

## WEEK 14 / FINAL REVIEW KEY

1. Camphor ( $C_{10}H_{16}O$ ) melts at  $179.8^{\circ}C$  and it has a particularly large freezing point depression constant,  $K_f = 40.0^{\circ}C/m$ . When  $0.186\text{ g}$  of an organic substance of unknown molar mass is dissolved in  $22.01\text{ g}$  of liquid camphor, the freezing point of the mixture is found to be  $176.7^{\circ}C$ . What is the molar mass of the solute?

$$\Delta T_f = K_f m \quad m = \frac{\text{mol solute}}{\text{kg solvent}}$$

$$\Delta T = 179.8 - 176.7^{\circ}C$$

$$\Delta T = 3.1^{\circ}C$$

$$m = \frac{0.186\text{ g (1/mm)}}{0.02201\text{ g}}$$

$$3.1^{\circ}C = 40 \frac{^{\circ}C}{m} \left( \frac{0.186\text{ g (1/mm)}}{0.02201\text{ g}} \right)$$

$$1/\text{mm} = 0.00917\text{ mol/g}$$

$$MM = 109\text{ g mol}^{-1}$$

2.

$$\pi = iMRT$$

$$\text{NaCl: } \pi = (2)(0.5 \frac{\text{mol}}{\text{L}})(0.08206 \frac{\text{L atm}}{\text{mol K}})(298\text{ K})$$

$$\pi = 24.5\text{ atm}$$

$$K_2SO_4: \pi = (3)(0.5 \frac{\text{mol}}{\text{L}})(0.08206 \frac{\text{L atm}}{\text{mol K}})(298\text{ K})$$

$$\pi = 36.7\text{ atm}$$

3.

$$\Delta T_f = K_f m$$

$$m = \frac{35.0\text{ g (1/mm)}}{0.350\text{ kg H}_2\text{O}} \quad \text{solve for}$$

$$0.5^{\circ}C = 1.86^{\circ}C/m \left( \frac{35\text{ g (1/mm)}}{0.350\text{ kg}} \right)$$

$$MM = 372\text{ g mol}^{-1}$$

2.

The rate of the reaction,  $\text{HgCl}_2(aq) + \frac{1}{2}\text{C}_2\text{O}_4^{2-}(aq) \rightarrow \text{Cl}^-(aq) + \text{CO}_2(g) + \frac{1}{2}\text{Hg}_2\text{Cl}_2(s)$ , is followed by measuring the number of moles of  $\text{Hg}_2\text{Cl}_2$  that precipitate per liter per second. What is the rate constant and overall rate order?

| $[\text{HgCl}_2]$ | $[\text{C}_2\text{O}_4^{2-}]$ | Initial Rate (mol/L · s) |
|-------------------|-------------------------------|--------------------------|
| 0.10              | 0.10                          | $1.3 \times 10^{-7}$     |
| 0.10              | 0.20                          | $5.2 \times 10^{-7}$     |
| 0.20              | 0.20                          | $1.0 \times 10^{-6}$     |
| 0.20              | 0.10                          | $2.6 \times 10^{-7}$     |

$$\frac{\text{exp 2}}{\text{exp 1}}: \frac{5.2 \times 10^{-7} \text{ M s}^{-1}}{1.3 \times 10^{-7} \text{ M s}^{-1}} = \frac{k(0.10)^m(0.20)^n}{k(0.10)^m(0.10)^n}$$

$$4 = 2^n$$

$\therefore n=2$ ,  $\text{C}_2\text{O}_4^{2-}$  is 2nd order

$$\frac{\text{exp 4}}{\text{exp 1}}: \frac{2.6 \times 10^{-7} \text{ M s}^{-1}}{1.3 \times 10^{-7} \text{ M s}^{-1}} = \frac{k(0.20)^m(0.10)^n}{k(0.10)^m(0.10)^n}$$

$$2 = 2^m$$

$\therefore m=1$ ,  $\text{HgCl}_2$  is 1st order

Overall rate order =  $m+n = 1+2$

Overall rate order = 3

$$\text{rate} = k[\text{HgCl}_2][\text{C}_2\text{O}_4^{2-}]^2$$

$$1.3 \times 10^{-7} \text{ M s}^{-1} = k(0.10 \text{ M})(0.10 \text{ M})^2$$

$$\therefore k = 1.3 \times 10^{-4} \text{ M}^{-2} \text{ s}^{-1}$$

3.

The rate law for the reaction:  $\text{NH}_4^+(aq) + \text{NO}_2^-(aq) \rightarrow \text{N}_2(g) + 2\text{H}_2\text{O}(l)$  is given by  $\text{rate} = k[\text{NH}_4^+][\text{NO}_2^-]$ . At  $25^\circ\text{C}$ , the rate constant is  $3.0 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$ . Calculate the rate of reaction at this temperature if  $[\text{NH}_4^+] = 0.36 \text{ M}$  and  $[\text{NO}_2^-] = 0.075 \text{ M}$ . What is the rate of  $\text{H}_2\text{O}$  production?

$$\text{rate} = k[\text{NH}_4^+][\text{NO}_2^-]$$

$$= 3.0 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1} (0.36 \text{ M})(0.075 \text{ M})$$

$$\text{rate} = 8.1 \times 10^{-6} \text{ M s}^{-1}$$

$$\text{rate} = \Delta[\text{H}_2\text{O}] / \Delta t$$

$$\frac{\Delta[\text{H}_2\text{O}]}{\Delta t} = 1.6 \times 10^{-5} \text{ M s}^{-1}$$

4.

Sulfuryl chloride undergoes ~~first order~~ decomposition at 320°C with a half-life of 8.75 hrs.



What is the value of the rate constant,  $k$ , in  $\text{s}^{-1}$  if the initial pressure of  $\text{SO}_2\text{Cl}_2$  is 791 torr and the decomposition occurs in a 1.25 L container, and ~~how many~~ ~~molecules~~ of  $\text{SO}_2\text{Cl}_2$  remain after 12.5 hours? (1 atm = 760 torr,  $R = 0.08206 \text{ L}\cdot\text{atm}/\text{mol}\cdot\text{K}$ )

$$PV = nRT \quad \therefore \frac{n}{V} = \frac{P}{RT}$$

$$\frac{n}{V} = \frac{791 \text{ torr} \left( \frac{1 \text{ atm}}{760 \text{ torr}} \right)}{0.08206 \left( \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}} \right) \cdot 593.15 \text{ K}} = 0.02138 \text{ M} = [\text{SO}_2\text{Cl}_2]_0$$

$$t_{1/2} = \frac{\ln(2)}{k} \quad \therefore k = \frac{\ln(2)}{t_{1/2}}$$

$$k = \frac{\ln(2)}{8.75 \text{ hr}} = 0.07922 \text{ hr}^{-1} \left( \frac{1 \text{ hr}}{60 \text{ min}} \right) \left( \frac{1 \text{ min}}{60 \text{ s}} \right)$$

$$k = 2.20 \times 10^{-5} \text{ s}^{-1}$$

$$\ln[\text{SO}_2\text{Cl}_2]_t = -kt + \ln[\text{SO}_2\text{Cl}_2]_0$$

$$\ln[\text{SO}_2\text{Cl}_2] = -(0.07922 \text{ hr}^{-1})(12.5 \text{ hr}) + \ln(0.02138 \text{ M})$$

$$\ln[\text{SO}_2\text{Cl}_2] = -4.8355$$

$$[\text{SO}_2\text{Cl}_2] = 0.007942 \text{ M} (1.25 \text{ L}) \left( \frac{0.022 \times 10^{23} \text{ molecules}}{\text{mol}} \right)$$

$$= 5.98 \times 10^{21} \text{ molecules SO}_2\text{Cl}_2$$

5. For a reaction  $A \rightarrow B$ , successive half-lives are observed to be 10.0, 20.0, and 40.0 min for an experiment in which  $[A]_0 = 0.10 \text{ M}$ . Calculate the concentration of A at 80.0 minutes and at 30.0 minutes.

\* longer half-lives = second order reaction

$$t_{1/2} = 1/[A]_0 k \quad \therefore k = 1/t_{1/2} [A]_0$$

$$k = 1/0.10 \text{ M} (10 \text{ min})$$

$$\therefore k = 1 \text{ M}^{-1} \text{ min}^{-1}$$

30 minutes:  $1/[A]_t = kt + 1/[A]_0$

$$1/[A]_t = 1 \text{ M}^{-1} \text{ min}^{-1} (30 \text{ min}) + 1/.10 \text{ M}$$

$$[A]_t = 0.025 \text{ M}$$

80 minutes:  $1/[A]_t = 1 \text{ M}^{-1} \text{ min}^{-1} (80 \text{ min}) + 1/.10 \text{ M}$

$$[A]_t = 0.011 \text{ M}$$

6. The rate constant for the reaction  $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightarrow 2\text{HI}(\text{g})$  is  $5.4 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$  at  $326^\circ\text{C}$ . At  $410^\circ\text{C}$  the rate constant was found to be  $2.8 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ . Calculate the activation energy and the frequency factor.

$$\ln\left(\frac{k_1}{k_2}\right) = \frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right) \quad \left| \quad \ln\left(\frac{5.4 \times 10^{-4}}{2.8 \times 10^{-2}}\right) = \frac{E_a}{8.314} \left(\frac{1}{683} - \frac{1}{599}\right)\right.$$

$$\ln(0.01929) = \frac{E_a}{8.314} (-2.05 \times 10^{-4})$$

$$-3.948 = -2.47 \times 10^{-5} E_a$$

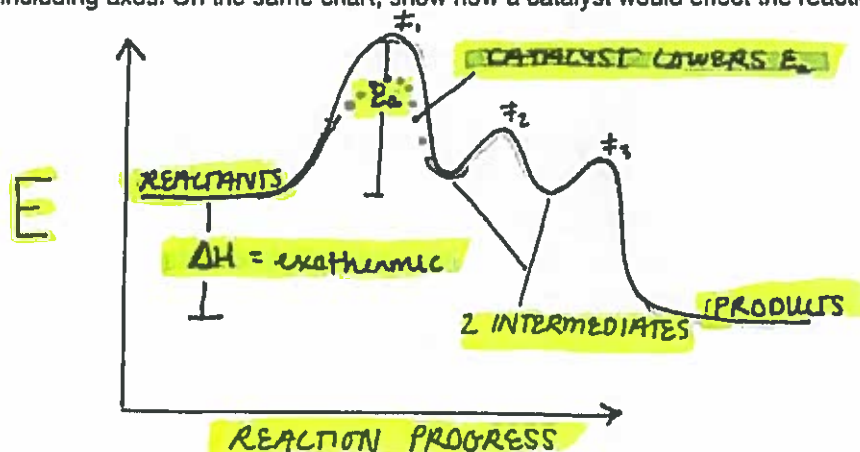
$$\therefore E_a = 159838 \text{ J/mol}$$

$$k = Ae^{-E_a/RT}$$

$$5.4 \times 10^{-4} = Ae^{-(159838/8.314 \cdot 599)}$$

$$\therefore 4.69 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$$

7. Draw an energy profile for a reaction that is overall exothermic, has 2 intermediates, and the first step is the rate determining step. Clearly label all parts of the energy profile, including axes. On the same chart, show how a catalyst would effect the reaction.



8. At 25°C,  $K_p = 5.3 \times 10^5$  for the reaction



When a certain partial pressure of  $\text{NH}_3(\text{g})$  is put into an otherwise empty rigid vessel at 25°C, equilibrium is reached when 50.0% of the original ammonia has decomposed. What was the original partial pressure of ammonia before any decomposition occurred?

$$K_p = \frac{(P_{\text{NH}_3})^2}{(P_{\text{N}_2})(P_{\text{H}_2})^3}$$

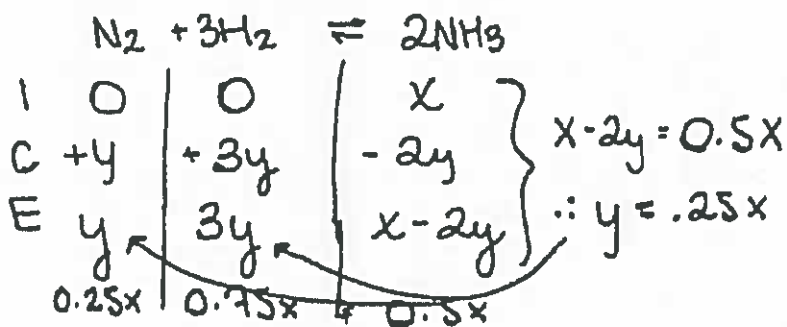
initial pressures:

$$P_{\text{NH}_3} = x$$

$$P_{\text{H}_2} = 0$$

$$P_{\text{N}_2} = 0$$

$\therefore$  reaction proceeds left

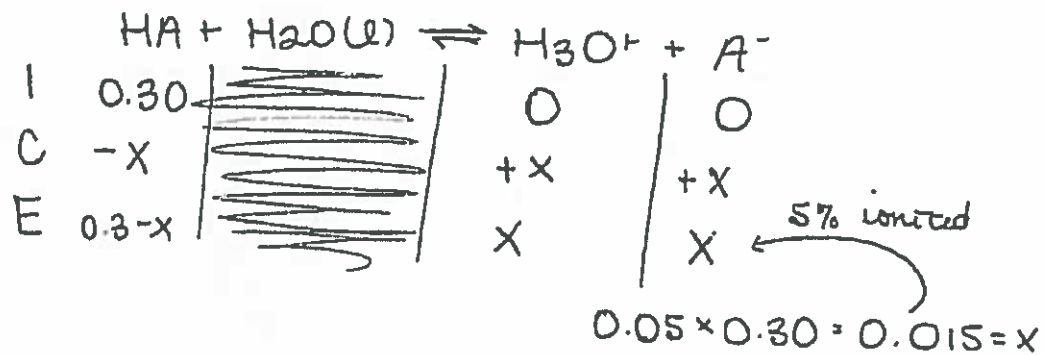


$$5.3 \times 10^5 = \frac{(0.5x)^2}{(0.25x)(0.75x)^3}$$

$$5.3 \times 10^5 = 2.37037/x^2$$

$$\therefore x = 2.1 \times 10^{-3} \text{ atm} = P_{\text{NH}_3}(\text{initial})$$

9. A 0.30 M solution of a weak acid is 5% dissociated; calculate the  $K_a$  of the acid.



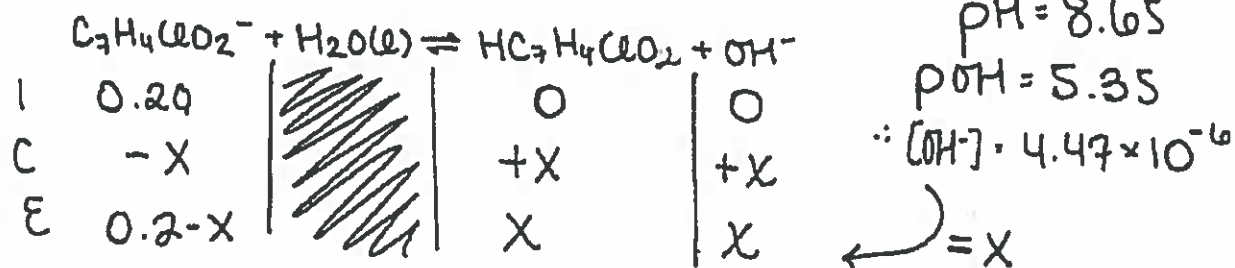
$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} = \frac{x^2}{0.3-x}$$

$$K_a = \frac{(0.015)^2}{(0.3-0.015)} = 7.89 \times 10^{-4}$$

10.

A 0.20 M sodium chlorobenzoate ( $\text{NaC}_7\text{H}_4\text{ClO}_2$ ) solution has a pH of 8.65. Calculate the pH of a 0.20 M chlorobenzoic acid ( $\text{HC}_7\text{H}_4\text{ClO}_2$ ) solution.

PART 1 - find  $K_a$  of  $\text{HC}_7\text{H}_4\text{ClO}_2$

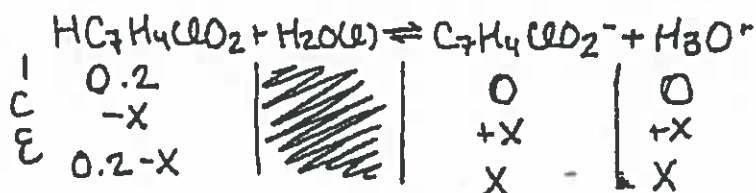


$$K_b = \frac{[\text{HC}_7\text{H}_4\text{ClO}_2][\text{OH}^-]}{[\text{C}_7\text{H}_4\text{ClO}_2^-]}$$

$$K_b = \frac{(4.47 \times 10^{-6})^2}{(0.2 - 4.47 \times 10^{-6})} = 9.99 \times 10^{-11}$$

$$K_a = \frac{K_w}{K_b} = \frac{1 \times 10^{-14}}{9.99 \times 10^{-11}} = 1.0 \times 10^{-4}$$

PART 2 - pH of  $\text{HC}_7\text{H}_4\text{ClO}_2$  solution



$$K_a = \frac{[\text{C}_7\text{H}_4\text{ClO}_2^-][\text{H}_3\text{O}^+]}{[\text{HC}_7\text{H}_4\text{ClO}_2]}$$

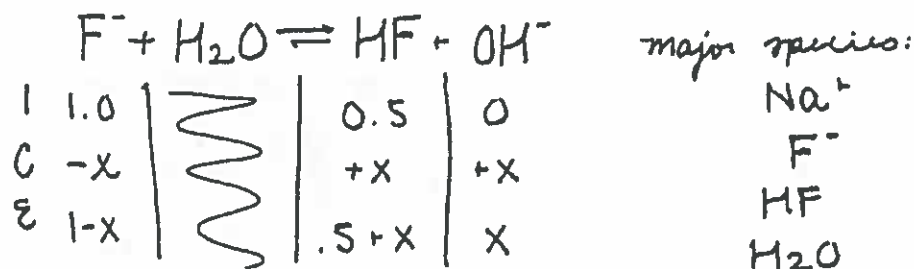
$$1 \times 10^{-4} = \frac{X^2}{0.2-X} \rightarrow \text{assume negligible}$$

$$\frac{5\% \text{ test}}{0.00447}{0.2} \times 100 = 2.2\% \quad \checkmark \checkmark \checkmark$$

$$X = [\text{H}_3\text{O}^+] = 0.00447 \text{ M}$$

$$\therefore \text{pH} = 2.35$$

- 11 2. When 1.00 mole of NaF is added to a 1 liter 0.5 M HF solution, what is the pH of the solution after equilibrium is established? Assume no change in volume.



\* when you have a buffer (aka acid/base AND conjugate), you can always write the  $K_a$  or  $K_b$  expression

$$K_b = \frac{[HF][OH^-]}{[F^-]}$$

$$1.39 \times 10^{-11} = \frac{x(0.5+x)}{(1-x)} \quad \text{assume } x \text{ is negligible}$$

$$x = [OH^-] = 2.78 \times 10^{-11}$$

$$pOH = 10.56$$

$$\therefore pH = 3.44$$

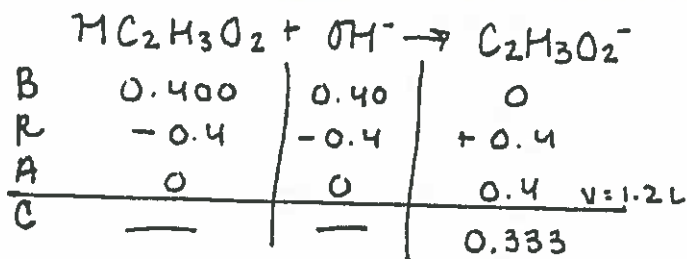
12. 3. What is the pH at the halfway point of titrating 200 mL of 2.0 M acetic acid with 0.4 M NaOH? How many mL of NaOH are necessary to reach the equivalence point and what is the pH?

@ halfway point  $pH = pK_a \therefore pH = 4.74$

equivalence point: moles acid = moles base

$$\text{moles acid} = 0.4 \text{ mol } HC_2H_3O_2$$

$\Rightarrow$  need to add 1.0 L (1000 mL) NaOH



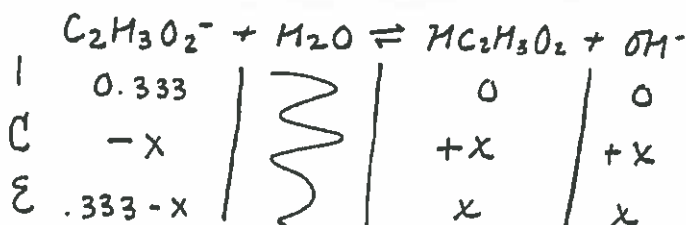
$$K_b = \frac{[HC_2H_3O_2][OH^-]}{[C_2H_3O_2^-]}$$

$$5.56 \times 10^{-10} = \frac{x^2}{0.333 - x}$$

$$x = [OH^-] = 1.36 \times 10^{-5}$$

$$pOH = 4.86$$

$$\therefore pH = 9.14$$



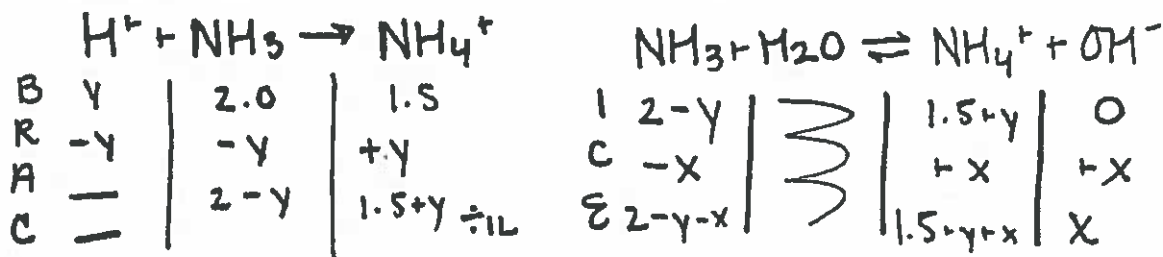
assume negligible

$$\frac{1.36 \times 10^{-5}}{0.333} \times 100 \text{ } \checkmark \checkmark \checkmark \text{ } \text{passes}$$



13. You have a 1.0 L buffered solution of 2.0 M ammonia ( $\text{NH}_3$ ) and 1.5 M ammonium chloride. How many ~~moles~~ HCl would you have to add to shift the pH to 8.0?

\* added HCl will react with  $\text{NH}_3$  in soln.



$$\text{pH} = 8.0 \therefore [\text{OH}^-] = 1 \times 10^{-6}$$

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$$

$$1.8 \times 10^{-5} = \frac{X(1.5 + Y + X)}{(2 - Y - X)}$$

assume negligible

$$1.8 \times 10^{-5} = 1 \times 10^{-6} \left( \frac{1.5 + Y}{2 - Y} \right)$$

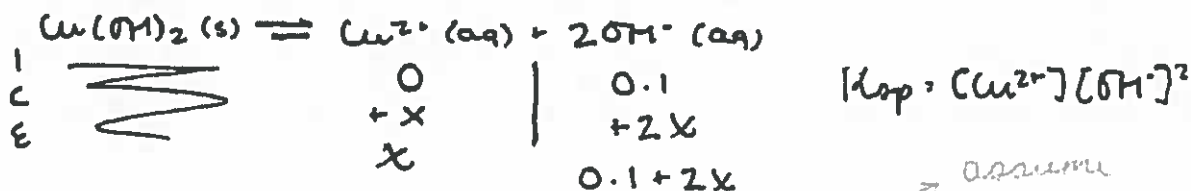
$$18 = 1.5 + Y / 2 - Y$$

$$36 - 18Y = 1.5 + Y$$

$$Y = 1.82 \text{ moles HCl}$$

14. You dissolve  $\text{Cu}(\text{OH})_2$  in each of the following aqueous solutions. What is the molar solubility in each?

a. Solution buffered at pH 13  $[\text{OH}^-] = 0.1 \text{ M}$

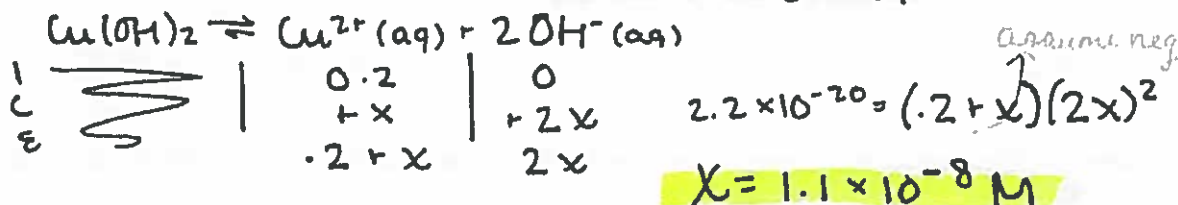


b. 0.2M copper (II) chloride

$$2.2 \times 10^{-20} = X(0.1 + 2X)^2$$

$$X = 2.2 \times 10^{-18} \text{ M}$$

assume negligible  
 $\frac{2X}{0.1} \times 100 \%$



14. 8 What is  $\Delta G^\circ$  for the reaction below at  $25^\circ\text{C}$ ?



15.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\Delta H^\circ = \left[ 3\text{mol}(-92.23 \frac{\text{kJ}}{\text{mol}}) + 1\text{mol}(-95.52 \frac{\text{kJ}}{\text{mol}}) + 1\text{mol}(-83.68 \frac{\text{kJ}}{\text{mol}}) \right] - \left[ 2\text{mol}(-74.85 \frac{\text{kJ}}{\text{mol}}) + 3\text{mol}(0) \right]$$

$$\Delta H^\circ = -306.19 \text{ kJ}$$

$$\Delta S^\circ = \left[ 3\text{mol}(187 \frac{\text{J}}{\text{mol}\cdot\text{K}}) + 1\text{mol}(270.28 \frac{\text{J}}{\text{mol}\cdot\text{K}}) + 1\text{mol}(234.36 \frac{\text{J}}{\text{mol}\cdot\text{K}}) \right] - \left[ 2\text{mol}(186.2 \frac{\text{J}}{\text{mol}\cdot\text{K}}) + 3\text{mol}(223 \frac{\text{J}}{\text{mol}\cdot\text{K}}) \right]$$

$$\Delta S^\circ = 24.24 \text{ J/K} = 0.02424 \text{ kJ/K}$$

$$\Delta G^\circ = -306.19 \text{ kJ} - 298.15 \text{ K}(0.02424 \text{ kJ/K})$$

$$\Delta G^\circ = -313.4 \text{ kJ}$$

16.

15. 4 Consider the following reaction:



$$\Delta G^\circ_{\text{rxn}} = 35.4 \text{ kJ/mol}$$

Calculate  $\Delta G$  at  $25^\circ\text{C}$  for the reaction if the partial pressures of the initial mixture are

$$P_{\text{PCl}_5} = 0.0029 \text{ atm}, P_{\text{PCl}_3} = 0.27 \text{ atm}, \text{ and } P_{\text{Cl}_2} = 0.40 \text{ atm}.$$

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

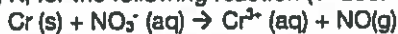
$$Q = \frac{P_{\text{Cl}_2} P_{\text{PCl}_3}}{P_{\text{PCl}_5}} = \frac{(0.40 \text{ atm})(0.27 \text{ atm})}{(0.0029 \text{ atm})} = 37.24$$

$$\Delta G = 35.4 \frac{\text{kJ}}{\text{mol}} + 8.314 \frac{\text{J}}{\text{mol}\cdot\text{K}} \left( \frac{1 \text{ kJ}}{1000 \text{ J}} \right) (298.15 \text{ K}) \ln(37.24)$$

$$\Delta G = 44.37 \text{ kJ mol}^{-1}$$

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15. 6 Calculate the eq. constant,  $K$ , for the following reaction ( $T=298\text{K}$ , acidic conditions):



$$n=3 \quad \left\{ \begin{array}{l} \text{oxidation: } \text{Cr} \rightarrow \text{Cr}^{3+} + 3e^- \quad E_{\text{ox}} = 0.73 \text{ V} \\ \text{reduction: } \text{NO}_3^- + 3e^- \rightarrow \text{NO} \quad E_{\text{red}} = 0.96 \text{ V} \end{array} \right.$$

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

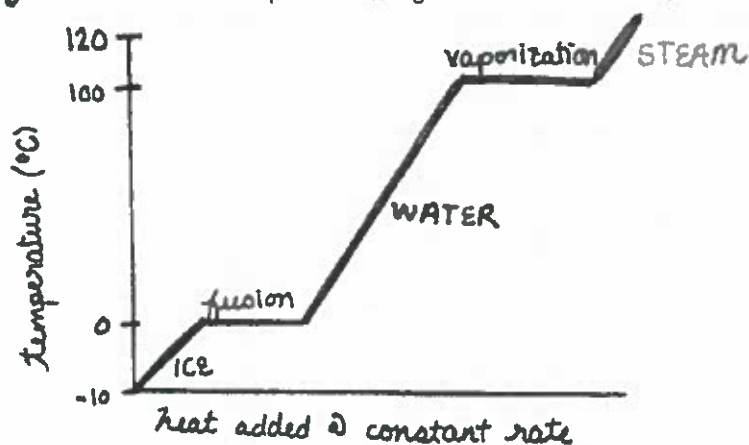
$$= -3(96485 \text{ J/V}\cdot\text{mol})(0.73 \text{ V} + 0.96 \text{ V})$$

$$\Delta G = -489179 \text{ J} = -RT \ln K$$

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

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

18. § How much heat is required to change 0.50 mol of ice at  $-10.0^{\circ}\text{C}$  into 0.5 mol of steam at  $120^{\circ}\text{C}$ ?



$$q_{\text{H}_2\text{O(s)}, -10^{\circ}\text{C} \rightarrow 0^{\circ}\text{C}} = 0.5 \text{ mol} \left( \frac{18.016 \text{ g}}{\text{mol}} \right) \left( \frac{2.03 \text{ J}}{\text{g} \cdot ^{\circ}\text{C}} \right) (0 - -10^{\circ}\text{C})$$

$$= 182.86 \text{ J to heat ice from } -10^{\circ}\text{C to } 0^{\circ}\text{C}$$

$$q_{\text{fusion}} = 0.5 \text{ mol} \left( \frac{6010 \text{ J}}{\text{mol}} \right) = 3010 \text{ J to melt ice to water}$$

$$q_{\text{H}_2\text{O(l)}, 0^{\circ}\text{C} \rightarrow 100^{\circ}\text{C}} = 0.5 \text{ mol} \left( \frac{18.016 \text{ g}}{\text{mol}} \right) \left( \frac{4.18 \text{ J}}{\text{g} \cdot ^{\circ}\text{C}} \right) (100^{\circ}\text{C} - 0^{\circ}\text{C})$$

$$= 3765.3 \text{ J to heat water to } 100^{\circ}\text{C}$$

$$q_{\text{vaporization}} = 0.5 \text{ mol} \left( \frac{40790 \text{ J}}{\text{mol}} \right) = 20395 \text{ J to turn water to steam}$$

$$q_{\text{H}_2\text{O(g)}, 100^{\circ}\text{C} \rightarrow 120^{\circ}\text{C}} = 0.5 \text{ mol} \left( \frac{18.016 \text{ g}}{\text{mol}} \right) \left( \frac{1.99 \text{ J}}{\text{g} \cdot ^{\circ}\text{C}} \right) (120^{\circ}\text{C} - 100^{\circ}\text{C})$$

$$= 358.52 \text{ J to heat steam to } 120^{\circ}\text{C}$$

$$q_{\text{TOTAL}} = 27.7 \text{ kJ}$$