

CHEMISTRY 204
Hour Exam I
February 20, 2020
Dr. D. DeCoste

Name _____

Signature _____

T.A. _____

This exam contains 23 questions on 12 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:

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

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

$$c = 2.998 \times 10^8 \text{ m/s} \quad h = 6.62608 \times 10^{-34} \text{ Js}$$

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

$$\Delta x \Delta p = h$$

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

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

Table 19.16

Approximate Relationship of Wavelength of Visible Light Absorbed to Color Observed

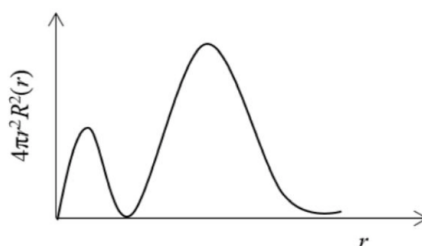
Absorbed Wavelength in nm (color)	Observed Color
400 (violet)	Greenish yellow
450 (blue)	Yellow
490 (blue-green)	Red
570 (yellow-green)	Violet
580 (yellow)	Dark blue
600 (orange)	Blue
650 (red)	Green

- The energy difference between a $2p$ and $2s$ orbital of a lithium atom is 2.96×10^{-19} J. When an excited electron in the $2p$ orbital of a lithium atom returns to the $2s$ orbital, what color of light is emitted?
 - red (625 nm to 700 nm)
 - orange (585 nm to 625 nm)
 - yellow (565 nm to 585 nm)
 - green (470 nm to 565 nm)
 - blue (420 nm to 470 nm)
- Imagine two set-ups, each with two identical neutral quantum particles (not electrons). In one case, the two particles are trapped in a 1-D box, and in the other case, the two particles are trapped in a 3-D cube. The dimensions of the cube are the same as the length of the box. Find the ratio of the longest wavelengths required in each to produce an excited state.

$$\text{Ratio} = \frac{\text{wavelength in 1-D box}}{\text{wavelength in 3-D cube}}$$

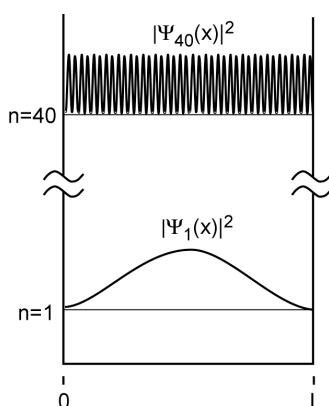
- 0.60
 - 0.83
 - 1.0
 - 1.2
 - 1.7
- You remove all but the last electron from an atom and find that to remove the final electron requires 2.10×10^4 kJ/mol. Which atom did you have?
 - He
 - Be
 - O
 - Cu
 - Cannot be determined.
 - A radial probability plot for an orbital is given below. This could be a plot (depending on the scale) for how many of the following ten orbitals?

$1s, 2s, 2p_x, 3s, 3p_x, 3d_{xy}, 4s, 4p_x, 4d_{xy}, 4f_{xyz}$



- 1
 - 3
 - 4
 - 5
 - 8
- Two of your friends are reviewing electron configurations, and Friend One says that the electron configuration of nitrogen is $1s^2 2s^2 2p^2 3s^1$. Friend Two laughs and says, "That's not right at all." Which of the following responses by Friend One is correct?
 - "It is a correct electron configuration for an excited state of nitrogen."
 - "It is a correct electron configuration for an ion of nitrogen."
 - "Did I say the nitrogen atom? I meant the sodium atom."
 - "Oops. You're right – it is not correct for nitrogen in any conceivable way."
 - "Yes it is."

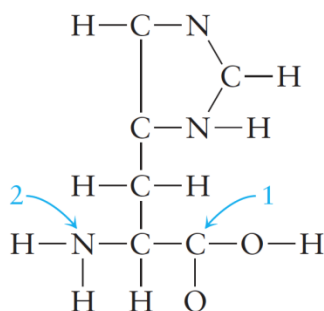
6. How many electrons can be described by the quantum numbers $n = 3, l = 2$?
- a) 2 b) 6 c) 8 d) 10 e) 18
7. You are pulled over for speeding (nice going). The police officer has clocked you at 25 mph (~ 11 m/s) in a school zone (where the speed limit is 20 mph). You decide to fight the ticket by using Heisenberg's Uncertainty Principle. Assuming the system (you, the car, anything else in the car) weighs about 2500 lbs. (for a mass on earth of about 1100 kg), what is your best defense, and will it work to get you out of the ticket?
- a) Yes, it will work! The best defense is to say the uncertainty in position is one atom (about 10^{-10} m). This maximizes uncertainty in velocity, and it is large enough so that it may be true that you were within the posted speed limit.
- b) Yes, it will work! The best defense is to say the uncertainty in position is about 10 meters (which is the approximate length you'd travel in the one second or so it takes the police officer to use the radar gun). This maximizes uncertainty in velocity, and it is large enough so that it may be true that you were within the posted speed limit.
- c) Yes, it will work! The best defense is to say the uncertainty in position is the distance of the school zone (about 500 meters). This maximizes uncertainty in velocity, and it is large enough so that it may be true that you were within the posted speed limit.
- d) No, it will not work. The best defense is to say the uncertainty in position is the distance of the school zone (about 500 meters). This maximizes uncertainty in velocity, but it is not large enough to bring the recorded 25 mph to 20 mph.
- e) No, it will not work. The best defense is to say the uncertainty in position is one atom (about 10^{-10} m). This maximizes uncertainty in velocity, but it is not large enough to bring the recorded 25 mph to 20 mph.
8. Consider the following figure (as seen in lecture!):



Which of the following statements (a-d) concerning this figure is correct?

- a) At $n = 1$ we can see that classical mechanics is simply a special case of quantum mechanics.
- b) The probability of finding a particle trapped in a box at $n = 40$ is greatest at $L/2$
- c) The probability that the particle is at $n = 1$ is always greater than the probability that the particle is at $n = 40$.
- d) Probability is evenly distributed for a quantum particle in the ground state.
- e) None of the above statements is correct.

9. The following is a skeletal structure of the amino acid histidine. Complete the Lewis structure such that **all atoms have a formal charge of zero**, and answer the following question.



Which of the following best describes the hybridization around the carbon atom labeled 1 and the nitrogen atom labeled 2?

- | Carbon atom (#1) | Nitrogen atom (#2) |
|-------------------------|---------------------------|
| a) sp^3 | dsp^3 |
| a) sp^2 | sp^2 |
| b) sp^3 | sp^3 |
| d) sp^3 | sp^2 |
| e) sp^2 | sp^3 |
10. Starch turns blue in the presence of iodine because of the formation of the triiodide ion (I_3^-). What is the hybridization of the center iodine in the triiodide ion?
- a) sp b) sp^2 c) sp^3 d) dsp^3 e) d^2sp^3
11. You are told that the shape around a specific atom in a molecule or ion is linear. From just this information, can you specify the hybridization of the atom?
- a) No, a linear shape can result in two different hybridizations.
 b) No, a linear shape can result in three different hybridizations.
 c) No, a linear shape can result in five different hybridizations.
 d) Yes, the atom must be sp hybridized.
 e) It turns out the atom is not hybridized if the shape is linear.
12. Consider removing one electron from the N_2 molecule and one electron from the O_2 molecule. What is expected to happen to the bond lengths?
- a) The bond lengths are expected to increase for both.
 b) The bond lengths are expected to decrease for both.
 c) The bond length is expected to increase when forming N_2^+ and to decrease when forming O_2^+ .
 d) The bond length is expected increase when forming O_2^+ and to decrease when forming N_2^+ .
13. Which of the following has the lowest ionization energy?
- a) N_2 b) N_2^- c) O d) O_2 e) O_2^-

14. Two of your friends are studying (again) and during the session, Friend One says, "We can think of a molecule as a collection of nuclei and delocalized electrons". Before Friend Two can continue, Friend One looks to you and asks, "When did we learn that?" Which of the following should you say to help Friend One?
- "That is a fundamental idea of the molecular orbital theory."
 - "That is part of the localized electron model we learned about in class."
 - "This is best demonstrated with the crystal field theory."
 - "That is a major tenet of hybridization theory."
 - "We didn't – Friend Two just made it up."
15. How many of the following geometries for complex ions in coordinate covalent compounds can exhibit *cis-trans* isomerism?
- linear
 - square planar
 - tetrahedral
 - octahedral
- a) 0 b) 1 c) 2 d) 3 e) 4
16. You dissolve a 3.14-g sample of pentaamminechlorochromium(III) chloride in water. What volume of 0.150M AgNO₃ is required for complete precipitation of AgCl?
- a) 0 mL b) 86.0 mL c) 101 mL d) 172 mL e) 258 mL
17. What is the expected ground state electron configuration for Sc⁺?
- [Ar] 4s²3d¹
 - [Ar] 4s²
 - [Ar] 3d²
 - [Ar] 4s¹3d¹
 - [Ar] 4s²3d²
18. How many of the following octahedral complexes are paramagnetic?
- Strong-field complexes of Ni²⁺
 - Weak-field complexes of Ni²⁺
 - Weak-field complexes of Co³⁺
 - Weak-field complexes of Zn²⁺
 - Strong-field complexes of Cr³⁺
- a) 1 b) 2 c) 3 d) 4 e) 5

19. As discussed in lecture and the text, the magnitude of the splitting of the d orbitals in CFT is somewhat dependent on the charge of the metal ion. The text states “ NH_3 is a weak-field ligand toward Co^{2+} but acts as a strong-field ligand toward Co^{3+} .” Given this, which of the following is true about the difference between the number of unpaired electrons when comparing $[\text{Co}(\text{NH}_3)_6]^{2+}$ and $[\text{Co}(\text{NH}_3)_6]^{3+}$?
- a) The difference in the number of unpaired electrons is one (1), and there are more unpaired electrons for $[\text{Co}(\text{NH}_3)_6]^{2+}$.
 - b) The difference in the number of unpaired electrons is one (1), and there are more unpaired electrons for $[\text{Co}(\text{NH}_3)_6]^{3+}$.
 - c) The difference in the number of unpaired electrons is three (3), and there are more unpaired electrons for $[\text{Co}(\text{NH}_3)_6]^{2+}$.
 - d) The difference in the number of unpaired electrons is three (3), and there are more unpaired electrons for $[\text{Co}(\text{NH}_3)_6]^{3+}$.
 - e) The complex ions have the same number of unpaired electrons (the difference is zero (0)).
20. How many of the following is/are optically active? (note: en = ethylenediamine = $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$)
- I. *cis*- $[\text{Co}(\text{en})_2\text{Cl}_2]^+$
 - II. *trans*- $[\text{Co}(\text{en})_2\text{Cl}_2]^+$
 - III. *cis*- $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$
 - IV. *trans*- $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$
- a) 0 b) 1 c) 2 d) 3 e) 4

21. We have discussed the need for more complex models to answer more questions. For example, in Chemistry 202, without the use of orbitals, we were able to discuss that, **in general**, ionization energies (IE) increase for elements across a row of the periodic table. However, there are some exceptions to this general trend as we can see from the data for the elements lithium through oxygen:

Element	First ionization energy (kJ/mol)
Li	520
Be	900
B	800
C	1100
N	1400
O	1300

- a. Explain these numbers. Make sure in your answer to **define** what is meant by ionization energy, **explain** why the **general trend** for IE values across a row is to increase, and the **nature of the exceptions**. Use concepts such as **shielding**, the **penetration effect**, and **orbital diagrams** () in your answer when appropriate. [7 points]

21. Now consider the second ionization energies as well:

Element	First ionization energy (kJ/mol)	Second ionization energy (kJ/mol)
Li	520	7300
Be	900	1800
B	800	2400
C	1100	2300
N	1400	2900
O	1300	3400

- b. Determine the ratio of 2nd IE/1st IE for the elements Li to O. **Why is this ratio greater than one** for all of the elements? **Explain the relative ratios** (using concepts such as **shielding**, the **penetration effect**, and **orbital diagrams**, when appropriate). [7 points]
- c. **Estimate** values for the first and second ionization energies for fluorine and **justify** your answers. [6 points]

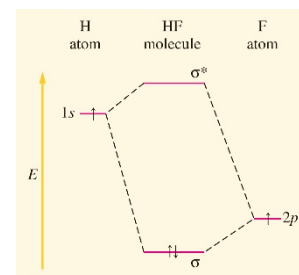
22. You learned a long, long time ago that nitrogen, oxygen, and fluorine gases are all diatomic (written as X_2), and with Lewis structures you can determine the number of bonds and relative bond strengths. But what about removing an electron (resulting in X_2^+) or adding an electron (resulting in X_2^-)? Lewis structures do not help us determine what happens to the relative bond strengths. No fear – molecular orbital (MO) theory can!
- a. Fill in the table below with N_2 , O_2 , and F_2 in the appropriate boxes – each molecule should be written twice; once for when an electron is removed, and once for when an electron is added. For example, we discussed in lecture that removing an electron from H_2 results in a weaker bond, so if I asked about H_2 , you would write H_2 in the upper left box. **[3 points]**

	Weaker bond than X_2	Stronger bond than X_2
Removing an electron (X_2^+)		
Adding an electron (X_2^-)		

- b. Use **MO energy-level diagrams** to **justify** your answers in the table in part a. **[8 points]**

22. c. One of the boxes in part a should be blank. Are there any homonuclear diatomic molecules (X_2 ; **not** an ion) that would be placed in that box? If yes, provide an example molecule with explanation. If not, explain why not, using the premises of MO theory. **[3 points]**

- d. For N_2 , O_2 , and F_2 , all bond strengths were greatly affected by both the adding and removing of an electron. It turns out that removing an electron from the HF molecule (resulting in HF^+) does not appreciably change the bond strength. A figure in the textbook (reproduced here) shows a partial MO energy level-diagram for the HF molecule (focusing only on the orbitals involved in bonding). **Sketch the complete MO energy-level diagram (with explanation)** for all valence electrons in H and F and **explain** why the bond strength does not change much. **[6 points]**



23. As seen in lecture (and lab!) solutions of transition metal ions (such as those of cobalt!) can be quite beautiful. And, as we have discussed in lecture, changing the ligands (among other changes) can change the colors of the solutions.

a. For example, consider the following complex ions and their colors in aqueous solutions:

Complex ion	Observed color in aqueous solution
$[\text{Co}(\text{H}_2\text{O})_6]^{3+}$	Red
$[\text{Co}(\text{NH}_3)_6]^{3+}$	Yellow
$[\text{Ni}(\text{NH}_3)_6]^{2+}$	Blue
$[\text{Ni}(\text{en})_3]^{2+}$	Violet

- i. Use this information, along with the data from Table 19.6 (front of the exam), to place the ligands NH_3 , H_2O , and en (en = ethylenediamine = $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$) on the spectrochemical series using the Crystal Field Theory (CFT) and CFT diagrams. That is, **arrange the three ligands according to splitting from large to small** (strong-field to weak-field) and **support** your answer. Even if you have memorized this series (but why?), you must support your answer to get credit for the ordering. Make sure to explain the nature of the colors – that is, **why do we see the colors that we do?**
- ii. **Predict the color** of $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ and **support your answer** using your developed spectrochemical series and the CFT.

Additional space is provided on the next page. [10 points]

23. a. Continue your answer to 23a below, if needed.

23. b. In part a we saw that the complex ion $[\text{Co}(\text{NH}_3)_6]^{3+}$ is yellow in aqueous solution. It turns out that if we add a solution with a high concentration of chloride ions, we can replace ammonia ligands with chloride ligands.
- i. If we replace two ammonia ligands with two chloride ligands, we make the complex ion $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$, which has two isomers. **Sketch** both of these ions and **name** them. **[4 points]**
- ii. One of the isomers appears violet in solution and the other appears green. With this information, **can you place Cl^- on the spectrochemical series** you developed in part a? **If so, place it and support your answer. If not, justify your answer. Also, match the isomers with their colors.** Use the CFT and energy level diagrams to **justify your answers.** **[6 points]**