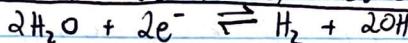


Week 3 Discussion Worksheet Answers

1)



$$E^\circ = -0.83 \text{ V}$$

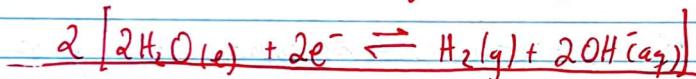
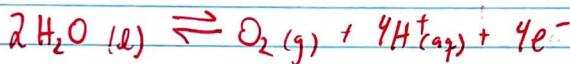


$$E^\circ = 1.229 \text{ V}$$

- a) In the electrolysis of water, a disproportionation reaction occurs in which water is simultaneously oxidized and reduced into 2 new species. What are the respective oxidation states of hydrogen and oxygen in water before electrolysis? During electrolysis, what atom is likely reduced? What atom is likely oxidized?

In water, H is +1 ; O is -2. Thus, hydrogen is likely reduced and oxygen must be oxidized.

- b) Use the half-cell reactions listed above to write a net equation for the electrolysis reaction.



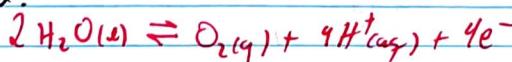
- c) What is the overall potential E° for this reaction? What is the minimum potential needed for electrolysis to occur?

$E^\circ = -2.06 \text{ V}$ so the minimal potential is +2.06 V

- d) If you were to collect the gases produced during electrolysis, what is the ratio of volumes (O_2 vs H_2 gas) you would expect to see?

Via the stoichiometric ratios a 1:2 ratio of $\text{O}_2:\text{H}_2$.

- 2) a) A 9V battery in this setup generates about 140 mA current. If we assume that the current remains steady for the 10 minutes that we electrolyzed the solution, calculate how many moles of O_2 could be produced.



$$10.0 \text{ min} \times \frac{60 \text{ s}}{\text{min}} \times \frac{0.140 \text{ C}}{\text{s}} \times \frac{1 \text{ mol e}^-}{96485} = 8.706 \times 10^{-4} \text{ mol e}^-$$

$$4 \text{ electrons per reaction} \Rightarrow 8.71 \times 10^{-4} \text{ mol} \times \frac{1 \text{ mol O}_2}{4 \text{ mole}^-} = \boxed{2.176 \times 10^{-4} \text{ mol O}_2}$$

b) What volume of hydrogen and oxygen gas would be collected when water is electrolyzed for 19.0 min with 10.0 mA current?

$$V = \frac{nRT}{P} = \frac{(2.176 \times 10^{-4} \text{ mol})(0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}})(298\text{K})}{1 \text{ atm}}$$

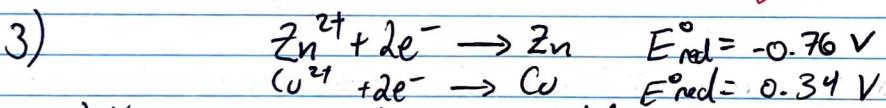
$$V_{O_2} = 5.3 \text{ mL}$$

$$\text{Moles } n_{H_2} = 8.71 \times 10^{-4} \text{ mole e}^- \times \frac{1}{2} = 4.35 \times 10^{-4} \text{ mol H}_2$$

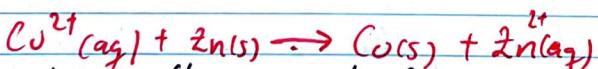
$$V_{H_2} = \frac{(4.35 \times 10^{-4} \text{ mol})(0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}})(298\text{K})}{1 \text{ atm}}$$

$$V_{H_2} = 10.6 \text{ mL}$$

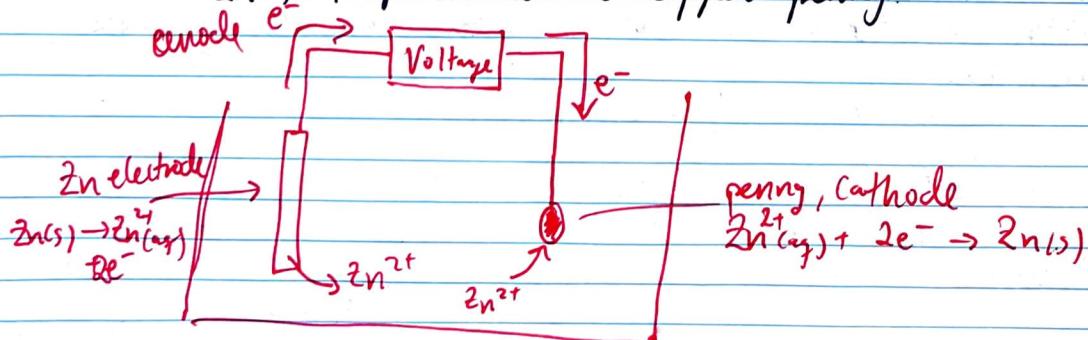
c) Do these volumes match your observation from part 1?
We created $\sim 2x$ as much H_2 gas as O_2 gas.



a) You want to plate zinc metal onto a copper penny. What is the spontaneous reaction that would occur between Zn/Zn^{2+} ; Cu/Cu^{2+} ?



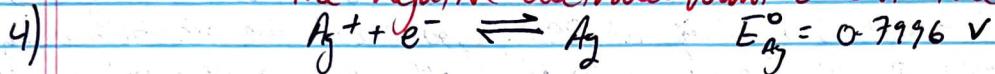
b) Electroplating allows us to force the non-spontaneous reaction to occur by using a voltage source to invert the redox reaction in the opposite direction. Draw a diagram showing what processes will occur at the anode and cathode if we force $Zn(\text{l})$ to plate onto a copper penny.



c) How much potential is required to make this reaction happen?
At least 1.1 V

d) What terminal of the voltage source should be connected to the penny during electrolysis?

The negative electrode. Want C^- onto the penny.



a) Consider a voltaic cell constructed from silver and copper. Calculate the cell potentials at the moment this battery starts to run, assuming we are using 1M solutions for all salts.

Since we are initial conditions

$$E_{cell} = E_{Ag}^\circ - E_{Cu}^\circ = 0.4594 \text{ V}$$

b) When a cell is under standard conditions, what is true of E_{cell}° ?

$$E = E^\circ - \frac{RT}{nF} \ln Q = E^\circ - \frac{RT}{nF} \ln 1 \Rightarrow E = E^\circ$$

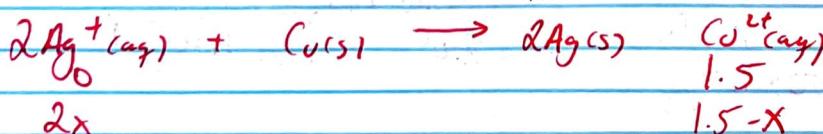
c) Suppose we leave the cell running for several hours and then come back and measure the cell potential. If we find the cell potential is now +0.20 V, what must be the concentration of Ag^{2+} ions in solution? Assume equal volumes at anode/bathode.

We want Q. Via Nernst Eqn:

$$E = E^\circ - \frac{RT}{nF} \ln Q \Rightarrow Q = \exp \left\{ \frac{nF}{RT} (E^\circ - E) \right\}$$

$$Q = \exp \left\{ \frac{2(96485 \text{ C/mol})}{(8.314 \text{ J/mol}\cdot\text{K})(298 \text{ K})} (0.4594 \text{ V} - 0.20 \text{ V}) \right\} = 5.95 \times 10^8$$

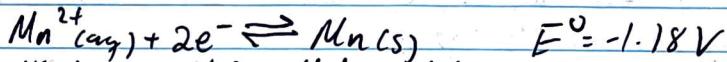
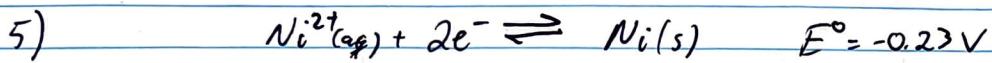
Since Q is so large, we assume complete conversion



$$5.95 \times 10^8 = \frac{1.5-x}{(2x)^2} \quad \text{Assuming } x \text{ small, } \boxed{x = 2.5 \times 10^{-5}}$$

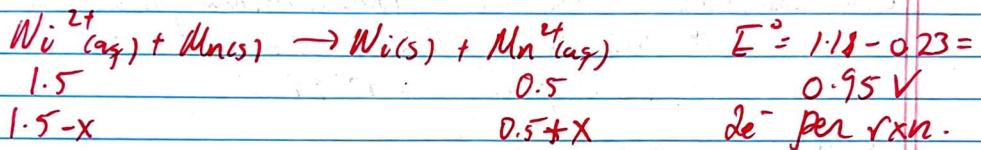
$$\boxed{[Cu^{2+}] = 1.5 \text{ M}}, \quad \boxed{[Ag^+] = (2.5 \times 10^{-5} \text{ M}) = 1.5 \times 10^{-5} \text{ M}}$$

$$\text{Hence, } [\text{Cu}^{2+}] = 1.5 \text{ M} \quad [\text{Ag}^+] = 5 \times 10^{-5} \text{ M}$$



How long will this voltaic cell be able to ~~possibly~~ supply a potential of at least 0.94 V if, at 298K, you start the reaction using 1.5M solution of Ni^{2+} and 0.50 M Mn^{2+} ? Assume the voltaic cell delivers a constant current of 150 mA and the volume of each cell is 1.00 L.

Long problem..



Want to know when reduction potential is 0.94 V for ~~this~~ x.

$$E = E^\circ - \frac{RT}{nF} \ln \left(\frac{[\text{Mn}^{2+}]}{[\text{Ni}^{2+}]} \right)$$

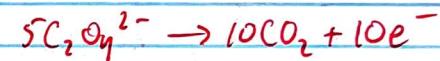
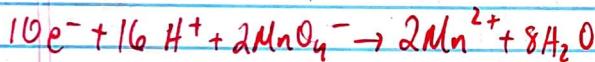
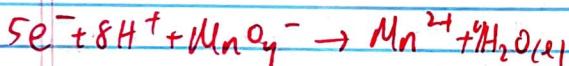
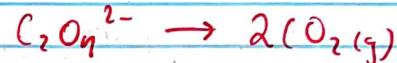
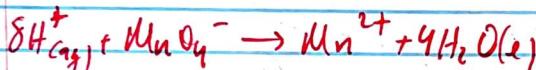
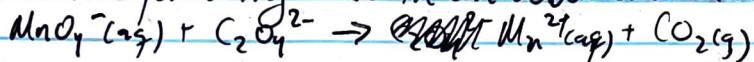
$$0.94 = 0.95 - \frac{(8.314 \text{ J/mol}\cdot\text{K})(298 \text{ K})}{(2)(96485 \text{ C/mol})} \ln \left(\frac{0.5+x}{1.5-x} \right)$$

$$\Rightarrow \frac{0.5+x}{1.5-x} = \exp(0.779) \Rightarrow \boxed{x = 0.871}$$

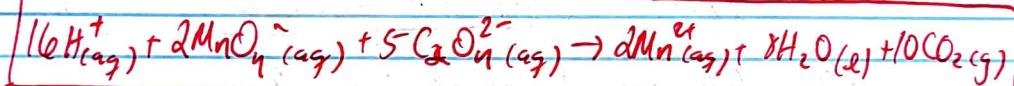
$(0.871 \text{ M})(1 \text{ L}) = 0.871 \text{ mol of reaction.}$
So 2e^- per rxn,

$$\frac{0.871 \text{ mol rxn} \times \left(\frac{2 \text{ mol e}^-}{1 \text{ mol rxn}} \right) \left(\frac{1.68 \times 10^5 \text{ C}}{1 \text{ mol e}^-} \right)}{150 \times 10^{-3} \text{ A}} = 1.12 \times 10^6 \text{ s} = \boxed{311 \text{ hours}}$$

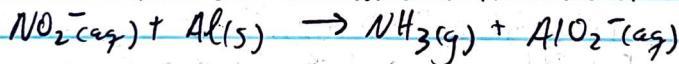
6) Balance the following rxn in an acidic environment.



Hence,

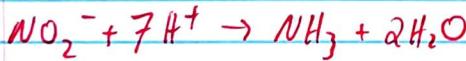


7) Balance in both acid & basic environment.

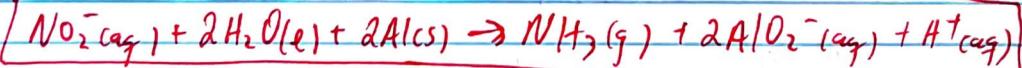


Start in acid first:

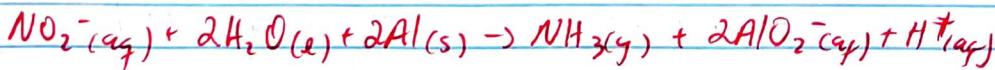
Like the above, separate:



Multiply 2nd by 2 & add to get:



In a basic environment, just add OH^- to both sides to consume all H^+ .

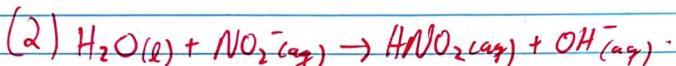
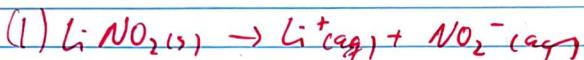


So, add OH^- to both sides



8) Do acidic or basic conditions favor the solubility of lithium nitrite (LiNO_2)? Please explain.

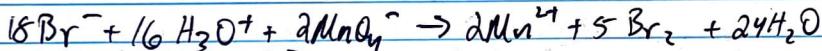
The following reactions occur in an aqueous soln. containing LiNO_2 :



So if made more acidic, $[\text{OH}^-]$ decreases. So rxn 2 is more favored, removing $[\text{NO}_2^-]$. Hence rxn 1 shifts to right, increasing solubility.

So acidic conditions favor LiNO_2 solubility.

9) The following balanced chemical eqn. occurs in a galvanic cell:



Calculate $[\text{Mn}^{2+}]$ given: $\Delta E^\circ_{\text{cell}} = 0.420 \text{ V}$, $\Delta E_{\text{cell}} = 0.442 \text{ V}$, $\text{pH} = 0$, $[\text{Br}^-] = 0.8 \text{ M}$, and $[\text{MnO}_4^-] = 0.3 \text{ M}$.

$$Q = \frac{[\text{Mn}^{2+}]^2}{[\text{MnO}_4^-]^2 [\text{H}_3\text{O}^+]^{16} [\text{Br}^-]^{10}} \quad 10 \text{ e}^- \text{ transferred.}$$

$$\Delta E_{\text{cell}} = \Delta E^\circ_{\text{cell}} - \frac{RT}{nF} \ln Q. \text{ Plug in values gives}$$

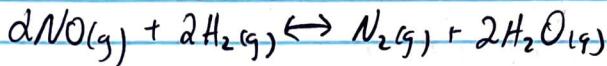
$$Q = e^{3.115} = 22.54$$

$$[\text{H}_3\text{O}^+] = 10^{-0} = 1 \text{ M.}$$

$$[\text{Mn}^{2+}]^2 = (22.54) [\text{MnO}_4^-]^2 [\text{H}_3\text{O}^+]^{16} [\text{Br}^-]^{10}$$

$$= 0.2187 \Rightarrow \boxed{[\text{Mn}^{2+}] = 0.467 \text{ M}}$$

10) a) What is the definition of an average reaction rate? An instantaneous rate? For the following reaction, what are all definitions of both the average and instantaneous reaction rate in terms of concentrations of products & reactants?



Average reaction rate is change in concentration of product over a given time interval.

Instantaneous reaction rate is the average reaction rate as $\Delta t \rightarrow 0$ ("derivative")

$$\text{Average: } -\frac{1}{2} \frac{\Delta [N_2O]}{\Delta t} = -\frac{1}{2} \frac{\Delta [H_2]}{\Delta t} = \frac{\Delta [N_2]}{\Delta t} = \frac{1}{2} \frac{\Delta [H_2O]}{\Delta t} = \text{rate}$$

$$\text{Instantaneous: rate} = -\frac{1}{2} \frac{d[N_2O]}{dt} = -\frac{1}{2} \frac{d[H_2]}{dt} = \frac{d[N_2]}{dt} = \frac{1}{2} \frac{d[H_2O]}{dt}$$

b) The rate of reaction depends on the concentrations of reactants and products. If the reaction is m^{th} order in $N_2O(g)$; n^{th} order in $H_2(g)$, with a rate constant of K , what is the rate law? What is the overall order of the reaction?

$$\text{rate} = K [N_2O]^m [H_2]^n$$

Overall order is $m+n$

c) Determine initial rate law, rate constant, and order of rxn.

$$\frac{k[0.01\text{ M}]^m [0.0100]^n}{k[0.01\text{ M}]^m [0.0200]^n} = \left(\frac{1}{2}\right)^n \cancel{\text{ex 2021}} = \frac{0.000\text{ M/min}}{0.012\text{ M/min}}$$

$$\Rightarrow \left(\frac{1}{2}\right)^n = \frac{1}{2} \Rightarrow \boxed{n=1}$$

$$\frac{k[0.01]^m[0.01]}{k[0.02][0.03]} = \left(\frac{1}{2}\right)^m \frac{1}{3} = \frac{0.006 \text{ M/min}}{0.144 \text{ M/min}} = \frac{1}{24}$$

Hence $\left(\frac{1}{2}\right)^m = \frac{1}{8} \Rightarrow m = 3.$

$$\text{rate} = k[N_2O]^3[H_2]$$

$$0.006 \frac{\text{M}}{\text{min}} = k(0.01 \text{ M})^3(0.01 \text{ M}) \Rightarrow k = 6.00 \times 10^5 \frac{\text{M}^{-3}}{\text{min}}$$

$$\text{rate} = \left(6.00 \times 10^5 \frac{\text{M}^{-3}}{\text{min}}\right) [N_2O]^3[H_2]$$

order of reaction is $3+1 = \boxed{4}$