CHEMISTRY 204
Hour Exam I
February 14, 2019
Dr. D. DeCoste

Name ________**KEY**__________

Signature ____________________________

T.A. ________________________________

This exam contains 23 questions on 11 numbered pages. Check now to make sure you have a complete exam. You have two hours to complete the exam. Determine the **best** answer to the first 20 questions and enter these on the special answer sheet. Also, **circle your responses** in this exam booklet.

Show all of your work and provide complete answers to questions 21, 22 and 23.

1-20	(60 pts.)	____________
21	(20 pts.)	____________
22	(20 pts)	____________
23	(20 pts.)	____________
Total	(120 pts)	____________

Useful Information:

$N_A = 6.022 \times 10^{23}$

$E = hc/\lambda$

$E = -2.178 \times 10^{-18}\ \text{J}\ (Z^2/n^2) = -1312\ \text{kJ/mol}\ (Z^2/n^2)$

$c = 2.998 \times 10^8\ \text{m/s}$

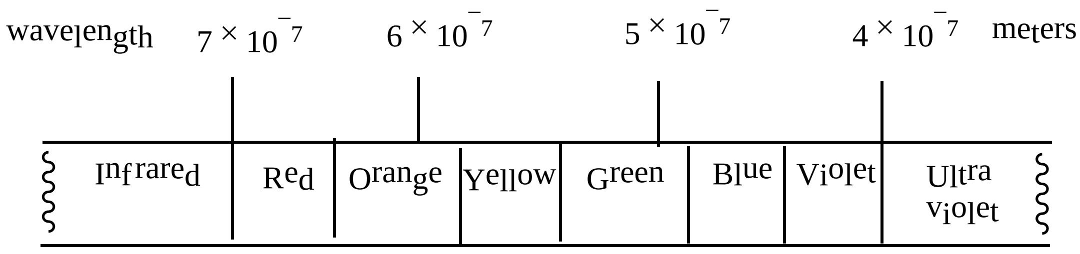
$h = 6.62608 \times 10^{-34}\ \text{Js}$

$\Delta x \Delta p = h$

$m_e = 9.10939 \times 10^{-31}\ \text{kg}$

$$E_n = \frac{n^2h^2}{8mL^2} \qquad E = \frac{h^2}{8m}\left[\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right]$$

$1\ \text{pm} = 10^{-12}\ \text{m}$ $\qquad$ $1\ \text{nm} = 10^{-9}\ \text{m}$



1. Imagine a planet for which the temperature is high enough so that the ground state for a hydrogen electron is $n = 3$. What is the ionization energy (in kJ/mol) for the hydrogen electron on this planet?

   a) –1312 b) 0 [✓ c) 146] d) 437 e) 1312

2. Consider a hydrogen atom. How many of the following are **true**?

   I. A transition of the electron from $n = 5$ to $n = 3$ involves the same energy as a transition from $n = 4$ to $n = 2$.
   II. A transition of the electron from $n = 4$ to $n = 2$ will emit radiation of a longer wavelength than one from $n = 5$ to $n = 1$.
   III. The wavelength of radiation required to cause the electron to go from energy level n to energy level $n + 1$ decreases with increasing n.
   IV. All transitions among the first five energy levels involve radiation in the visible portion of the spectrum.

   a) 0 [✓ b) 1] c) 2 d) 3 e) 4

3. How many of the following statements are **true**?

   I. In a hydrogen (H) atom, the 4*s* orbital is at higher energy than the 3*d* orbital.
   II. The Z_{eff} for a 2s electron in uranium (U) is greater than the Z_{eff} for a 2s electron in beryllium (Be).
   III. The 1*s* orbital of the lithium (Li) atom is higher in energy than the 1*s* orbital of the hydrogen (H) atom.
   IV. The energy of red light is greater than the energy of violet light.

   a) 0 b) 1 [✓ c) 2] d) 3 e) 4

4. Which of the following has the **shortest wavelength**?

   a) An electron traveling at 1% the speed of light.
   b) An electron traveling at 10% the speed of light.
   c) A baseball traveling at 50 mph.
   [✓ d) A baseball traveling at 100 mph.]
   e) All have the same wavelength.

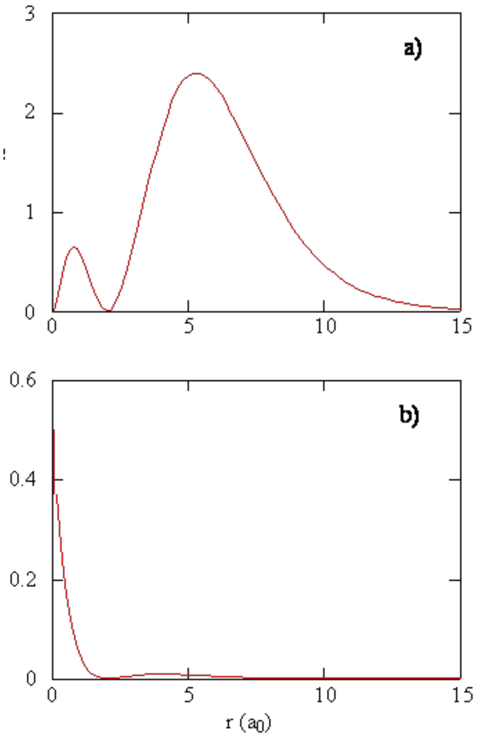
5. Which of the following set of quantum numbers describes an electron with the **highest** energy in an excited hydrogen atom?

   a) $n = 3$ $l = 0$ $m_l = 0$
   b) $n = 3$ $l = 1$ $m_l = 0$
   c) $n = 3$ $l = 1$ $m_l = 1$
   d) $n = 3$ $l = 2$ $m_l = 1$
   [✓ e) Each of the sets above (a-d) describes an electron with the same energy.]

6. Consider a ground state quantum particle trapped in a one-dimensional box of length L. The most probable position for the quantum particle is at x =

a) L
[✓ b) L/2]
c) L/3
d) 0
e) The particle is equally likely to be found anywhere in the box.

7. The plots below are for the same orbital in the hydrogen atom. Which of the following statements correctly describes these plots?



a) The plots are for the 1*s* orbital in hydrogen. The top plot is the electron radial probability distribution ($4\pi r^2R^2$ vs distance from the nucleus) and the bottom plot is the probability density of the electron (R^2 vs. distance from the nucleus).
[✓ b) The plots are for the 2*s* orbital in hydrogen. The top plot is the electron radial probability distribution ($4\pi r^2R^2$ vs distance from the nucleus) and the bottom plot is the probability density of the electron (R^2 vs. distance from the nucleus).]
c) The plots are for the 2*s* orbital in hydrogen. The top plot is the probability density of the electron (R^2 vs. distance from the nucleus) and the bottom plot is the electron radial probability distribution ($4\pi r^2R^2$ vs distance from the nucleus).
d) The plots are for a 2*p* orbital in hydrogen. The top plot is the electron radial probability distribution ($4\pi r^2R^2$ vs distance from the nucleus) and the bottom plot is the probability density of the electron (R^2 vs. distance from the nucleus).
e) The plots are for a 2*p* orbital in hydrogen. The top plot is the probability density of the electron (R^2 vs. distance from the nucleus) and the bottom plot is the electron radial probability distribution ($4\pi r^2R^2$ vs distance from the nucleus).

8. What is the expected ground state electron configuration for the most stable ion of bromine in an ionic compound?

a) $[Ar]\ 4s^2 4d^{10} 4p^5$
b) $[Ar]\ 4s^2 3d^{10} 4p^5$
c) $[Ar]\ 4s^2 4d^{10} 4p^6$
d) $[Ar]\ 4s^2 3d^{10} 4f^{14} 4p^5$
[✓ e) $[Ar]\ 4s^2 3d^{10} 4p^6$]

9. The hybridization of the **central nitrogen atom** in the N_2O molecule is

[✓ a) sp]
b) sp^2
c) sp^3
d) dsp^3
e) The hybridization can vary depending on the chosen resonance structure of the molecule.

10. Cyanogen chloride is a highly toxic chemical with the formula NCCl (the carbon atom is central). Predict the hybridization for each of the atoms in the molecule.

	N	C	Cl
a)	sp^2	sp	sp^3
b)	sp	sp^2	sp^2
c)	sp^3	sp^2	sp^2
d)	sp^3	sp^3	sp^3
[✓ e)]	sp	sp	sp^3

11. Compare the ionization energy of the nitrogen (N) atom to the oxygen (O) atom, nitrogen gas (N_2) and the N_2^- ion. In each case, which species has the **highest ionization energy**?

	N vs. O	N vs. N_2	N vs N_2^-
[✓ a)]	N	N_2	N
b)	O	N_2	N
c)	N	N	N
d)	O	N	N_2^-
e)	N	N_2	N_2^-

12. The F-F bond in $F_2(g)$ is much weaker than the B-B bond in $B_2(g)$. Why is this?

a) The fluorine atom is much more electronegative than the boron atom.
b) The boron atom is smaller than the fluorine atom.
c) According to MO theory, the bond order for F_2 is less than that for B_2.
[✓ d) The electron-electron repulsions are greater in F_2 than in B_2.]
e) The B-B bond in $B_2(g)$ is nonpolar.

13. Which of the following bonds gets **stronger** if an electron is **added**?

[✓ a) B_2] b) O_2^- c) N_2 d) F_2^+ e) All the bonds get weaker.

14. Consider the description: “Two wave functions of similar energy in a given atom overlap to give a new wavefunction that solves the Schrödinger equation. This new wave function is able to overlap with the wavefunction in a different atom to form a molecule.”

    This description best describes:

    a) Simple valence bond theory
    b) Localized electron model
    [✓ c) Hybridization]
    d) Molecular orbital theory
    e) Crystal field theory

15. Which of the following compounds requires the *cis*/*trans* designation when naming?

    a) pentaamminebromocobalt(II) chloride
    b) diamminedichlorocobalt(II) (tetrahedral)
    [✓ c) diamminedichloroplatinum(II) (square planar)]
    d) $[Co(en)_3]Cl_2$
    e) At least two of the above (a-d) require the *cis*/*trans* designation when naming.

16. Which of the following coordination compounds will form a precipitate when treated with an aqueous solution of $AgNO_3$?

    a) $[Cr(NH_3)_3Cl_3]$
    b) $[Cr(NH_3)Cl]NO_3$
    c) $Na_3[CrCl_6]$
    [✓ d) $[Cr(NH_3)_6]Cl_3$]
    e) At least two of the above will form a precipitate when treated with an aqueous solution of $AgNO_3$.

17. Consider the complex ion $[Co(en)_2Cl_2]^+$, where en = ethylenediamine = $NH_2CH_2CH_2NH_2$. How many geometric isomers and optical isomers does this complex ion exhibit?

	Geometric isomers	**Optical isomers**
a)	0	0
[✓ b)]	2	2
c)	2	3
d)	3	2
e)	4	4

18. You discover a new ligand (congratulations!) and wish to place it on the spectrochemical series. Which of the following would be a good choice to determine if the ligand were a weak-field or strong-field ligand by determining the number of unpaired electrons?

    [✓ a) Cr^{2+}] b) V^{2+} c) Ni^{2+} d) Zn^{2+} e) Cu^+

19. The complex ions of Zn^{2+} are colorless in solution. The most likely explanation for this is

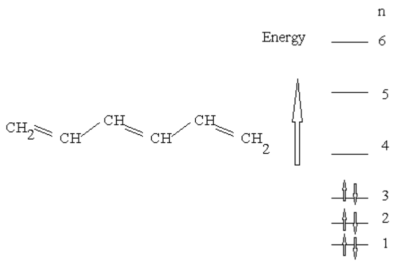
a) the Zn^{2+} complex ion is paramagnetic.
b) the *d*-orbital splitting in such complexes is outside of the visible region in the spectrum.
c) the *d*-orbital splitting in such complexes allows for the absorbing of all wavelengths in the visible region.
[✓ d) the Zn^{2+} ion is a d^{10} ion.]
e) only strong-field ligands can bind with the Zn^{2+} ion.

20. Consider the complex ions $[Co(A)_6]^{2+}$, $[Co(A)_6]^{3+}$, $[Co(B)_6]^{2+}$, and $[Co(C)_6]^{3+}$. The ligands A, B, and C are all neutral. The number of unpaired electrons for each of the complex ions (respectively) are found to be 3, 0, 1, 4. Rank the ligands from **strongest field to weakest field.**

a) A, B, C
b) C, B, A
c) B, C, A
d) A, C, B
[✓ e) B, A, C]

21. In lecture, we discussed the one dimensional “particle-in-a-box” model and how we can use the appropriate electrons in a conjugated single-double bond system as an approximation of this model. In this question you will discuss this model and then apply it and evaluate it with a known molecule.

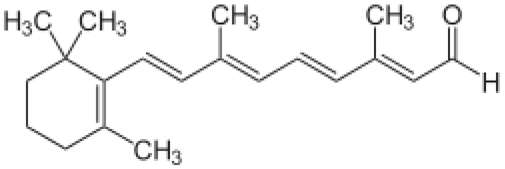
a. Consider the molecule shown below along with the energy level diagram for the particle-in-a-box approximation.



Using premises of the localized electron model (specifically hybridization theory) and molecular orbital theory, discuss how we use the particle-in-a-box model with a molecule like the one above. A complete answer will address the hybridization of the carbon atoms, the nature of the double bonds, what is meant in this case by the “box”, the number of particles (electrons) we consider trapped in the box (and how/why they are trapped), along with a discussion of the energy level diagram (specifically the number, placement, and nature of the arrows). Please consider your thoughts to write a coherent, succinct (limit your answer to this page), yet complete description of this model. **[10 points]**

See textbook and lectures.

21. b. Retinal is a molecule found in the photoreceptor cells of the retina and is crucial in our vision by allowing us to convert visible light into a chemical signal in the brain. The structure of retinal is:



i. **Determine the longest wavelength** of light that can be absorbed to cause a ground state electron to go to its first excited state. Assume the average carbon-carbon bond length is 140 pm and the average carbon-oxygen bond length is 120 pm. Include an **appropriate and filled-in energy-level diagram** (like the one given in part a). **Justify** the number and placement of the arrows. **Show and explain all work**. **[8 points]**

See textbook and lectures.

λ = 5.860 x 10^{-7} m [586 nm]

ii. Is the particle in a box model reasonable to use in this case to verify that retinal will absorb light in the visible region of the spectrum? **Explain**. **[2 points]**

Yes, it is reasonable. See textbook and lectures.

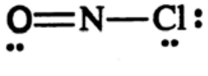
22. In Chemistry 202 we discussed radicals (species with an odd number of electrons) like NO and OH, but we couldn't draw Lewis structures for them. Fear not! Molecular orbital (MO) theory is here to help.

a. **Draw and label the MO energy-level diagram for the valence electrons for NO**. Assume the orbital order includes p-s mixing and is just like the MO diagram for N_2. **Use your diagram to answer the following (and explain your answers)**: **[6 points]**

- In hour exam 3 for Chemistry 202, you estimated the bond energy for NO to be 628 kJ/mol. Given that the bond energy for N–O is 201 kJ/mol and for N=O is 607 kJ/mol, is 628 kJ/mol reasonable?
- Would the bond get stronger by the addition or the removal of an electron? Or, would both processes make the bond weaker?

See textbook and lectures.

b. Consider the reaction ONCl(*g*) → NO(*g*) + Cl(*g*). It looks as though all that is happening in this reaction is that the N–Cl bond is being broken. The bond energy for N–Cl is 200 kJ/mol but ΔH_{rxn}, while still positive, is not equal to 200 kJ/mol. Do you expect ΔH_{rxn} to be greater or less than 200 kJ/mol? Use your answer to part a above and the Lewis structure for ONCl, and assume there are no significant intermolecular attractions among any molecules. **[3 points]**



ΔH_{rxn} is expected to be **less than** 200 kJ/mol.

See textbook and lectures.

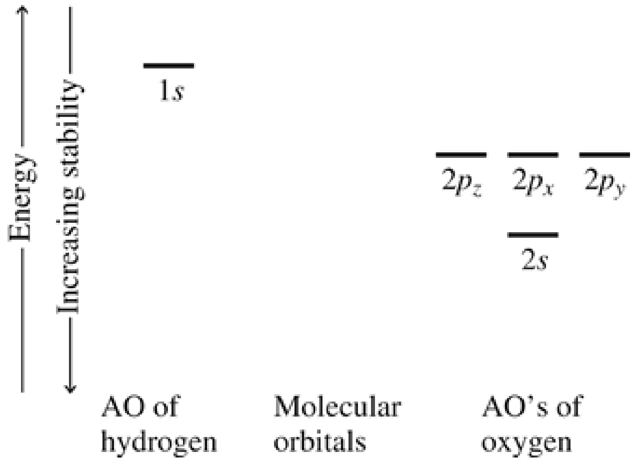
22. c. Like NO, the OH radical is a heteronuclear diatomic, but the atoms are quite different (more so than N and O). We consider the overlap in orbitals to form the MOs in OH to be between the 1*s* orbital of the hydrogen atom and one of the 2*p* orbitals of the oxygen atom.

i. Why does the hydrogen 1*s* orbital overlap with only one of the oxygen 2*p* orbitals? Does the overlap form a sigma(σ) or pi (π) bond? Use pictures in your explanation to show how the hydrogen 1*s* orbital interacts with the three oxygen 2*p* orbitals and why only one allows for overlap. **[4 points]**

See textbook and lectures.

ii. Draw the appropriate relative molecular orbitals on the diagram below and label each with either **b** for bonding, **a** for antibonding, or **n** for nonbonding. Fill in the appropriate number of electrons (for both atomic and molecular orbitals). **[4 points]**

See textbook and lectures.



iii. How would you expect the ionization energy of the oxygen atom to compare with the ionization energy of the OH radical? Use your filled in MO diagram above to explain your answer. **[3 points]**

See textbook and lectures.

23. Please answer the questions succinctly, yet fully. Full credit is awarded to complete, coherent answers written in complete sentences. Take some time to draft out an answer on scratch paper before you begin writing. **Please limit each answer to one side of the page.**

    a. Describe the general ideas of the crystal field model. Include in this discussion the nature of the ligands and the nature of the bond between the ligands and the metal ion. In addition, include a crystal field diagram for an octahedral complex and explain/justify the relative positions of the *d*-orbitals in the complex ion and in the free ion (make sure to label these). **[8 points]**

See textbook and lectures.

    b. Models in science are kept as simple as possible, and then they are refined/changed as questions cannot be answered correctly. What are two problems with crystal field theory that require a different model? Briefly describe these problems. **[2 points]**

See textbook and lectures.

23. c. Recall the lecture demonstration in which I added concentrated HCl to an aqueous solution of cobalt(II) ions. The reaction that occurred can be represented as follows.

$$[Co(H_2O)_6]^{2+} + 4Cl^- \rightarrow \underset{\text{(tetrahedral)}}{[CoCl_4]^{2-}} + 6H_2O$$

This reaction is accompanied by a color change (one of the complex ions is blue in solution and the other is red).

i. Sketch crystal field diagrams for each of the complex ions. Label the *d*-orbitals and include the proper number and placement of electrons. Label each as weak field or strong field. There may be more than one possible answer for each complex ion – explain why. **[5 points]**

See textbook and lectures.

ii. Explain the color change. In part a you discussed why such complex ions can exhibit color. For this question, explain why the color changes, and explain if the color change upon the addition of HCl is red→blue or blue→red (you don't have to recall the demonstration – you can determine this). Support your answer using the premises of crystal field theory. **[5 points]**

See textbook and lectures.