

Question 1 (page 1 of 2)

USNCO ID Number:

1. [10%] An unknown salt MX_2 is a group 2 metal halide.

- a. 10.00 g MX_2 dissolves in 50.0 g water to give a homogeneous solution. The freezing point of this solution is -4.50°C . What is the molar mass of MX_2 ? For water, $K_f = 1.86^\circ\text{C}/m$.

$$m = \frac{\Delta T}{K_f} = \frac{4.50^\circ\text{C}}{1.86^\circ\text{C}/m} = 2.42 m$$

$$m = \frac{10.00 / M \times 3}{0.0500} = 2.42 \Rightarrow \boxed{M = 248 \text{ g/mol}}$$

SrBr_2 ?

- b. 10.00 g Na_2CO_3 and 10.00 g MX_2 are mixed in 200.0 mL of water. A precipitate of MCO_3 forms. What is the pH of the supernatant? The K_a of H_2CO_3 is 4.3×10^{-7} and the K_a of HCO_3^- is 4.7×10^{-11} .

$$n(\text{Na}_2\text{CO}_3) = 10.00 / 106.0 = 9.43 \times 10^{-2} \text{ mol}$$

$$n(\text{MX}_2) = 10.00 / 248 = 4.03 \times 10^{-2} \text{ mol} < n(\text{Na}_2\text{CO}_3)$$

$$\text{In the supernatant: } C(\text{CO}_3^{2-}) = \frac{9.43 \times 10^{-2} - 4.03 \times 10^{-2}}{0.2000 \text{ L}} = 2.70 \times 10^{-1} \text{ M}$$

$$\text{CO}_3^{2-} + \text{H}_2\text{O} \rightleftharpoons \text{HCO}_3^- + \text{OH}^-$$

$$\frac{X^2}{5.40 \times 10^{-2} - X} = K_b = \frac{10^{-14}}{4.7 \times 10^{-11}} = 2.13 \times 10^{-4}$$

$$X = 3.29 \times 10^{-3} \quad \text{pH} = 11.52$$

- c. A solution of 10.00 g MX_2 in water is treated with excess silver nitrate. The precipitate is dried; the mass of the dried compound is 15.2 g. What is the identity of MX_2 ?



$$\frac{15.2}{107.9 + X} = 2 \times \frac{10.00}{248} = 4.03 \times 10^{-2} \times 2 \Rightarrow X = 80.7 = \text{Br}$$

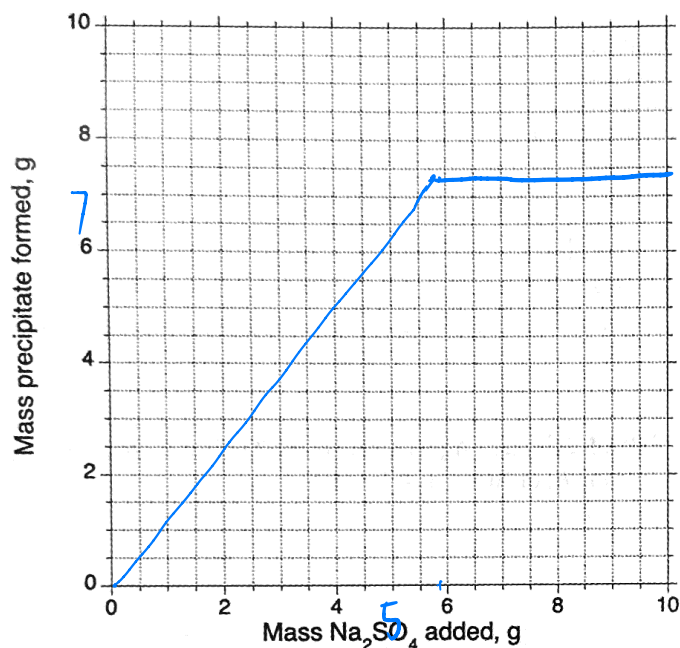
$$M = 248 - 80.7 \times 2 = 86.6 = \text{Sr}$$

$$\boxed{\text{MX}_2 = \text{SrBr}_2}$$

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- d. A sample of 10.00 g MX_2 dissolved in 50 mL water is treated with increasing amounts of Na_2SO_4 up to 10 g in total. How will the mass of precipitate formed vary with the mass of added Na_2SO_4 ? Graph your answer on the grid provided.



$$n(\text{MX}_2) = 4.53 \times 10^{-2}$$

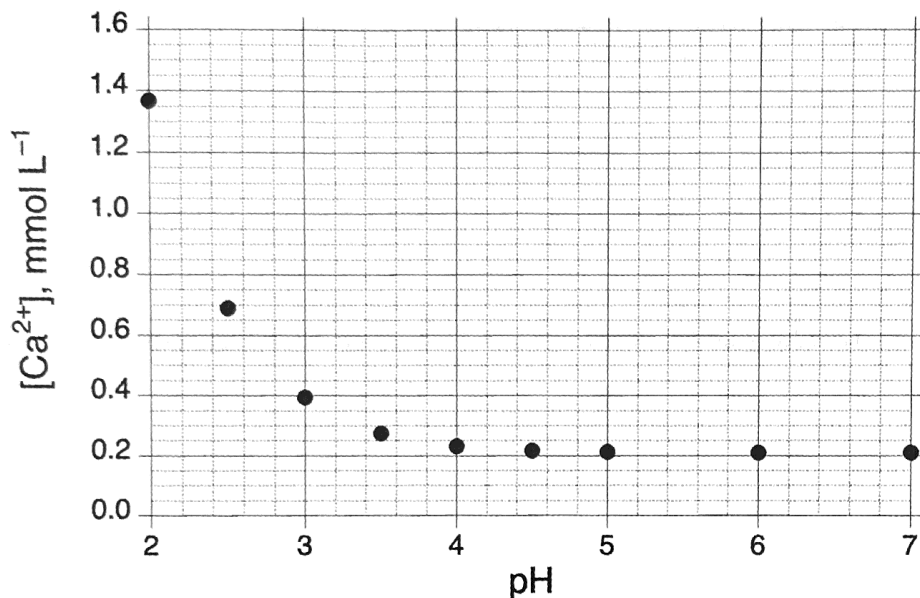
$$m(\text{Na}_2\text{SO}_4) = 4.53 \times 10^{-2} \times 142 = \boxed{6.43 \text{ g}}$$

$$m(\text{SrSO}_4) = 4.53 \times 10^{-2} \times 184 = \boxed{8.33 \text{ g}}$$

- e. What color flame test does MX_2 give?

red!

2. [13%] A sample of solid calcium fluoride is suspended in water in an unreactive container and stirred until it achieves equilibrium. The pH of the solution is lowered by careful addition of nitric acid, and the pH and concentration of $\text{Ca}^{2+}(\text{aq})$ are noted at several points as shown on the graph below. Note that the units on the y axis are millimoles per liter.



- a. Determine the K_{sp} of CaF_2 from the data provided.

When pH is high, $[\text{Ca}^{2+}] = 0.2 \times 10^{-3}$

$$[\text{F}^-] \approx 2[\text{Ca}^{2+}] = 0.42 \times 10^{-3}$$

$$K_{\text{sp}} = 0.2 \times 10^{-3} \times (0.42 \times 10^{-3})^2 = \boxed{2.7 \times 10^{-11}}$$

- b. Qualitatively, what is the cause for the increase in solubility of CaF_2 at low pH?

pH lower, $[\text{H}^+]$ higher, $\text{CaF}_2 + 2\text{H}^+ \rightleftharpoons \text{Ca}^{2+} + 2\text{HF}$

F^- binds with H^+ to form weak acid HF .

Shifting the dissolution equilibrium of CaF_2 to the right!
increasing S.

- c. From the data provided, determine the
- K_a
- of HF.

At pH = 2, $[HF] \gg [F^-]$

$$[F^-] = \sqrt{\frac{K_{sp}}{[Ca^{2+}]}} = \sqrt{\frac{2.7 \times 10^{-11}}{1.37 \times 10^{-3}}} = 1.64 \times 10^{-4} M$$

$$[HF] + [F^-] = 2[Ca^{2+}] = 1.37 \times 10^{-3} \times 2 = 2.74 \times 10^{-3}$$

$$\Rightarrow [HF] = 2.58 \times 10^{-3} M$$

$$K_a = \frac{[H^+][F^-]}{[HF]} = \frac{10^{-2} \times 1.64 \times 10^{-4}}{2.58 \times 10^{-3}} = \boxed{6.4 \times 10^{-4}}$$

At pH = 3, $[Ca^{2+}] = 0.4 \times 10^{-3} M$

$$[F^-] = \sqrt{\frac{K_{sp}}{[Ca^{2+}]}} = \sqrt{\frac{2.7 \times 10^{-11}}{0.4 \times 10^{-3}}} = 3.04 \times 10^{-4} M$$

$$[HF] + [F^-] = 2[Ca^{2+}] = 8.0 \times 10^{-4}$$

$$[HF] = 8.0 \times 10^{-4} - 3.04 \times 10^{-4} = 4.96 \times 10^{-4}$$

$$K_a = \frac{[H^+][F^-]}{[HF]} = \frac{10^{-3} \times 3.04 \times 10^{-4}}{4.96 \times 10^{-4}} = \boxed{6.1 \times 10^{-4}}$$

- d. How many moles of
- HNO_3
- must be added to the
- CaF_2
- /water mixture to achieve a pH = 3.00 in this experiment? The volume of solution is 1.00 L.

$$pH = 3.00, [Ca^{2+}] = 0.4 \times 10^{-3} M; [F^-] = \sqrt{\frac{2.7 \times 10^{-11}}{0.4 \times 10^{-3}}} = 3.04 \times 10^{-4} M$$

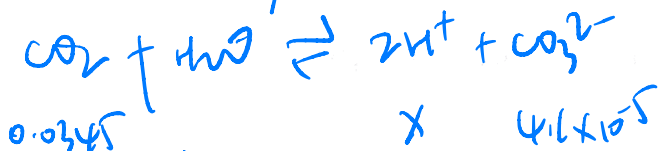
$$[HF] = \frac{[H^+][F^-]}{K_a} = \frac{10^{-3.00} \times 3.04 \times 10^{-4}}{6.4 \times 10^{-4}} = 4.75 \times 10^{-4} M$$

$$n(HNO_3) = ([H^+] + [HF]) \times 1.00 L = 4.75 \times 10^{-4} + 10^{-3.00} = \boxed{1.5 \times 10^{-3} \text{ mol}}$$

- e. Carbon dioxide dissolves in water at 25 °C and 1 atm pressure to the extent of
- $0.0345 \text{ mol L}^{-1}$
- . An aliquot of the solution taken from the above experiment at pH = 5 is stirred under 1 atm
- CO_2
- and the pH slowly raised by addition of solid NaOH until
- $CaCO_3$
- just begins to precipitate. What is the pH of the solution at this point? The
- K_{sp}
- of
- $CaCO_3$
- is
- 8.7×10^{-9}
- , the
- K_a
- of aqueous
- CO_2
- ("
- H_2CO_3
- ") is
- 4.3×10^{-7}
- , and the
- K_a
- of
- HCO_3^-
- is
- 4.7×10^{-11}
- .

$$pH > 5.00, [Ca^{2+}] = 2.1 \times 10^{-4} M$$

$$[CO_3^{2-}] = \frac{K_{sp}}{[Ca^{2+}]} = \frac{8.7 \times 10^{-9}}{2.1 \times 10^{-4}} = 4.1 \times 10^{-5} M$$



$$0.0345 \quad \quad \quad \times \quad 4.1 \times 10^{-5}$$

(steady)

$$\Rightarrow \tilde{X} = 1.7 \times 10^{-14} \Rightarrow X = 1.3 \times 10^{-7}$$

$$pH = \boxed{6.88}$$

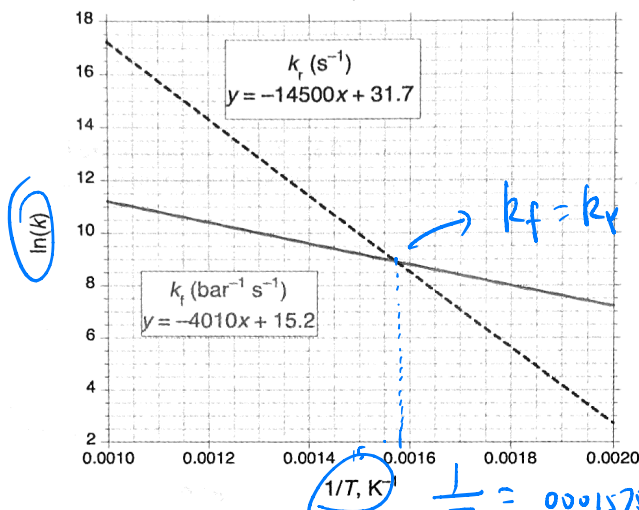
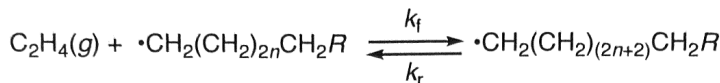
$$\begin{aligned} \frac{X^2 \cdot 4.1 \times 10^{-5}}{0.0345} &= K_{a1} \cdot K_{a2} \\ &= 4.3 \times 10^{-7} \\ &\quad \times 4.7 \times 10^{-11} \\ &= 2.0 \times 10^{-17} \end{aligned}$$

* Best method for b). $\ln K = \ln\left(\frac{k_f}{k_r}\right) = \ln k_f - \ln k_r = -4010\left(\frac{1}{T}\right) + 15.2 - (-14500\left(\frac{1}{T}\right) + 31.7)$
 $\Rightarrow \Delta H^\circ = -10490 \times 8.314 = \boxed{-87.2 \text{ kJ/mol}}$; $\Delta S^\circ = 165 \times 8.314 = \boxed{137 \text{ J/mol} \cdot \text{K}}$

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3. [13%] Ethene, C_2H_4 , can react in the gas phase in the presence of radicals R to form polyethylene as shown in the equation below. Here n is the degree of polymerization. The forward reaction is second-order while the reverse reaction is first-order. The values of these rate constants are independent of the degree of polymerization n and the identity of R .

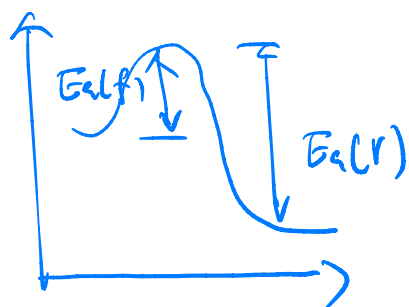


- a. A sample of polyethylene has an average degree of polymerization $n = 1200$. How many polymer chains are present in 1.0 g of this material?

$N = \frac{1.0}{1200 \times 28.05} \times 6.02 \times 10^{23} = \boxed{1.8 \times 10^{19}} \text{ chains}$

- b. Calculate ΔH° and ΔS° for the polymerization reaction.

1) According to Arrhenius eq: $\ln k = -\frac{E_a}{R} \cdot \left(\frac{1}{T}\right) + C$
 The slope is $-\frac{E_a}{R}$; $E_a(r) = -14500 \times (-8.314) = 121 \text{ kJ/mol}$
 $E_a(f) = -4010 \times (-8.314) = 33.3 \text{ kJ/mol}$



$\Delta H^\circ = E_a(f) - E_a(r)$

$= 33.3 - 121 = \boxed{-87.7 \text{ kJ/mol}}$

2) When $\frac{1}{T} = 0.001575$, $T = 635 \text{ K}$; $k_f = k_r$, $K = 1$, $\Delta G^\circ = 0$

$\Delta S^\circ = \frac{\Delta H^\circ}{T} = \frac{-87.7 \times 10^3}{635} = \boxed{-138 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}}$

* d) better and alternative method: $\Delta G^\circ (720\text{K}) = -87.7 - 720 \times 10^3 \times (-138) = +11.7 \text{ kJ/mol}$

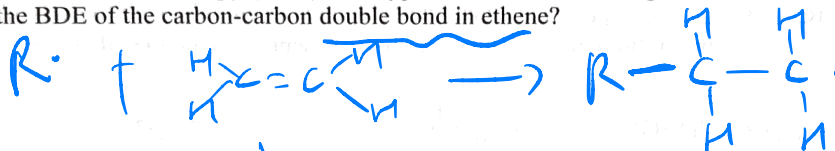
$$K_p = e^{-\frac{\Delta G^\circ}{RT}} = e^{-\frac{11.7 \times 10^3}{8.314 \times 720}} = 0.142$$

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$$\% = \frac{25 - 7.4}{25} = 72\%$$

- c. The bond dissociation enthalpy (BDE) for a typical carbon-carbon single bond is 345 kJ mol^{-1} . From the data given, what is the BDE of the carbon-carbon double bond in ethene?



a C=C converts to 2 C-C single.

$$\Delta H^\circ = \text{BDE}(\text{C}=\text{C}) - 2 \times 345 = -87.7 \Rightarrow \text{BDE}(\text{C}=\text{C}) = 602 \text{ kJ/mol}$$

- d. Ethene is charged to a fixed vessel at 25 bar and 720 K. Traces of radical are then added to initiate polymerization. What is the percent conversion of ethene into polymer at equilibrium under these conditions?

$$\frac{k_f}{k_r} = K_p(720) = \frac{e^{(-4010 \div 720 + 15.2)}}{e^{(-14500 \div 720 + 31.7)}} = \frac{e^{9.63}}{e^{11.6}} = 0.830 \times \frac{1.52 \times 10^4}{1.09 \times 10^5} = 0.139$$



$$K_p = 0.139 = \frac{1}{P(\text{C}_2\text{H}_4, \text{g})_{\text{eq}}} \Rightarrow P(\text{C}_2\text{H}_4, \text{g})_{\text{eq}} = \frac{1}{0.139} = 7.19 \text{ bar}$$

$$\% = \frac{25 - 7.19}{25} \times 100\% = 71\%$$

- e. In the presence of a catalyst for the polymerization reaction, the forward rate constant as a function of temperature is $\ln(k_f) = -3050(1/T) + 21.0$. By what factor does the catalyst accelerate the rate of the forward reaction at 500 K?

$$\ln(k_f)' = -3050 \times \frac{1}{500} + 21.0 = 14.9; k_f' = 2.96 \times 10^6 \text{ bar}^{-1}\text{s}^{-1}$$

$$\ln(k_f) = -4010 \times \frac{1}{500} + 15.2 = 7.18; k_f = 1.31 \times 10^3 \text{ bar}^{-1}\text{s}^{-1}$$

$$k_f'/k_f = \frac{2.96 \times 10^6}{1.31 \times 10^3} = 2.26 \times 10^3$$

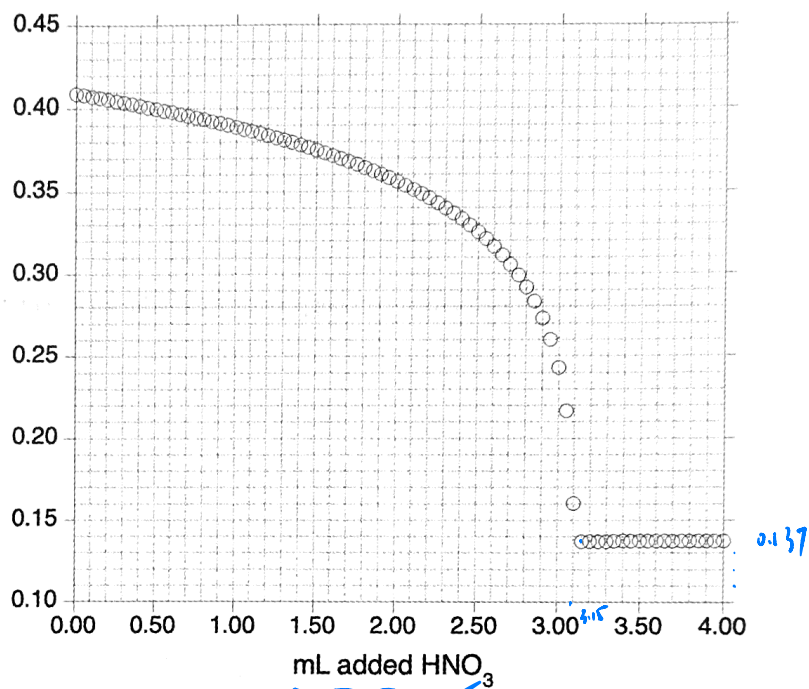
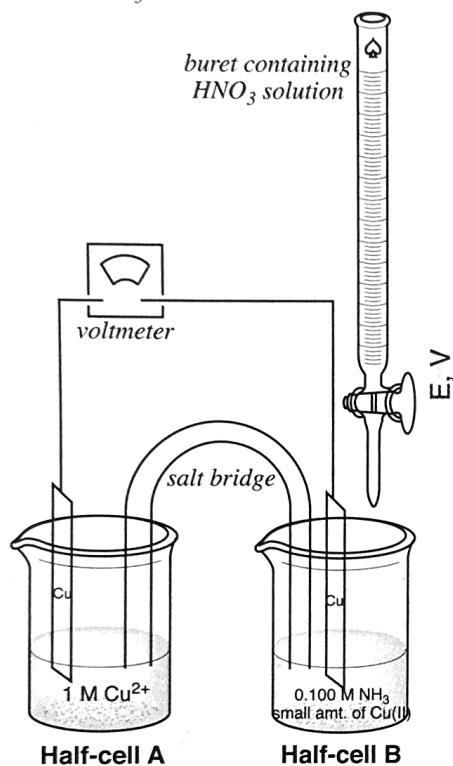
- f. By what factor does the catalyst change the rate of the reverse reaction at 500 K?

The same as above, 2.26×10^3

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4. [13%] Copper(II) forms a complex ion with ammonia, $\text{Cu}(\text{NH}_3)_4^{2+}$, with $K_f = 1.7 \times 10^{13}$. An electrochemical cell is set up as shown below at 298 K. Half-cell A contains 100 mL of 1.00 M $\text{Cu}(\text{NO}_3)_2$, while half-cell B contains 100 mL of a solution that contains a small amount of copper(II) and is 0.100 M in NH_3 . A solution of nitric acid is slowly added to half-cell B and the potential measured by the voltmeter is recorded as a function of the added volume of HNO_3 .



- a. Which half-cell is the cathode and which is the anode? Justify your answer.

A is the cathode ; B is the anode :
 $[\text{Cu}^{2+}]_A = 1.00 \text{ M}$; $[\text{Cu}^{2+}]_B$ is much smaller
 $\text{Cu}^{2+}(\text{A}) \rightleftharpoons \text{Cu}^{2+}(\text{B})$

It's a concentration cell, Cu^{2+} in A converts into Cu^{2+} in B through redox, Cu^{2+} in A gains e^- to form Cu while Cu in B loses e^- to form Cu^{2+} , thus ...

* d) further explain why there is a significant drop when approaching to the plateau?

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b. Qualitatively explain the shape of the graph.

As HNO_3 is added to B, $\text{NH}_3 \rightarrow \text{NH}_4^+$, more Cu^{2+} is converted from its complex. $[\text{Cu}^{2+}]_B \uparrow$,

according to LCP or Nernst equation. $E_{\text{cell}} \downarrow$

When enough HNO_3 added, all $\text{NH}_3 \rightarrow \text{NH}_4^+$, and all Cu^{2+} is released, so $[\text{Cu}^{2+}]_B$ doesn't change with V_{HNO_3}

c. What is the total concentration of copper(II) in the solution in half-cell B?

In the end, $E_{\text{cell}} = 0.137 \text{ V}$, thus levels off.

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{RT}{nF} \ln Q$$

$$= 0 - \frac{0.0591}{2} \lg \frac{[\text{Cu}^{2+}]_B}{1.00} = 0.137 \Rightarrow [\text{Cu}^{2+}]_B = 2.31 \times 10^{-5} \text{ M}$$

V_{HNO_3} added is negligible compared to 100 mL.

$$\text{so } [\text{Cu}^{2+}]_{\text{total}} \text{ in B} = \boxed{2.31 \times 10^{-5} \text{ M}}$$

d. What is the concentration of nitric acid in the buret?

When $V_{\text{HNO}_3} = 3.15 \text{ mL}$ is added, E_{cell} levels off.

It means all NH_3 is converted to NH_4^+



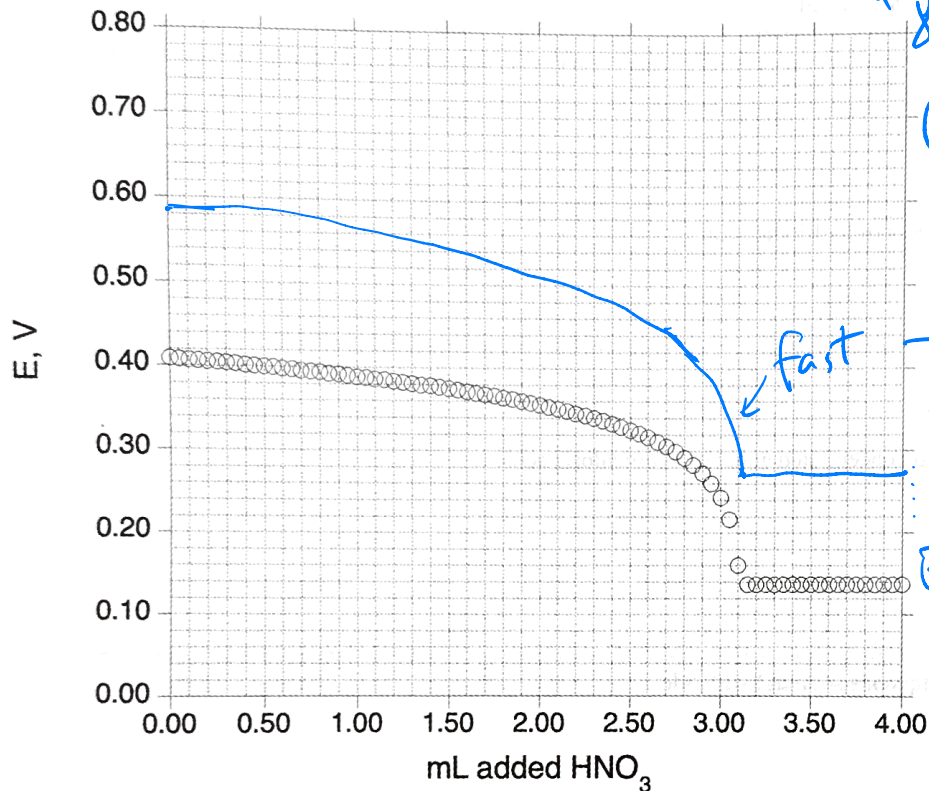
$$n_{\text{HNO}_3} = n_{\text{Cu}(\text{NH}_3)} = 100 \text{ mL} \times 0.100 \text{ M} = 1.00 \times 10^{-2} \text{ mol}$$

$$C(\text{HNO}_3) = \frac{n}{V} = \frac{1.00 \times 10^{-2}}{3.15 \times 10^{-3}} = \boxed{3.17 \text{ M}}$$

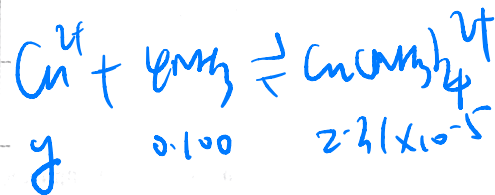
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- *e. Suppose that the experiment is set up again with silver metal in place of copper metal and silver(I) ion in place of copper(II) ion, but with all concentrations and all other reagents identical. What would the graph of E vs. mL added HNO_3 look like in this experiment? Sketch your result on the grid below (the graph shown above is redrawn for your convenience), and explain your answer. Silver(I) forms a complex ion with ammonia, $\text{Ag}(\text{NH}_3)_2^+$, with $K_f = 1.7 \times 10^7$.



*~~8~~ 2.31



$$\frac{2.31 \times 10^{-5}}{y \times (0.100)^4} = K_f = 1.7 \times 10^7$$

$$y = 1.36 \times 10^{-14}$$

$$E_0 = -\frac{0.0591}{2} \lg(1.36 \times 10^{-14})$$

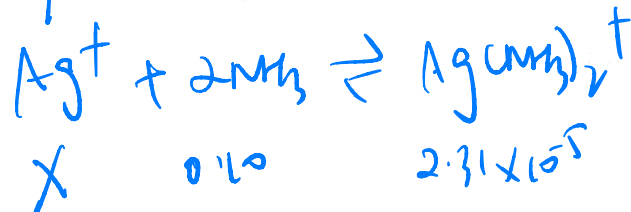
$$= 0.410 \text{ V} \quad \checkmark$$

Perfect!

$$[\text{Ag}^+]_{\text{level off}} = 2.31 \times 10^{-5} \text{ M} ; E_{\text{level off}} = -\frac{0.0591}{1} \lg \frac{2.31 \times 10^{-5}}{1.00}$$

Initially, $V_{\text{HNO}_3} = 0$

$$= 0.774 \text{ V} \quad \checkmark$$



$$\frac{2.31 \times 10^{-5}}{x \cdot (0.10)^2} = K_f = 1.7 \times 10^7$$

$$x = 1.36 \times 10^{-10} \text{ M}$$

$$E_0 = E^\circ - \frac{0.0591}{1} \lg \frac{1.36 \times 10^{-10}}{1.00} = 0.587 \text{ V} \quad \checkmark$$

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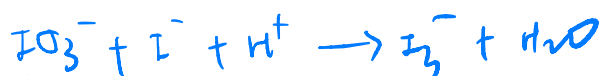
USNCO ID Number:

5. [12%] Write net equations for each of the reactions below. Use appropriate ionic and molecular formulas and omit formulas for all ions or molecules that do not take part in a reaction. Write structural formulas for all organic substances, and clearly show stereochemistry where relevant. You need not balance the equations or show the phase of the species.

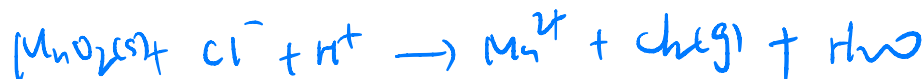
a. Aqueous ammonia and acetic acid are mixed.



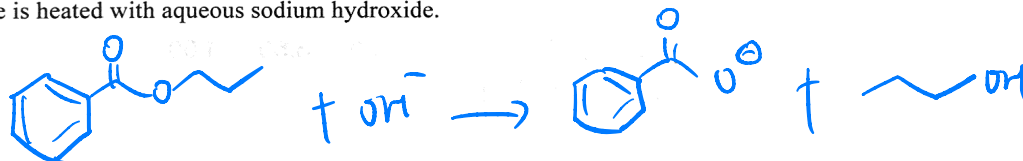
b. Sodium iodate is added to an excess of hydriodic acid.



c. Manganese(IV) oxide is added to concentrated aqueous hydrochloric acid.



d. Propyl benzoate is heated with aqueous sodium hydroxide.



e. Calcium oxide and graphite are heated to 2200 °C.



f. Iodine-124 undergoes radioactive decay by electron capture.



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6. [14%] Consider the properties of the group 1 elements, whose valence shell electron configuration is ns^1 in the table below.

Element M	n	First ionization energy, kJ mol^{-1}	Energy required to excite the valence electron to the $(n+1)s$ orbital, kJ mol^{-1}	Molar density of solid MCl , mol cm^{-3}
H	1	1312	984	0.0403
Li	2	520	325	0.0507
Na	3	496	308	0.0371
K	4	420	252	0.0266
Rb	5	403	241	0.0232
Cs	6	376	222	0.0237

- a. Rationalize the observed trend in first ionization energies with increasing n .

ns^1 is ionized, as $n \uparrow$, the energy level of $ns \downarrow$, thus the IE \downarrow .

- b. Suppose a hydrogen atom were excited to its $2s^1$ state. If that excited state atom were to transfer its electron to Cs^+ to form a ground-state Cs atom, how much energy would that reaction absorb or release?



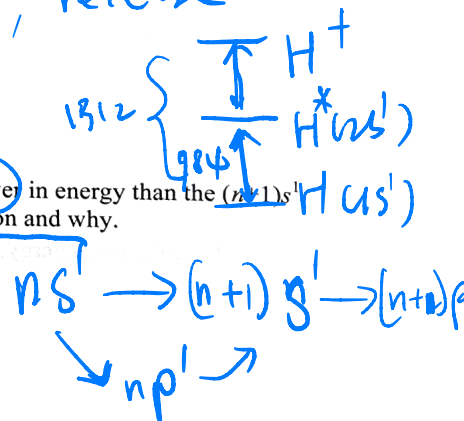
$$\Delta H = -376 + (1312 - 984) = -48 \text{ kJ/mol}, \text{ release}$$

$$q = -\frac{48 \times 10^3 \text{ J/mol}}{6.02 \times 10^{23} \text{ /atom}} = -8.0 \times 10^{-20} \text{ J/atom}$$

- c. All but one of the atoms listed in the table have an excited state that is significantly lower in energy than the $(n+1)s^1$ state described in the table. Explain this observation, noting which atom is the exception and why.

有 p 轨道比 s 轨道低! $ns^1 \rightarrow (n+1)s^1$

H, as all others have np^1 which is significant lower than $(n+1)s^1$, but H doesn't have $1p$!



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- d. All but one of the atoms listed in the table have an excited state that is modestly higher in energy ($38 - 55 \text{ kJ mol}^{-1}$) than the $(n+1)s^1$ state described in the table. Explain this observation, noting which atom is the exception and why.

其他都有 $(n+1)p$ 轨道比 $(n+1)s$ 高。只有 H 没有 ($(n+1)p$)!

$(n+1)p$ is modestly higher than $(n+1)s$ for all $\text{Li} \rightarrow \text{Cs}$ but H's $(n+1)p$ has the same energy as $(n+1)s$ as

it has only e^- , $ns = np$ (energy)

- e. The compounds $\text{MCl}(s)$ show a smooth decrease in their molar densities, except that $\text{HCl}(s)$ is less dense than expected from the trend and $\text{CsCl}(s)$ is more dense than expected. Explain this periodic trend, and give reasons for the two exceptions to the trend.

$\text{LiCl} \rightarrow \text{RbCl}$, similar lattice structures, volume increases more than that of the molar mass, thus $d \downarrow$

$\text{HCl}(s)$ is not ionic, but molecular, distance between molecules are larger, so density smaller; Cs^+ has a

- f. ^{137}Cs (136.9070895 amu) undergoes radioactive decay to give a stable product whose atomic mass is 136.9058274 amu. What type of radioactive decay is this, and what is the identity of the decay product?



β -decay

larger size, having more e^- surrounding thus, density higher

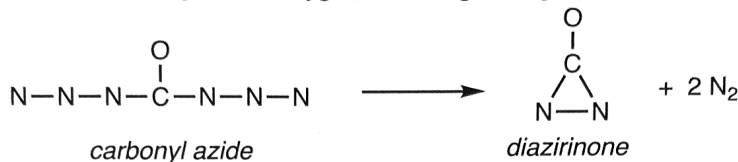
- g. Calculate the energy, in kJ mol^{-1} , released by the radioactive decay of ^{137}Cs .

$$\begin{aligned} \Delta E = \Delta mc^2 &= (136.9070895 - 136.9058274) \times (2.998 \times 10^8)^2 \times 6.022 \times 10^{23} \\ &= 1.136 \times 10^{14} \text{ J/mol} \\ &= 1.136 \times 10^{11} \text{ kJ/mol} \end{aligned}$$

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USNCO ID Number:

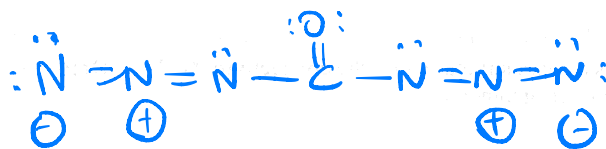
7. [13%] Flash vacuum pyrolysis of carbonyl azide (CON_6) at 420°C gives low yields of a cyclic compound, diazirinone, as shown in the equation below. Note that the illustrations of carbonyl azide and diazirinone correctly show the connectivity of the atoms but are NOT correct Lewis structures. The bond dissociation enthalpies (BDE, in kJ mol^{-1}) of various bonds among carbon, oxygen, and nitrogen are given in the table.



Bond	BDE, kJ mol^{-1}	Bond	BDE, kJ mol^{-1}	Bond	BDE, kJ mol^{-1}	Bond	BDE, kJ mol^{-1}
C-O	350	C-N	290	N-N	160	N-O	200
C=O	741	C=N	615	N=N	418	N=O	480
C \equiv O	1080	C \equiv N	891	N \equiv N	949		

- a. Draw complete Lewis structures for carbonyl azide and for diazirinone, including all lone pairs and nonzero formal charges. You need only draw one Lewis structure for each molecule, even if there are multiple possible resonance structures.

CA:



DA:



- b. Diazirinone decomposes in the gas phase over the course of several days at room temperature to give carbon monoxide and nitrogen gas. Based on the given BDEs, calculate ΔH° for this decomposition reaction.



$$\Delta H^\circ = 418 + 290 \times 2 + 741 - 1080 - 949 = \boxed{-290 \text{ kJ mol}^{-1}}$$

Question 7 (page 2 of 2)

USNCO ID Number:

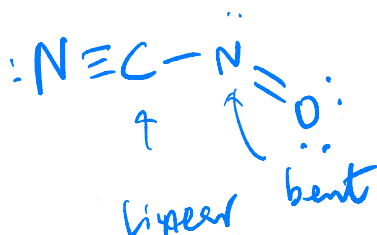
- c. The actual ΔH° for the decomposition of diazirinone is -347 kJ mol^{-1} . Comment on any discrepancy you find between this value and the value you determined in part b. Be sure your comment addresses the direction of deviation of the two values.

Actual is more exothermic than calculated!
 it is caused by the significant instability of $\text{N}=\text{N}$ due to the ring strain (small ring), this is why...

- d. Will ΔG° for decomposition at 298 K be algebraically greater than, less than, or equal to ΔH° for decomposition? Briefly justify your answer.

As more gas molecules are produced, $\Delta S^\circ > 0$,
 $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \Rightarrow \Delta G^\circ < \Delta H^\circ$

- e. There is an isomer of diazirinone that has a chain structure with the connectivity NCNO. Draw a Lewis structure for this molecule and clearly describe or sketch its geometry.



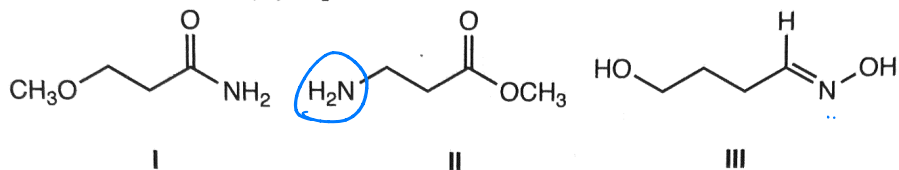
- f. Would you expect acyclic NCNO to be more or less stable than diazirinone? Clearly justify your prediction.

More stable, ring strain due to the less ideal bond angle distortion!

Question 8 (page 1 of 2)

USNCO ID Number:

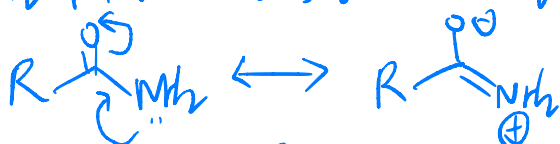
8. [12%] Consider the three isomers of $C_4H_9NO_2$ shown below:



a. Which compound is the most basic? Justify your answer.

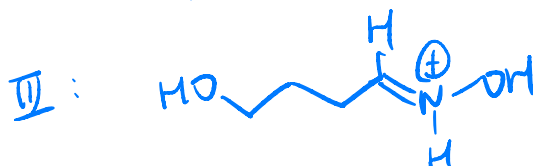
II; H_2N in II is the most basic.

The NH_2 in I is less basic as the N is resonanced with $C=O$,

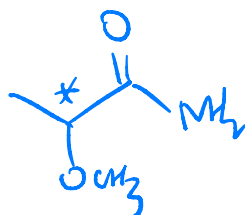


The N in II is sp^2 -hybridized, thus it is more electronegative, and less basic than that in I.

b. Draw the structures of the conjugate acids of the three compounds.



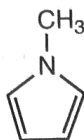
c. Draw the structure of a chiral isomer of $C_4H_9NO_2$.



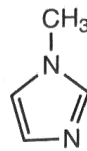
Question 8 (page 2 of 2)

USNCO ID Number: _____

Consider the two nitrogen heterocycles shown below:



IV



V

- d. Which compound is more basic? Draw the structure of its conjugate acid.

V is more basic.

CA of V:



- e. Which compound is more reactive towards Br_2 ? Explain why it is more reactive and draw the structure of a major product of its reaction with Br_2 .

IV is more reactive.

The circled N in V below is electron withdrawing, which decreases the e^- density in V, thus V is less reactive towards Br_2 as aromatic ring is the nucleophile (higher e^- density, more reactive)

major product of IV:

