1. (15 pts) True/False
   a  T  F  Ionization energy decreases as one moves down from Li to Cs in Group 1.
   b  T  F  Group I elements react with $O_2$ to form different compounds depending on
            the element. These include oxides, peroxides, and superoxides.
   c  T  F  Hydrogen has an ionization energy more similar to fluorine’s than to
            lithium’s.
   d  T  F  Hydrogen forms an extremely strong H-H bond.
   e  T  F  Alkaline earth oxides (e.g. CaO) are base anhydrides.
   f  T  F  In the compound NaH, the δ$^+$ is on the H atom.
   g  T  F  Boranes contain boron and hydrogen in which hydrogen sometimes bridges
            two boron centers in a 3-center, 2-electron bond.
   h  T  F  Aluminum reacts with bases but is non-reactive towards acids.
   i  T  F  Silicon and carbon have equal abilities to form double bonds.
   j  T  F  Carbon exists in a variety of allotropes including the tetramer, C$_4$.
   k  T  F  The nitride ion has formula N$_2$.
   l  T  F  White phosphorus, P$_4$, is expected to be more volatile than red phosphorus,
            (P$_4$)$_n$.
   m  T  F  Unlike O$_2$, S$_8$ is diamagnetic.
   n  T  F  Chlorine has a range in oxidation states from $+7$ (e.g. KClO$_4$) to $-3$ (e.g.
            Rb$_3$Cl).
   o  T  F  Speckled nitrogen is formed by boiling CH$_2$ in an osmotic fog until the
            atoms are fully extracted and the neutrons precipitate.

2. Short answer:
   a. (1 pt) What is the periodic trend for atomic radius across the transition metals from Sc to Zn?
      a. Atomic radius increases  b. Atomic radius decreases
   b. (1 pt) Transition metals tend to form cations. How does the ionic radius for any given metal
            change with the magnitude of the charge?
      a. Ionic radius increases with increasing charge
      b. Ionic radius decreases with increasing charge
   c. (1 pts) Going down any given triad of transition metals one notices a peculiar trend with respect to
            ionic radius. For example, the ionic radii of Ni$^{+2}$, Pd$^{+2}$, and Pt$^{+2}$ are 83, 100, and 94 pm,
            respectively. What is the name of this effect? (Or what is the explanation?)

3. (3 pts) Give the oxidation state of iron in each of these complexes:
   \[
   [\text{Fe(NH}_3)_6\text{SO}_4] \quad \text{K[Fe(NH}_3)_2(\text{Cl})_4] \quad \text{Fe(CN)}_2(\text{NH}_3)_3\text{Cl}
   \]
4. (2 pts) The ligand diethylenetriamine, \( \text{NH}_2\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2 \), commonly abbreviated “dien”, forms octahedral complexes with metal ions with the formula \( \text{M(dien)}_2^{+n} \). How many structural isomers are possible for \( \text{M(dien)}_2^{+n} \)?

5. (2 pts) The equilibrium \( \text{Cr(NH}_3)_6^{+3} + 3 \text{ en} \rightleftharpoons \text{Cr(en)}_3^{+3} + 6 \text{ NH}_3 \) (where en = \( \text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2 \)) lies far to the right, despite the fact that \( \Delta H \) for the reaction is very close to zero. What is the explanation?

   a. \( \Delta S > 0 \)  
   b. \( \Delta S = 0 \)  
   c. \( \Delta S < 0 \)  
   d. rate constant > 0  
   e. rate constant = 0  
   f. rate constant < 0

6. (2 pts) Which two of these generic octahedral compounds would exhibit chirality (enantiomerism)?

   \[ \text{MA}_3\text{B}_3 \quad \text{MA}_3\text{BCD} \quad \text{MA}_2\text{BC}_3 \quad \text{MABCDEF} \]

7. (3 pts) An alternative rare geometry for coordination number six is the trigonal prism shown below. It is shaped like a familiar prism: two equilateral triangles in an eclipsed position with the metal in the center and equal distance from all six ligands. How many structural isomers are possible for trigonal prismatic compounds of the formula \( \text{MA}_2\text{B}_4 \)?

8. (3 pts) (a) Sketch the crystal field splitting pattern for an octahedral complex. (b) Label all of the orbitals. (c) Populate it for \( d^5 \) low spin.

9. (2 pts) Calculate the crystal field stabilization energy in units of \( \Delta_0 \) and \( P \).

10. (1 pts) An octahedral complex of \( \text{Fe}^{+2} \) is diamagnetic. Is the complex high-spin or low-spin?

   a. high spin  
   b. low spin
11. (2 pts) Ni(NH$_3$)$_4^{+2}$ is paramagnetic while isoelectronic (having the same number of electrons) Pd(NH$_3$)$_4^{+2}$ is diamagnetic. Explain in a few words how this could be so.

12. (3 pts) List the three conditions that are necessary for an octahedral complex to be high spin.
   a. 
   b. 
   c. 

13. (3 pts) What do you think the crystal field splitting pattern for the trigonal prism (See Question 9 for a diagram) would look like? (Hint: There are degenerate orbitals.) Label each d-orbital.

14. (12 pts) Predict the geometry and the number of unpaired electrons for each of these transition metal complexes. Given: Spectrochemical Series:

   I$^-$ < Br$^-$ < SCN$^-$ < Cl$^-$ < F$^-$ < OH$^-$ < ox < H$_2$O < NCS$^-$ < py, NH$_3$ < en < NO$_2^-$ < CH$_3^-$ < CN$^-$ < CO

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<th>Compound</th>
<th>Geometry</th>
<th>Number of unpaired electrons</th>
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<tr>
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<tr>
<td></td>
<td>Square plane</td>
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</table>
15. The transition metal complex PdCl$_4^{2-}$ is square planar. The bonding of the four chlorides can be considered as $\sigma$-only (no $\pi$-bonding). Use the D$_{4h}$ character table and the started MO diagram to complete the questions that follow.

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<th>E</th>
<th>2C$_4$</th>
<th>C$_2$</th>
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<th>i</th>
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</table>

SALCs

p - - -

s -

d- - - - - -
(a) (2 pts) Use the character table to write symmetry labels by the 4d, 5s and 5p atomic orbitals on the diagram.

(b) (2 pts) Sketch the set of four atomic orbitals that are used to form the SALC set on this Cartesian coordinate system:

\[ \text{Diagram of atomic orbitals} \]

(b) (1 pts) If you determined the reducible representation for the SALC set, you would have concluded that the SALC set transforms as \( A_{1g} + B_{1g} + E_u \). Add these labels to the SALC orbitals in the diagram (such as “a\(_{1g}\)” — use lower case.)

(c) (4 pts) Finish the MO diagram. Caution! There are three orbitals that transform as \( A_{1g} \)!

Recall how we handled this! Double check: Did you create 13 MOs from the 13 AOs?

Add symmetry labels to each MO (such as “a\(_{1g}\)” — use lower case.)

(d) (2 pts) Square planar compounds such as PdCl\(_4^{2-}\) are diamagnetic, d\(^8\), 16-electron compounds (8 e\(^-\) from the d\(^8\) metal and 2 each from the four ligands. Populate the MO diagram in order to give a diamagnetic result.

(e) (3 pts) Suppose one of the ligands in PdCl\(_4^{2-}\) is replaced with a π-back bonding ligand such as CO, producing Pd(CO)Cl\(_3^{-}\). Ignore the minor adjustments that would take place for the \( \sigma \)-SALC set by having two types of \( \sigma \)-donor ligands. Sketch in the two π* orbitals that the one CO would add to the ligand column (under the word SALC), and then indicate how you think these would form π-bonding and antibonding orbitals with the metal. To do this, decide what orbital(s) is/are involved from the metal and use arrows and lines or whatever you feel is necessary to explain the role of π-back bonding in the MO diagram.

16. (3 pts) What is the ground state free ion term symbol for the electron configuration \( f^2 \), such as 4f\(^2\)?

17. (3 pts) Suppose you were filling in a table of microstates for a d\(^4\) situation. List the microstates that would go in the box for \( M_L = 4 \) and \( M_S = 1 \).
18. The following questions pertain to Cu(H₂O)₆²⁺

a. (3 pts) Into what term symbols does the free ion term ²D change in an octahedral field of ligands? Sketch the split that occurs and label each energy level with the appropriate term symbol.

b. (2 pts) Sketch a sample microstates by each of the energy levels sketched above.

c. (2 pts) Add a label for Δₒ.

19. (2 pts) With d³ configurations, we could easily obtain values for Δₒ directly from the spectrum. (Unlike d² where we had to do some subtracting of absorbances.) Suppose a d³ complex featured absorbance maxima at 10,500, 18,800, and 28,900 cm⁻¹. What is the value of Δₒ?

20. (4 points) What four tetrahedral dⁿ configurations have a ground state term symbol of ¹A?

   d¹  d²  d³  d⁴  d⁵  d⁶  d⁷  d⁸  d⁹  d¹⁰

21. (8 pts) Count electrons in each of these organometallic formulas involving technecium. Some of them do not exist because they do not obey the 18-electron rule.

<table>
<thead>
<tr>
<th>Tc(CO)₆</th>
<th>(OC)₄TcBr</th>
</tr>
</thead>
<tbody>
<tr>
<td>(π-C₅H₅)Tc(CO)₃</td>
<td>(OC)₅TcCH₃</td>
</tr>
</tbody>
</table>

22. (3 pts) The compound “(π-C₅H₅)Ir(CO)” exists as a dimer, [(π-C₅H₅)Ir(CO)]₂ with a metal-metal bond between. The compound obeys the 18-electron rule. Is the Ir-Ir bond a single, double or triple bond? Show work.
Answers:

1. T, T, T, T, T       F T F F F       F T T F (F) (last one was a silly statement meant to be false – it was not counted.)
2. b. b            3. +2, +3, +3       4. Two: fac and mer       5. a
6. MA₃BCD       MABCDEF
7. There are three structural isomers: (1) the two A groups can be on the same triangular face, (2) they can be on separate triangular faces directly above one another or (3) they can be on separate triangular faces not directly above one another. This third possibility is chiral.
8. lower: the t₂g orbitals (dₓᵧ, dₓz, dᵧz) higher: the e₉ orbitals: dₓ²₋ᵧ² and d₂z². Population: (t₂g)⁵ (e₉)0
9. 5 x 0.4 Δₒ – 2 P ( = –5 x 0.4 Δₒ + 2 P)
10. b
11. Ni(NH₃)₄⁺²⁺ is tetrahedral Pd(NH₃)₄⁺² is square planar
12. a. first row metal, b. low oxidation state, c. weak field ligands
13. Here, several answers would be acceptable. If the prism is short and wide, the splitting will be different than if it were tall and skinny. Either way, there are two doubly degenerate pairs: dₓz, dᵧz are degenerate and dₓ²₋ᵧ² and dₓᵧ are degenerate. The remaining orbital dₓ² is unique. The best guess is that dₓz, dᵧz are highest in energy while the others are lower.
14. [Cr(NH₃)₆]²⁺(SO₄)₃, Octahedron, 3 unpaired electrons; K₂[CoCl₄], Tetrahedron, 3 unpaired electrons; Pt(NH₃)₂Cl₂, Square plane, 0 unpaired electrons; K₄[Mn(CN)₆], Octahedron, 1 unpaired electrons
15. (a) dₓᵧ: b₂g; dₓz and dᵧz: e₉; dₓ²₋ᵧ² : b₁g d₂z² : a₁g; (b) four circles, one on each end of the x and y axes.; (c) See MO diagram in textbook; (d) populated up through and including : a₁g(n); (e) The π* orbital will overlap with the filled e₉(n) in the original σ-only diagram.
16. ³H
17. There are only two microstates possible for the four electrons: (m₁, mₛ): (2, ½); (2, -½); (1, ½); (-1, ½) and (2, ½); (1, ½); (1, -½); (0, ½)
18. a. Lower energy state: ²E, higher energy state ²T. b. The lower energy state has configuration (t₂g)⁶ (e₉)³ and the higher energy state has configuration (t₂g)⁵ (e₉)⁴. c. Energy difference between ²E ²T is Δ₀.
19. Δ₀ = 10,500 cm⁻¹
20. d² d⁵ d⁷ d¹⁰
21. Tc(CO)₆: 19 e⁻     (OC)₄TcBr: 16 e⁻     (π-C₅H₅)Tc(CO)₃: 18 e⁻     (OC)₅TcCH₃: 18 e⁻
22. double bond