Quiz 6.2 – Electrochemistry

Name: Key

Reduction Potentials

Find the standard reduction potential for (A) $Cu^{2+} + 2\,e^- \longrightarrow Cu(s)$ using the following potentials:

(B) $Cu^+ + e^- \longrightarrow Cu \qquad E^\ominus = 0.52\,V$

(C) $Cu^{2+} + e^- \longrightarrow Cu^+ \qquad E^\ominus = 0.16V$

$2 \cdot E_A = 1 \cdot E_B + 1\,E_C \rightarrow 2E_A = 0.52V + 0.16V$

$E_A = 0.34\,V$

Electrochemical Cells

Find the *standard* cell potential for a cell constructed after the following schema:

$Ag(s)|AgCl(s)|Cl^-(aq)||Ce^{4+}(aq)/Ce^{3+}(aq)|Pt(s)$ $\quad Ag(s) + Cl^-_{(aq)} + Ce^{4+}_{(aq)} \rightarrow AgCl(s) + Ce^{3+}_{(aq)}$

$E^\circ = 1.61\,V - 0.22\,V = 1.39\,V$

What is the equilibrium constant K for this cell?

$E^\circ_{cell} = \frac{RT}{\nu F} \ln K \rightarrow 1.39\,V = \frac{8.314\ J/mol\cdot K \cdot 298\,K}{1 \cdot 96{,}485\ C/mol} \ln K \rightarrow K = 3.23 \cdot 10^{23}$

Ag/AgCl electrodes will often buffer the $Cl^-(aq)$ concentration by saturating the solution in KCl. KCl has a solubility product of $K_{sp} = 21.7$, ~~and at saturation KCl has $\gamma_\pm = 1.45$~~ $[Cl^-] = \sqrt{21.7} = 4.66\,M$

Find the cell potential when the cell uses a saturated KCl solution in the anode, and has $[Ce^{4+}] = 0.25\,M$ and $[Ce^{3+}] = 0.75\,M$ in the cathode $Q = \frac{[Ce^{3+}]}{[Cl^-][Ce^{4+}]} = \frac{0.75\,M}{4.66\,M - 0.25\,M} = 0.644$

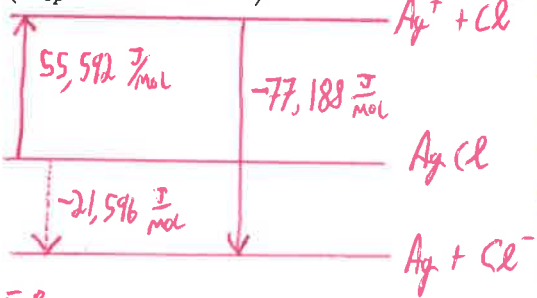
$E_{cell} = E^\circ_{cell} - \frac{RT}{\nu F}\ln(Q) = 1.39\,V - \frac{8.314\ \frac{J}{mol\cdot K} \cdot 298\,K}{1 \cdot 96{,}485\ \frac{C}{mol}} \ln 0.644 = 1.40\,V$

Is this cell a voltaic cell or an electrolytic cell?

Voltaic Cell

Can you explain the standard redution potential of a Ag/AgCl electrode ($+0.22\,V$) using the Ag^+/Ag standard reduction potential ($+0.80\,V$) and the solubility product of AgCl ($K_{sp} = 1.8 \times 10^{-10}$)?

ΔG° links all reactions together



$AgCl(s) \rightarrow Ag^+_{(aq)} + Cl^-_{(aq)} \quad \Delta G^\circ = 55{,}592\ J/mol$

$Ag^+_{(aq)} \rightarrow Ag(s) \quad \Delta G^\circ = -77{,}188\ J/mol$

Via Hess's law, $AgCl(s) \rightarrow Ag(s) + Cl^-_{(aq)} \quad \Delta G^\circ = -21{,}596\ J/mol \rightarrow E^\circ_{cell} = 0.224\,V$