Question 1 (25 points) **ANSWERS**

Picric acid, $C_6H_3N_3O_7(s)$, can explode in air, forming $NO_2(g)$, $CO_2(g)$, and $H_2O(g)$.

a) (4) Balance the chemical reaction for the explosion:

$$\underline{4}\ C_6H_3N_3O_7(s) + \underline{25}\ O_2(g) \rightarrow \underline{12}\ NO_2(g) + \underline{24}\ CO_2(g) + \underline{6}\ H_2O(g)$$

b) (4) A glass bulb is evacuated and weighed. Oxygen (O_2) gas is added, and the bulb reweighed. The empty bulb weighed 44.118 g, and the filled bulb 50.153 g. How many moles of $O_2(g)$ are present?

mass $O_2(g)$ = 50.153 – 44.118 = 6.035 grams

molar mass O_2 = 2 x 15.9994 g/mole = 31.9988 g/mole

moles $O_2(g)$ = 6.035/31.9988 = 0.1886008 → 0.1886 moles [4 s.f.]

c) (7) 6.00 grams of picric acid is added to the container. Which will be the limiting reagent in the explosion?

M = 6(12.011) +3(1.00794) + 3(14.0067) + 7(15.9994) = 229.106 g/mole

n = w/M = (6.00 g)/(229.10578 g/mole) = 0.02618875 moles.

Suppose the picric acid was limiting:

From the reaction, (moles O_2 reacting)/(moles picric acid acid reacting) = 25/4,

so moles O_2 reacting = (25/4)(0.02618875) = 0.16367969

There is more than enough O_2, so the picric acid is limiting.

If you calculated moles of one product produced by each, and said picric was limiting without saying why, I deducted 2 points. You logic must be explicit! For example, "since picric acid produces less NO_2, it is limiting."

d) (10) Based on the amounts given in parts b and c, how many moles each of the following are present after the explosion goes to completion?

moles $C_6H_3N_3O_7(s)$ none: it is limiting **moles $O_2(g)$** 0.025

moles $NO_2(g)$ 0.0786 **moles $CO_2(g)$** 0.157

moles $H_2O(g)$ 0.0393

Calculations: (3 sig, figs for moles reacting, due to 6.00g picric acid)

0.02618875 moles picric acid react with O_2 forming (6/4)(0.02618875) = 0.0392831 moles H_2O

moles NO_2 = 2 x moles H_2O = 0.0785663, and moles CO_2 = 2 x moles H_2O = 0.1571325

Moles O_2 remaining = initial moles – moles reacting

= 0.1886008 – 0.16367969 = 0.0249211 moles → 0.025 moles

Question 2 (20 points) **ANSWERS**

A drug used in the treatment of AIDS is azidothymidine, or AZT. Elemental analysis of AZT shows that it contains the following percents by weight: C (45.11%), N (26.30%), O (24.04%), and the rest H.

a) (15) What is the empirical formula of AZT?

Consider a 100 gram sample of AZT. [← *say this!]* Then the %'s by weight become grams:

(the mass of H [or the percent] is found by subtracting all the others from 100)

	w / M =	moles / smallest =	molar ratio → round*	integer ratio	× 4
C	45.11/ 12.011	= 3.7557239 /1.5025563	= 2.499556 → 2.500	= 2 1/2	**10**
N	26.30/ 14.0067	= 1.8776728 /1.5025563	= 1.249652 → 1.250	= 1 1/4	**5**
O	24.04/ 15.9994	= 1.5025563 /1.5025563	= [1.0] → 1	= 1	**4**
H	4.55/ 1.00794	= 4.5141575 /1.5025563	= 3.004318 → 3.00	= 3	**12**

so the empirical formula is $\mathbf{C_{10}H_{12}N_5O_4}$ or $\mathbf{(C_{10}H_{12}N_5O_4)_n}$

* *You must round to the correct number of significant figures immediately after finding the molar ratios. Then the significant figure rule that says that the rightmost digit is uncertain allows you to decide what integer ratio is a possible equivalent. (Example: 1.250 is equal to 1 1/4, while 1.24965 is not! Likewise 1.250 ≠ 6/5 = 1.200, but this would be a possible answer if we had only 3 significant figures.) I deducted points for omitting correct rounding even if you got the correct ratio, since you did not give me evidence that you have carefully taken significant figures into account in your reasoning.*

b) (5) It is determined that the molecular weight of AZT is approximately 270. What is the molecular formula of AZT?

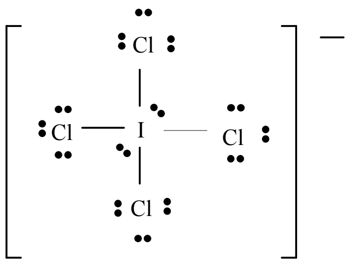
based on the empirical formula, the approximate molecular weight is 10(12)+5(14)+4(16)+12(1) = 266 × n. *(No need to find a more accurate value here.)*

If the experimental weight is 270, then n must be 1. Therefore the correct molecular formula is $C_{10}H_{12}N_5O_4$

Question 3 (27 points) **ANSWERS**

Specify the total number of valence electrons and write the Lewis electron dot structure for each of the following. If there are multiple resonance structures, include them. Specify the *molecular* geometry, including approximate angles. Finally, indicate whether the molecule is polar. In each case, the first atom listed is in the center, the others bound to it.

a) ICl_4^- (I in the center, bound to each Cl) **# valence electrons:** 5(7) + 1 = 36

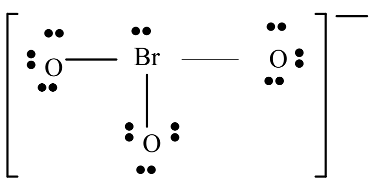


After filling all octets, there are 4 extra electrons. Thus it is necessary to violate the octet rule. Since I is farther down in the periodic chart, it can accommodate an expanded valence shell. Electron domain # (number of electron pair groups) at I is 6, so framework is octahedral.
The lone pairs repel each other strongly: they occupy opposite positions.

Molecular geometry: **square planar** **Cl-I-Cl angles:** 90° (and 180°).

Polar? No.

b) bromate: BrO_3^- **# valence electrons:** 7 + 3(6) + 1 = 26

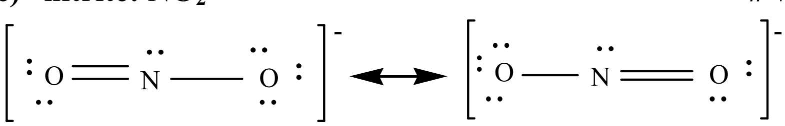


All octets satisfied, no need for multiple bonds.
Electron domain # at Br is 4, so tetrahedral framework.
One lone pair.

Molecular geometry: **trigonal pyramid** **O-Br-O angles**: ~109° (or a little < 109°)

Polar? Yes.

c) nitrite: NO_2^- **# valence electrons:** 5 + 2(6) + 1 = 18



Two resonance structures. Please put two-way arrow between them, not "or"!

Electron domain # at N is 3: framework is planar trigonal; one position occupied by lone pair..

Molecular geometry: **bent** **O-N-O angle**: ~120° (or a little < 120°)

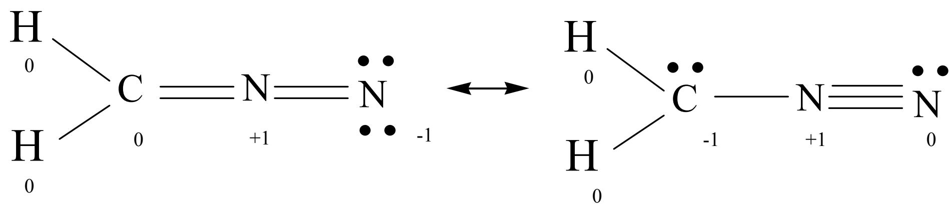
Polar? Yes

All triatomic molecules are planar, since three points always fall in the same plane, so planar is a useless statement here. Triatomic molecules may be either linear (180°) or bent (<180°).

Question 4 (27 points) **ANSWERS**

The three parts of this question are not related to each other

A) (10 points) Resonance structures for diazomethane, CH_2N_2, are



sum of formal charges must always equal molecular charge, here 0.

Label each atom in each structure with its formal charge.
What would you predict for the approximate bond order of the N-N bond? Why?

How do these differ? The left structure puts the –1 formal charge on N, the right on C. Since N is more electronegative than C, N tolerates a negative formal charge better. Thus the left structure is better, so the N-N bond is closer to double than triple: Bond order between 2 and 2.5 or a little more than 2. *If you said 2.5, you ignored the consequences of formal charge.*

B) (12 points) Nanoscience is in the news: the science dealing with structures whose dimensions are on the order of nanometers (10^{-9} m). Consider a cube of gold with length 15 nm. If the density of gold is 19.3 g/mL, what mass of gold is in the cube? How may gold atoms are present?

15 nm = 15×10^{-9} m = 1.5×10^{-8} m = 1.5×10^{-6} cm.

V = $(1.5 \times 10^{-6}\text{ cm})^3 = 3.\underline{3}75 \times 10^{-18}\text{ cm}^3 = 3.\underline{3}75 \times 10^{-18}$ mL

mass = density x volume = (19.3 g/mL)(3.375×10^{-18} mL) = 65.1375×10^{-18} grams

mass = $\underline{6.5 \times 10^{-17}\text{ g}}$

moles = mass/(at. wt.) = (6.51375×10^{-17} grams)/196.9665 g/mole = $3.3070344 \times 10^{-19}$ moles

atoms = N_A(moles) = (6.0221415×10^{23})($3.\underline{3}0703.. \times 10^{-19}$ moles) = 199,154 atoms

There are $\underline{2.0 \times 10^5}$ atoms in the cube. *2 s.f., due to the 15 nm*

Fractional atoms do not exist, so any nonsensical value < 1 resulted in an extra deduction.

C) (5 points) In an imaginary world the element Bo (Bogusium) has two isotopes. ^{14}Bo weighs 13.976532 with natural abundance 56.45%, and ^{16}Bo weighs 15.995432 with natural abundance 43.55%. Calculate the atomic weight of Bo.

atomic weight = (0.5645)(13.976532) + (0.4355)(15.995432)

= $7.88\underline{9}75... + 6.96\underline{6}010 = 14.8557629 \rightarrow \underline{14.856}$

Please come ask if you do not understand how to calculate a weighted average.

Question 5 (24 points) **ANSWERS**

A. (12) Complete the blank entries in the list of chemical formulas and compound names below. Indicate whether each compound is ionic or molecular by circling I or M.

CHEMICAL FORMULA	COMPOUND NAME	IONIC or MOLECULAR	
MgI_2	___magnesium iodide________	<u>I</u>	M
SO_3	___sulfur trioxide ___________	I	<u>M</u>
PCl_5	___phosphorus pentachloride__	I	<u>M</u>
NH_4NO_2	___ammonium nitrite________	<u>I</u>	M
$Ca_3(PO_4)_2$	Calcium phosphate	<u>I</u>	M
CS_2	Carbon disulfide	I	<u>M</u>
K_2SO_3	Potassium sulfite	<u>I</u>	M
$Pb(OH)_2$	Lead (II) hydroxide	<u>I</u>	M

B) (12) Explain the following observations. Use complete sentences. Sketches or diagrams may be helpful in some cases.

a) Alkali metals form +1 cations exclusively (never +2 or +3).

Alkali atoms have <u>one valence electron</u>: one electron more than the rare gases that precede them in the periodic chart. Losing one electron, becoming the +1 cation, gives them a <u>stable rare gas electronic configuration</u>. They are not +2 or +3, since that would entail removing an electron from a closed shell (rare gas) configuration.

b) CaO(s) mixed with water makes a basic solution.

Metal oxides are generally basic. The oxide anion, O^{2-}, is not stable in water; it combines with water to form hydroxide. For CaO(g) the relevant reaction is

$$CaO(s) + H_2O(\ell) \rightarrow Ca^{2+} + 2\ OH^{-}(aq)$$

Basic solutions have excess OH^-.

The answer must either show or say how OH is formed. Never write $Ca(OH)_2(aq)$ in chemical reaction equations: show separate ions, since that is how they exist in solution. CaO(s) does not contain hydroxide, it produces it when the oxide reacts with water.

c) Aqueous solutions containing transition metal ions are frequently colored.

Transition metals have <u>partially filled d orbitals</u>. When <u>light is absorbed</u>, a <u>valence electron</u> is promoted to the <u>first excited state</u>. The corresponding <u>energy gap</u> for many transition metal ions corresponds to the <u>energy of visible light</u>. We see the color of the light which is not absorbed: the transmitted light. (This can be seen in the equation $\Delta E = hc/\lambda$, where λ is the wavelength of the light.) *Essential points underlined. I did not expect you to write equations. This was discussed in Lab lecture, week 3. The ions are in the solution already: no ions forming, no reactions happening.)*

Comments about Results and Grading: PLEASE READ CAREFULLY

If you think I have added wrong on a question or have entered the numbers into the computer incorrectly (so the total is wrong), please come see me: I want this to be correct.

I was quite pleased with the results: many of you did very well, and a class average of 77% is excellent. I make some comments below on my grading policies and practices.

Since I give a lot of partial credit when the answer is wrong, I also deduct points even when the answer is correct, if you have not shown your work or justified your answer. I don't need detailed expositions, and I can often figure out what you were doing, but if you provided no explanation or I was unable to figure it out, then you have not shown me your work adequately.

Since I try to grade more than a hundred papers quickly, I cannot write long corrections or explanations on each paper. General comments based on common errors are written in italics in the answers above. Some of the possibly cryptic grading comments may be explained below.

Never give me two answers to a question: I will not pick the correct one or give partial credit! A question has one answer: I don't do multiple choice.

When I write **ok** next to a value, it is wrong, but was found correctly based on a previous error. I deduct points once, where the error occurs.

I write **redundant** when you do unnecessary extra calculations. This is not wrong (points not deducted), but it suggests that you do really understand what you are doing, and it wastes time.

s.f. or sig. figs. means a significant figure error.

In empirical formula problems, the ratio of integers must agree with the calculated value to the correct number of significant figures --- it may differ only in the last digit --- so if you fail to indicate how many are significant by rounding the ratios to the correct values (or showing with an underline), then your selection of the corresponding ratio has not been properly justified.

% → g or **how?** next to 45.11 g means that you failed to explain how a % by weight becomes a mass in grams. You must say something like "Consider 100 g."

In question 3, I asked for the *molecular* geometry. If you wrote something like "tetrahedral/trigonal pyramid" I can guess what you were thinking (tetrahedral framework, trigonal pyramid molecule), but since you wrote what could be interpreted as two different possible answers to the question, I did not give you any credit. Answer the question *as asked*!

If a small calculation error results in an absurd answer, and you do not comment on the fact that it is clearly wrong, I deduct extra points. A cube 15 nm on a side cannot weigh 65 grams, nor can it have a small fraction of an atom! Always think about the size of your answers: ask yourself if they are reasonable. If they are not, and you do not have time to find you error, tell me, for example: "too big!" or "impossible". That will avoid an extra deduction for nonsense.

In question 5, part B, I asked you to *explain* the observations. Answers that restated the facts in different words, or supplied different facts, do not answer the question. If you go overboard writing extraneous stuff, I deduct points. Science writing must be concise and to the point.

You MUST write your name on every page. In the future, a point will be deducted per page if you fail to follow this instruction.