#1. (20 points) Short Answer Questions.

a) The number of atoms in 10.0 g of $CaCO_3$ (100.0 g/mol) is:

[✓ **1.81×10^{23}**] **6.02×10^{22}** **3.01×10^{23}** **1.21×10^{23}**

b) The solubility of cobalt (II) hydroxide is highest in a buffer solution with a pH of

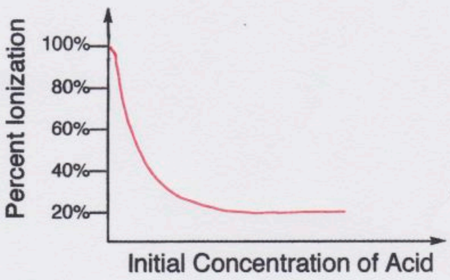
[✓ **3.5**] **8.5** **6.5** **10.5**

c) Balance the following reaction:

$\underline{2}$ Fe (s) + $\underline{6}$ HCl (aq) → $\underline{2}$ $FeCl_3$ (s) + $\underline{3}$ H_2 (g)

When 4.55 g of Fe (s) was reacted with HCl (aq), 0.101 g of H_2 (g) was formed. The percent yield of the reaction is 40.9% **.**

d) On the axes provided a right, draw a line (or curve) representing the percent ionization of a weak acid as a function of the initial concentration of the acid.



e) The standard heat of formation of solid potassium chlorate is -835 kJ. Write the chemical equation for the reaction to which this value applies.

$K(s) + \frac{1}{2} Cl_2(g) + \frac{3}{2} O_2(g) \rightarrow KClO_3(s)$

f) Find the overall balanced redox reaction (acidic conditions) from these half-reactions:

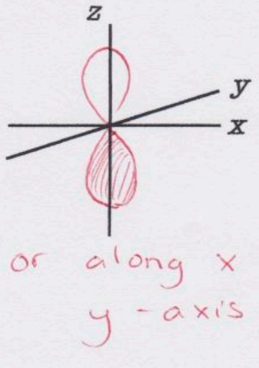
$2\,Cu^+ \rightarrow 2\,Cu^{2+} + 2e^-$

$2e^- + 2H^+ + BrO_2^- \rightarrow BrO^- + H_2O$

OVERALL: $2Cu^+ + 2H^+ + BrO_2^- \rightarrow 2Cu^{2+} + BrO^- + H_2O$

g) On the 3D axes provided at right, sketch an orbital that corresponds to the following set of quantum numbers: n = 2 and ℓ = 1.

a p orbital



(or along x or y-axis)

h) One way to make a buffer is to start with a concentrated solution of a weak base and titrate it to the half-equivalence point with a strong acid. **[✓ TRUE]** **FALSE**

i) For a given reaction, the plot of lnk versus 1/T yields a slope of - 13.9 and a y-intercept of 2.6×10^6. Knowing this information, the reaction has

$\ln k = \ln A - \frac{E_a}{R}\cdot\frac{1}{T}$

[✓ $E_a > 0$] $\Delta H < 0$ $E_a < 0$ $\Delta H > 0$

← in fact, this is ALWAYS true!

j) Name two factors that influence the speed of a chemical reaction:

i) catalyst

ii) temperature

concentration

surface area

} any 2

k) Name the following compounds.

$Fe(OH)_3$ iron (III) hydroxide

N_2O_5 dinitrogen pentoxide

l) Which of the following ions is the strongest base? F^- IO_3^- N_3^- [✓ CN^-]

HCN is weakest acid

m) Write the equilibrium constant expression for the following reaction, and choose the best means by which you could encourage the formation of hydrogen gas.

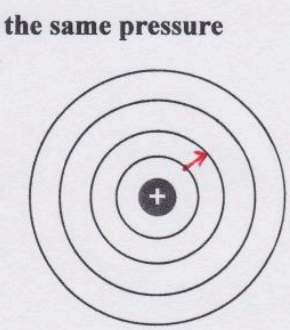
n) $C(s) + H_2O(g) \leftrightarrows CO(g) + H_2(g)$ $\Delta H^o = 211$ kJ

- **i) Add steam and remove heat**
- **[✓ ii)] Increase volume and add heat**
- **iii) Remove carbon monoxide and decrease volume**
- **iv) Add hydrogen gas and increase volume**

$$K = \boxed{\frac{P_{CO}\cdot P_{H_2}}{P_{H_2O}}}$$

o) A one litre balloon is filled with neon gas. A hole is made in the balloon and the gas effuses at a rate of 0.0106 mol/hr. If the same balloon is refilled with argon at the same pressure and temperature, its rate of effusion would be 0.0075 mol/hr.

p) On the Bohr Atom shown, draw an electronic transition that would correspond to the absorption of a photon with the longest wavelength.



$\Delta n > 0$ lowest energy

$\therefore n=1 \longrightarrow n=2$

#2.

a) (4 points) What is the minimum value of n for the following ℓ values and what is the maximum number of orbitals having these ℓ and n values?

$\ell = 1$ $n = 2$: This is the 2p subshell.

$m_\ell = -1, 0, +1$ ∴ there are $\underline{\underline{3}}$ 2p orbitals

$\ell = 3$ $n = 4$: This is the 4f subshell.

$m_\ell = -3, -2, 0, +1, +2, +3$ ∴ there are $\underline{\underline{7}}$ 4f orbitals

b) (2 points) How many electrons can be described by the each of the following sets of quantum numbers?

$\overset{\checkmark}{n = 3}, \overset{\checkmark}{\ell = 2}$ $m_\ell = -2, -1, 0, +1, 2$ This is the 3d subshell.

5 orbitals x $2e^-$ each = $10e^-$ overall

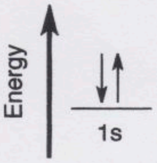
$\underbrace{n = 3, \ell = 3}$, $m_\ell = -1$, $m_s = -1/2$

impossible! $\ell \neq 3$ when $n = 3$. ∴ no orbital exists

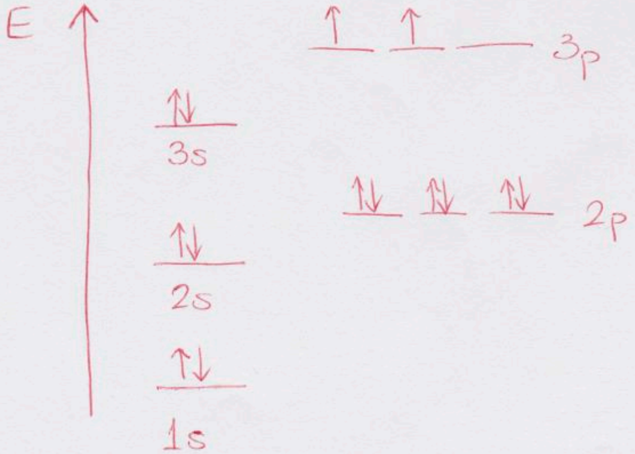
∴ $0e^-$

c) (4 points) Following the example of helium shown below, give the FULL spdf electronic configuration of silicon AND draw its orbital energy-level diagram.

Example: **Helium's spdf electronic configuration is $1s^2$ and its orbital energy-level diagram is:**



Si = $1s^2 2s^2 2p^6 3s^2 3p^2$



#3. In the Marion lab, you mix 25.0 g of CaO with exactly 80 mL of water at 25.0°C and you observe the following reaction, as well as the release of some steam:

$$CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(s)$$

a) (4 points) What is the reagent in excess and how many grams of it will be left at the end of the reaction?

$$? \text{ mol } Ca(OH)_2 \text{ from } CaO = 25.0 g \text{ } CaO \cdot \frac{\text{mol } CaO}{56.078 g \text{ } CaO} \cdot \frac{1 \text{ mol } Ca(OH)_2}{1 \text{ mol } CaO} = 0.446 \text{ mol} \quad *LR*$$

$$? \text{ mol } Ca(OH)_2 \text{ from } H_2O = 80 mL \cdot \frac{1g}{1mL} \cdot \frac{\text{mol } H_2O}{18.02 g \text{ } H_2O} \cdot \frac{1 \text{ mol } Ca(OH)_2}{1 \text{ mol } H_2O} = 4.44 \text{ mol}$$

$$? g \text{ } H_2O \text{ reacted} = 0.446 \text{ mol } CaO \cdot \frac{1 \text{ mol } H_2O}{1 \text{ mol } CaO} \cdot \frac{18.02 g \text{ } H_2O}{\text{mol } H_2O} = 8.04 g$$

$$? g \text{ } H_2O \text{ leftover} = 80.0 - 8.04 g = 72.0 g$$

Reagent in excess: H_2O **Mass:** 72.0g

b) (6 points) Using the data in the table below and on page 14, calculate the mass of the steam that escaped during the reaction.

CaO (s)	**ΔH_f^o = - 635 kJ/mol**
H_2O (l)	**ΔH_f^o = - 286 kJ/mol**
$Ca(OH)_2$ (s)	**ΔH_f^o = - 987 kJ/mol**

$$\Delta H_{rxn}^\circ = [\Delta H_f^\circ(Ca(OH)_2)] - [\Delta H_f^\circ(CaO) + \Delta H_f^\circ(H_2O)]$$
$$= [-987] - [(-635) + (-286)] \text{ kJ/mol}$$
$$= -66 \text{ kJ/mol}$$

$$\Delta H_{rxn} = \frac{q}{n} \quad \therefore q = n \times \Delta H_{rxn} = 0.446 \text{ mol } Ca(OH)_2 \cdot -66 \text{ kJ/mol } Ca(OH)_2$$
$$= -29.4 \text{ kJ} \quad \therefore q_{H_2O} = +29.4 \text{ kJ}$$

① Heat leftover water from 25°C → 100°C:

$$q = ms\Delta T = (72.0g)(4.184 J/g°C)(75°C) = 22.6 kJ$$

② Extra heat = +29.4 − 22.6 kJ = 6.8 kJ

③ Use extra heat to vaporize water: ΔH_{vap} = 40.7 kJ/mol

$$? g \text{ } H_2O(g) = 6.8 kJ \cdot \frac{\text{mol}}{40.7 \text{ kJ}} \cdot \frac{18.02 g}{\text{mol } H_2O} = 3.0 g$$

Answer: 3.0g

#4. The following reaction, occurring in a sealed vessel, has a percent yield of 94.9%:

$$2NaN_3\,(s) \rightarrow 2\,Na\,(l) + 3\,N_2(g)$$

a) (8 points) What volume of N_2, measured at 735 mmHg and 26.0°C, is produced when 75.0 g of sodium azide decomposes?

? theo mol $N_2 = 75.0g\ NaN_3 \cdot \frac{mol\ NaN_3}{65.02g\ NaN_3} \cdot \frac{3mol\ N_2}{2mol\ NaN_3} = 1.73\ mol$

? actual mol $N_2 = 1.73\ mol \times 0.949 = 1.64\ mol$

$V\ N_2 = \frac{nRT}{P} = \frac{(1.64mol)(0.08206\ L\cdot atm/(mol\cdot K))(299.15\ K)}{0.967\ atm}$

$= 41.6L$

Answer: 41.6L

b) (2 points) After the reaction is complete, argon gas is added to the vessel until the final total pressure is 1000 mmHg. What is the mole fraction of nitrogen in the gas mixture?

$\chi_{N_2} = \frac{P_{N_2}}{P_T} = \frac{735\ mmHg}{1000\ mmHg} = 0.735$

Answer: 0.735

#5. You are provided 500.0 mL of a 0.100 M solution of $NaHCO_3$, which you will use to prepare a carbonate buffer with pH = 10.10. Your TA gives you a 0.300 M stock solution of H_2CO_3 and a jar of solid Na_2CO_3. (For H_2CO_3, $K_{a1} = 4.2x10^{-7}$ and $K_{a2} = 4.8x10^{-11}$)

$\cdot H_2CO_3/HCO_3^- \nearrow$ $\nwarrow HCO_3^-/CO_3^{2-}$

a) (2 points) Which component, H_2CO_3 or Na_2CO_3, will you need to make the pH = 10.10 buffer? (Show your calculation to get the points, don't just guess!)

$pKa_1 = -\log(4.2\times10^{-7}) = 6.38$

$pKa_2 = -\log(4.8\times10^{-11}) = 10.32$

} choose HCO_3^-/CO_3^{2-} conjugate pair (it's closer to desired pH, 10.10)

Circle needed component: H_2CO_3 [✓ Na_2CO_3]

b) (4 points) How much of the needed component will you add to the 0.100 M $NaHCO_3$ solution to achieve the desired buffer pH? You may assume any volume change is negligible.

$pH = pKa + \log\left(\frac{[CO_3^{2-}]}{[HCO_3^-]}\right)$

$10.10 = 10.32 + \log\left(\frac{[CO_3^{2-}]}{[HCO_3^-]}\right)$

$\therefore \frac{[CO_3^{2-}]}{[HCO_3^-]} = 0.60$

$[CO_3^{2-}] = 0.60 \times [HCO_3^-]$

$= 0.060\ mol/L$

$\rightarrow \therefore ?\,g\ Na_2CO_3 =$

$0.500L \times \frac{0.060mol}{L} \times \frac{105.99g}{mol}$

$= 3.2g$

_______________ **mL of 0.300M H_2CO_3** ***OR*** 3.2g **g of Na_2CO_3**

c) (4 points) What will be the new pH of the buffer if 0.0030 mol of HCl is added to it?

$?\ mol\ HCO_3^- = (0.100\ M)(0.500\ L) = 0.050\ mol$

$?\ mol\ CO_3^{2-} = (0.060M)(0.500L) = 0.030\ mol$

	CO_3^{2-}	+ HCl	$\rightarrow HCO_3^-$	+ Cl^-
B	0.030	0.003	0.050	-
C	-0.003	-0.003	+0.003	-
A	0.027	0	0.053	-

$\therefore pH = pKa + \log\frac{[CO_3^{2-}]}{[HCO_3^-]}$

$= 10.32 + \log\frac{(0.027)}{(0.053)}$

$= 10.03$

Answer: 10.03

#6. The reaction of NO_2 and CO to make NO and CO_2 is believed to occur via a two-step mechanism:

① $NO_2 + \cancel{NO_2} \xrightarrow{k_1} NO + \cancel{NO_3}$

② $\cancel{NO_3} + CO \xrightarrow{k_2} \cancel{NO_2} + CO_2$

a) (2 points) What is the overall reaction? What is the reaction intermediate?

Overall rxn: $NO_2 + CO \rightarrow NO + CO_2$

Intermediate = NO_3

b) (3 points) The rate law is determined experimentally to be: rate = $k[NO_2]^2$. Is the proposed mechanism reasonable? Why or why not? What would be the rate-determining step?

rate step ① = $k_1[NO_2]^2$

rate step ② = $k_2[NO_3][CO]$

Yes, the mechanism is reasonable (so far): the expt'lly observed rate law matches one of the steps in the proposed mechanism → Step ① is ∴ the RDS.

c) (5 points) When the initial concentration of NO_2 is 0.010 M, the initial rate of reaction is 5.5×10^{-6} M/s. What is the concentration of NO_2 after 3.00 min if the initial concentration is changed to 0.033 M?

rate = $k[NO_2]^2$

$$k = \frac{5.5\times10^{-6}\,Ms^{-1}}{(0.010M)^2}$$

$= 0.055\,M^{-1}s^{-1}$

3 min = 180 s

$$\frac{1}{[NO_2]_t} = \frac{1}{[NO_2]_0} + kt$$

$$\frac{1}{[NO_2]_t} = \frac{1}{(0.033\,M)} + (0.055\,M^{-1}s^{-1})(180s)$$

$= 40.2\,M^{-1}$

$$\therefore [NO_2]_t = \frac{1}{40.2\,M^{-1}} = 0.025\,M$$

Answer: 0.025 M

#7.

a) (5 points) A student prepares a 0.120 M solution of an unknown monoprotic acid. At equilibrium, she measures the pH to be 3.820. What is the acid's ionization constant?

	$HA + H_2O$	$\rightleftarrows A^-$	$+ H_3O^+$
I	0.120	0	0
C	-1.51×10^{-4}	$+1.51\times10^{-4}$	$+1.51\times10^{-4}$
E	≈ 0.120	1.51×10^{-4}	1.51×10^{-4}

$pH = 3.820$

$\therefore [H^+] = 10^{-3.820}$

$= 1.51\times10^{-4}\,M$

$$\therefore K_a = \frac{[A^-][H_3O^+]}{[HA]} = \frac{(1.51\times10^{-4})^2}{0.120} = 1.9\times10^{-7}$$

Answer: 1.9×10^{-7}

(b) (5 points) Vinegar is a dilute aqueous solution of acetic acid. The legal minimum acetic acid content of vinegar is 4.0% *by mass*. Dr. Fox takes a 5.00 mL sample of President's Choice brand vinegar and titrates it to completion with 38.08 mL of 0.1000 M NaOH. Does the sample exceed the minimum content? (Vinegar has a density of about 1.01 g/mL).

$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$

$$?\,g\ CH_3COOH\ \text{present} = 0.03808\,L \times \frac{0.1000\,mol\ NaOH}{L} \times \frac{1\,mol\ CH_3COOH}{1\,mol\ NaOH} \times \frac{60.06\,g\ CH_3COOH}{mol\ CH_3COOH}$$

$= 0.2287\,g$

$$?\,g\ vinegar = 5.00\,mL \times \frac{1.01\,g}{mL} = 5.05\,g$$

$$\therefore m\%\ \text{of}\ CH_3COOH\ \text{in vinegar} = \frac{0.2287\,g}{5.05\,g} \times 100\% = 4.53\%$$

Answer: YES, it is >4%

#8.

a) (3 points) What is the molar solubility of Ag_2SO_4 in pure water?

$$Ag_2SO_4 \rightleftharpoons \underset{2s}{2Ag^+} + \underset{s}{SO_4^{2-}}$$

$$K_{sp} = (2s)^2(s) = 4s^3 = 1.4\times10^{-5}$$

$$\therefore s = 0.0152\,M$$

Answer: 0.0152 M

b) (3 points) What is the molar solubility of Ag_2SO_4 in 1.00 M Na_2SO_4?

	$Ag_2SO_4 \rightleftharpoons$	$2Ag^+$	$+\ SO_4^{2-}$
I	–	0	1.00
C	–	+2s	+s
E	–	2s	1.00+s

$$K_{sp} = (2s)^2(1.00+s)$$

$$1.4\times10^{-5} \approx 4s^2(1.00)$$

$$\therefore s = 1.87\times10^{-3}\,M \quad ✓$$

PASSES
ASSUMPTION.

Answer: 1.87×10^{-3} M

c) (4 points) KIO_3 is added to 1.00 L of the solution formed in part (b), and we observe the formation of a precipitate, $AgIO_3$. Calculate the mass of KIO_3 (in mg) needed to start the precipitation.

$$AgIO_3 \rightleftharpoons Ag^+ + IO_3^-$$

$$K_{sp} = 3.0\times10^{-8} = [Ag^+][IO_3^-]$$

$$[Ag^+] = 2s = 2(1.87\times10^{-3}\,M)$$

$$= 0.00374\,M$$

$$\therefore \underset{max}{[IO_3^-]} = \frac{K_{sp}}{[Ag^+]} = \frac{3.0\times10^{-8}}{0.00374} = 8.02\times10^{-6}\,M$$

$\therefore$? mg KIO_3 needed =

$$1.00\,L \times \frac{8.02\times10^{-6}\,mol}{L} \times \frac{214.0\,g}{mol} \times \frac{1000\,mg}{g}$$

$$= 1.72\,mg$$

Answer: 1.72 mg

#9. Indigo, the dye for blue jeans, has a percent composition, by mass, of 73.27% C, 3.84% H, 10.68% N, and the remainder is oxygen. the molecular mass of indigo is 262.3 u.

a) (5 points) What is the molecular formula of indigo?

$? \text{ mol C} = 73.27\text{g} \cdot \frac{\text{mol C}}{12.011\text{g}} = 0.061 \text{ mol C}$

$? \text{ mol H} = 3.84\text{g H} \cdot \frac{\text{mol H}}{1.0079\text{g}} = 0.038 \text{ mol H}$

$? \text{ mol N} = 10.68\text{g N} \cdot \frac{\text{mol N}}{14.01\text{g}} = 0.0076 \text{ mol N}$

$? \text{ mol O} = 12.21\text{g} \cdot \frac{\text{mol O}}{15.999\text{g}} = 0.0076 \text{ mol O}$

$\text{EF} = C_{\frac{0.061}{0.0076}} H_{\frac{0.038}{0.0076}} N_{\frac{0.0076}{0.0076}} O_{\frac{0.0076}{0.0076}}$

$= C_8H_5NO$

EF mass = 131.14 u

$\frac{\text{MF mass}}{\text{EF mass}} = \frac{262}{131} = 2$

$\therefore \text{MF} = 2 \times \text{EF}$

$= C_{16}H_{10}N_2O_2$

Answer: $C_{16}H_{10}N_2O_2$

b) (3 points) A 0.451 g sample of indigo undergoes complete combustion in a bomb calorimeter. It is found that the bomb calorimeter absorbs 264.8 J of heat during the reaction. What is the enthalpy of combustion, in kJ/mol, of indigo?

$? \text{ mol } C_{16}H_{10}N_2O_2 = 0.451\text{g} \cdot \frac{\text{mol}}{262.3\text{g}} = 0.00172 \text{ mol}$

$q_{rxn} = -q_{cal} = -264.8\text{ J}$

$\therefore \Delta H_{comb} = \frac{q_{rxn}}{n} = \frac{-264.8\text{J}}{0.00172\text{mol}} \cdot \frac{\text{kJ}}{1000\text{J}} = -154 \text{ kJ/mol}$

Answer: −154 kJ/mol

c) (2 points) What is the change in internal energy for the reaction in part (b)?

$\Delta U = q + W$ but $W = 0$ $(\Delta V = 0)$

$\therefore \Delta U = q = -264.8\text{ J}$

Answer: −264.8 J