

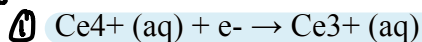
-  $E^\circ_{\text{cell}}$  must be positive

- if you multiply the rxn by coefficients to balance,  $E^\circ$  does not change

Yasuda

# FINAL REVIEW WORKSHEET Winter 2021 14B woo ;-;

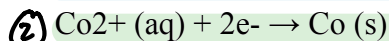
galvanic cell



reduction

$E^\circ_{\text{standard}} = 1.44 \text{ V}$

reduced (cathode)



$E^\circ_{\text{standard}} = -0.28 \text{ V}$

oxidized (anode)



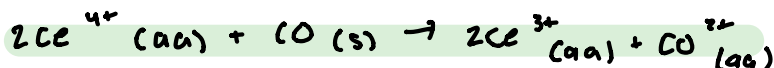
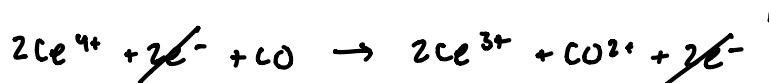
1a. Using the half reactions above, balance the following redox reaction and calculate  $E^\circ$



$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$$

$$1.44 \text{ V} - (-0.28 \text{ V})$$

$$E^\circ_{\text{cell}} = 1.72 \text{ V}$$



1b. Calculate  $\Delta G^\circ$  and  $K$   $E^\circ_{\text{cell}} (+)$  = spontaneous  $\Delta G^\circ_{\text{rxn}} (-)$  = spontaneous

$$\Delta G^\circ_{\text{rxn}} = -nFE^\circ_{\text{rxn}}$$

$$= -(2)(96,485 \frac{\text{C}}{\text{mol}})(1.72 \text{ V})$$

$$= -331.9 \text{ kJ/mol}$$

$$E^\circ_{\text{rxn}} = \frac{RT}{nF} \ln K$$

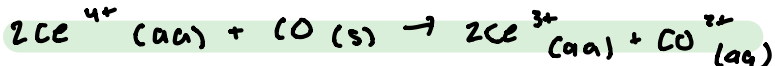
$$\frac{E^\circ_{\text{rxn}}(nF)}{RT} = \ln K$$

$$K = e^{\frac{E^\circ_{\text{rxn}} nF}{RT}}$$

$$= e^{\frac{1.72 \text{ V} (2)(96485 \frac{\text{C}}{\text{mol}})}{8.314 \text{ J/mol} (298 \text{ K})}} = 1.515 \times 10^{58}$$

1c. When the voltage is 3.04V, what is the concentration of  $\text{Co}^{2+}(\text{aq})$  when the concentrations of  $\text{Ce}^{3+}(\text{aq}) / \text{Ce}^{4+}(\text{aq})$  is .025 M?  $\Leftarrow$

$n$  = moles of electrons transferred in galvanic cell



$E = 3.04 \text{ V}$

$$Q = \frac{[\text{Co}^{2+}][\text{Ce}^{3+}]^2}{[\text{Ce}^{4+}]^2}$$

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

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

$$-nF(E - E^\circ) = \ln Q$$

$$e^{-\frac{nF(E-E^0)}{RT}} = \frac{[Co^{2+}][Ce^{3+}]^2}{[Ce^{4+}]^2}$$

$$[Co^{2+}] = e^{-\frac{2(96485)(3.04V - 1.72V)}{8.314(298K)}}$$

$$= \boxed{2.254 \times 10^{-45} M}$$

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equilibrium  
 $\Delta G = 0$   
 $E = 0$  }  $\ln K$

not equil.  
 $E \neq 0$   
 $\Delta G \neq 0$  }  $\ln Q$

1d. What is the change in cell potential when  $[Ce^{4+}] = .015 M$   $[Ce^{3+}] = .010 M$   $[Co^{2+}] = .10 M$

$$E = E^0 - \frac{RT}{nF} \ln Q$$

$$E - E^0 = -\frac{RT}{nF} \ln Q$$

$$Q = \frac{[Co^{2+}][Ce^{3+}]^2}{[Ce^{4+}]^2}$$

$$= \frac{-8.314(298.15)}{2(96485)} \ln \frac{(.10)(.010)^2}{(.015)^2}$$

$$\boxed{E - E^0 = .039995 V}$$

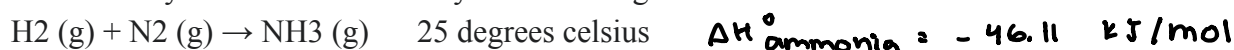
2. What would increase the pH of the following buffer solution which contains the conjugate acid/base pair:  $CH_3COOH/CH_3COO^-$

- ☒ (a) Add  $NaCH_3COO^-$
- ☒ (b) Remove  $NaCH_3COO^-$
- ☒ (c) Add  $CH_3COOH$
- ☒ (d) Add  $OH^-$
- ☒ (e) Add  $H^+$

buffer.. any addition of acid/base will be neutralized bc the conjugate acid/base is present and they are weak



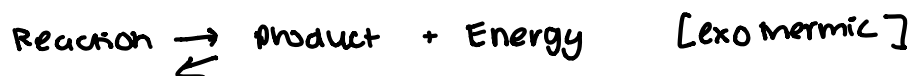
Ammonia Synthesis is described by the following unbalanced reaction



3a. Is this reaction exothermic or endothermic?

Exothermic process

3b. Do you expect the K value to increase or decrease with an increase in temperature?



$$K = \frac{[\text{product}]}{[\text{reactant}]}$$

↑ temp is same as  
 "adding energy"

↑ temp causes less product to form, so lower K value



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$$\Delta H_{\text{NH}_3} = (-46.11 \text{ kJ/mol}) \cdot 2 = -92.22 \text{ kJ}$$

3c. What is the  $\Delta H_{\text{rxn}}^\circ$ ?  $\Delta H_{\text{rxn}}^\circ = \Delta H_{\text{NH}_3}^\circ - \Delta H_{\text{N}_2}^\circ - \Delta H_{\text{H}_2}^\circ$

$$-92.22 \text{ kJ} - 0 - 0$$

$$\Delta H_{\text{rxn}}^\circ = -92.22 \text{ kJ}$$

3d. What is the ratio of  $K_1$  to  $K_2$  when you raise the temperature to 425 K?

$$\ln \frac{K_2}{K_1} = \frac{\Delta H_{\text{rxn}}^\circ}{R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right]$$

$$\ln \frac{K_2}{K_1} = \frac{-92.22 \times 10^3 \text{ J}}{8.314 \text{ J/mol}\cdot\text{K}} \left[ \frac{1}{298 \text{ K}} - \frac{1}{425 \text{ K}} \right]$$

$$\frac{K_2}{K_1} = .000014772$$

$$\frac{K_1}{K_2} = 67696.32$$

3e. Does this mean the reaction yield increased or decreased with the increase in temperature?

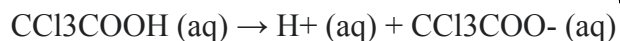
$$\frac{K_1}{K_2} : K_1 \gggg K_2$$

$$K = \frac{[\text{prod}]}{[\text{react}]}$$

product yield decreases  
at high temp

4. [Winter 2019] Trichloroacetic acid is used in cosmetic treatments (such as chemical peels and tattoo removal) and as topical medication for chemoablation of warts. What is the pH of a concentrated stock solution when .500 moles of trichloroacetic acid are dissolved in water and diluted to 1.00 L?

$$[\text{CCl}_3\text{COOH}] = \frac{.500 \text{ mol}}{1.00 \text{ L}} = .500 \text{ M}$$



$K_a = 1.3\text{E}-1$  at 25 degrees Celsius

$$\text{I} \quad .500 \text{ M} \quad 0 \quad 0$$

$$\text{C} \quad -x \quad +x \quad +x$$

$$\text{E} \quad .500 - x \quad (x) \quad (x)$$

$$K_a = \frac{[\text{CCl}_3\text{COO}^-][\text{H}^+]}{[\text{CCl}_3\text{COOH}]}$$

$$1.3 \times 10^{-1} = \frac{(x)(x)}{.500 - x}$$

$$\frac{x^2}{.500 - x} = 1.3 \times 10^{-1}$$

$$x^2 = .065 - 1.3 \times 10^{-1}x$$

$$x^2 + 1.3 \times 10^{-1}x - .065 = 0$$

$$x = \frac{-1.3 \times 10^{-1} \pm \sqrt{(1.3 \times 10^{-1})^2 - 4(1)(-.065)}}{2}$$

$$x = \underline{.198} \quad \text{OR} \quad x = \cancel{-.328}$$

ANSWER:

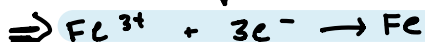
$$[\text{H}^+] = .198 \text{ M}$$

$$\begin{aligned} \text{pH} &= -\log [\text{H}^+] \\ &= -\log (.198) \\ &= \boxed{.703} \end{aligned}$$

5. What is the function of the porous disk?

in a galvanic cell, ions not involved in the rxn [ $\text{Cl}^-$  ions] can pass through the disk to prevent charge buildup

HALF RXN



- [ ① 6.  $\text{Fe}^{3+}(\text{aq}) + \text{e}^- \rightarrow \text{Fe}^{2+}(\text{aq})$   
 ②  $\text{Fe}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Fe}(\text{s})$

$$E^\circ = +.77\text{V}$$

$$E^\circ = -.44\text{V}$$

CANNOT JUST ADD RXNS AND  
 $E^\circ$  BC NOT STATE FUNCTION

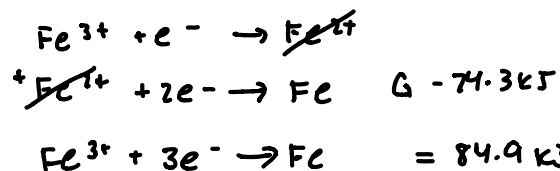
Calculate the standard potential for the reaction above using the reduction potentials given in the table.

Q1 on worksheet:  $E^\circ_{\text{cell}}$  always positive ALL BATTERIES/GALVANIC CELLS

Q6. Half rxn... this rxn  $\text{Fe}^{3+} + 3\text{e}^- \rightarrow \text{Fe}$  is not in battery so can be neg.

$$\begin{aligned} \textcircled{1} \quad \Delta G &= -nFE = -1(96485)(.77) \\ &= -74.3 \text{ kJ} \end{aligned}$$

$$\begin{aligned} \textcircled{2} \quad \Delta G &= -nFE = -2(96485)(-.44\text{V}) \\ &= 84.9 \text{ kJ} \end{aligned}$$



$$\Delta G_{\text{tot}} = 10.6 \times 10^3 \text{ J} = 10.6 \text{ kJ}$$

$$E = -\frac{\Delta G}{nF} = -\frac{10.6 \times 10^3 \text{ J}}{3(96485)}$$

$$= -0.0366 \text{ V}$$

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$$18.5^{\circ}\text{C} = 291.65 \text{ K}$$

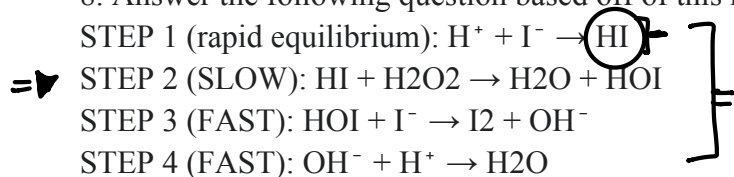
$$28.1^{\circ}\text{C} = 301.25 \text{ K}$$

$$C_v: \text{N}_2 = \text{diatomic ideal gas} : \frac{5}{2} R$$

7. [Midterm W19] During the test of an internal combustion engine, 3.00 L of nitrogen gas (1.00 mol N<sub>2</sub> gas) at 18.5 degrees Celsius compressed suddenly (and irreversibly) to .500 L by driving in a piston. In the process the temperature of the gas increased to 28.1 degrees Celsius. Assume ideal behavior. What is the change in entropy of the gas?

$$\begin{aligned} \Delta S_{\text{tot}} &= \Delta S_{V_1 \rightarrow V_2} + \Delta S_{T_1 \rightarrow T_2} \\ &= nR \ln \frac{V_2}{V_1} + n C_v \ln \frac{T_2}{T_1} \\ &= 1 \text{ mol} \left( 8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}} \right) \ln \left( \frac{.500 \text{ L}}{3.00 \text{ L}} \right) + (1.00 \text{ mol}) \left( \frac{5}{2} \left( 8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}} \right) \right) \ln \left( \frac{301.25}{291.65} \right) \\ &= -14.2 \text{ J/K} \end{aligned}$$

8. Answer the following question based off of this reaction mechanism:



8a. List the intermediate(s) products but consumed right after



8b. What is the molecularity of Step 2? bimolecular

8c. Write the overall reaction



Experimental rate law:  $k [\text{H}^+][\text{I}^-][\text{H}_2\text{O}_2]$

8d. Write the rate law based on the proposed mechanism. pre-equilibrium (rapid step before slow step)

OVERALL RATE LAW WE WANT TO GET  $\Rightarrow \text{rate} = k [\text{H}_2\text{O}_2][\text{H}^+]^2[\text{I}^-]^2$

rate law  
of slow  
step

$$\Rightarrow \text{rate} = k_2 [\text{H}_2\text{O}_2][\text{HI}]$$

FAST  
STEP

Forward rate

$$\Rightarrow \text{rate} = k_1 [\text{H}^\cdot][\text{I}^\cdot]$$

Reverse

$$\text{rate} = k_1' [\text{HI}]$$

$$k_1 [\text{H}^\cdot][\text{I}^\cdot] = k_1' [\text{HI}]$$

$$[\text{HI}] = \frac{k_1}{k_1'} [\text{H}^\cdot][\text{I}^\cdot]$$

$$\text{rate} = k_2 [\text{H}_2\text{O}_2] \left( \frac{k_1}{k_1'} \right) [\text{H}^\cdot][\text{I}^\cdot]$$

$$\underline{\text{rate} = K [\text{H}_2\text{O}_2][\text{H}^\cdot][\text{I}^\cdot]} \Leftarrow$$

PRE-equilibrium

CONDITION: FAST STEP BEFORE SLOW STEP

slow step = rate determining step

① Write the rate law for slow step

② if intermediates are present in answer for ①

then write forward and reverse rate law  
for the fast step before it

③ Equate rate law forward to rate law reverse

④ isolate for intermediate. then substitute back  
into slow step rate law