

- 1) A 35.0-g sample of ethylene glycol, $\text{HOCH}_2\text{CH}_2\text{OH}$, is dissolved in 500.0 g of water. The vapor pressure of water at 32°C is 35.7 mm Hg. What is the vapor pressure of the water-ethylene glycol solution at 32°C ? (Ethylene glycol is nonvolatile.) (1 atm = 1.01325 bar)

$$\text{Moles } \text{HOCH}_2\text{CH}_2\text{OH} = 35.0\text{g} \times \frac{1 \text{ mol}}{62.07 \text{ g}} = .564 \text{ mol}$$

$$\text{Moles } \text{H}_2\text{O} = 500 \text{ g} \times \frac{1 \text{ mol}}{18.016 \text{ g}} = 27.8 \text{ mol}$$

$$X_{\text{H}_2\text{O}} = \frac{27.8 \text{ mol}}{27.8 \text{ mol} + .564 \text{ mol}} = 0.980$$

$$P = X_{\text{H}_2\text{O}} P^\circ = (0.980)(35.7 \text{ mm Hg}) = \boxed{35.0 \text{ mm Hg}}$$

- 2) An aqueous solution contains 3.00% phenylalanine ($\text{C}_9\text{H}_{11}\text{NO}_2$) by mass. (Phenylalanine is nonionic and nonvolatile.) Find the following:

- (a) the freezing point of the solution $K_{fp} = -1.86^\circ\text{C}/m$

Assume 100.0 g solution: 3.00 g $\text{C}_9\text{H}_{11}\text{NO}_2$ and 97.0 g H_2O

$$\text{Moles } \text{C}_9\text{H}_{11}\text{NO}_2 = 3.00\text{g} \times \frac{1 \text{ mol}}{165.19 \text{ g}} = .0182 \text{ mol}$$

$$\text{Molality } \text{C}_9\text{H}_{11}\text{NO}_2 = \frac{.0182 \text{ mol}}{.0970 \text{ kg}} = .188 \text{ m}$$

$$\Delta T_{fp} = K_{fp} m = (-1.86^\circ\text{C}/m)(.188 \text{ m}) = -0.349^\circ\text{C}$$

$$T_{fp} = \overset{\text{Exact}}{\downarrow} 0^\circ\text{C} - 0.349^\circ\text{C} = \boxed{-0.349^\circ\text{C}}$$

- (b) the boiling point of the solution $K_{bp} = 0.5121^\circ\text{C}/m$

Use molality calculated above

$$\Delta T_{bp} = K_{bp} m = (0.5121^\circ\text{C}/m)(.188 \text{ m}) = .0963^\circ\text{C}$$

$$T_{bp} = \overset{\text{Exact}}{\downarrow} 100^\circ\text{C} + .0963^\circ\text{C} = \boxed{100.0963^\circ\text{C}}$$

- (c) the osmotic pressure of the solution at 25°C $P = 1.0\text{g}/1\text{mL}$

$$V = 100.0\text{g} \times \frac{1\text{mL}}{1.0\text{g}} \times \frac{1\text{L}}{1000\text{mL}} = .100 \text{ L}$$

$$\text{Molarity } \text{C}_9\text{H}_{11}\text{NO}_2 = \frac{.0182 \text{ mol}}{.100 \text{ L}} = .182 \text{ M}$$

$$\Pi = MRT = .182 \text{ M} \times \left(0.08206 \frac{\text{L-atm}}{\text{mol-K}}\right) (298 \text{ K})$$

$$= \boxed{4.45 \text{ atm}}$$

- 3) An aqueous solution contains 0.180 g of an unknown, nonionic solute in 50.0 g of water. The solution freezes at -0.040°C . What is the molar mass of the solute? $K_{fp} = -1.86^{\circ}\text{C/m}$

$$\text{Moles of unknown} = \frac{0.180\text{g}}{\text{MM}}$$

$$\text{Molality of unknown} = \frac{0.180\text{g}}{\text{MM} \times 0.0500\text{kg}} = \frac{3.60}{\text{MM}}$$

$$\Delta T_{fp} = K_{fp} m$$

$$-0.040^{\circ}\text{C} = (-1.86^{\circ}\text{C/m}) (3.6/\text{MM})$$

$$0.0597 = \frac{1}{\text{MM}}$$

$$\text{MM} = 167 \text{ g/mol}$$

- 4) List the following aqueous solutions in order of increasing melting point.

- (a) 0.1 m sugar (b) 0.1 m NaCl
(c) 0.08 m CaCl_2 (d) 0.04 m Na_2SO_4

$$\text{a) } 0.1 \text{ m} \times 1 = 0.1 \text{ m}$$

$$\text{b) } 0.1 \text{ m} \times 2 = 0.2 \text{ m}$$

$$\text{c) } 0.08 \text{ m} \times 3 = 0.24 \text{ m}$$

$$\text{d) } 0.04 \text{ m} \times 3 = 0.12 \text{ m}$$

$$c < b < d < a$$

- 5) Data for the reaction $\text{NO(g)} + \frac{1}{2}\text{O}_2\text{(g)} \rightarrow \text{NO}_2\text{(g)}$ are given (for a particular temperature) in the table.

Experiment	Concentration (mol/L)		Initial Rate (mol NO / (L*h))
	[NO]	[O ₂]	
1	3.6×10^{-4}	5.2×10^{-3}	3.4×10^{-8}
2	3.6×10^{-4}	1.04×10^{-2}	6.8×10^{-8}
3	1.8×10^{-4}	1.04×10^{-2}	1.7×10^{-8}
4	1.8×10^{-4}	5.2×10^{-3}	?

- (a) What is the rate law for this reaction?

To determine order of NO, compare exp. # 2 and 3.

When [O₂] is held constant and [NO] doubles (3 to 2), the rate quadruples. Therefore the order is 2 for NO.

To determine order of O₂, compare exp. # 1 and 2.

When [NO] is held constant and [O₂] doubles (1 to 2), the rate also doubles. Therefore the order is 1 for O₂.

$$\text{Rate} = k [\text{NO}]^2 [\text{O}_2]$$

(b) What is the rate constant for the reaction?

$$\text{Rate} = k [\text{NO}]^2 [\text{O}_2]$$

Using Experiment #1

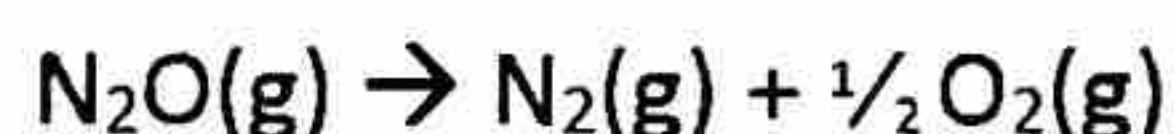
$$3.4 \times 10^{-8} \text{ M/h} = k (3.6 \times 10^{-4} \text{ M})^2 (5.2 \times 10^{-3} \text{ M})$$

$$k = 50 \text{ M}^{-2}/\text{h}$$

(c) What is the initial rate of the reaction in experiment 4?

$$\begin{aligned} \text{Rate} &= 50 \text{ M}^{-2}/\text{h} [\text{NO}]^2 [\text{O}_2] \\ &= 50 \text{ M}^{-2}/\text{h} (1.8 \times 10^{-4} \text{ M})^2 (5.2 \times 10^{-3} \text{ M}) \\ &= 8.4 \times 10^{-9} \text{ mol NO/L} \cdot \text{h} \end{aligned}$$

6) Data for the decomposition of dinitrogen monoxide:



on a gold surface at 900 °C are given below. Determine the order of the reaction and the rate constant. Using the rate law and value of k , determine the decomposition rate at 900 °C when $[\text{N}_2\text{O}] = 0.035 \text{ mol/L}$.

Time (min)	$[\text{N}_2\text{O}] \text{ (mol/L)}$	Zero	First $\ln [\text{N}_2\text{O}]$	Second $1/[\text{N}_2\text{O}]$
15.0	0.0835		-2.483	12.0
30.0	0.0680		-2.688	14.7
80.0	0.0350		-3.352	28.6
120.0	0.0220		-3.817	45.5

Only the first order graph ($\ln [\text{N}_2\text{O}]$ vs. Time(min)) will have a straight line, therefore the reaction is first order.

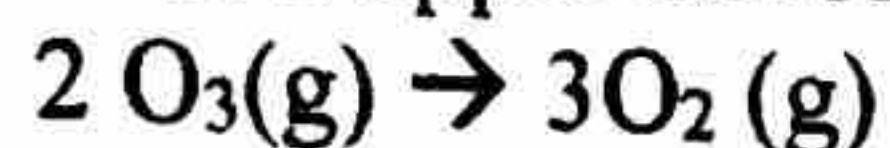
$$\text{rate} = k [\text{N}_2\text{O}]$$

$$\text{slope} = \frac{\text{rise}}{\text{run}} = \frac{(-3.817 - -2.483)}{(120.0 - 15.0)} = -0.0127$$

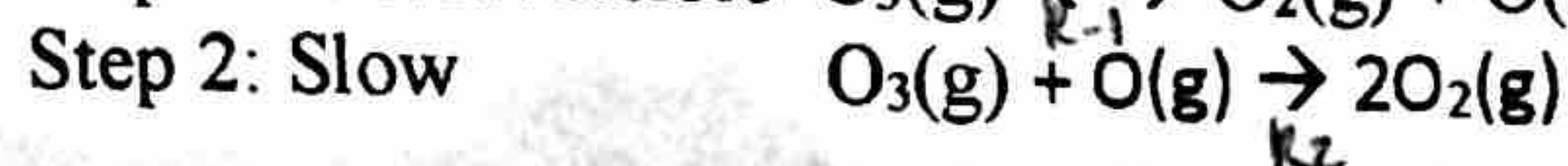
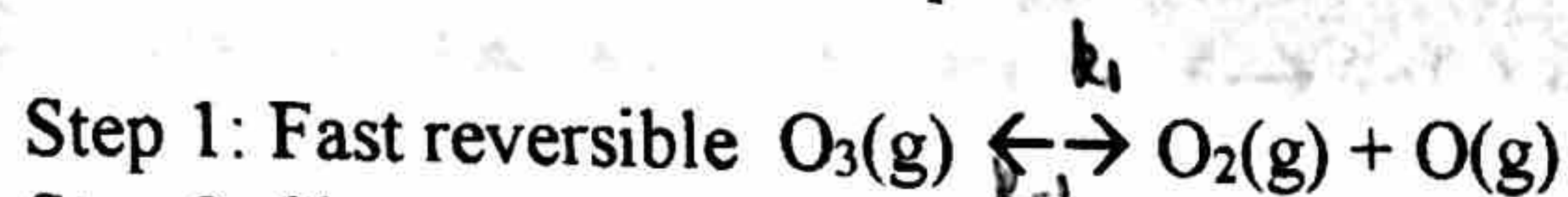
$$k = |-0.0127| = 0.0127 \text{ min}^{-1}$$

$$\begin{aligned} \text{rate} &= 0.0127 \text{ min}^{-1} [\text{N}_2\text{O}] \\ &= 0.0127 \text{ min}^{-1} (0.035 \text{ mol/L}) \\ &= 4.4 \times 10^{-4} \text{ M/min} \end{aligned}$$

7) Ozone, O_3 , in the Earth's upper atmosphere decomposes according to the equation:



The mechanism of the reaction is thought to proceed through an initial fast, reversible step, followed by a slow, second step.



(a) Which of the steps is rate-determining?

Step 2

(b) Write the rate equation for the rate-determining step.

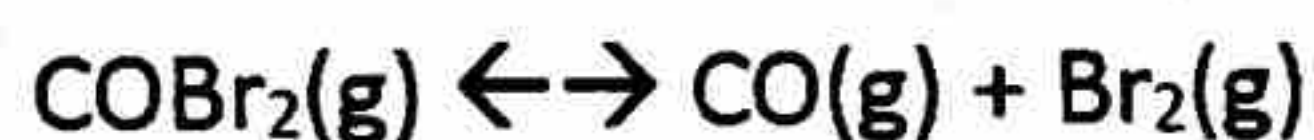
$$\text{Rate} = k_2 [O_3] [O]$$

O is not in the overall reaction and must be removed.

$$\frac{k_1}{k_{-1}} = \frac{[O_2][O]}{[O_3]} \quad [O] = \frac{k_1}{k_{-1}} \frac{[O_3]}{[O_2]}$$

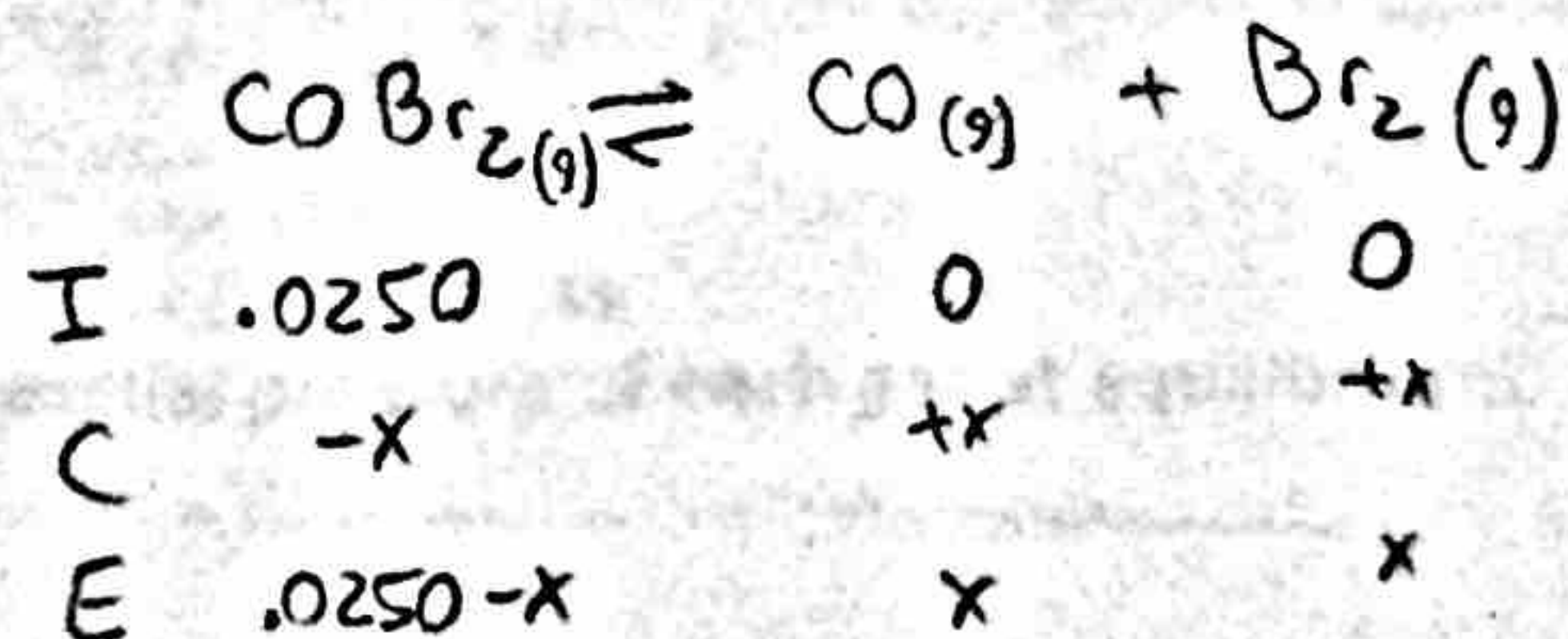
$$\text{Rate} = k_2 [O_3] \frac{k_1}{k_{-1}} \frac{[O_3]}{[O_2]} = \boxed{k \frac{[O_3]^2}{[O_2]}}$$

8) Carbonyl bromide decomposes to carbon monoxide and bromine:



K_c is 0.190 at 73 °C. If you place 0.0500 mol of $COBr_2$ in a 2.00-L flask and heat it to 73 °C, what are the equilibrium concentrations of $COBr_2$, CO , and Br_2 ? What percentage of the original $COBr_2$ decomposed at this temperature?

$$[COBr_2]_i = 0.0500 \text{ mol} / 2.00 \text{ L} = 0.0250 \text{ M}$$



$$K_c = \frac{[CO][Br_2]}{[COBr_2]}$$

$$0.190 = \frac{x^2}{0.0250 - x}$$

$$(0.0250 - x)(0.190) = x^2$$

$$x^2 + 0.190x - 0.00475 = 0$$

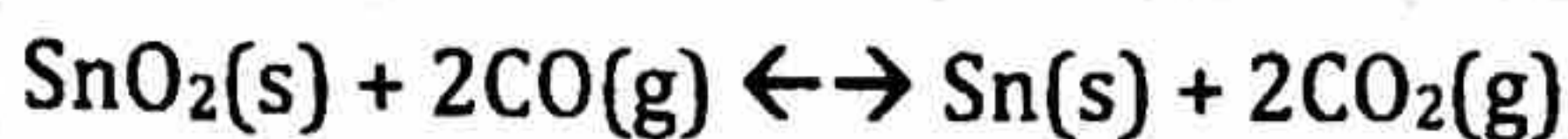
$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = 0.0224$$

$$[COBr_2] = 0.0250 - 0.0224 = 0.0026 \text{ M}$$

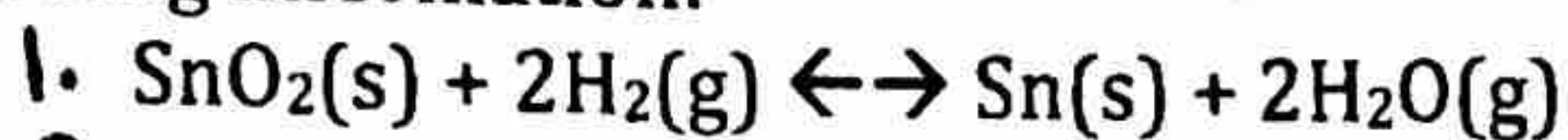
$$[CO] = [Br_2] = 0.0224 \text{ M}$$

$$\% COBr_2 \text{ decomposed} = \frac{0.0224}{0.0250} \times 100 = 89.6\%$$

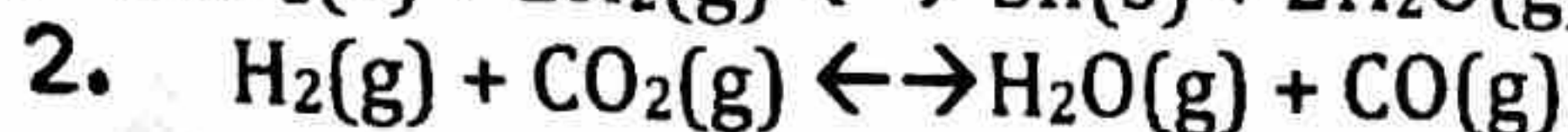
9) Calculate K for the reaction



given the following information:



$$K_1 = 8.12$$



$$K_2 = 0.771$$

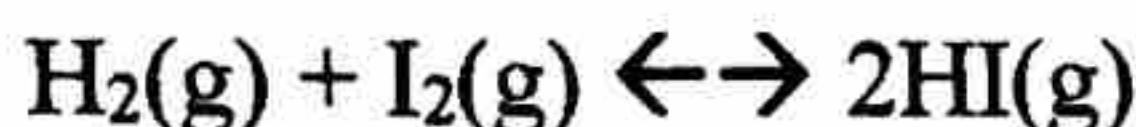
Equation 1 is fine as is.

Equation 2 needs to be reversed and doubled

Reversed: Invert K (K)
Doubled: Square K (K²)
Reversed and doubled: (K⁻²)

$$K = K_1 \times \frac{1}{K_2^2} = 8.12 \times \frac{1}{(0.771)^2} = \boxed{13.7}$$

10) The reaction of hydrogen and iodine to give hydrogen iodide has an equilibrium constant, K_c , of 56 at 435 °C.



(a) What is the value of K_p ?

only gases $\rightarrow \Delta n = 2 - 2 = 0$

$$K_p = K_c (RT)^{\Delta n} = 56 (RT)^0 = \boxed{56}$$

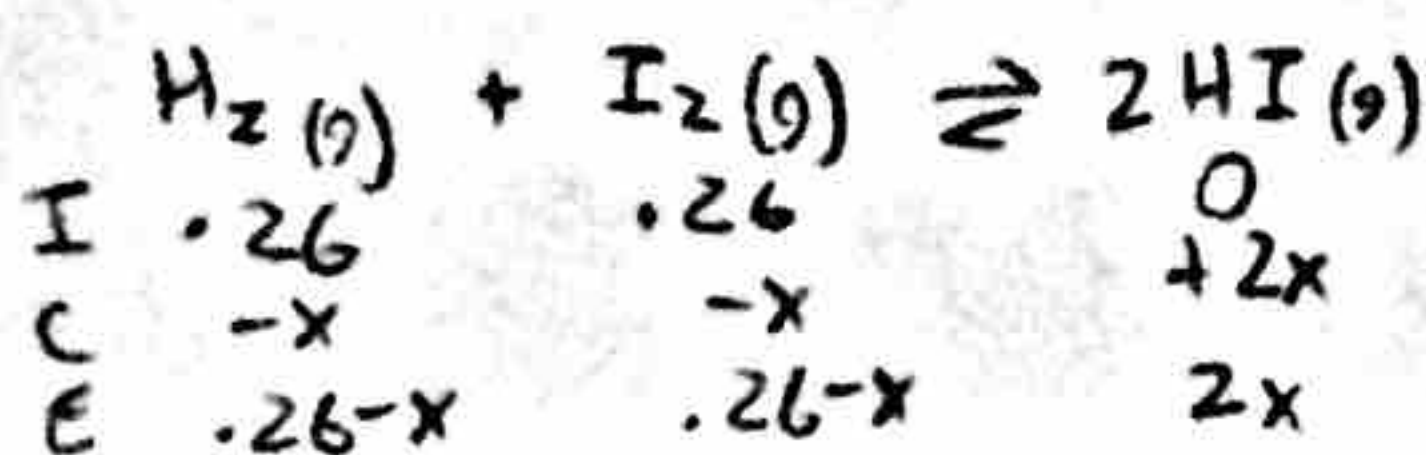
(b) Suppose you mix 0.045 mol of H_2 and 0.045 mol of I_2 in a 10.0-L flask at 425 °C. What is the total pressure of the mixture before and after equilibrium is achieved?

$$PV = nRT$$

$$T = 425^\circ\text{C} + 273 \text{ K} = 698 \text{ K}$$

$$P_i = \frac{nRT}{V} = \frac{(0.045 \text{ mol} + 0.045 \text{ mol}) (0.082057 \text{ L-atm/K-mol}) (698 \text{ K})}{10.0 \text{ L}} = \boxed{.52 \text{ atm}}$$

$$P_{\text{H}_2} = P_{\text{I}_2} = \frac{.52}{2} = .26 \text{ atm}$$



$$\sqrt{56} = \frac{(2x)^2}{(.26-x)^2}$$

$$7.48 = \frac{2x}{.26-x} \quad x = .21$$

$$P_f = 2(.26-x) + 2x = 2(.26 - .21) + 2(.21)$$

$$P_f = \boxed{.52 \text{ atm}}$$

(c) What is the partial pressure of each gas at equilibrium?

$$P_{\text{H}_2} = P_{\text{I}_2} = .26 - .21 = .05 \text{ atm}$$

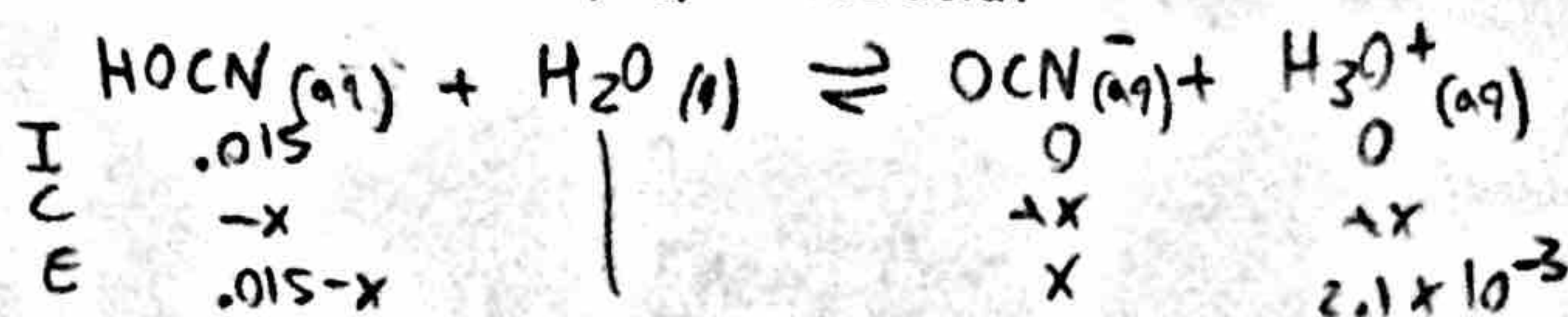
$$P_{\text{HI}} = 2(.21) = .42 \text{ atm}$$

Total pressure remained the same because same number of moles of gas on each side.

- 11) A 0.015M solution of hydrogen cyanate, HOCN, has a pH of 2.67.
 (a) What is the hydronium ion concentration in the solution?

$$[H_3O^+] = 10^{-2.67} = 2.1 \times 10^{-3} M$$

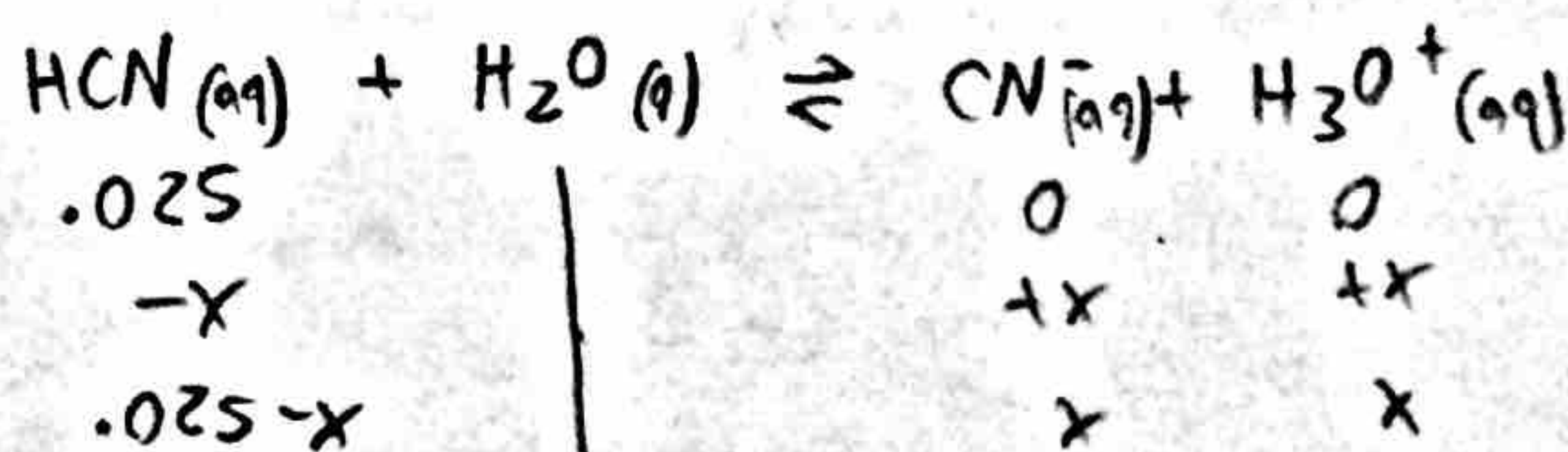
- (b) What is the ionization constant, K_a , for the acid?



$$x = 2.1 \times 10^{-3}$$

$$K_a = \frac{[OCN^-][H_3O^+]}{[HOCN]} = \frac{[2.1 \times 10^{-3}]^2}{(.015 - 2.1 \times 10^{-3})} = \boxed{3.5 \times 10^{-4}}$$

- 12) What are the equilibrium concentrations of H_3O^+ , CN^- , and HCN in a 0.025 M solution of HCN? What is the pH of the solution? (HCN $K_a = 4.0 \times 10^{-10}$)



$$K_a = \frac{[CN^-][H_3O^+]}{[HCN]}$$

$$4.0 \times 10^{-10} = \frac{x^2}{.025-x}$$

$$x = 3.2 \times 10^{-6}$$

$$[CN^-] = [H_3O^+] = 3.2 \times 10^{-6} M$$

$$[HCN] = .025 M$$

$$pH = -\log [H_3O^+] = 5.50$$

- 13) Sodium cyanide is the salt of the weak acid HCN. Calculate the concentrations of H_3O^+ , OH^- , HCN, and Na^+ in a solution prepared by dissolving 10.8 g of NaCN in enough water to make $5.00 \times 10^2 \text{ mL}$ of solution at 25°C . ($\text{HCN } K_a = 4.0 \times 10^{-10}$)

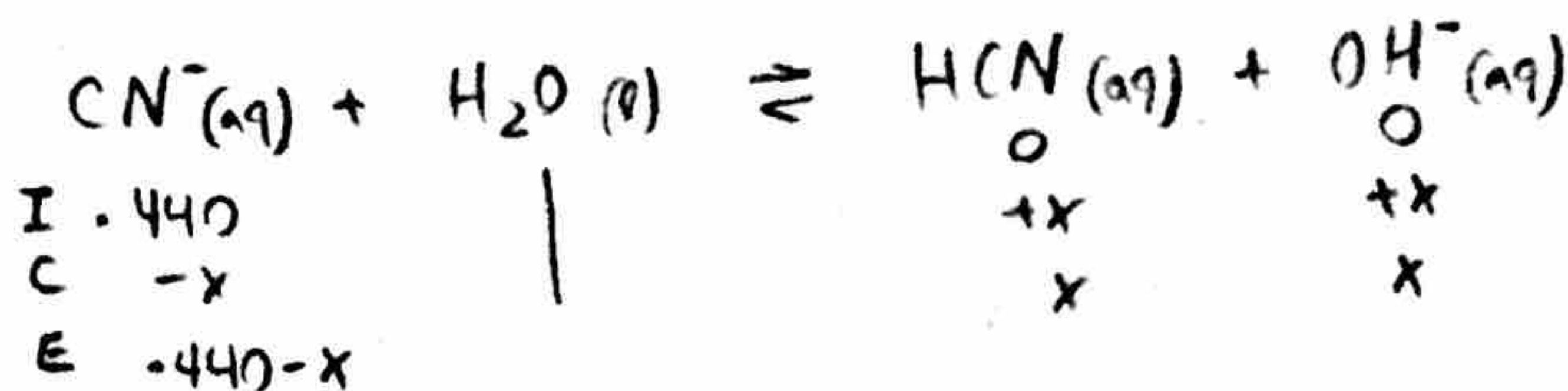
$$10.8 \text{ g NaCN} \times \frac{1 \text{ mol NaCN}}{49.01 \text{ g}} = .220 \text{ moles} \quad [\text{NaCN}] = \frac{.220 \text{ mol}}{.500 \text{ L}} = .440 \text{ M}$$

Na^+ is simply a spectator ion because NaCN will fully ionize.

$$K_b \text{ for } \text{CN}^- = K_w / K_a$$

$$= 1 \times 10^{-14} / 4.0 \times 10^{-10}$$

$$K_b = 2.5 \times 10^{-5}$$



$$K_b = \frac{[\text{HCN}][\text{OH}^-]}{[\text{CN}^-]}$$

$$2.5 \times 10^{-5} = \frac{x^2}{.440 - x}$$

$$x = 3.3 \times 10^{-3}$$

$$[\text{Na}^+] = 0.440 \text{ M}$$

$$[\text{CN}^-] = .440 - 3.3 \times 10^{-3} = .437 \text{ M}$$

$$[\text{HCN}] = [\text{OH}^-] = 3.3 \times 10^{-3} \text{ M}$$

$$[\text{H}_3\text{O}^+] = 1 \times 10^{-14} / [\text{OH}^-] = 3.0 \times 10^{-12} \text{ M}$$

- 14) What mass of sodium acetate, NaCH_3CO_2 , must be added to 1.00 L of 0.10 M acetic acid to give a solution with a pH of 4.50? ($\text{HC}_2\text{H}_3\text{O}_2 K_a = 1.8 \times 10^{-5}$)

$$pK_a = -\log(1.8 \times 10^{-5}) = 4.74$$

$$\text{pH} = pK_a + \log \frac{[\text{base}]}{[\text{acid}]}$$

$$4.50 = 4.74 + \log \frac{[\text{base}]}{[\text{acid}]}$$

$$-0.24 = \log \frac{[\text{base}]}{[\text{acid}]}$$

$$.58 = \frac{[\text{base}]}{[\text{acid}]}$$

$$[\text{base}] = .58 [\text{acid}]$$

$$\frac{n_b}{V} = .58 [\text{acid}]$$

$$n_b = .58 [\text{acid}] \cdot V$$

$$= .58(.10)(1.00 \text{ L})$$

$$n_b = .058 \text{ moles}$$

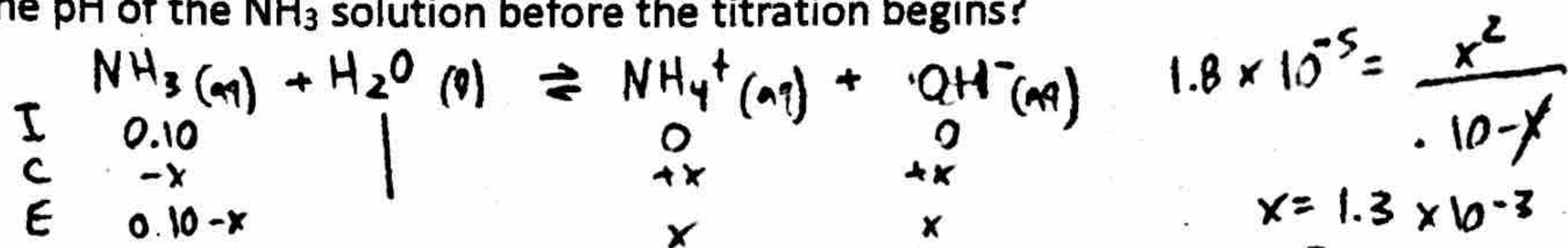
$$\text{mass NaCH}_3\text{CO}_2 = \text{moles} \times \text{MM}$$

$$= (.058 \text{ mol})(82.03 \text{ g/mol})$$

$$= \boxed{4.7 \text{ g}}$$

15) You titrate 25.0 mL of 0.10 M NH_3 with 0.10 M HCl . ($\text{NH}_3 K_b = 1.8 \times 10^{-5}$)

(a) What is the pH of the NH_3 solution before the titration begins?



$$x = 1.3 \times 10^{-3}$$

$$[\text{OH}^-] = x$$

$$\text{pOH} = -\log(1.3 \times 10^{-3}) = 2.87 \quad \text{pH} = 14 - \text{pOH} = 14 - 2.87 = \boxed{11.13}$$

(b) What is the pH at the equivalence point?

$$\text{moles NH}_3 = 0.10 \text{ M} \times 0.025 \text{ L} = 0.0025 \text{ moles}$$

At equivalence point: moles NH_3 = moles HCl

$$[\text{NH}_4^+]_i = \frac{0.0025 \text{ mol}}{0.050 \text{ L}} = 0.05 \text{ M}$$

$$K_a = \frac{[\text{NH}_3][\text{H}_3\text{O}^+]}{[\text{NH}_4^+]}$$

$$V_{\text{HCl needed}} = 0.0025 \text{ mol} / 0.10 \text{ M} = 0.025 \text{ L}$$

$$\text{Total V} = 0.025 \text{ L} + 0.025 \text{ L} = 0.050 \text{ L}$$



$$5.6 \times 10^{-10} = \frac{x^2}{0.05-x}$$

$$x = 5.3 \times 10^{-6}$$

$$[\text{H}_3\text{O}^+] = x$$

$$\text{pH} = -\log(5.3 \times 10^{-6}) = \boxed{5.28}$$

(c) What is the pH at the half equivalence point of the titration?

At half equivalence point

$$\text{pOH} = \text{p}K_b = -\log(1.8 \times 10^{-5}) = 4.74$$

$$\text{pH} = 14 - \text{pOH} = 14 - 4.74 = \boxed{9.26}$$

(d) Calculate the pH of the solution after adding 5.00, 15.0, 20.0, 22.0, and 30.0 mL of the acid.

25.0 mL is equivalence point. For 5.00, 15.0, 20.0, and

22.0 it is in the buffer region (Use Henderson Hasselbach).

For the 30.0 mL, there is excess HCl .

For HH, can use moles instead of $[\]$ because V cancels in ratio since it is the same.

mL 0.10 M HCl	5.00	15.0	20.0	22.0
n_a moles HCl	0.0005	0.0015	0.0020	0.0022
n_b moles NH_3	0.0020	0.0010	0.0005	0.0003
pH	9.86	9.08	8.66	8.39

$$\text{moles HCl} = n_a = 0.10 \text{ M} \times V$$

$$n_b = 0.0025 - n_a$$

$$\text{pH} = \text{p}K_a + \log \frac{n_b}{n_a}$$

$$= 9.26 + \log \frac{n_b}{n_a}$$

Total V = 55.0 mL

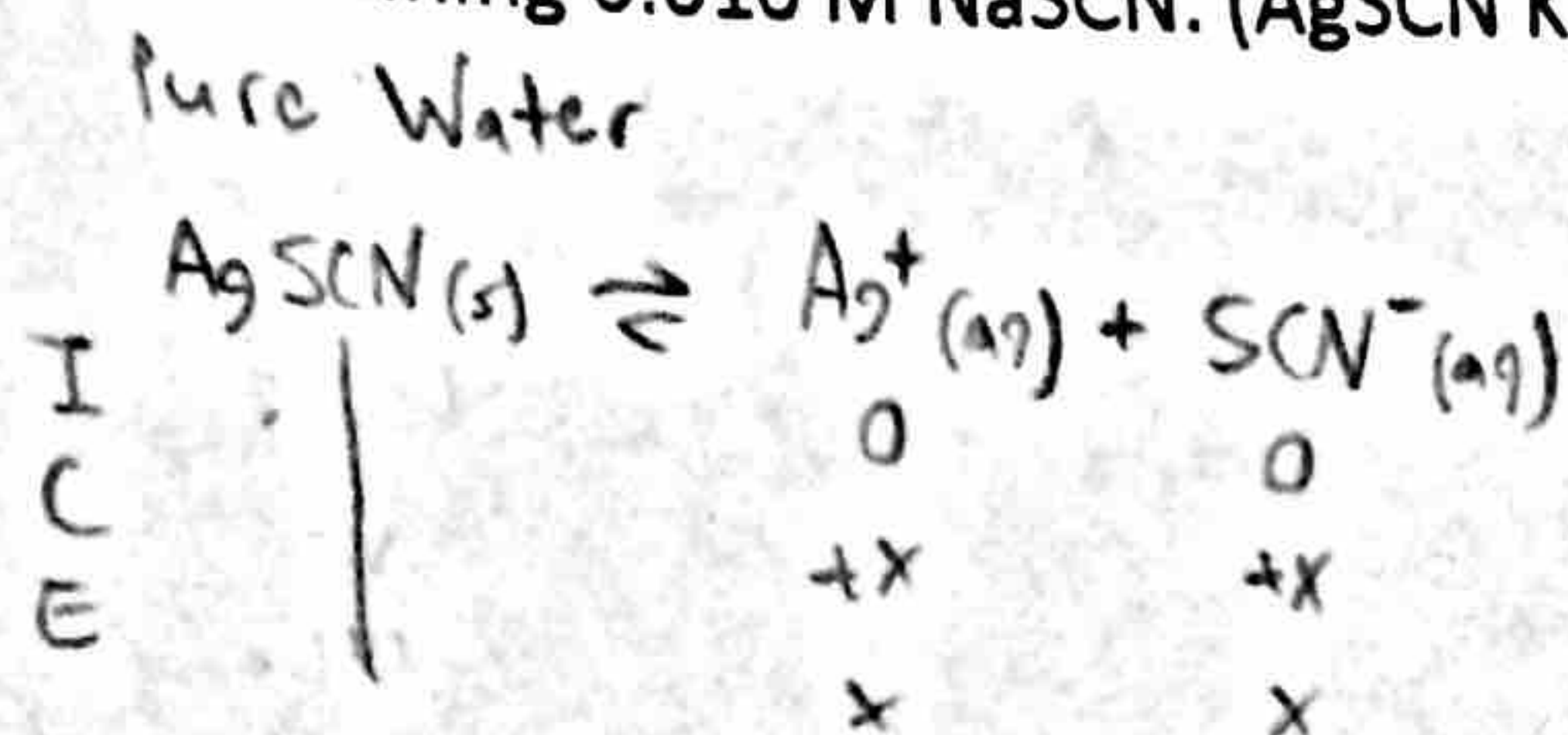
30.0 mL of acid means 5.0 mL excess of HCl

$$\text{moles excess HCl} = 0.005 \text{ L} \times 0.10 \text{ M} = 0.0005 \text{ moles}$$

$$[\text{HCl}] = \frac{0.0005 \text{ mol}}{0.055 \text{ L}} = 0.0091 \text{ M} = [\text{H}_3\text{O}^+]$$

$$\text{pH} = -\log(0.0091) = \boxed{2.04}$$

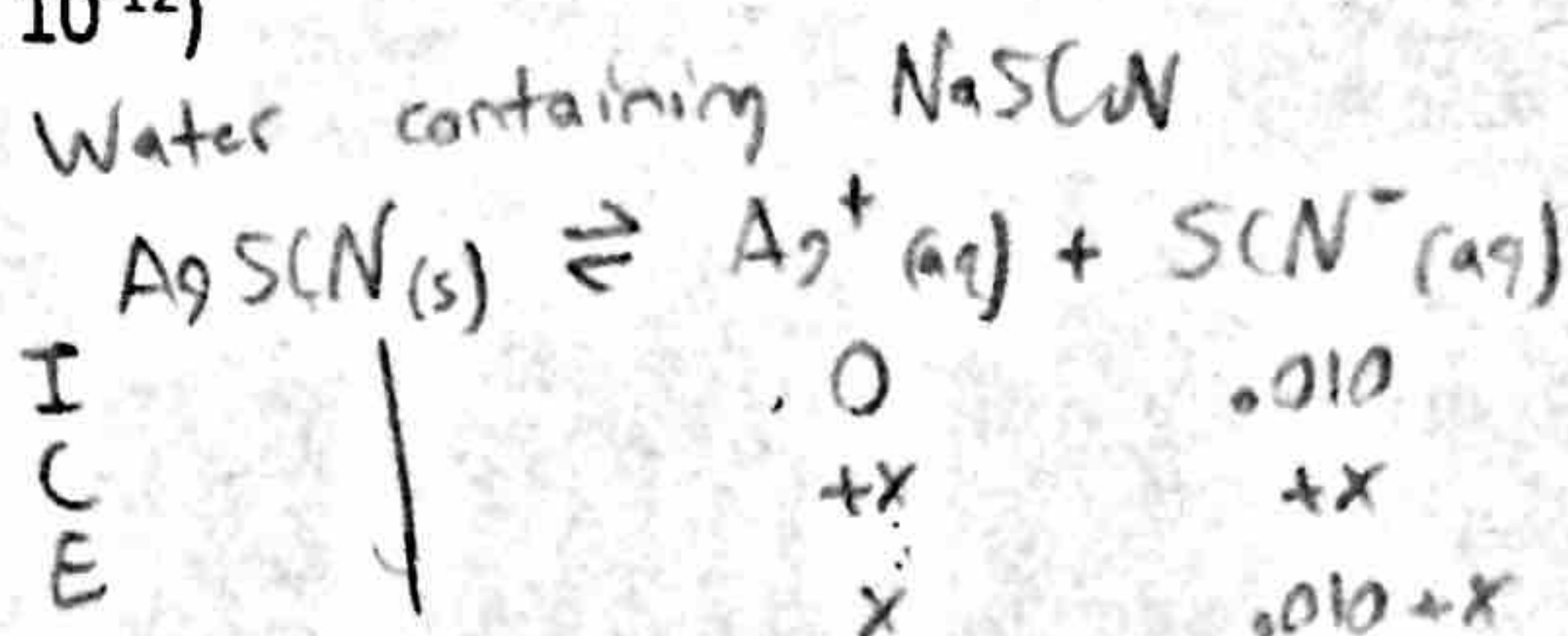
- 16) Calculate the molar solubility of silver thiocyanate, AgSCN, in pure water and in water containing 0.010 M NaSCN. (AgSCN $K_{sp} = 1.0 \times 10^{-12}$)



$$K_{sp} = [\text{Ag}^+][\text{SCN}^-]$$

$$1.0 \times 10^{-12} = x^2$$

$$x = 1 \times 10^{-6} \text{ mol/L}$$



$$K_{sp} = [\text{Ag}^+][\text{SCN}^-]$$

$$1 \times 10^{-12} = x(0.010 + x)$$

$$1 \times 10^{-12} = 0.010x$$

$$x = 1 \times 10^{-10} \text{ mol/L}$$

- 17) A solution contains Ca^{2+} and Pb^{2+} ions, both at a concentration of 0.010 M. You wish to separate the two ions from each other as completely as possible by precipitating one but not the other using aqueous Na_2SO_4 as the precipitating agent. (CaSO_4 $K_{sp} = 4.9 \times 10^{-5}$, PbSO_4 $K_{sp} = 2.5 \times 10^{-8}$)

- (a) Which will precipitate first as sodium sulfate is added, CaSO_4 or PbSO_4 ?

Since both CaSO_4 and PbSO_4 have the same general K_{sp} expression for 1:1 salts: $K_{sp} = [\text{M}^{2+}][\text{SO}_4^{2-}]$ and the cations both have the same concentration (0.010 M), you can just look at K_{sp} . Since PbSO_4 has a smaller K_{sp} it will precipitate first.

- (b) What will be the concentration of the first ion that precipitates (Ca^{2+} or Pb^{2+}) when the second, more soluble salt begins to precipitate?

The more soluble salt that will precipitate second is CaSO_4 .

$$K_{sp} = [\text{Ca}^{2+}][\text{SO}_4^{2-}] \quad [\text{SO}_4^{2-}] = \frac{K_{sp}}{[\text{Ca}^{2+}]} = \frac{4.9 \times 10^{-5}}{0.010} = 4.9 \times 10^{-3} \text{ M}$$

The $[\text{SO}_4^{2-}]$ for the PbSO_4 will be the same

$$K_{sp} = [\text{Pb}^{2+}][\text{SO}_4^{2-}] \quad [\text{Pb}^{2+}] = \frac{K_{sp}}{[\text{SO}_4^{2-}]} = \frac{2.5 \times 10^{-8}}{4.9 \times 10^{-3}} = 5.1 \times 10^{-6} \text{ M}$$

Answer Key

Chapter 18: Thermodynamics

Question 18:

Fill in the following table. Assume no two rows are the same

ΔH	ΔS	ΔG	Low Temp	High Temp
-	+	-	spontaneous	spontaneous
-	-	Temp. dependent	spontaneous	Non-spontaneous
+	+	Temp. dependent	non-spontaneous	spontaneous
+	-	+	non-spontaneous	non-spontaneous

Question 19 (18.25):

Heating some metal carbonates, among them magnesium carbonate, leads to their decomposition.



$$\Delta S_f^\circ \text{ MgO} = 26.85 \text{ J/mol K}$$

$$\Delta H_f^\circ \text{ MgO} = -601.85 \text{ kJ/mol}$$

$$\Delta S_f^\circ \text{ CO}_2 = 213.74 \text{ J/mol K}$$

$$\Delta H_f^\circ \text{ CO}_2 = -393.51 \text{ kJ/mol}$$

$$\Delta S_f^\circ \text{ MgCO}_3 = 65.84 \text{ J/mol K}$$

$$\Delta H_f^\circ \text{ MgCO}_3 = -1111.69 \text{ kJ/mol}$$

(a) Calculate $\Delta_r G^\circ$ for the reaction.

$$\Delta_r G^\circ = \Delta_r H^\circ - T \Delta_r S^\circ = 116.33 \frac{\text{kJ}}{\text{mol}} - 298.15 \text{ K} \times 0.17475 \frac{\text{kJ}}{\text{mol K}} = \boxed{64.23 \frac{\text{kJ}}{\text{mol}}}$$

$$\Delta_r H^\circ = \sum \Delta H_f^\circ (\text{products}) - \sum \Delta H_f^\circ (\text{reactants}) = -601.85 \frac{\text{kJ}}{\text{mol}} - 393.51 \frac{\text{kJ}}{\text{mol}} - (-1111.69 \frac{\text{kJ}}{\text{mol}}) = 116.33 \frac{\text{kJ}}{\text{mol}}$$

$$\Delta_r S^\circ = \sum \Delta S_f^\circ (\text{products}) - \sum \Delta S_f^\circ (\text{reactants}) = 26.85 \frac{\text{J}}{\text{mol K}} + 213.74 \frac{\text{J}}{\text{mol K}} - 65.84 \frac{\text{J}}{\text{mol K}} = 174.75 \frac{\text{J}}{\text{mol K}}$$

(b) Over what temperature range is the reaction predicted to be product-favored at equilibrium?

$$\Delta_r G^\circ = 0 \text{ when } T = \frac{\Delta_r H^\circ}{\Delta_r S^\circ} = \frac{116.33 \frac{\text{kJ}}{\text{mol}}}{0.17475 \frac{\text{kJ}}{\text{mol K}}} = 665.7 \text{ K}$$

As T increases, $\Delta_r G^\circ$ decreases. So $\Delta_r G^\circ < 0$ when $T > 665.7 \text{ K}$

The reaction is product-favored at equilibrium when $\Delta_r G^\circ < 0$, so when $T > 665.7 \text{ K}$

(c) What is the equilibrium constant of the above reaction at $T = 500 \text{ K}$? $R = 8.314 \text{ J/mol K}$

$$\Delta_r G^\circ = -RT \ln(K)$$

$$-\frac{\Delta_r G^\circ}{RT} = \ln(K)$$

$$K = e^{\frac{-\Delta_r G^\circ}{RT}} = e^{\frac{-64.87 \text{ kJ/mol}}{8.314 \frac{\text{J}}{\text{mol K}} \times 500 \text{ K}}} = e^{-15.61} \approx 1.67 \times 10^{-7}$$

Question 20 (18.31):

For the synthesis of ammonia from its elements at 25 °C, $\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \rightarrow 2 \text{NH}_3(\text{g})$

$\Delta_f G^\circ \text{N}_2(\text{g}) = \Delta_f G^\circ \text{H}_2(\text{g}) = 0 \text{ kJ/mol}$

$\Delta_f G^\circ \text{NH}_3(\text{g}) = -16.37 \text{ kJ/mol}$

(a) Calculate $\Delta_r G^\circ$. Is the reaction product-favored at equilibrium?

$$\Delta_r G^\circ = \sum \Delta_f G^\circ \text{ products} - \sum \Delta_f G^\circ \text{ reactants} = -16.37 \frac{\text{kJ}}{\text{mol}} - (0 \frac{\text{kJ}}{\text{mol}} + 0 \frac{\text{kJ}}{\text{mol}}) = -32.74 \frac{\text{kJ}}{\text{mol}}$$

(b) Calculate $\Delta_r G$ when the reactants and product are each present at a partial pressure of 0.10 atm and the reaction is at 350 K. Is the reaction spontaneous under these conditions?

$$\begin{aligned} \Delta_r G &= \Delta_r G^\circ - RT \ln(Q) & Q &= \frac{(P_{\text{NH}_3})^2}{(P_{\text{N}_2})(P_{\text{H}_2})^3} = \frac{(0.10 \text{ atm})^2}{(0.10 \text{ atm})^4} = 100 \\ &= -32.74 \frac{\text{kJ}}{\text{mol}} - 0.008314 \frac{\text{kJ}}{\text{mol} \cdot \text{K}} \times & & \\ & & & 350 \text{ K} \times \ln(100) \\ &= -19.34 \frac{\text{kJ}}{\text{mol}} & \text{Yes, it is spontaneous} \end{aligned}$$

Question 21 (18.33):

For each set of compounds below, circle the one of highest entropy. Assume that all are at the same temperature. Briefly explain your reasoning.

(a) HF(g) HCl(g) HBr(g)

Entropy increases with molar mass

(b) NH₄Cl(s) NH₄Cl(aq)

Solutions have greater entropy than solids

(c) C₂H₄(g) N₂(g) (same molar mass)

Entropy increases with molecular complexity

(d) NaCl(s) NaCl(g)

~~Solids~~ Solids have lower entropy than gases

Chapter 19: Electrochemistry

Question 22 (19.21):

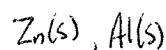
Consider the following half reactions

Half Reaction	E° (V)
$\text{Cu}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Cu}(\text{s})$	+ 0.34 V
$\text{Sn}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Sn}(\text{s})$	- 0.14 V
$\text{Fe}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Fe}(\text{s})$	- 0.44 V
$\text{Zn}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Zn}(\text{s})$	- 0.76 V
$\text{Al}^{3+}(\text{aq}) + 3 \text{e}^- \rightarrow \text{Al}(\text{s})$	- 1.66 V

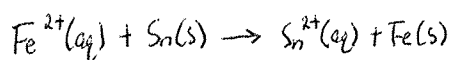
(a) Based on E° values, which metal is the most easily oxidized?



(b) Which metals on this list are capable of reducing $\text{Fe}^{2+}(\text{aq})$ to $\text{Fe}(\text{s})$?



(c) Write a balanced chemical equation for the reaction of $\text{Fe}^{2+}(\text{aq})$ with $\text{Sn}(\text{s})$. Is this reaction product- favored or reactant-favored?



$$E_{\text{cell}}^\circ = -0.44 \text{ V} - (-0.14 \text{ V}) = -0.30 \text{ V}$$

The reaction is reactant favored

(d) Write a balanced chemical equation for the reaction of $\text{Zn}^{2+}(\text{aq})$ with $\text{Sn}(\text{s})$. Is this reaction product- favored or reactant-favored?

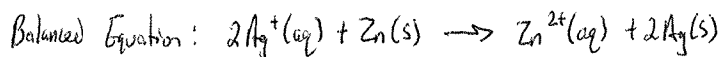
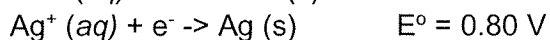
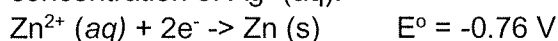


$$E_{\text{cell}}^\circ = -0.76 \text{ V} - (-0.14 \text{ V}) = -0.62 \text{ V}$$

The reaction is reactant favored

Question 23 (19.33):

One half-cell in a voltaic cell is constructed from a silver wire electrode in a AgNO_3 solution of unknown concentration. The other half-cell consists of a zinc electrode in a 1.0 M solution of $\text{Zn}(\text{NO}_3)_2$. A potential of 1.48 V is measured for this cell. Use this information to calculate the concentration of $\text{Ag}^+(\text{aq})$.



$$E_{\text{cell}}^\circ = 0.80 \text{ V} - (-0.76 \text{ V}) = 1.56 \text{ V}$$

$$Q = \frac{[\text{Zn}^{2+}]}{[\text{Ag}^+]^2}$$

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.0257}{n} \ln(Q)$$

$$\ln(Q) = \left(\frac{n}{0.0257}\right) (E_{\text{cell}}^\circ - E_{\text{cell}})$$

$$\ln\left(\frac{[\text{Zn}^{2+}]}{[\text{Ag}^+]^2}\right) = \left(\frac{2}{0.0257}\right) (1.56 \text{ V} - 1.48 \text{ V}) = 6.226$$

$$\frac{[\text{Zn}^{2+}]}{[\text{Ag}^+]^2} = e^{6.226} = 505.6$$

~~$$\frac{1}{e^{6.226}} = [\text{Ag}^+]^2 = e$$~~

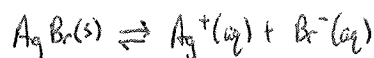
~~$$[\text{Ag}^+] = 0.044 \text{ M}$$~~

Question 24 (19.37):

Use standard reduction potentials below to calculate the value of K_{sp} for AgBr (s)

- $\text{AgBr(s)} + e^- \rightarrow \text{Ag(s)} + \text{Br}^-(\text{aq})$ 0.0713 V
- $\text{Ag}^+(\text{aq}) + e^- \rightarrow \text{Ag(s)}$ 0.7994 V

Complete Reaction:



$$E_{\text{cell}} = 0.0713 \text{ V} - 0.7994 \text{ V} \\ = -0.7281 \text{ V}$$

$$E_{\text{cell}}^0 = \frac{0.0257}{n} \ln(K_{sp})$$

$$\ln(K_{sp}) = \frac{n E_{\text{cell}}^0}{0.0257}$$

$$K_{sp} = e^{\frac{n E_{\text{cell}}^0}{0.0257}} = e^{\frac{-0.7281}{0.0257}} = 4.967 \times 10^{-13}$$

Question 25 (19.49):

Electrolysis of a solution of CuSO_4 (aq) to give metal Cu (s) is carried out using a current of 0.66

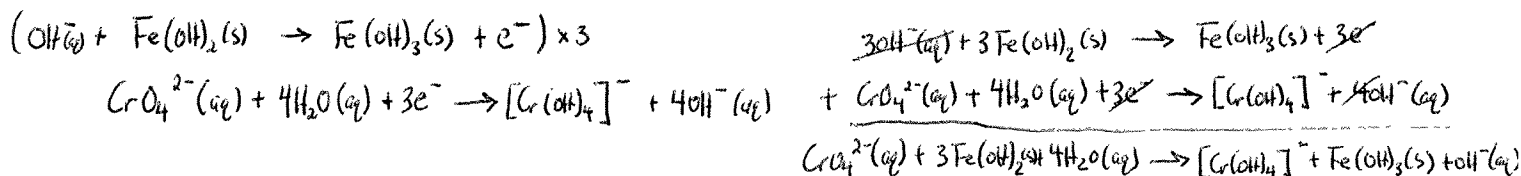
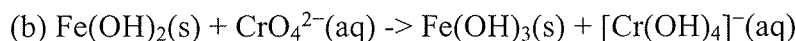
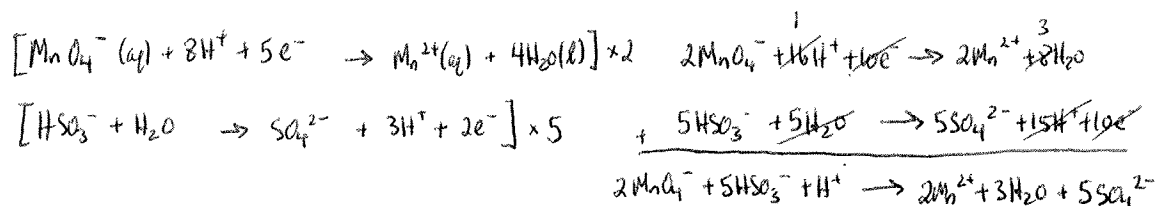
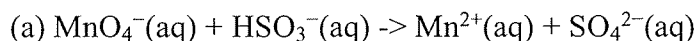
A. How long should electrolysis continue to produce 0.50 g of copper?

$$0.50 \text{ g Cu} \times \frac{1 \text{ mol Cu}}{63.546 \text{ g Cu}} \times \frac{2 \text{ mol } e^-}{1 \text{ mol Cu}} \times \frac{96485 \text{ C}}{1 \text{ mol } e^-} \times \frac{1 \text{ s}}{0.66 \text{ C}} = 2300 \text{ s}$$

$\uparrow$ $\uparrow$ $\uparrow$
 molar mass $\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$ $F = \frac{96485 \text{ C}}{1 \text{ mol } e^-}$

Question 26 (19.3 & 19.5):

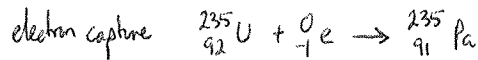
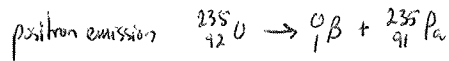
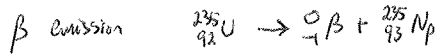
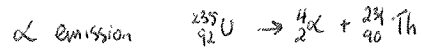
Balance the following redox equations. (a) is in acidic solution (b) is in basic solution



Chapter 25: Nuclear Chemistry

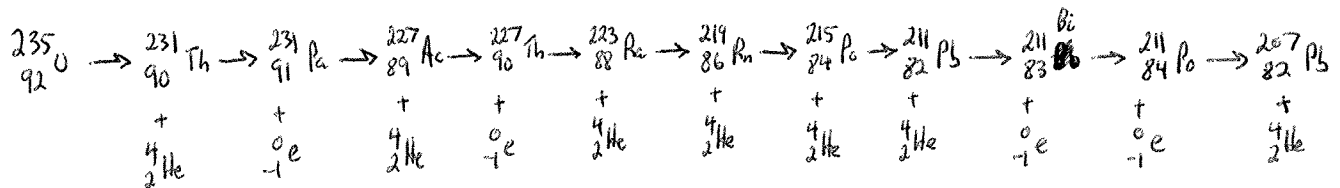
Question 27:

Give an example of each of the four types of nuclear reactions (α emission, β emission, positron emission, electron capture) for $^{235}_{92}\text{U}$.



Question 28 (25.15):

The uranium-235 radioactive decay series, beginning with $^{235}_{92}\text{U}$ and ending with $^{207}_{82}\text{Pb}$, occurs in the following sequence: α , β , α , β , α , α , α , α , β , β , α . Write an equation for each step in this series.



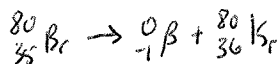
Question 29 (25.19): Predict the probable mode of decay for each of the following radioactive isotopes, write an equation to show the products of decay, and briefly explain your reasoning.

(a) bromine-80



35 protons, 45 neutrons

$n \gg p$, beta emission

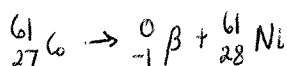


(c) cobalt-61



27 protons, 34 neutrons

$n \gg p$, beta emission

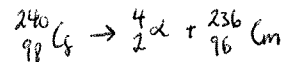


(b) californium-240



98 protons, 142 neutrons

protons > 92 , alpha emission

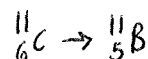


(d) carbon-11



6 protons, 5 neutrons

fewer neutrons than protons,
positron emission or electron capture



Question 30: Given ${}^1_1\text{H} = 1.00783 \text{ amu}$ ${}_0^1\text{n} = 1.00867 \text{ amu}$, calculate the binding energy per mole of nucleons for the following.

(a) ${}^{11}\text{B}$ (11.00931 g/mol)

${}^{11}\text{B}$: 11 nucleons, 6 neutrons and 5 protons

$$6n + 5p = 6(1.00867 \text{ g/mol}) + 5(1.00783 \text{ g/mol}) \\ = 11.09117 \text{ g/mol B}$$

$$\Delta m = (11.09117 - 11.00931) \text{ g/mol B} = 0.08186 \text{ g/mol B} = 8.186 \times 10^{-5} \text{ kg/mol B}$$

$$\text{Binding energy} = \Delta mc^2 = (8.186 \times 10^{-5} \frac{\text{kg}}{\text{mol B}}) (3.00 \times 10^8 \text{ m/s})^2 (\frac{1 \text{ J}}{1 \text{ kg m}^2 \text{ s}^{-2}}) \\ = 7.367 \times 10^{12} \frac{\text{J}}{\text{mol B}}$$

$$\frac{\text{Binding energy}}{\text{mol nucleon}} = 6.26 \times 10^8 \frac{\text{J}}{\text{mol B}} \times \frac{1 \text{ mol B}}{11 \text{ mol nucleon}} = 6.70 \times 10^8 \frac{\text{J}}{\text{mol nucleon}}$$

(b) ${}^{40}\text{Ca}$ (39.96259 g/mol)

${}^{40}\text{Ca}$: 40 nucleons, 20 neutrons and 20 protons

$$20n + 20p = 20(1.00867 \text{ g/mol}) + 20(1.00783 \text{ g/mol}) \\ = 40.33 \text{ g/mol Ca}$$

$$\Delta m = (40.33 - 39.96259) \text{ g/mol Ca} = 0.3674 \text{ g/mol Ca} = 3.674 \times 10^{-4} \text{ kg/mol Ca}$$

$$\text{Binding energy} = \Delta mc^2 = (3.674 \times 10^{-4} \frac{\text{kg}}{\text{mol Ca}}) (3.00 \times 10^8 \text{ m/s})^2 (\frac{1 \text{ J}}{1 \text{ kg m}^2 \text{ s}^{-2}}) \\ = 3.307 \times 10^{13} \frac{\text{J}}{\text{mol Ca}}$$

$$\frac{\text{Binding energy}}{\text{mol nucleon}} = 3.307 \times 10^{13} \frac{\text{J}}{\text{mol Ca}} \times \frac{1 \text{ mol Ca}}{40 \text{ mol nucleon}} = 8.26 \times 10^8 \frac{\text{J}}{\text{mol nucleon}}$$

(c) ${}^{16}\text{O}$ (15.99492 g/mol)

${}^{16}\text{O}$: 16 nucleons, 8 neutrons and 8 protons

$$8n + 8p = 8(1.00867 \text{ g/mol}) + 8(1.00783 \text{ g/mol}) \\ = 16.132 \text{ g/mol O}$$

$$\Delta m = 16.132 \frac{\text{g}}{\text{mol O}} - 15.99492 \frac{\text{g}}{\text{mol O}} = 0.13708 \frac{\text{g}}{\text{mol O}} \\ = 1.3708 \times 10^{-4} \text{ kg/mol O}$$

$$\text{Binding energy} = \Delta mc^2 = 1.234 \times 10^{10} \frac{\text{J}}{\text{mol O}}$$

$$\frac{\text{Binding energy}}{\text{mol nucleon}} = 7.70 \times 10^8 \frac{\text{J}}{\text{mol nucleon}}$$

Question 31: Gallium-67 ($t_{1/2} = 78.25$ hours) is used in the medical diagnosis of certain kinds of tumors. If you ingest a compound containing 0.015 mg of this isotope, what mass (in milligrams) remains in your body after 13 days? (Assume none is excreted.)

Method 1

$$13 \text{ days} \times \frac{24 \text{ hrs}}{1 \text{ day}} \times \frac{1 \text{ half life}}{78.25 \text{ hrs}} = 3.987 \text{ half-lives}$$

$$\text{mass remaining} = 0.015 \text{ mg} \times \left(\frac{1}{2}\right)^{3.987}$$

$$= 0.000946 \text{ mg}$$

$$= 9.46 \times 10^{-4} \text{ mg}$$

Method 2

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{78.25 \text{ hr}} = 0.00886 \text{ hr}^{-1}$$

$$13 \text{ days} \times \frac{24 \text{ hrs}}{1 \text{ day}} = 312 \text{ hrs} = t$$

$$\ln(\text{mass}) = -kt + \ln(\text{mass}_0)$$

$$\ln(\text{mass}) = -0.00886 \text{ hr}^{-1} \times 312 \text{ hrs} + \ln(0.015)$$

$$\ln(\text{mass}) = -6.823$$

$$\text{mass} = 9.46 \times 10^{-4} \text{ mg}$$

$$\text{mass} = 9.46 \times 10^{-4} \text{ mg}$$