Chemistry 448/548 Test 3 Name: __________
Fall 2025

Very Short Answer Questions: (3 points each)

1. The distance of closest approach between two unbound atoms of the same element is their van der Waal's radius
2. In a complex, Δ (energy gap) generally increases as elements progress down a group.
3. The transition metals are most frequently found in nature as their oxide (salts).
4. A defect caused by missing ions from the lattice is called an Schottky defect.
5. Of the high temperature superconductors, a major class are the "1-2-3 superconductors" which are so called because they have the general formula $YBa_2Cu_3O_{7-\delta}$.
6. The distance component of London disperson forces is directly proportional to $1/r^6$.
7. Viscosity is directly proportional to the strength of intermolecular forces.
8. The *d*-electron configuration in $Cr(CO)_6$ is d^6.
9. What is the minimum number of electrons a stable, octahedral transition metal complex can be expected to have? 12 (filled a_{1g}, e_g, and t_{1u})
10. State the Jahn-Teller theorem. For a non-linear molecule in an electronically degenerate ground state, the molecule must distort so as to lower the symmetry.

Discussion Questions: (You must show work to receive credit!)

1. Consider the square planar coordination complex MX_4. Ignoring π-bonding effects, its *d*-orbitals are ordered energetically $xz = yz < z^2 < xy < x^2-y^2$. If π-bonding is introduced, which metal orbitals will be involved and give the relative order of interaction. Justify your predictions. Are Jahn-Teller distortions for such complexes likely? Why or why not? (*Hint*: Assume the bond axes = xy axes.) (10 points)

   p or π* orbitals on the ligands would either lie parallel to the z-axis or in the xy-plane perpendicular to either the x or y axes. The orbitals that would be affected would be the *xy*, *xz*, and *yz* orbitals. The z^2 and x^2-y^2 would not have a π interaction. (While the z^2-orbital would line-up correctly, the signs of its wavefunctions would yield no net interaction. Each ligand orbital would experience the same level of interaction. The metal *xy*-orbital would experience twice the interaction of the *xz* or *yz* orbitals.

   Jahn-Teller distortions would occur only rarely, since the condition for it is met only for d^1 and d^6 metals.

2. Discuss n- and p-type semiconductors. (10 points)

   n-type semiconductor - A semiconductor incorporating 2 materials, generally of similar sizes, one of which is present in much smaller quantity (dopant) and possesses a greater number of electrons than the bulk material. The extra electrons reside near the conduction band and are responsible for the flow of electricity through the material. Resistance to the flow of electrons arises from the higher electronegativity of the dopant which hinders the electrons from breaking free.

Example: arsenic in germanium.

p-type semiconductors - Like n-type semiconductors except that the dopant has fewer electrons than the bulk material. The electron vacancy resides near the valence band and electricity flows when electrons flow into and out of the hole. Resistance to the flow of electrons arises from the lower electronegativity of the dopant which hinders the flow of electrons onto that material.

Example: gallium in germanium

3. Boron nitride, $(BN)_n$, can have a structure similar to that of graphite. Which would conduct electricity better and why? Would the difference in conductivities between the two be large or small and why? (10 points)

Graphite has a planar structure with each C bound to 3 others in a trigonal arrangement. This leaves a *p* orbital with one electron on each C to form an extended π-network through which electrons can move. The same is true of boron nitride.

Graphite is a much better conductor for several reasons.

1) B and N have an electronegativity difference of about 1. Thus, it requires extra energy to force an electron from N onto B. Since all C atoms have the same electronegativity, this is not a problem in graphite.
2) The electrons are more localized on BN because the electrons start off on a N lone pair and are not shared equally electronegativity aside. Again, this is not a problem for carbon since it has one electron in each orbital to start with.
3) The atom and orbital sizes of B and N are different causing poorer overlap and making the conducting of electricity more difficult.

4. List the following in order of **increasing** melting point and briefly explain why each molecule was placed into the position that you chose. (i.e. Why does it melt at a higher temperature than the molecule preceding it and why does it melt at a lower temperature than the molecule following it?) AlN, diamond, H_2, H_2O, LiCl, NaCl, Ne, O_2, $SiCl_4$.

$H_2 < Ne < O_2 < SiCl_4 < H_2O < LiCl < NaCl < AlN <$ diamond

H_2, Ne, O_2, and $SiCl_4$ are all non-polar and are held together by London disperson forces. They occur in this order because of increasing size. (Larger e^- clouds are more polarizable.)

H_2O is held together by hydrogen bonding which is strong for second row elements and causes anomalously high melting points.

LiCl is an ionic compound and has a much higher melting point than water because the charges on ions are larger than dipoles so the electrostatic attraction is greater.

NaCl is also ionic and melts higher than LiCl because Na^+ does not polarize as well as Li^+. Thus, NaCl has less covalent character than LiCl and melts at a higher temperature.

AlN is ionic and melts higher than NaCl because the forces of attraction between ions goes as z^2 and the charge on each ion is ±3.

Diamond melts highest because it is an extended covalent network. (Actually it doesn't melt it sublimes.)

5. Identify each element. (*Note*: Only 10 of the 11 elements are used.) (1 point each)

Cr	The high luster of this metal is noteworthy as is the colorful nature of its coordination compounds.
V	Its +4 oxidation state is unexpectedly its most stable. It is found in a variety of minerals and oil.
Ti	Forms a chloride that is a liquid at room temperature.
Co	Bluish metal which frequently forms coordination compounds.
Cu	Soft and ductile; it is difficult to oxidize, but its oxide forms a distinctive green color.
Mn	Usually isolated by reduction of its oxide (found naturally) by chemical methods or of its sulfate electrochemically.
Zn	Chemically very similar to magnesium.
Fe	It is found naturally in the minerals haematite and magnetite among others.
U	Very dense; pyrophoric when finely divided.
Ni	Reacts at room temperature with CO to form a liquid tetracarbonyl that is very toxic.

6. Which of the following would have the larger crystal field splitting energy (Δ_O)? Justify your answer. (10 points)

   a) $[CoF_6]^{2-}$ or $\mathbf{[RhF_6]^{2-}}$ - Probably because the d-orbitals of second-row transition metals extend further into space allowing greater overlap with the ligands.

   b) $[Co(H_2O)_6]^{2+}$ or $\mathbf{[Co(NH_3)_6]^{2+}}$ - Both water and ammonia have no low lying π^*-orbitals and are sp^3 hybridized with no p-orbitals available for π-bonding. Thus, the difference in Δ_O is predominantly a σ effect. N is less electronegative than O, so the lone pair on NH_3 will project further into space than the lone pairs on O. Thus, the *d*-electrons on Cr will be repelled more by the e^- on N than those on O when the ligands approach the metal.

7. Methane has a boiling point of -182°C, CF_4 has a bp of -184 °C, and CCl_4 has a bp of -23 °C. Why are the boiling points of the first two so close to each other and so far from the last compound? (10 points)

   These molecules are all non-polar and therefore are held together only by London disperson forces. The general rule of thumb is that as molecules get larger, London disperson forces increase and the melting points go up. However, size is not the cause of London disperson forces. London disperson forces arise from instantaneous dipoles within molecules. Fluorine is very electronegative and holds onto its electrons tightly preventing them from being easily polarized this causes its melting point to be lower than would be expected only on the basis of size. The melting point of Cl is so much higher because its electronegativity is lower than that of F and it is larger making polarization easier.