5.111
PRINCIPLES OF CHEMICAL SCIENCE

	SCORE	TOTAL
Q1	18	22
Q2	0	16
Q3	34	38
Q4	17.5	24
Q5	13	30
Q6	6	12
Q7	6	20
Q8	7	27
Q9	7	11
Q10	12	12
Q11	12	12
Q12	9	12
Q13	8	22
Q14	15	30
Q15	12	12

174 / 300 = 58.%

NOTE FROM SCOTT:

THIS WAS A COMPILATION OF MIDTERMS, RATHER THAN A FINAL EXAM, INITIALLY DONE AS PRACTICE UNFORTUNATELY, AS I COULDN'T OBTAIN A VIABLE FINAL EXAM IT STANDS AS THE BASIS OF EVALUA ALTHOUGH I DID SIGNIFICANT PREPARATION AFTERWARD.

Written Nov 20th, 2011

Scott Young

1. (22 points) **The photoelectric effect**

A beam of light with an intensity of 15 W is incident on a copper plate ($\phi = 7.43 \times 10^{-19}$ J). Electrons with a minimum wavelength of 3.75×10^{-10} m are ejected from the surface of the copper.

(a) (12 points) Calculate the frequency of the incident light.

$$\lambda = \frac{h}{p} \qquad E = \frac{p^2}{2m} =$$

$$E = hf$$

$$\cancel{E = h \cdot c / \lambda}$$

$$p = \sqrt{2Em}$$

$$\cancel{\frac{E}{hc} = \frac{1}{\lambda}}$$

$$\lambda = \frac{h}{\sqrt{2Em}}$$

$$2Em = \left(\frac{h}{\lambda}\right)^2$$

$$E = \frac{(h/\lambda)^2}{2m}$$

$$f = \cancel{\frac{2\pi}{h}} \frac{E}{h}$$

$$E = \frac{(h/3.75 \cdot 10^{-10})^2}{2(9.1094 \cdot 10^{-31})}$$

$$\frac{E}{2\pi hc} = f$$

$$= \frac{\left(\frac{6.6261 \cdot 10^{-34}}{3.75 \cdot 10^{-10}}\right)^2}{2(9.1094 \cdot 10^{-31})}$$

$$f = \frac{2.45667 \cdot 10^{-18}}{\cancel{2\pi} \cdot 6.6261 \cdot 10^{-34} \cdot \cancel{2.998 \cdot 10^8}}$$

$$= \frac{3.1221 \cdot 10^{-48}}{1.82188 \cdot 10^{-30}} = \underline{1.7136 \cdot 10^{-18}} \text{ J} \checkmark$$

$$= 21.972 \text{ mHz}$$

$$1.7136 \cdot 10^{-18} + 7.43 \times 10^{-19} =$$

$$= 3.71 \cdot 10^{15} \text{ Hz}$$

$$\underline{2.45667 \cdot 10^{-18} \text{ J}}$$

$$\checkmark \quad \text{incident light} \atop \text{beam}$$

A beam of light with an intensity of 15 W is incident on a copper plate (ϕ = 7.43 x 10^{-19} J). Electrons with a minimum wavelength of 3.75 x 10^{-10} m are ejected from the surface of the copper.

(b) (6 points) Calculate the maximum number of electrons that can be ejected by a 3.0-second pulse of the incident light.

# of photons =

$$\frac{45 J}{Energy\ per\ photon}$$

✓

⑥

$$= \frac{45}{hc/\lambda}$$ ~~same wrong~~
formula ~~from before~~

$$= \frac{45}{(2.9979 \cdot 10^{14}) \cdot (6.6261 \cdot 10^{-34})}$$

$$3.189 \cdot 10^{-6}$$

$$= 2.27 \cdot 10^{20}\ photons$$ ✗   CARRY
FORWARD

(c) (4 points) If a new light source (E_i = 7.19 x 10^{-19} J) with an intensity of 35 W is incident on the copper surface, what is the maximum number of electrons that can be ejected from a 6.0 second pulse of light?

None can be ejected because

$$E_i < \phi$$

④

✓

2. (16 points) **One-electron atoms:**

Consider a Ca^{19+} ion with its electron in the 5th excited state. *this corresponds to n=6, not 5!*

(a) (12 points) Calculate the longest wavelength of light that could be emitted when the Ca^{19+} electron transitions to a lower energy state. Report your answer with three significant figures.

$$E_n = -\frac{Z^2 R_H}{n^2} \quad \text{use } \mathcal{R} \text{ not } R_H!! \quad = \quad E = \frac{hc}{\lambda}$$

$$E_{5 \to 1} = -\frac{Z^2 R_H}{25} - Z^2 R_H \qquad \mathcal{R} = \quad \lambda = \frac{hc}{E}$$

$$\times \qquad = -Z^2 R_H \left(\frac{1}{25} - 1\right) \qquad \lambda = 2.373 \cdot 10^{-11}$$

$$= Z^2 R_H \left(\frac{24}{25}\right) \qquad \boxed{= 2.37 \cdot 10^{-10} \, m}$$

$$= 20^2 (2.1799 \cdot 10^{-18}) \left(\frac{24}{25}\right)$$

$$= 384 (2.1799 \cdot 10^{-18})$$

$$= 8.371 \times 10^{-16} \, J$$

(b) (4 points) Suppose the same transition as in part (a) took place in a **hydrogen atom**. Would the wavelength of emission be longer than, shorter than, or the same as your answer to part (a). Very briefly explain why. *(Note: This question does NOT require a calculation. Also, you do not need to use the answer to part (a) to answer this question.)*

The photon would have less energy (corresponding to a lower z) and, as a result, the emitted photon would have a higher frequency and thus shorter waveleng
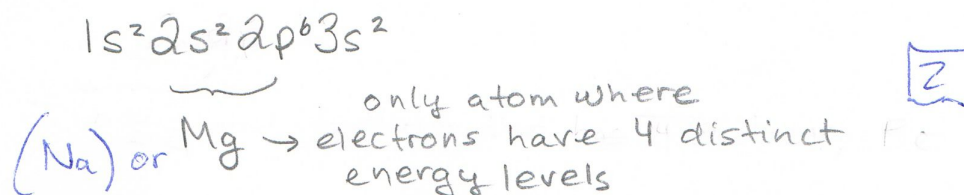
really?!

3. (32 points) **Multi-electron atoms**

(**a**) (16 points) An x-ray photoelectron spectroscopy experiment with an unidentified element, **X**, displays an emission spectrum with four distinct kinetic energies: 5.9×10^{-17} J, 2.53×10^{-18} J, 2.59×10^{-20} J, and 2.67×10^{-20} J. (Assume the incident light has sufficient energy to eject any electron in the atom.)

(**i**) (4 points) Name all of the possible ground state atoms that could yield this spectrum.

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

$\underbrace{\qquad}$ only atom where

(Na) or Mg → electrons have 4 distinct energy levels

$\boxed{2}$

(**ii**) (8 points) Calculate the **binding energy** of an electron in the 2p orbital of element **X** if the x-rays used for the spectroscopy experiment had an energy of 2.68×10^{-16} J.

$E_{BIND} = \text{Light Energy} - \text{Ejection Energy}$

$= 2.68 \cdot 10^{-16} - 2.53 \cdot 10^{-18}$

$\doteq 2.65 \cdot 10^{-16}$ J

↳ 2nd highest energy electron

$KE = E_{light} - E_{BINDING}$

$E_{light} - KE = E_{BINDING}$

✓

$\boxed{8}$

(**iii**) (4 points) Consider both the filled and unfilled orbitals of element **X**. Determine the number of:

total nodes in a 4d orbital:
angular nodes = ℓ
radial nodes = $n-\ell-1$ total nodes = $n-1 = \boxed{3}$ xy, yz, xz, z^2, x^2-y^2

angular nodes in the 2p$_y$ orbital:
one angular node

degenerate 5p orbitals:
three degenerate 5p orbitals ✓

$\boxed{4}$

(b) (22 points) The first, second, and third ionization energies of phosphorus are 1011 kJ/mol, 1903 kJ/mol, and 2912 kJ/mol respectively.

(i) (8 points) Calculate the effective nuclear charge (Z_{eff}) experienced by a 3p electron in phosphorus.

1011 kJ/mol

$$IE = \frac{(Z_{eff})^2 R_H}{n^2}$$

$$= \frac{(Z_{eff})^2 R_H}{9} = \frac{1011000}{avogadro's \#}$$

didn't average the three ionize... energies

3 shell

forgot √

$$(Z_{eff})^2 = \sqrt{\frac{9 \cdot 1011\,000}{R_H \cdot 6.022 * 10^{23}}}$$

[6]

$$= \frac{9099000}{2.1799 \cdot 10^{-18} \cdot 6.022 \cdot 10^{23}}$$

$$= \frac{90.99}{2.1799 \cdot 6.022} = \boxed{6.931}$$

(ii) (4 points) Would it be expected that the minimum energy necessary to eject a 3s electron from phosphorus in a photoelectron spectroscopy experiment be **larger**, **smaller**, or **the same** as the 4th ionization energy (IE_4) of phosphorus? Briefly explain your answer.

The minimum energy would be smaller because the 4th ionization energy does eject a 3s electron except there is less electron shielding, resulting in a higher Z_{eff}.

[4]

(iii) (4 points) Which experience **less** shielding, 3s-electrons or 3p-electrons in phosphorus? Very briefly explain why.

> 3s electrons experience less shielding because they have more probability density closer to the nucleus.

✓

④

(iv) (4 points) On the plot below, graph the radial probability distribution for a phosphorus 3p orbital with a solid line. Label the r_{mp}, and point to each node with an arrow. Label the axes, but do not include numbers or units.

radial nodes $= n - \ell - 1 = 3 - 1 - 1 =$

electron probability density

✓

4

r_{mp} radius

radial node
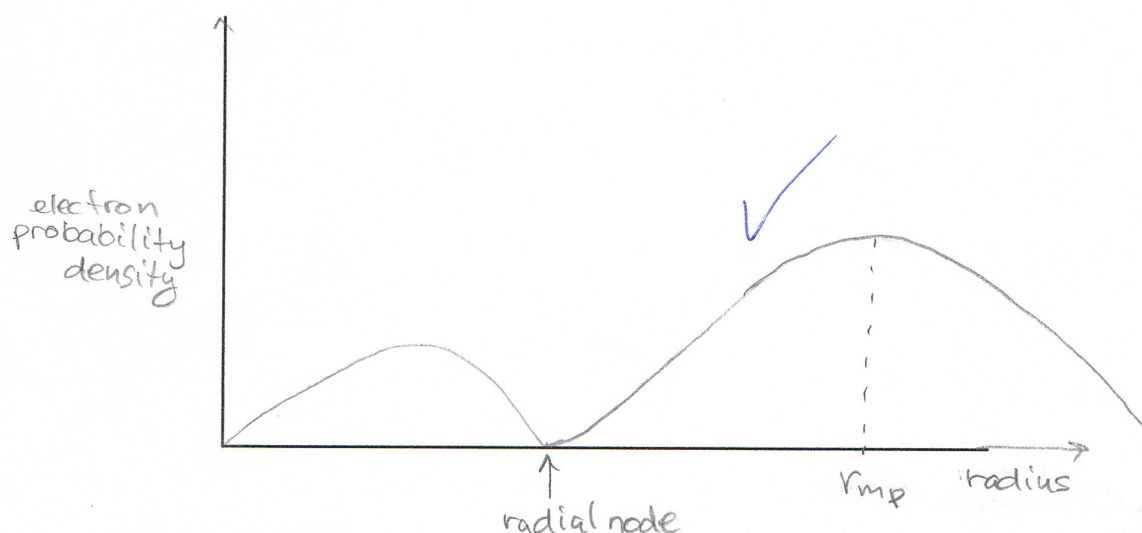
(v) (2 points) Is the r_{mp} for a **hydrogen** 3p orbital **longer** or **shorter** than the r_{mp} for a 3p phosphorus orbital? Very briefly explain why.

> The r_{mp} is longer for a Hydrogen 3p orbital because there is less positive charge at the nucleus pulling the electrons inward.

2

4. (24 points) **Periodic trends and miscellaneous short answer**

(a) (5 points) Consider the **second** ionization energies (IE_2) for the following 3rd row elements: Si, S, Mg, Al.

(i) Which has the highest IE_2?

Sulfur has the highest second ionization energy ✓

2.5

(ii) Which has the third highest IE_2?

Aluminum has the third highest

✗

(b) (5 points) Order the following atoms and ions in order of **increasing** atomic radius: Cl, Te, Te^{2-}, S. Note: use the < symbol for clarity.

$Cl < S < Te < Te^{2-}$

✓   5

(c) (6 points) Give the electron configuration expected for the following atoms or ions. *(You may use the noble gas configuration as a means to abbreviate the full configuration.)*

(i) Pb (Z = 82)

Xe $6s^2 5d^{10} 4f^{14} 6p^2$ ✗   2

(ii) Mo (Z = 42)

Kr $5s^1 4d^5$ ✓

(iii) Zr^+ (Z = 40)

Kr $5s^2 5d^1$ ✗ $[Kr] 4d^2 5s^1$

(d) (4 points) In one sentence (or less!), briefly explain the physical interpretation of Ψ^2 for a hydrogen atom.

Ψ^2 is the probability density of an electron in the orbital specified. ✓

(e) (4 points) How many **electrons** in a single atom can have the following two quantum numbers: n = 7, m_l = -3?

$n = 7$ $\ell \geq 3, \ell \leq 6$
$m_\ell = -3$

$\underline{n = 7}$
$\underline{\ell = 3, 4, 5, 6}$ 8
$\underline{m_\ell = -3}$
$m_s = \frac{1}{2}, -\frac{1}{2}$ ✓

8

1. (30 points) **Lewis structures and VSEPR theory**
Draw the **most stable** Lewis structure for each of the following molecules, subject to the information given for each. Be sure to **include the lone pairs** and, if applicable, draw any **resonance forms** that are equal in energy. **Indicate any nonzero formal charges**.

(a) (i) (6 points) Draw the Lewis structure of $POCl_3$. Include any relevant resonance forms, and indicate any nonzero formal charges.
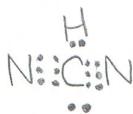
$$O::P:Cl \quad (Cl \text{ above}, \ddot{C}l \text{ below})$$

$$O=P-Cl \quad (Cl \text{ above and below})$$ ✓
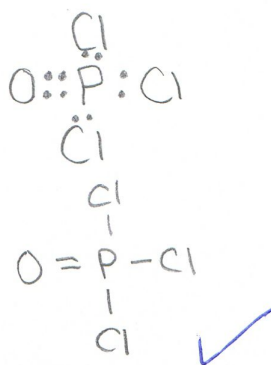
1) $5+21+6=32$
2) $32-32=$

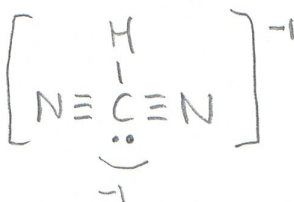(ii) (2 points) Name the geometry around the phosphorus atom.

tetrahedral ✓

(b) (8 points) Draw the Lewis structure of $(NCNH)^{-1}$ (atom order as indicated). Include any relevant resonance forms, and indicate any nonzero formal charges.
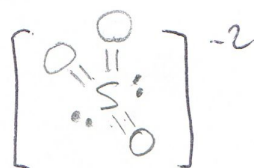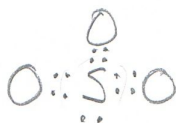
$$N::C::N \quad (H \text{ above})$$

$$\left[N=C\equiv N \right]^{-1} \quad (H \text{ above}) \quad -1$$ ✗

1) $5+5+4+1=15$
2) $16-1$

(c) (i) (6 points) Draw the Lewis structure of $(SO_3)^{-2}$. Include any relevant resonance forms, and indicate any nonzero formal charges.

1) $6 \cdot 4 = 24 + 2 = 26$
2) $32 - 26 = 6$ bonding electi

$O :: \ddot{S} :: O$ with O above and lone pairs

$O = \ddot{S} = O$ with O above

$\left[\begin{array}{c} O \cdots \overset{O}{\underset{}{\ddot{S}}} \cdots O \end{array} \right]^{-2}$ ✗

(ii) (2 points) Name the geometry around the sulfur atom.

trigonal planar ✗ ✓
CARRY FWD ERROR

pyramidal ①

(iii) (3 points) Circle the one value that best describes the O-S-O bond angle in $(SO_3)^{-2}$.

$< 90°$; $90°$; $> 90°$; $\boxed{< 109.5°}$; $109.5°$; $> 109.5°$; $< 120°$; $\boxed{120°}$; $> 120°$; $< 180°$; $180°$; $> 180°$

✗
CARRY FWD ✓ ②

(iv) (3 points) Is $(SO_3)^{-2}$ a **polar** or a **non-polar** molecule?

non polar, if trigonal planar, as above

✗ CARRY FWD

②

3

2. (12 points) **Ionic bonds**

KF has an ionic bond with a bond length of 0.217 nm. Calculate the ΔE, in kJ/mol, for the **formation** of a KF bond from the neutral atoms K and F. For this calculation, assume that the potassium and fluorine ions are point charges. IE and EA information for K and F is provided in the table below.

	Ionization energy (kJ/mol)	Electron affinity (kJ/mol)
potassium (K)	418	48
fluorine (F)	1680	328

$$\chi_K = \frac{418 + 48}{2} = 233 \text{ kJ/mol}$$

$$\chi_F = \frac{1680 + 328}{2} = 1004 \text{ kJ/mol}$$

$$U(r) = \frac{19.9 \cdot (1)^2}{4\pi \varepsilon_o \cdot 0.217 \cdot 10^{-6}} = \frac{171}{1.11265 \cdot 10^{-10} \cdot 0.217 \cdot 10^{-1}}$$

Potassium is ionized,

$$-418 \text{ kJ/mol}$$

also Fluorine accepts electron

$$328 - 418 \text{ kJ/mol} = -90 \text{ kJ/mol}$$

$$U(r) = \frac{19.9 \cdot (1)^2}{4\pi \varepsilon_o r} = \frac{171 \cdot e^2}{4\pi \cdot 8.8542 \cdot 10^{-12} \cdot 0.217 \cdot 10^{-6}}$$

wrong input

$$= 1.1347 \cdot 10^{-19}$$
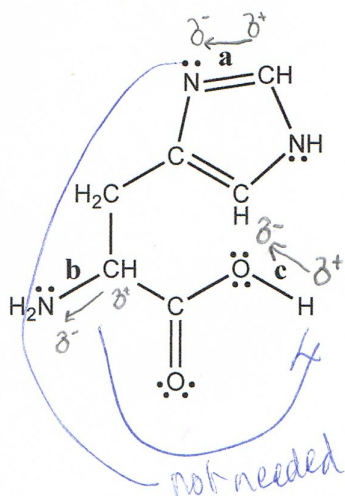
$$= 6833 \text{ kJ/mol}$$

[6]

$$\Delta E = 6824 \text{ kJ/mol}$$

4

3. (20 points) **Hybridization**

(**a**) (12 points) The structure of the amino acid histidine is provided below. For the indicated bonds, a-c, write the symmetry of each bond, and give the hybrid or atomic orbitals (with their principal quantum numbers) that overlap to form each of the bonds. Where appropriate, include the x, y, or z designations with the orbitals.


N-C bond a:
$C \rightarrow sp^3$ hybrid
$N \rightarrow p^3$

$\pi(C_{2sp_x^3} \times N_{2p_x^3})$, $\sigma(C_{2sp_z^3}, N_{2p_z^3})$

N-C bond b:
$C \rightarrow sp^3$ hybrid
$N \rightarrow p^3$

$\sigma \pi(C_{sp^3}, N_{p}^3)$ ✓

O-H bond c:

$\sigma(H_{1s}, O_{2p_z^3})$ ✓

⑥

this is symmetry

— not needed

(**b**) (8 points)

(i) For the molecule below, indicate the symmetry in the C-Cl bond (labeled **a**), and give the hybrid or atomic orbitals (with their principal quantum numbers) that overlap to form the bond. If appropriate, include the x, y, or z designations with the orbitals.

$F_2C=C=C$

C-Cl bond a:

$\pi \sigma(sp^2, Cl_{3p_z^3})$ ✗ 0
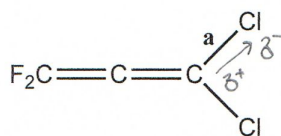
(ii) Do the chlorine atoms in the $F_2C=C=CCl_2$ molecule above lie in the **same plane** as the fluorine atoms or in a **perpendicular plane** to the fluorine atoms? Briefly explain your answer (with words or a picture).

They lie in the same plane ✗, the interior double bonds cannot rotate and the behavior of each atom is symmetric

— perpendicular to the bonds

$C = C$

5

4. (27 points) **Molecular orbital theory**

(a) (21 points)

(i) (9 points) Draw an energy correlation diagram for the molecular orbitals of the **valence electrons** in CN. Label the atomic and molecular orbitals, including the x, y and z designations where appropriate. The relative ordering of the energies of the states must be correct. **Use the full space available** to spread out your energy levels so that the labels for the orbitals fit easily.

: C ⋮⋮ N

forgot
σ_{2s} orbitals
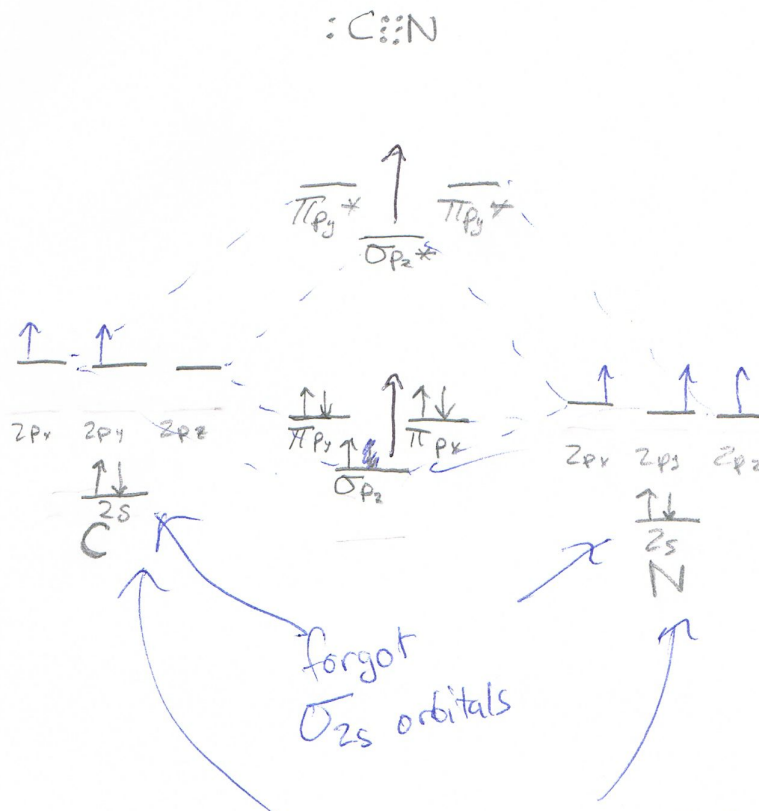
the original orbitals
should not be changed,
the key MO are in addition to
on the diagram

③

(ii) (2 points) Of the CN molecular orbitals **occupied by valence electrons**, name the orbitals that have a nodal plane along the internuclear (bond) axis.

π_{py} & π_{px} ✓

②

6

(ii) (4 points) Determine the <u>bond order</u> of the cyanide molecule, CN, *and* the cyanide **ion**, CN^{-1}.

BO of CN: $3(2.5)$ BO $= \frac{1}{2}$ (# bonding - # antibonding)

BO of CN^{-1}: 3 ✓ ②

(iii) (4 points) Below is an energy diagram of the CN covalent bond in a neutral CN molecule. On the same graph, plot the energy vs. internuclear distance, r, of the CN covalent bond in a **CN^{-1}** ion. Indicate the equilibrium bond distances with arrows. The **relative** values of the bond distances and energies must be correct, but no numbers are needed.
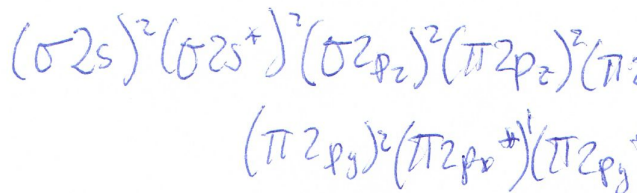

Energy

0

CN

internuclear distance, r ⟶

✗
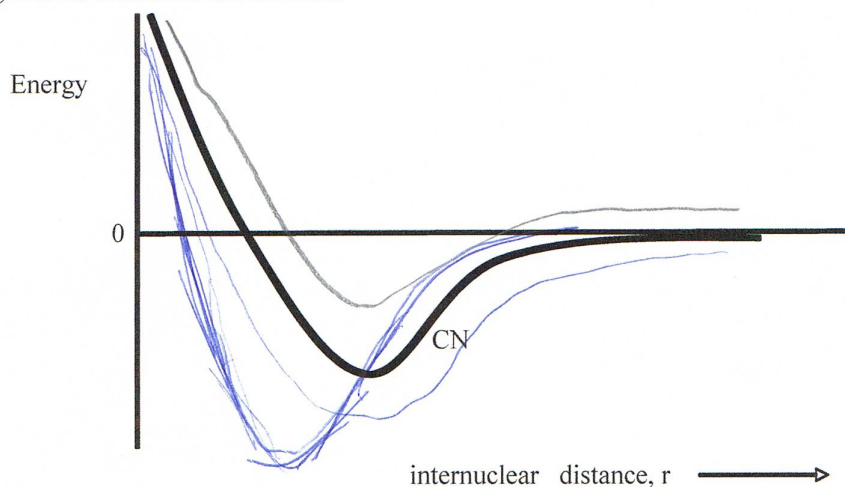
(iv) (2 points) Which of the following are radical species: CN, CN^{-1}, both, or neither?

✗

(b) (6 points)
Write the **valence** electron configuration for O_2.

:Ö—Ö: ✗

$(\sigma 2s)^2 (\sigma 2s^*)^2 (\sigma 2p_z)^2 (\pi 2p_z)^2 (\pi$

$(\pi 2p_y)^2 (\pi 2p_x^*)^1 (\pi 2p_y$

7
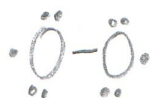
5. (11 points) Thermochemistry

(a) (7 points) Consider the reaction below for the conversion nitrogen dioxide to nitric oxide and O_2.

$$2NO_2(g) \rightarrow 2NO(g) + O_2(g)$$

	ΔH_f° (kJ/mol)
$NO_2(g)$	+33.18
$NO(g)$	+90.25

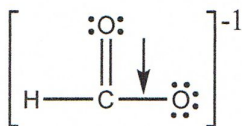Calculate ΔH° (per mol of O_2 formed) for the reaction at 298 K.

$$2 \cdot \Delta H_f (NO_2) = 2\Delta H_f (NO) + \Delta H_f (O_2)$$

$$66.36 = 180.50 + \Delta H_f$$

$$\Delta H_f = 66.36 - 180.50 = 114.14 \text{ kJ/}$$

✓

(b) (4 points) Using the table of mean bond enthalpies provided, predict the bond enthalpy (in kJ/mol) for the CO bond marked with an arrow in the molecule below.

Bond	Mean Bond Enthalpy (in kJ/mol)
C-H	412
C-C	348
C=C	612
C-O	360
C=O	743

360 kJ/mol

✗

360 < bond enthalpy < 743

1. THERMODYNAMICS (12 points total)
Consider the formation of MgO (s).
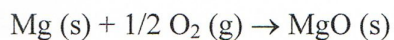
Mg (s) + 1/2 O₂ (g) → MgO (s) $\Delta H_r° = -602$ kJ/mol
                                     $\Delta S_r° = -108$ JK⁻¹mol⁻¹.

(Assume that $\Delta H_r°$ and $\Delta S_r°$ are independent of temperature.)

(a) (6 points) Calculate $\Delta G_r°$ for the formation of MgO (s) at 0 °C (273 K). Is the reaction spontaneous or non-spontaneous at 0 °C?

$$\Delta G° = \Delta H° - \Delta S° T$$

$$= -602 + (108)(273°)$$

$$= -602 + 29.4$$

$$= -572 \text{ kJ/mol}$$

yes, the reaction is spontaneous

✓

(b) (6 points) Is there a temperature at which the formation of MgO switches from spontaneous to non-spontaneous or vice versa? If no, explain briefly why not. If yes, calculate the temperature (T*) at which the spontaneity of the reaction switches.

Yes, because the signs are the same, this reaction will become non-spontaneous at:

$$\Delta G = 0$$

$$\Delta H = \Delta S T$$

$$-602 = (-.108)T$$

$$T = \frac{602}{.108} = \boxed{5.57 \cdot 10^3 \text{ K}}$$

✓

2. CHEMICAL EQUILIBRIUM (12 points total)

Explain the effect of each of the following stresses on the position of the following equilibrium:

$$3 NO(g) \rightleftharpoons N_2O(g) + NO_2(g)$$

The reaction as written is exothermic.

(a) (4 points) The equilibrium mixture is cooled. Explain your answer.

The equilibrium reaction will shift toward products (RHS) because an exothermic reaction will increase in response to cooling (Le châtelier

✓

(b) (4 points) The volume of the equilibrium mixture is reduced at constant temperature. Explain your answer.

Shift toward products, (RHS) because 3 moles are becoming 2 moles ∴ the system minimizes the stress in that direction

✓

(c) (4 points) Gaseous argon (which does not react) is added to the equilibrium mixture while both the total gas pressure and the temperature are kept constant. Explain your answer.

The only way total pressure and temp could remain constant during an increase in moles of total gas is if the volume were increasing. In which case, partial pressure on the reactants and products is reduced ∴ The reaction will shift toward reactants (LHS)

✓

3. ACID-BASE EQUILIBRIUM (12 points total)

(a) (6 points) Calculate the pH in a solution prepared by dissolving 0.050 mol of acetic acid (CH_3COOH) and 0.20 mol of sodium acetate ($NaCH_3COO$) in water and adjusting the volume to 500. mL. The pKa for acetic acid (CH_3COOH) is 4.75.

Buffer Problem   Molarities: $CH_3COOH = \dfrac{0.05}{.5} = 0.1\,M$

$CH_3COO^- = \dfrac{0.2}{.5} = 0.4\,M$

$$CH_3COOH \rightleftharpoons H_3O^+ + CH_3COO^-$$

	CH_3COOH	H_3O^+	CH_3COO^-
Initial	0.1	0	0.4
ΔM	$-x$	$+x$	$+x$
Total	$0.1-x$	x	$0.4+x$

$pKa = -\log(Ka) =$

$Ka = 1.778 \cdot 10^{-5} = \dfrac{x(0.4+x)}{0.1-x} \overset{try}{=} \dfrac{0.4x}{0.1}$

$x = 4.446 \cdot 10^{-6}$ ($< 5\%$)

$pH = -\log[4.446 \cdot 10^{-6}] = \boxed{5.35}$ ✓

(b) (6 points) Suppose 0.010 mol of NaOH is added to the buffer from part (a). Calculate the pH of the solution that results.

0.01 moles NaOH completely dissociates
neutralizing 0.01 moles of CH_3COOH

$$CH_3COOH \rightleftharpoons H_3O^+ + CH_3COO^-$$

	CH_3COOH	H_3O^+	CH_3COO^-
Initial	0.09	0	0.4
ΔM	$-x$	$+x$	$+x$
Total	$0.09-x$	x	$0.4+x$

$Ka = 1.778 \cdot 10^{-5} = \dfrac{x(0.4+x)}{0.09-x}$

③/6

should have used Henderson-Hasselbalch

try $\dfrac{x(0.4)}{0.09} = 1.778 \cdot 10^{-5}$

$4.001 \cdot 10^{-6}$

$pH = -\log[4.001 \cdot 10^{-6}] = \boxed{5.40}$

4. ACID-BASE TITRATION (22 points total)

A 10.0 mL sample of 0.20 M HNO_2 (aq) solution is titrated with 0.10 M NaOH (aq).
(K_a of HNO_2 is 4.3×10^{-4}).

(a) (5 points) Calculate the volume of NaOH needed to reach the equivalence point.

Equivalence Point = 10 ml · 0.2M = $2 \cdot 10^{-3}$ moles of HNO_2

$2 \cdot 10^{-3} = x \cdot 0.1M =$

$\boxed{x = 2 \, mL \, of \, NaOH}$

Wrong units (cL not mL) ✓

(b) (12 points) Calculate the pH at the equivalence point. Check assumptions for full credit.
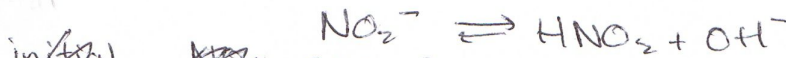
At equivalence point: (12 mL total)

	$HNO_2 \rightarrow$	$H_3O^+ +$	NO_2^-
Initial	0.2	0	0
ΔM	$-x$	$+x$	$+x$
Total	$0.2-x$	x	x
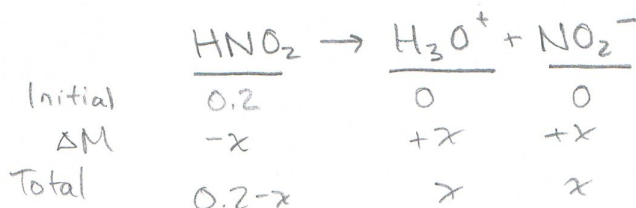
$K_a = \dfrac{x^2}{0.2-x}$ try $\dfrac{x^2}{0.2} = 4.3 \cdot 10^{-4}$

$x^2 =$

$x = 9.2736 \cdot 10^{-3}$

initial $[H_3O^+]$ $\underset{CHECK}{\boxed{x < 5\% \, of \, 0.2}}$

✗

$HNO_2 + NaOH \rightarrow \underset{salt}{NaNO_2} + \underset{water}{H_2O}$

$NO_2^- \rightleftharpoons HNO_2 + OH^-$

initial	$7.7 \cdot 10^{-3}$	0	0
ΔM	$-x$	$+x$	$+x$
total	$7.7 \cdot 10^{-3}-x$	$+x$	$+x$
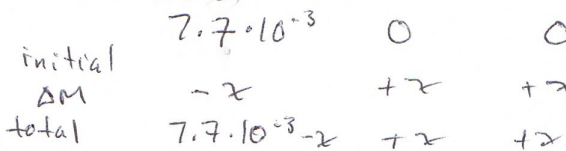
$9.3 \cdot 10^{-3} \cdot \dfrac{10}{12} =$

$K_B = \dfrac{10^{-14}}{4.3 \cdot 10^{-4}}$

$= 2.325 \cdot 10^{-11}$

$2.325 \cdot 10^{-11} = \dfrac{x^2}{7.7 \cdot 10^{-3}-x}$

Try

$p = 5.5 \cdot$

$< 5\%$ ✓

$pOH = -\log(5.$

$= 4.$

$pH = 9.7$

(c) (5 points) Calculate the pH with 2.00 mL of NaOH added past the equivalence point.

2 ml of 0.1 M NaOH

total volume = 14 mL   CARRY
FWD
ER ROR

Assume complete dissociation:

$1.42 \cdot 10^{-2}$ M [OH]⁻

$pOH = -\log(1.42 \cdot 10^{-2}) = 1.845$

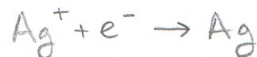$pOH + pH = 14$

$pH = 14 - pOH = \boxed{12.2}$ ✓

5. OXIDATION/REDUCTION REACTIONS (30 points total)

For a cell constructed with a Cu (s) | Cu^{2+} (aq) anode and Ag$^+$ (aq) | Ag (s) cathode at 25.00 °C.

(a) (5 points) Write the overall balanced equation under acidic conditions.

Cu is oxidized   Ag⁺ is reduced

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

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

$Cu + 2H_3O^+ \rightarrow Cu^{2+} + 2H_2O$ $H_2O + Ag^+ \rightarrow H_3O^+ + Ag$

Overall reaction:

$Cu + 2H_3O^+ + 2H_2O + 2Ag^+ \rightarrow 2H_3O^+ + 2Ag + Cu^{2+} + 2H_2O$

③

(b) (13 points) Calculate the cell potential at 25.0°C under non-standard conditions:
$[Cu^{2+}] = 0.300$ M and $[Ag^+] = 0.0500$ M

Cell potential

don't factor in quantity here

there shouldn't be a minus sign here

$$\Delta E° = 2(0.8) - (+0.34)$$

$$= 1.6 + 0.34 = 1.94 \text{ V} \times$$

$$\Delta E = \Delta E° - (RT/F)_n \ln\left(\frac{[Cu^{2+}]}{[Ag^+]}\right) \quad \text{—forgot to square this term}$$

$$= 1.94 - (0.025693)(2) \ln(6.0000)$$

$$= 1.94 - 9.207 \cdot 10^{-2}$$

$$= 1.84 \text{ V}$$

(c) (6 points) Is the above cell a galvanic or electrolytic cell under standard conditions? Explain your choice of answer.

galvanic   because total voltage is positive
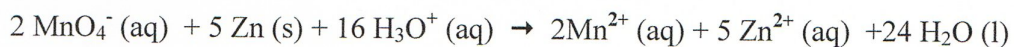∴ Gibbs free energy is negative and the reaction is   spontaneous.

(d) (6 points) Of the following, list **all** of the atoms or ions that will oxidize Ag (s):
Au^+ (aq), Pb^{2+}(aq), Zn (s), Cr^{3+}(aq), Ni (s), Au (s).
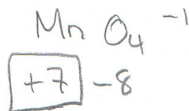
Only Au^+ will oxidize Ag.

6. OXIDATION-REDUCTION (12 points total)

The following reaction has an $\Delta E°$(cell) of 2.27 V and a K = 10^{383} at 25°C:

$$2\ MnO_4^-\ (aq) + 5\ Zn\ (s) + 16\ H_3O^+\ (aq) \rightarrow 2Mn^{2+}\ (aq) + 5\ Zn^{2+}\ (aq) + 24\ H_2O\ (l)$$

(a) (4 points) What is the oxidation number for Mn in MnO_4^-?

$$Mn\ O_4\ ^{-1}$$
$$\boxed{+7}\ -8$$

(b) (4 points) How many electrons are transferred in this reaction (in other words, what is "n")?

$$2x\ +7 \rightarrow +2$$
$$2 \cdot 5e^- = \boxed{10\ e^-}$$

(c) (4 points) Would you expect a large quantity of MnO_4^- ions at equilibrium at 25°C? Why or why not?

No, K >> 1 ∴ the reaction is almost entirely products.