

LAST NAME:

Rogers

FIRST NAME:

STUDENT ID:

answer key

mass #5
#9 typo somewhere;
grade as bonus

Fix typo #11 2p not 3p!

#13d accept orbital boxes partial credit
#8d all three, not four

Chem 241 - INORGANIC CHEMISTRY I

MIDTERM EXAMINATION

Tues. Oct. 14, 2014

note: \checkmark 0.25
 \checkmark = 0.5 marks
 \checkmark = 1.0 marks

PLEASE READ THIS BOX WHILE WAITING TO START

INSTRUCTIONS:

- Calculators are permitted; cell phones and other electronic devices are not allowed.
- This test paper includes 8 pages; please read over the whole test before starting.
- Answer the multiple-choice questions on the scan sheet, in pencil.
- Please write clearly and organize your work logically.
- A periodic table is included and may be detached.
- Read the whole exam over quickly before starting.
- Duration: 70 minutes. GOOD LUCK!

NOTE:

- "explain" means WHY, i.e. talk about causes, don't just give trends (those are observations)
- don't just list relevant factors; explain cause + effect (be specific, not vague).

Average Professor use - Grades:

| Page | Score | Max | Notes |
|-----------------|-------------|-----------|-----------------|
| Page 2 | 10.4 | 16 | Multiple-choice |
| Page 3 | 2.2 | 5 | |
| Page 4 | 5.8 | 9 | |
| Page 5 | 7.2 | 11 | |
| TOTAL: | 25.6 | 41 | |
| PERCENT: | % | | |

GRADE OUT OF 38 (MAX. 41) (BECAUSE OF LATE-IDENTIFIED ERROR IN #9.)

Average sect. 01
67.3%

PART A: MULTIPLE-CHOICE QUESTIONS (Each question has one correct answer.)
Write your final answer in pencil on the scan sheet; circle answer here too as a back-up.

#1. (2 marks) Which **one** statement below about nuclear chemistry is **FALSE**?

- a) ✓ Even-even nuclides (even numbers of p^+ and n^0) are more stable than even-odd or odd-odd nuclides.
 b) ✓ Electron capture converts a proton into a neutron and thereby raises the $n^0:p^+$ ratio of the nucleus.
 c) ✗ Nuclides with $n^0:p^+$ ratio **higher** than the band of stability often decay via positron-emission. $p^+ \rightarrow n^0 + e^+$
 d) ✓ Radioactive nuclei that are heavier than Fe tend to release energy via fission reactions.

#2. (2 marks) The radial part of the 2p wavefunction is shown here, where σ is proportional to r (distance from nucleus). What is the physical significance of the circled term in the equation?

$$R_{2p} = \frac{1}{\sqrt{3}} \left[\frac{Z}{2a_0} \right]^{3/2} \sigma e^{-\sigma/2}$$

Small when r is small (pointing to σ)
 Small when r is large (pointing to $e^{-\sigma/2}$)

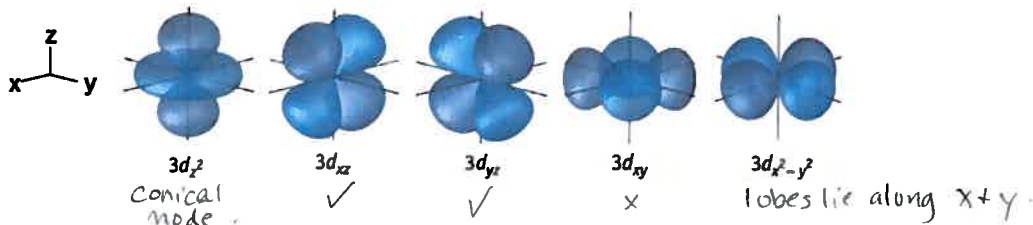
- a) ✗ It is responsible for the electron density being extremely low very close to the nucleus.
 b) ✓ It is responsible for the electron density decreasing far from the nucleus.
 c) ✗ It is responsible for the radial (spherical) node within the orbital.
 d) ✗ All of the above.

#3. (2 marks) Which **one** statement below about valence bond theory is **FALSE**?

- a) ✓ Hybrid atomic orbitals are used by non-terminal atoms for forming σ -bonds and housing lone pairs.
 b) ✗ A sp^3d hybrid orbital set formed using the $d_{x^2-y^2}$ orbital provides the square **planar** geometry.
 c) ✓ Multiple bonds are formed via overlap of unhybridized p or d orbitals.
 d) ✓ Face-on overlap of two d orbitals results in a δ -bond.

#4. (2 marks) Which of the orbitals shown has/have an angular node in the xy plane?

- a) ✗ d_{xy} & $d_{x^2-y^2}$
 b) ✓ d_{xz} & d_{yz}
 c) ✗ d_{xz} & d_{xy}
 d) ✗ d_z^2 only



#5. (2 marks) Which choice below represents the electron configuration of a ground-state V²⁺ ion?

- a) ✗ [Ar] 4s²3d³ = V atom
 b) [Ar] 4s²3d¹
 c) [Ar] 4s¹3d²
 d) ✓ [Ar] 4s⁰3d³ → ground state transition metal cations (stable ones) do not have valence e⁻ in s orbitals
- } all missing 2e⁻ ∴ V²⁺ possibilities

#6. (2 marks) Which statement below **INCORRECTLY** matches the scientist with their work?

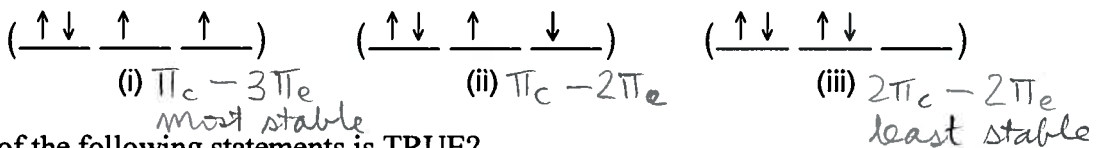
- a) ✓ Heisenberg determined that we cannot know an electron's momentum and position at the same time.
 b) ✓ Schrödinger pioneered the quantum model that treats electrons as standing waves about the nucleus.
 c) ✗ Einstein derived an equation that shows that a moving electron has a significant wavelength. = De Broglie
 d) ✓ Bohr proposed an atomic model based on electrons in circular orbits around the nucleus.

#7. (2 marks) Which choice below shows the correct ordering of the radii of Fe, Fe²⁺ and Fe³⁺?

- a) ~~X~~ Fe = Fe²⁺ = Fe³⁺
- b) ~~X~~ Fe < Fe²⁺ < Fe³⁺
- c) Fe³⁺ < Fe²⁺ < Fe largest
- d) ~~X~~ Fe²⁺ < Fe³⁺ < Fe

↑ largest
 ↗ cations always smaller than atom
 ∴ shielding is less (fewer e⁻)
 ⇒ fewest e⁻ ⇒ lowest shielding ⇒ smallest

#8. (2 marks) The diagrams below show three possible configurations of the 2p electrons of oxygen.



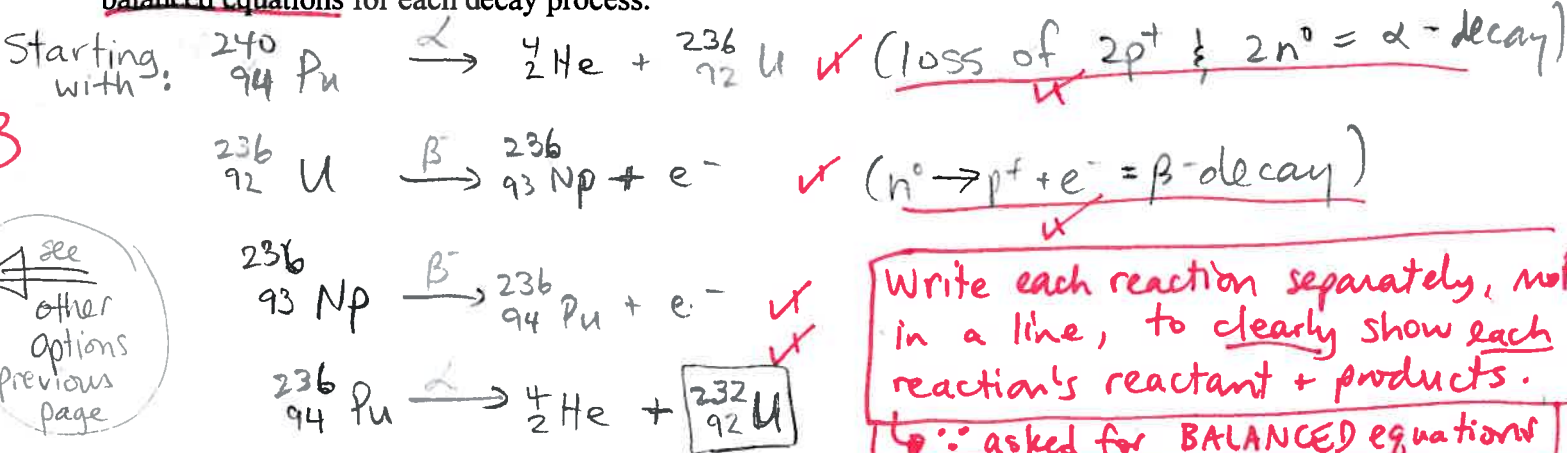
Which **one** of the following statements is TRUE?

- a) (i) has the least destabilizing pairing energy (Π_c) & the most stabilizing exchange energy (Π_e).
- b) ~~X~~ (ii) has the least destabilizing pairing energy (Π_c) & the most stabilizing exchange energy (Π_e).
- c) ~~X~~ (iii) has the least destabilizing pairing energy (Π_c) & the most stabilizing exchange energy (Π_e).
- d) ~~X~~ All ~~four~~ ^{three} configurations have the same pairing energy and the same exchange energy.

NOTE: answer key has more detail than expected from students during exam.

PART B: FULL WRITTEN ANSWERS (answer on exam)

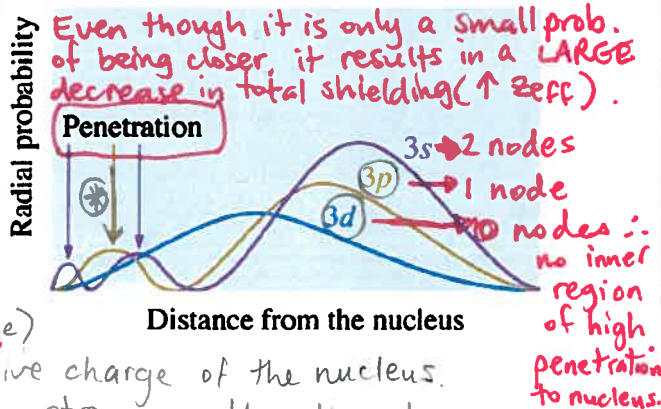
#9. (3 marks) Show that ²³⁰U results from successive α, β, β, α decays of ²³⁸U. Write balanced equations for each decay process.



Write each reaction separately, not in a line, to clearly show each reaction's reactant + products.
 ∴ asked for **BALANCED** equations

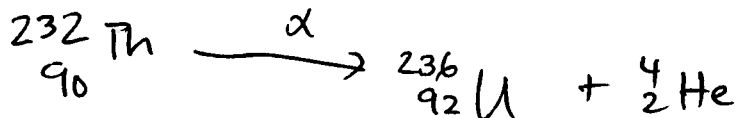
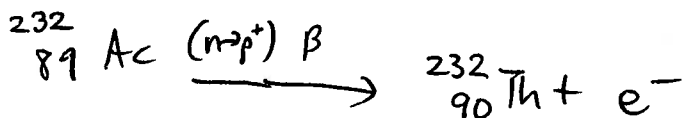
#10. (2 marks) Use the radial probability functions shown in the diagram to explain the difference in energy between 3p and 3d orbitals in a ground-state multi-electron atom.

Despite the maximum in probability being farther away, the 3p orbital penetrates closer to the nucleus than a 3d orbital - see ⊗ that shows the inner region of enhanced probability for a 3p electron at short distance from the nucleus. This means the electron feels overall less shielding from other electrons (i.e. feels higher effective nuclear charge) in addition to being a little closer to the positive charge of the nucleus. These factors both make the 3p electron feel a stronger attraction to the nucleus than a 3d electron would feel. Stronger attraction means greater stabilization, which means the 3p orbital is at LOWER ENERGY.



no inner region of high penetration to nucleus.

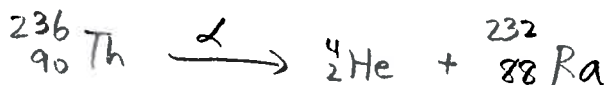
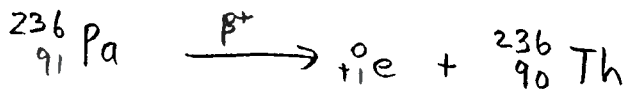
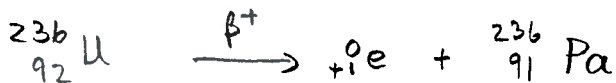
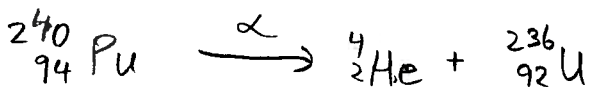
If worked backwards from $^{236}_{92}\text{U}$:



~~Some people tried α , β^+ capture, β^+ capture, α ...~~ ^{non-radiative} ~~with an α step midway:~~

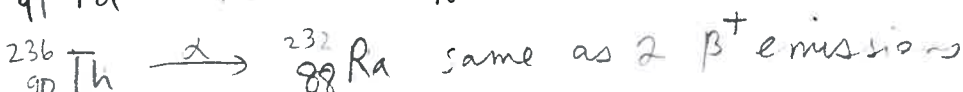
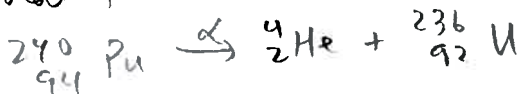
Some people tried α , β^+ capture, β^+ capture, α ...
 Problem here: β^+ (positrons) are ANTIMATTER. So, we have no source of them in an atom (just e^- , n^0 , p^+). If you imagined you had a positron beam as a source, somehow, there would be an even bigger problem. Positrons would strike e^- when they hit the atom, and self-annihilate, releasing enormous amounts of energy. (+ never reach nucleus)

What if treat $\alpha, \beta, \beta, \alpha$ as $\alpha, \beta^+, \beta^+, \alpha$?



(β^+ em: $^1_0p \rightarrow ^0_{+1}e + ^1_0n$)

What if treat it as α, β^- capture, β^- capture, α ?



#11. Effective nuclear charge is an excellent aid to understanding differences in properties of the elements.

a) (3 marks) Using Slater's rules, estimate the effective nuclear charges experienced by a $3p$ electron of fluorine and a $3p$ electron of oxygen. (similar shielding, starting with different nuclear charges)

• a $2p$ e^- is shielded a lot by each $1s$ e^- and a little by each $2s + 2p$ e^- (not itself!)

| | OXYGEN (Z=8) | FLUORINE (Z=9) |
|---|---------------------------------|---------------------------------|
| Slater configuration | $\{(1s^2)\} \{(2s^2, 2p^4)\}$ ✓ | $\{(1s^2)\} \{(2s^2, 2p^5)\}$ ✓ |
| Shielding parameter σ | $2(0.85) + 5(0.35) = 3.45$ ✓ | $2(0.85) + 6(0.35) = 3.80$ ✓ |
| Effective nuclear charge, $Z_{\text{eff}} = Z - \sigma$ | $8 - 3.45 = 4.55$ ✓ | $9 - 3.80 = 5.20$ ✓ |

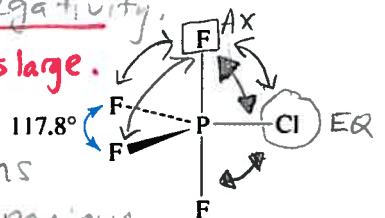
b) (2 marks) Use your answer from (a) to explain what causes the difference in electronegativity between oxygen and fluorine (recall that the Allred-Rochow definition of electronegativity is based on effective nuclear charge). **F has ↑ shielding BUT nucleus has ↑ charge ∴ NET EFFECT still ↑ Z_{eff} vs. O.**

Electronegativity in all its definitions represents the ability of an atom to pull electrons towards itself, whether those electrons are its own or shared via covalent bonding. As Z_{eff} increases, the electron-nucleus attraction increases, and so the electrons are pulled closer to the nucleus. Thus, because the Z_{eff} felt by the valence e^- s of fluorine is larger than for oxygen, fluorine pulls e^- s towards itself more than oxygen, and thus fluorine has higher electronegativity.

#12. (4 marks) Consider the trigonal bipyramidal molecule shown. Briefly explain:

a) why the chlorine occupies an equatorial site. **2 reasons: $\chi_{\text{Cl}} < \chi_{\text{F}}$ + Cl is large.**

This is related to minimizing repulsions between bonding electron pairs AND between peripheral atoms (consider their sizes). Equatorial sites are more spacious, because there are 2 neighbouring peripheral atoms 90° away (see \blacktriangleright) vs. $3 \times 90^\circ$ interactions for axial sites (see \blacktriangleleft). To give both the P-Cl bonding electrons (held nearly midway between P+Cl) AND the large Cl atom the most space possible, the Cl atom occupies an equatorial site.

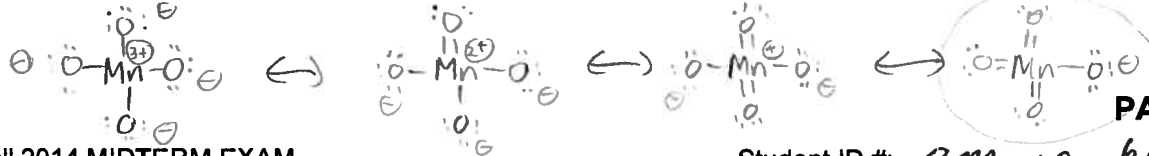


b) why the F-P-F bond angle is less than the ideal trigonal 120° . **2 reasons: chlorine is large + S-F polarity**

The ideal angle between 2 equatorial sites in a trigonal bipyramid is 120° , but here the angle is a little less. This is related to the positioning of the bonding e^- s in the highly polar P-F bonds.

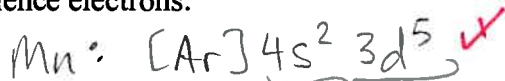
Because F is so much more electronegative than P, the bonding e^- s in all the P-F bonds lie very close to the peripheral atoms, which makes them physically quite far apart. Thus, to minimize repulsions with the P-Cl bonding e^- s, which do lie closer to the central P, the F-F bonds can squeeze together a bit more without much P-F bond repulsion.

2
and also steric repulsion due to Cl's ↑ size



#13. Permanganate anion, MnO_4^- , is a powerful oxidizing agent that consists of a transition-metal atom covalently bonded to four oxygen atoms.

a) (1 mark) Write the ground-state electron configuration of elemental Mn, and specify its number of valence electrons.

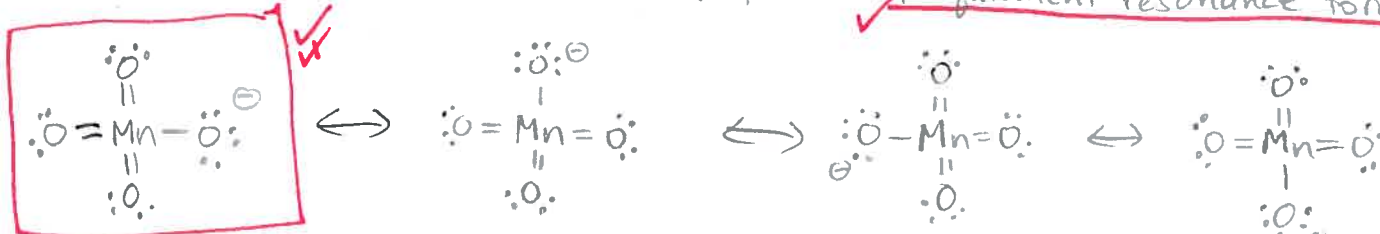


7 valence electrons

b) (4 marks) Draw the optimized Lewis structure for MnO_4^- (and all equivalent canonical structures), showing all lone pairs and non-zero formal charges.

$\text{MnO}_4^-: 7 + 4(6) + 1 = 32$ valence e^- total (preliminary structures shown above)

The canonical structure with minimized formal charges (with expanded shell of Mn, allowed for 4th row element) is shown, in its 4 equivalent resonance forms:



F.C.s

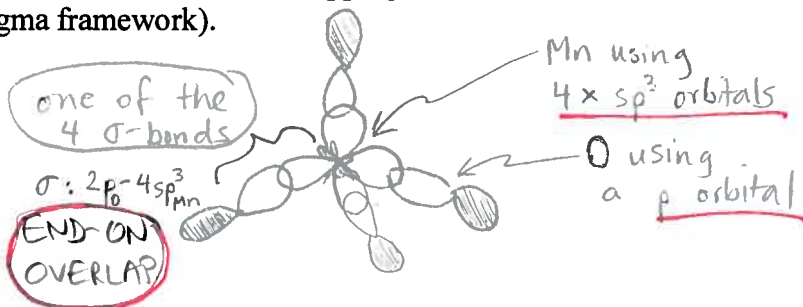
c) (3 marks) To describe the resonance hybrid from part (b), complete the following table.

| | | | |
|----------------------------|----------------|--------------------------------|---------------|
| Average metal-O bond order | $7/4 = 1.75$ | Geometry of metal atom (Td) | tetrahedral |
| Average charge on O | $-1/4 = -0.25$ | Oxygen-metal-oxygen bond angle | 109.5° |
| Number of π -bonds | 3 | Hybridization of metal atom | sp^3 |

1/2 each

(3 π bonds over 4 atom pairs = 3/4 π bonds per Mn-O linkage) ← also accepted

d) (2 marks) Sketch the overlapping orbitals involved in the metal-oxygen σ -bonds (i.e., the whole sigma framework).



Mn using sp^3 hybrids
O using p orbitals (or if sp^2 hybridized O)
If show O as sp^2 -hyb., can draw all 3 sp^2 orbitals on O, then make a σ -bond with one + house the 2 lone pairs in the remaining 2 sp^2 s

e) (1 mark) BONUS - Apply background knowledge: Given that the metal-O bonds are polar, what is the oxidation state of the metal atom in this anion? Why does this make it an oxidizing agent? (oxidizes others)

- Mn has total of 7 bonds to O, in which O "hogs" the electrons
- Oxidation states are assigned by pretending the more electronegative atom in each bond steals away the other atom's bonding e^-

Thus: neutral Mn - 7 e^- s "lost" to O ($1e^-$ per bond) = Mn +VII (+7 ox. state)

Mn (+VII) is very e^- poor, so is good at stealing e^- s i.e. oxidizing other species.