Topic 6N - Applications of Standard Potentials

Nernst Equation

Recall that

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

and that

$$\Delta G = -nFE \quad \text{and} \quad \Delta G^\circ = -nFE^\circ$$

Thus,

$$-nFE = -nFE^\circ + RT \ln Q$$

Hence,

$$\boxed{E = E^\circ - \frac{RT}{nF} \ln Q} \qquad \text{(Nernst Eq.)}$$

At Equilibrium, E = 0 and Q = K. Thus,

$$E^\circ = \frac{RT}{nF} \ln K = -\frac{\Delta G^\circ}{nF}$$

$$\ln K = \frac{nFE^\circ}{RT} = -\frac{\Delta G^\circ}{RT}$$

Since F = 96,485 C/mol and R = 8.314 J/mol-K, and if T = 298K and ln is converted Into $\log_{10}$ (÷ 2.303), then

$$2.303 \frac{RT}{F} = 0.0592 \text{ V}$$

and

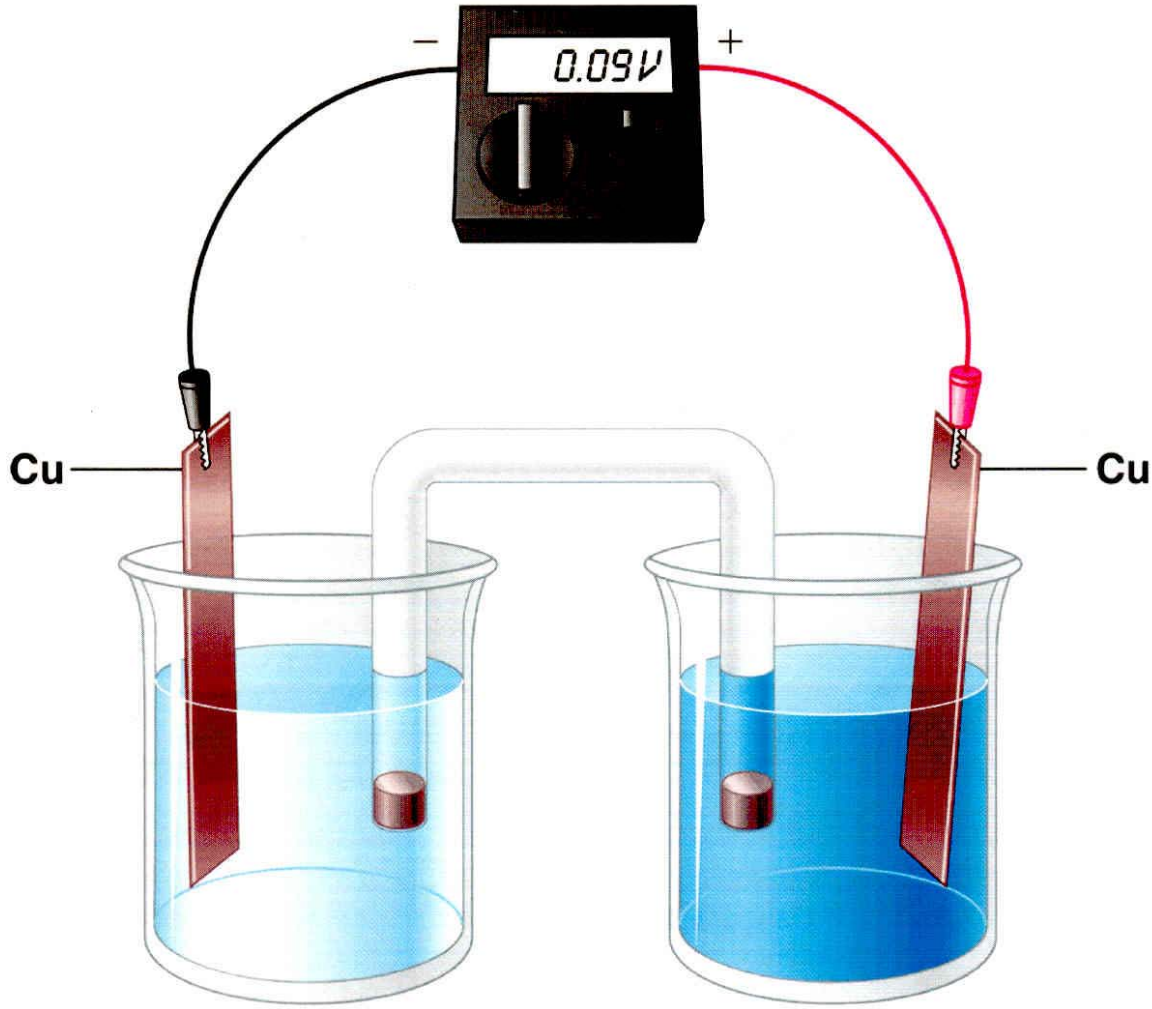
$$\boxed{E = E^\circ - \frac{0.0592}{n} \log_{10} Q}$$

which is a commonly encountered form of the Nernst equation.

Thus, at equilibrium at 25°C (298K) and with all components in their standard states,

$$\log_{10} K = \frac{nE^\circ}{0.0592}$$

Concentration Cell



0.0010 M Cu^{2+} 1.0 M Cu^{2+}

Anode: $Cu\ (s) \rightarrow Cu^{2+}\ (aq)$ Cathode: $Cu^{2+}\ (aq) \rightarrow Cu\ (s)$

Net "Reaction": $Cu^{2+}\ (aq) + Cu\ (s) \rightarrow Cu\ (s) + Cu^{2+}\ (aq)$ $E° = 0.00$

$$E = 0.00 - \frac{0.05916}{2}\log_{10}\frac{[Cu^{2+}]_{anode}}{[Cu^{2+}]_{cathode}}$$

$$= 0.00 - \frac{0.05916}{2}\log_{10}\frac{0.001}{1.0} = 0.089\ V$$

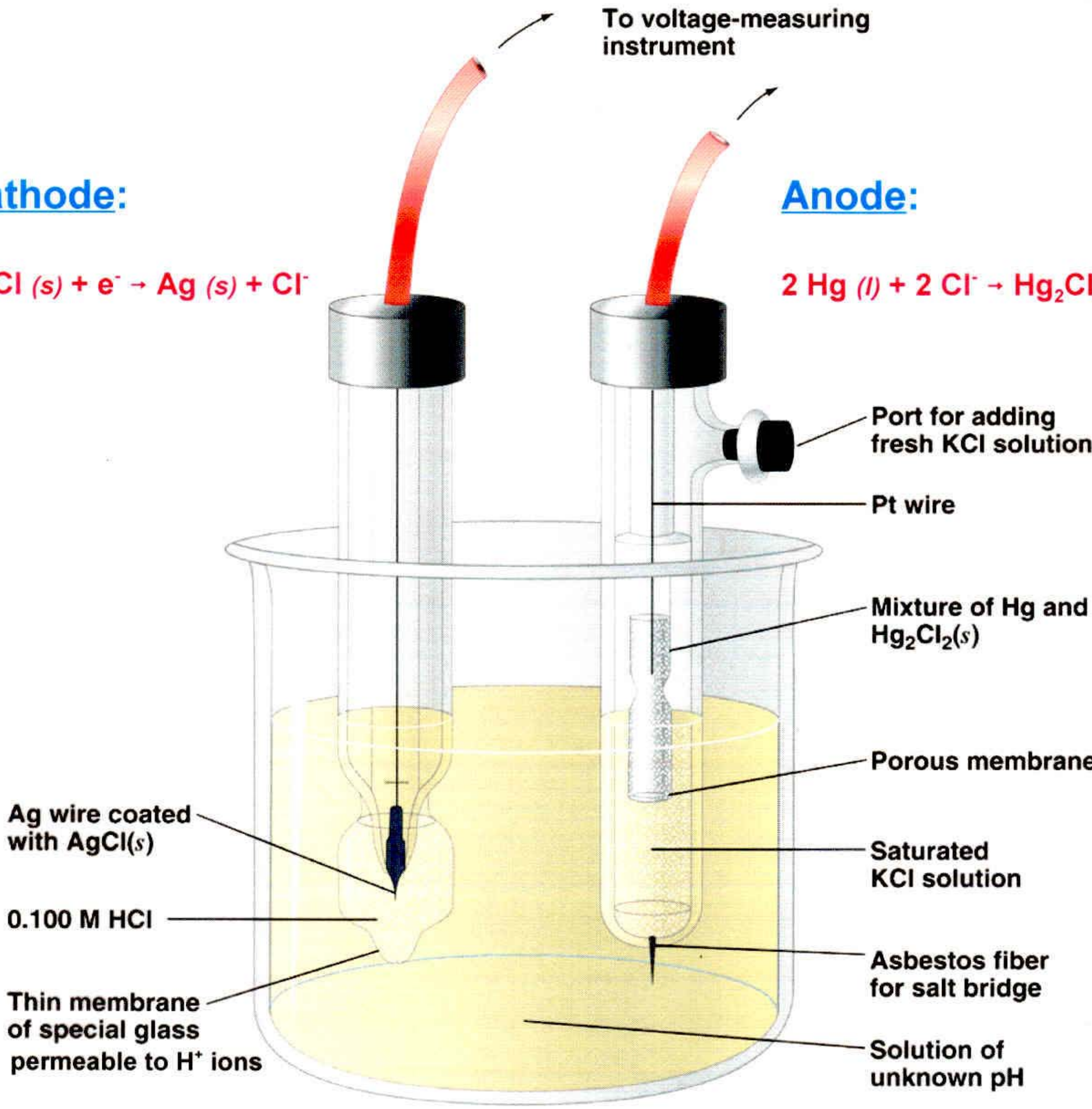
pH Meter

Cathode:

$AgCl\ (s) + e^- \rightarrow Ag\ (s) + Cl^-$

Anode:

$2\ Hg\ (l) + 2\ Cl^- \rightarrow Hg_2Cl_2\ (s) + 2\ e^-$



$$Ag\,|\,AgCl\ (s),\ HCl\ (1.0\ M)\,|\,\text{glass membrane}\,|\ [H^+]\ \|\ KCl\ (satd.),\ Hg_2Cl_2\,|\,Hg\ (Pt)$$

$$E = 0.00 - \frac{0.05916}{2}\log_{10}\frac{[H^+]^2_{anode}}{[H^+]^2_{cathode}}$$

$$= -\frac{0.05916}{2}\log_{10}\frac{[H^+]^2}{(1.0)^2}$$

$$= -0.05916\log_{10}[H^+]$$

$$= +0.05916\ pH$$