CHEMISTRY 204

Name _____

Hour Exam I

February 15, 2024

Signature _____

Dr. D. DeCoste

T.A. _____

This exam contains 23 questions on 10 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:

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

$E = hc/\lambda$

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

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

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

$\Delta x \Delta p = h$

$\lambda = h/mv$

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

$E_n = \dfrac{n^2 h^2}{8mL^2}$

$E = \dfrac{h^2}{8m}[\dfrac{n_x^2}{L_x^2} + \dfrac{n_y^2}{L_y^2} + \dfrac{n_z^2}{L_z^2}].$

1 pm = 10^{-12} m   1 nm = 10^{-9} 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

wavelength 7×10^{-7} 6×10^{-7} 5×10^{-7} 4×10^{-7} meters

| Infrared	Red	Orange	Yellow	Green	Blue	Violet	Ultra violet
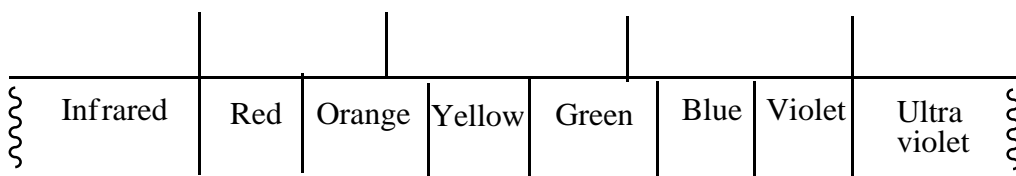
1. What color of visible light is emitted when an excited electron in a hydrogen atom drops from
    $n = 5$ to $n = 2$?

    a) It is not visible.   b) Red   c) Orange   d) Yellow   e) Blue

2. The ionization energy of a one-electron species is 7.84×10^{-17} J. Identify the element that forms
    this ion.

    a) Boron   b) Carbon   c) Oxygen   d) Fluorine   e) Chlorine

3. For which of the following energy levels is the probability of finding a particle in a one-dimensional
    box of length L the greatest between x $= 0$ and x $= L/2$?

    a) $n = 1$ b) $n = 2$ c) $n = 3$ d) The probability is the same for these (a-c).

4. Consider electrons in an atom in the first three energy levels. How many of these electrons
    can have the magnetic quantum number, m_l, equal to -1?

    a) 2   b) 4   c) 6   d) 10   e) 12

5. Consider the **expected** ground state electron configurations for the atoms of the transition metals
    scandium (Sc), cobalt (Co), nickel (Ni) and zinc (Zn) and determine the **total number** of unpaired
    electrons.

    a) 0   b) 2   c) 4   d) 6   e) 9

6. Recall the one-dimensional "particle-in-a-box" model we discussed and how we can use
    the appropriate electrons in a conjugated single-double bond system as an approximation of
    this model. Consider the following molecule as represented below:

    H_2C⟍⟋⟍⟋⟍⟋CH_2
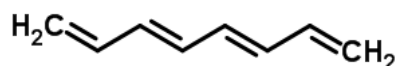
    Which of the following represents the energy difference between the ground state and first
    excited state?

    a) $(\frac{h^2}{8mL^2})$ b) $7(\frac{h^2}{8mL^2})$ c) $9(\frac{h^2}{8mL^2})$ d) $15(\frac{h^2}{8mL^2})$ e) $17(\frac{h^2}{8mL^2})$

7. Consider all possible orbitals in the first four energy levels of the hydrogen atom ($n = 1, 2, 3,$ and
    4). How many of them have the following shape for their radial probability distribution?
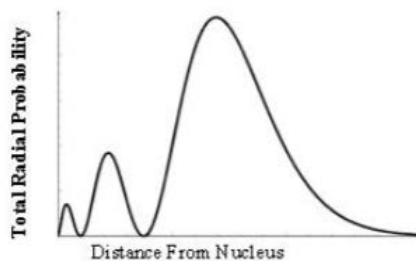

    a) 4   b) 8   c) 12   d) 17   e) 18

8. Determine the hybridization of sulfur for each of the following. Cross out the species for which the hybridization of sulfur is unique (that is, which none of the other given molecules or ions share). How many have you **not** crossed out?

$$SF_4^{2-}, SF_4, SO_2, H_2S, SO_3$$

   a) 0   b) 2   c) 3   d) 4   e) 5

9. All you know about a given molecule is the shape around the central atom. For which of the following shapes could the central atom have the most possible hybridizations?

   a)   trigonal pyramid
   b)   see-saw
   c)   bent
   d)   square planar
   e)   The number of possible hybridizations for the central atom is equally great in at least two of the above (a-d).

10. 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.
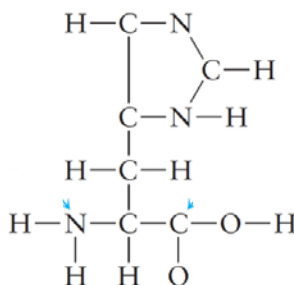
   Of carbon, hydrogen, nitrogen, and oxygen, how many of them have more atoms that are sp^2 hybridized than sp^3 hybridized?

   a) 0   b) 1   c) 2   d) 3   e) 4

11. According to MO theory, for how many of the following is bond strength expected to **increase** (that is, a **stronger bond** is formed) when changing the number of electrons as shown below?

$$B_2, N_2, O_2, B_2^-, B_2^+, O_2^{2+}$$
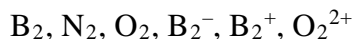
	Adding an electron	Removing an electron
a)	Three (3)	One (1)
b)	Three (3)	Three (3)
c)	Three (3)	Two (2)
d)	One (1)	Three (3)
e)	Two (2)	Three (3)

12. According to MO theory, which of the following is expected to have the **longest** bond length?

    a) N_2^- b) O_2^+ c) O_2^- d) F_2^+ e) F_2^-

13. You are told that the ionization energy for a diatomic molecule is less than the ionization energy for the individual atom that makes it up (that is, the ionization energy for X_2 is less than the ionization energy for X). Considering boron, carbon, nitrogen, oxygen, and fluorine, for how many is this true?

    a) 1   b) 2   c) 3   d) 4   e) 5

14. A cyanide contains carbon and nitrogen bonded to each other (CN). For inorganic compounds, the cyanide group is a cyanide anion, CN^-. Consider the Lewis structure and MO energy diagram for the cyanide ion.

    a) The bond order from the MO diagram is the same as the number of bonds in the Lewis structure, and MO theory predicts the ion is diamagnetic.
    b) The bond order from the MO diagram is the same as the number of bonds in the Lewis structure, and MO theory predicts the ion is paramagnetic.
    c) The bond order from the MO diagram is the different from the number of bonds in the Lewis structure, and MO theory predicts the ion is diamagnetic.
    d) The bond order from the MO diagram is the different from the number of bonds in the Lewis structure, and MO theory predicts the ion is paramagnetic.
    e) We cannot draw a Lewis structure for the cyanide ion.

15. How many of the following are **correct names** for a coordinate covalent compound?

    - potassium hexacyanoferrate(III)
    - pentaamminechlorocobalt(III) chloride
    - hexachlorocobalt(II) fluoride
    - triamminebromoplatinum(II) chloride

    a) 0   b) 1   c) 2   d) 3   e) 4

16. The electron configuration of ground state Ti^{2+} is

    a) [Ar] $4s^2 3d^2$
    b) [Ar] $4s^2$
    c) [Ar] $4d^2$
    d) [Ar] $4s^1 3d^1$
    e) [Ar] $3d^2$

17. Consider all possible isomers of the following three species: $[Co(NH_3)_4(H_2O)_2]^{2+}$, $[Pt(NH_3)_2Br_2(H_2O)_2]^{2+}$, and $[Co(en)_2Cl_2]$, where en = ethylenediamine = $NH_2CH_2CH_2NH_2$. How many **optically active** isomers are there?

    a) 0   b) 2   c) 3   d) 4   e) 6

18. Consider eight octahedral complex ions: $[NiA_6]^{2+}$, $[CoA_6]^{3+}$, $[CrA_6]^{3+}$, $[ZnA_6]^{2+}$, $[NiB_6]^{2+}$, $[CoB_6]^{3+}$, $[CrB_6]^{3+}$, and $[ZnB_6]^{2+}$, where A is a neutral strong-field ligand and B is a neutral weak-field ligand. How many of these octahedral complex ions are **diamagnetic**?

   a) 3   b) 4   c) 5   d) 6   e) 7

19. You are in lab and asked to determine if a ligand is strong-field or weak-field. You are told to test it by making complex ions with a transition metal ion and determining the number of unpaired electrons. Your lab partner suggests Co^{3+}, Cu^+, Cr^{2+}, Zn^{2+}, and Ni^{2+}. How many of these would work to differentiate between strong-field and weak-field ligands?

   a) 0   b) 1   c) 2   d) 3   e) 4

20. Given the spectrochemical series below, which of the following is the best prediction for the number of **unpaired electrons** in the complex ion $[CoI_6]^{3-}$?

   Spectrochemical series: $CN^- > NO_2^- >$ en $> NH_3 > H_2O > OH^- > F^- > Cl^- > Br^- > I^-$
                           (strong-field)   (weak-field)

   a) 0   b) 1   c) 2   d) 3   e) 4

21. Full credit will be reserved for complete answers.

    a.   Consider a 3-D cube of length *L*. What is the **minimum** number of ground state quantum particles (uncharged – not electrons – all with the same mass, *m*) needed to require the **longest possible wavelength** of light to excite a particle to the **first excited state** in such a box? **Justify** your answer. **Draw and explain** the energy level diagram as **part of your explanation**.   [10 pts.]

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21. b. Here is a snippet of dialogue from the hilarious joke I told in lecture that began "Heisenberg and Schrödinger are going for a drive and are stopped for speeding":

> Police officer: Do you know how fast you were going?
> Heisenberg: No.
> Police office: You were going 85 miles per hour.
> Heisenberg: Great – now we're lost.

The best way to make a funny joke even funnier is to explain it, and that's what you are to do in this problem. **[10 pts.]**

  i. Explain why Heisenberg said that they were lost. What does he mean by "lost" and what prompted him to say this? **Explain**.

  ii. It is often humorous when we say things that are exaggerations. Use reasonable estimations to provide **quantitative support** that the two were not actually lost. Conversions that may be of use: there are about 1600 meters in a mile, 3600 seconds in an hour, about two pounds to a kilogram on earth, and an average atomic radius is about 100 pm. **Show and explain** all work.

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22. The molecular orbital (MO) model is very powerful but can be complicated even for simple molecules like water. As we discussed, this complexity is often due to the shape, and MO diagrams for linear molecules can approximated similarly to what we do for diatomics. In this problem you will consider carbon dioxide (CO_2). **[20 pts.]**

The unlabeled MO diagram for carbon dioxide is shown below. Note that the 2s orbitals for the oxygen atoms have been included, and that these **do not participate** in bonding (they are nonbonding orbirals). **Draw and label the remainder of the atomic orbitals** (AOs) for the carbon atom to the left of the MO diagram, and those for the oxygen atoms to the right of the MO diagram, making sure to pay attention to their **relative energy levels**. Use **dotted lines to show** which AOs **overlap** to form the MOs. Fill in the **proper number of electrons** and **label the MO diagram** (using σ, σ^*, π, π^*, and *nb* for "nonbonding", if appropriate). It is a good idea to take some time determining these on scratch paper before completing the MO diagram below.

On the following page, justify your completion of the diagram, explaining/showing the appropriate AO overlap and **providing support** for any MOs you label as nonbonding. Finally, draw a Lewis structure for the carbon dioxide molecule and **explain** how the MO diagram is **consistent** with this Lewis structure.

Carbon AOs   **MO diagram for CO₂**   **Oxygen AOs**

___

___

___   ___

___   ___

___   ___

___

___

_↑↓_   _↑↓_ (nb)   _↑↓_ 2s   _↑↓_ 2s

[Please write your discussion of the MO diagram on the next page]

22.   b.   Please discuss your answer below. **Justify** your completion of the MO diagram on the previous page, explain/show the appropriate AO overlap, and **provide support** for any MOs you label as nonbonding. Finally, draw a Lewis structure for the carbon dioxide molecule and **explain** how the MO diagram is **consistent** with this Lewis structure.

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23.   In this problem you will be considering coordinate covalent complex ions.

   a.   We developed the crystal field theory (CFT) from the MO diagrams of octahedral
        transition metal complexes. These MOs can be drawn because of the symmetry of
        the ions (as discussed in class and in question #22 on this exam). Sketch the MO
        diagram for a general octahedral complex ion $[ML_6]^{n+}$. Include the **relative energies**
        of the free metal ion orbitals and those of the ligands, and use **dotted lines to show**
        which AOs **overlap** to form the MOs. **Label the MO diagram** (using σ, σ^*, π, π^*,
        and *nb* for "nonbonding", if appropriate). Finally, **explain why** we are able to
        simplify this diagram to the type of diagram we use in Crystal Field Theory. **Justify**
        your answer. **[10 pts.]**
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23.   b.   Consider the following cobalt complexes: $[Co(NH_3)_6]^{3+}$, $[CoF_6]^{3-}$, $[Co(H_2O)_6]^{3+}$, and $[Co(CN)_6]^{3-}$. The colors of the four complex ions are (in no particular order): green, blue, yellow, and green-yellow. **Match these colors** with the complex ions, **fill in** the colors in the table below, and **justify** your answer. A **complete** answer will **discuss** the **origin of the color** of an aqueous solution. **[10 pts.]**

The spectrochemical series is as follows:

$$CN^- > NO_2^- > en > NH_3 > H_2O > OH^- > F^- > Cl^- > Br^- > I^-$$
(strong-field)   (weak-field)
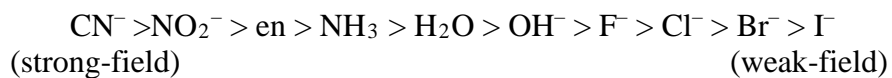
Complex Ion	Color
$[Co(NH_3)_6]^{3+}$	
$[CoF_6]^{3-}$	
$[Co(H_2O)_6]^{3+}$	
$[Co(CN)_6]^{3-}$	