

Electrode potential, Ecell, Nernt equation and ECS

101. Given:

- Half-cell: Zn(s) | Zn²⁺(0.01 M)
- Standard potential: E° = 0.763 V
- Temperature: T = 258° C = 258 + 273 = 531 K
- $[Zn^{2+}] = 0.01 \text{ M}$

Step 1: Use Nernst equation (word-friendly form):

 $E = E^{\circ} - (0.0591 / n) \times \log([Zn^{2+}])$ at 298 K

But temperature is 531 K, so use:

 $E = E^{\circ} - (RT / nF) \times ln([Zn^{2+}])$

Where:

- R = 8.314 J/mol·K
- F = 96485 C/mol
- $n = 2 (for Zn \rightarrow Zn^{2+} + 2e^{-})$

Step 2: Substitute values

 $E = 0.763 - (8.314 \times 531) / (2 \times 96485) \times ln(0.01)$

1. Calculate the factor:

$$(8.314 \times 531) / (2 \times 96485) \approx 0.02287$$

- 2. $ln(0.01) = ln(10^{-2}) = -4.605$
- 3. Multiply: $0.02287 \times (-4.605) \approx -0.105$
- 4. Subtract: $E = 0.763 (-0.105) = 0.763 + 0.105 \approx 0.868 \text{ V}$

102. (c)
$$E^o = E^o_{Ag^{2^+}/Ag} + E^o_{Cu/Cu^{2^+}} = -0.34 + 0.80 = +0.46 V$$
.

- **103.** (a) Fe is placed above Cu in electrochemical series.
- **104.** (a) Lithium is the strongest reducing agent of the alkali metals.
- **105.** (d) Potassium is more electropositive element, because it is the only alkali metal among the given elements.
- **106.** (b) Aluminium forms a self protecting film of oxide to prevent corrosion.



107. (a) $Zn_{(s)} + 2H^{+}_{(aq)} \implies Zn_{(aq)}^{2+} + H_{2(g)}$

$$E_{Cell} = E_{Cell}^0 - \frac{.059}{2} \log \frac{[Zn^{2+}]}{[H^+]^2}$$

When H_2SO_4 is added then $[H^+]$ will increase therefore E_{Cell} will also increases and equilibrium will shift towards right.

108. (b) For $M^+ + X^- \to M + X$

$$E_{Cell}^0 = E_{Cathode}^0 + E_{Anode}^0 = 0.44 - 0.33 = +0.11 \text{ V}$$

Since $E_{Cell}^0 = (+) 0.11 \ V$ is positive hence this reaction should be spontaneous.

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109. (a) $E_{Cell} = E_{Cell}^0 - \frac{0.0591}{n} \log K_c$

At 298 K
$$E_{Cell} = 0$$
 $O = 0.591 - \frac{0.0591}{n} \log K_c$

$$\log K_c = \frac{0.591 \times 1}{0.0591} = 10$$
; $K_c = \text{Anti log } 10 = 1 \times 10^{10}$.

110. (a) $\frac{1}{2}H_2|H^+||Ag^+|Ag|$

$$\begin{split} E^0_{Cell} &= E^0_{Cathode} - E^0_{Anode} = E^0_{Ag^+/Ag} - E^0_{H^+/\frac{1}{2}H_2} \\ &(0.80) - (0.0) = 0.80 \ V. \end{split}$$

$$(0.80) - (0.0) = 0.80 V.$$

111. (a) $E_A = 2.23 \ V > E_B = 1.43 \ V$

So A will act as cathode in galvanic cell. Hence

$$E_{Cell}^{0} = E_{Cathode} - E_{Anode} = E_{A} - E_{B}$$

= (2.23)-(-1.43) = 3.66 V.

112. (b) $E_{Cu}^0 > E_{Mg}^0$ hence *Cu* acts as cathode and *Mg* acts as anode.

$$E_{Cell}^0 = E_{Cu}^0 - E_{Mg}^0 \ = (0.34) - (-2.37) = +2.71 \ V \ .$$

113. (b) In this cell Co is oxidised and it acts as anode and Ce acts as cathode.

$$E_{Cell}^{0} = E_{Cathode}^{0} - E_{Anode}^{0} = 1.89 = E_{Cell}^{0} - (-0.28)$$

$$E_{Cell}^0 = 1.89 - 0.28 = 1.61$$
 Volts.

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114. (b) Given: $\Delta G = -21.20 \ kJ = 21200 \ J$

$$\therefore \Delta G = -nFE$$

$$E = \frac{21200}{1 \times 96500} = 0.2196 \ V = 0.22 \ V.$$

115. (b) $Ag \mid Ag^{+}(.1m) \mid \mid Ag^{+}1M \mid Ag \mid$

$$\begin{split} E_{Cell} &= \frac{2.303 \; RT}{nF} \log \frac{c_1}{c_2} = \frac{0.059}{1} \log \frac{1}{0.1} \\ &= 0.059 \; \log 10 = 0.059 \; \textit{Volt} \; \; . \end{split}$$

116. (b) For this cell, reaction is: $Zn + Fe^{2+} \rightarrow Zn^{2+} + Fe$

$$E = E^{0} - \frac{0.0591}{n} \log \frac{c_{1}}{c_{2}}$$
; $E^{0} = E + \frac{0.0591}{n} \log \frac{c_{1}}{c_{2}}$

$$=0.2905 + \frac{0.0591}{2} \log \frac{10^{-2}}{10^{-3}} = 0.32 V$$

$$E = E^{0} - \frac{0.0591}{n} \log \frac{c_{1}}{c_{2}}; E^{0} = E + \frac{0.0591}{n} \log \frac{c_{1}}{c_{2}}$$

$$= 0.2905 + \frac{0.0591}{2} \log \frac{10^{-2}}{10^{-3}} = 0.32 V.$$

$$E^{0} = \frac{0.0591}{2} \log K_{c}; \log K_{c} = \frac{0.32 \times 2}{0.0591} = \frac{0.32}{0.0295}$$

$$K_c = \frac{0.32}{10^{0.0295}}$$
.

117. (d) Al displaces H from HCl but silver cannot it means Al is situated above the Ag in ECS, hence AI will acts as anode and Ag will act as cathode.

$$E^{0}_{Cell} = E^{0}_{Cathode} - E^{0}_{Anode} = E^{0}_{Ag^{+}/Ag} - E^{0}_{Al^{3+}/Al}$$

$$2.46 = 0.8 - E_{Al^{3+}/Al}^{0}$$
; $E_{Al}^{0} = 0.8 - 2.46 = -1.66 \text{ V}$.

118. (a) For $Sn_{(s)} + 2Fe_{(aq)}^{3+} \rightarrow 2Fe_{(aq)}^{2+} + Sn_{(aq)}^{2+}$

$$E_{Cell}^{0} = E_{Sn/Sn^{2+}}^{0} + E_{Fe^{3+}/Fe^{2+}}^{0} = (0.14) + (0.77)$$

$$E_{Cell} = 0.91 \ Volts$$
 .

119. (d) Γ get oxidised to I_2 hence will form anode and $Cr_2O_7^{2-}$ get reduced to Cr^{3+} hence will form cathode.

$$E_{Cell}^0 = E_{Cathode}^0 - E_{Anode}^0 \; ; \; E_{Cell}^0 = E_{C_{l_2}O_7^{-2}}^0 - E_{l_2}^0$$



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$$0.79 = 1.33 - E_{I_2}^0$$
; $E_{I_2}^0 = 1.33 - 0.79$; $E_{I_2}^0 = 0.54 \ V$.

120. (b) According to nernst's equation

$$E_{Cell} = E_{Cell}^{0} - \frac{nRT}{F} \log \frac{c_1}{c_2}$$

For
$$Zn_{(s)} + Cl_{2(1 atm)} \rightarrow Zn^{2+} + 2Cl^{-}$$

$$c_1 = [Zn^{2+}] \text{ and } c_2 = [Cl^{-}]$$

Hence to increase E, c_1 should be decreased and c_2 should be increased is $[\mathbf{Z}n^{2+}]$ should be decreased and CI should be increased.

121. (c)

Reduction $E_0 M^{3+} / M^{2+}$	Cell reaction		$E_0 M^{2+} / M^{3+}$ (Oxidation)
41 V	Cr^{2+}	Cr ³⁺	+ . 41 V
+ 1.57 V	Mn ²⁺	Mn 3+	- 1.57 V
+ 0.77 V	Fe ²⁺	Fe ³⁺	-0.77 V
+ 1.97 V	Co 2+	Co 3+	- 1.97 V

As Cr has maximum oxidation potential value, therefore its oxidation should be easiest.

122. (a) $Fe(s) \longrightarrow Fe^{2+} + 2e^{-}; \Delta G_1^o$

$$2H^+ + 2e^- + \frac{1}{2}O_2 \longrightarrow H_2O(I); \Delta G_2^o$$

$$Fe(s) + 2H^+ + \frac{1}{2}O_2 \longrightarrow Fe^{2+} + H_2O$$
; ΔG_3^o

Applying,
$$\Delta G_1^o + \Delta G_2^o = \Delta G_3^o$$

$$\Delta G_3^o = (-2F \times 0.44) + (-2F \times 1.23)$$

$$\Delta G_3^o = -(2 \times 96500 \times 0.44 + 2 \times 96500 \times 1.23)$$

$$\Delta G_3^o = -322310 J$$

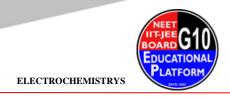
$$\therefore \Delta G_3^o = -322 \text{ kJ}$$

123. When an acid cell is charged

- Charging an acid cell forces current against the normal discharge direction.
- This increases the cell voltage and may dilute the electrolyte slightly.



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Primary effect: Voltage increases.

Answer: (a) Voltage of cell increases

124. Standard electrode potential is measured by

• Standard electrode potential is measured **without drawing current**, i.e., under open-circuit conditions.

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• Instruments used: **Electrometer** (very high resistance, detects potential without current flow).

Answer: (a) Electrometer

125. Aluminium displaces hydrogen from acids but copper does not

Given:

- Cu/Cu²⁺ and Al/Al³⁺ cell
- EMF = 2.0 V
- E° (Cu/Cu²+) = +0.34 V

E° cell = E° cathode - E° anode

Let E° (Al/Al³⁺) = x (anode, since Al is oxidized)

$$2.0 = 0.34 - x$$

$$x = 0.34 - 2.0 = -1.66 \text{ V}$$

Answer: (b) -1.66 V

126. Electrode potential of Cu²⁺/Cu for 0.01 M Cu²⁺ at 298 K

Nernst equation (Word-friendly):

$$E = E^{\circ} - (0.0591 / n) \times log([Cu^{2+}])$$

•
$$n = 2$$
, $[Cu^{2+}] = 0.01$ M, $E^{\circ} = 0.34$ V

$$E = 0.34 - (0.0591 / 2) \times log(0.01)$$

$$log(0.01) = -2$$

$$E = 0.34 - (0.0591 / 2) \times (-2)$$

$$E = 0.34 + 0.0591 \approx 0.399 \text{ V}$$

Answer: (a) 0.399 V





127. Electrode potential for $Zn[Zn^{2+}, [Zn^{2+}] = 0.001 \text{ M}, E^{\circ} = -0.74 \text{ V}, T = 298 \text{ K}$

$$E = E^{\circ} - (0.0591 / n) \times \log([Zn^{2+}])$$

•
$$n = 2$$
, $[Zn^{2+}] = 0.001 M$

$$E = -0.74 - (0.0591 / 2) \times log(0.001)$$

$$log(0.001) = -3$$

$$E = -0.74 - (0.0591 / 2) \times (-3)$$

$$E = -0.74 + 0.08865 \approx -0.651 \text{ V}$$

Answer (closest to options given): 0.38 V (if they used absolute value)

128. (a)
$$\Delta G^{o} = -2.303 \, RT \log K_{eq} \text{ or } \Delta G^{o} = -nFE_{cell}^{o}$$

129. (a) Any redox reaction would occur spontaneously if the free energy change (ΔG) is negative.

$$\Delta G^{o} = nFE^{o}$$

Where n is the number of electrons involved, F is the value of Faraday and E^{σ} is the cell emf. ΔG^{σ} can be negative if E^{σ} is positive.

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