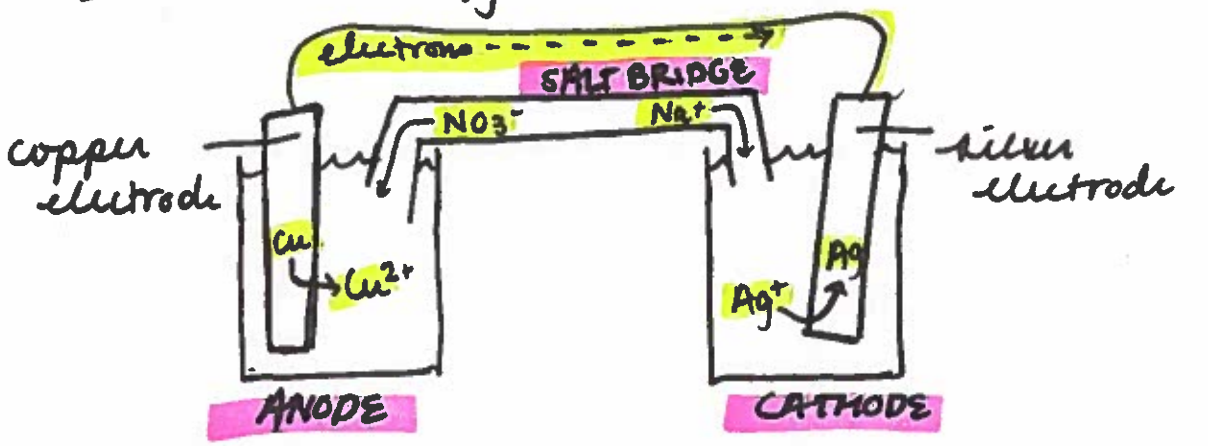
WEEK 11 KEY

1. For the following reaction, draw a galvanic cell and label ALL parts (make sure to include where oxidation and reduction are happening, and how all species flow through the system, including electrons).

$$2AgNO_3\,(aq) + Cu\,(s) \rightarrow Cu(NO_3)_2\,(aq) + 2Ag\,(s)$$

oxidation: $Cu \rightarrow Cu^{2+} + 2e^-$ @ ANODE

reduction: $Ag^+ + e^- \rightarrow Ag$ @ CATHODE



2. Calculate the standard emf for a galvanic cell based on the following rxn:

$$2Na\,(s) + 2H_2O\,(l) \rightarrow 2NaOH\,(aq) + H_2\,(g)$$

oxidation: $Na \rightarrow Na^+ + e^-$ $\quad \mathcal{E}^\circ_{ox} = 2.71\,V$

reduction: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ $\quad \mathcal{E}^\circ_{red} = -0.83\,V$

$$\mathcal{E}^\circ_{cell} = \mathcal{E}^\circ_{ox} + \mathcal{E}^\circ_{red}$$

$$\mathcal{E}^\circ_{cell} = 1.88\,V$$

3. Calculate the eq. constant, K, for the following reaction (T=298K, acidic conditions):

$$Cr\,(s) + NO_3^-\,(aq) \rightarrow Cr^{3+}\,(aq) + NO(g)$$

$n=3$ $\left\{ \begin{array}{ll} \text{oxidation: } Cr \rightarrow Cr^{3+} + 3e^- & \mathcal{E}_{ox} = 0.73\,V \\ \text{reduction: } NO_3^- + 3e^- \rightarrow NO & \mathcal{E}_{red} = 0.96\,V \end{array} \right.$

$$\Delta G = -nFE^\circ_{cell}$$

$$= -\underset{mol}{3}(96485\,J/V\cdot mol)(0.73\,V + 0.96\,V)$$

$$\Delta G = -489179\,J = -RT\ln K$$

$$K = e^{(489179/8.314 \cdot 298.15\,K)}$$

$$\therefore K = 5.01 \times 10^{85}$$

4. Calculate E°_{ox} for the reaction below:

$Au(s) + NO_3^- (aq) + 4H^+ (aq) \rightarrow Au^{3+} (aq) + NO (g) + 2H_2O (l)$ $E^\circ_{cell} = -0.54$

$$E^\circ_{cell} = E^\circ_{ox} + E^\circ_{red}$$

$$-0.54 V = E^\circ_{ox} + 0.96$$

$$\therefore E^\circ_{ox} = 1.50 V$$

5. Rank the following in order of increasing strength as oxidizing/reducing agents:

a. Ag, Cr^{3+}, Li, F^-, H_2 – reducing agents (rank E°_{ox})

$$F^- < Cr^{3+} < Ag < H_2 < Li$$

b. F_2, Cr^{3+}, I_2, MnO_4^- – oxidizing agents (rank E°_{red})

$$Cr^{3+} < I_2 < MnO_4^- < F_2$$

c. Cu^+, Ni, Cd, Cr – reducing agents (rank E°_{ox})

$$Cu^+ < Ni < Cd < Cr$$

6. Calculate the standard E° for the electrochemical cell below:

a. Al (s) | Al^{3+} (aq) || Mg^{2+} (aq) | Mg (s)

$E_{ox} = 1.66 V$

$E_{red} = -2.37 V$

$E^\circ_{cell} = -0.71 V$

b. Zn (s) | Zn^{2+} (aq) || SO_4^{2-} (aq) | H_2SO_3 (aq) | Pt(s)

$E_{ox} = 0.76 V$

$E_{red} = 0.20 V$

$E^\circ_{cell} = 0.96 V$

7. Calculate ΔG° and K for the following reaction. Is this reaction spontaneous?

$$MnO_4^- (s) + H^+ (aq) + H_2O_2 (aq) \rightarrow MnO_2 (s) + H_2O (l) + O_2 (g)$$

$\mathcal{E}_{ox} = -0.68$ $\mathcal{E}_{red} = 1.68$

$\mathcal{E}°_{cell} = 1.00 V$

$\Delta G° = -nFE°_{cell} = -6(96485 J/V\cdot mol)(1 V)$

$\Delta G° = -578910 J/mol$

$\Delta G° = -RT\ln(K)$

$K = 2.67 \times 10^{101}$ → probably gives a calculator error

8. A number of chemical species can behave as both an oxidizing reagent and a reducing reagent. In the following situations, what reaction would predominate? → what has highest E_{cell} / lowest ΔG

a. Chamber containing Mn^{2+} (aq), PbO_2 (s), and Ag (s)

$Mn^{2+} + 2e^- \rightarrow Mn$ $\mathcal{E}_{red} = -1.18 V$

$Mn^{2+} + 4H_2O \rightarrow MnO_4^- + 8H^+ + 5e^-$ $\mathcal{E}_{ox} = -1.51 V$

$PbO_2 + 4H^+ + 2e^- \rightarrow Pb^{2+} + 4H_2O$ $\mathcal{E}_{red} = 1.69$

$Ag \rightarrow Ag^+ + e^-$ $\mathcal{E}_{ox} = -0.80$

HIGHEST E_{cell}

$PbO_2 + Ag + 4H^+ \rightarrow Pb^{2+} + H_2O + Ag$ dominates

b. Chamber containing I_2 (s), Zn^{2+} (aq) and Cl_2 (g)

$I_2 + 2e^- \rightarrow 2I^-$ $\mathcal{E}_{red} = 0.54 V$

$\frac{1}{2} I_2 + 3H_2O \rightarrow IO_3^- + 6H^+$ $\mathcal{E}_{ox} = -1.2V$

$Zn^{2+} + 2e^- \rightarrow Zn$ $\mathcal{E}_{red} = -0.76$

$Cl_2 + 2e^- \rightarrow 2Cl^-$ $\mathcal{E}_{red} = 1.36 V$

highest $E°_{rxn}$

$Cl_2 + \frac{1}{2} I_2 + H_2O \rightarrow IO_3^- + H^+ + Cl^-$ DOMINATES

c. Chamber containing Cr^{3+} (aq), ClO_2^- (aq), and Au (s)

$Cr^{3+} \rightarrow Cr + 3e^-$ $\mathcal{E}_{red} = -0.73 V$

$Cr^{3+} \rightarrow Cr^{2+} + 2e^-$ $\mathcal{E}_{red} = -0.50 V$

$Au \rightarrow Au^{3+} + 3e^-$ $\mathcal{E}_{ox} = -1.50 V$

$ClO_2^- \rightarrow e^- + ClO_2$ $\mathcal{E}_{ox} = -0.954$

$2Cr^{3+} + 7H_2O \rightarrow Cr_2O_7^- + 14H^+ + 6e^-$ $\mathcal{E}_{ox} = -1.33 V$

* NO SPONTANEOUS REACTIONS