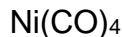


Advanced Inorganic Chemistry: Exercises

Chapter 1: Role of Inorganic Chemistry

- 1) Which are the most common coordination polyhedra for molecules with coordination numbers 2 to 9? Name examples from inorganic chemistry!
- 2) What are Lewis acids and bases? Which are the strongest species?
- 3) VSEPR revisited: Sketch the spatial structures of the compounds given below at room temperature. Remark: Count lone pairs as ligands. Please mention the hybridization of the central atom of the respective structure!



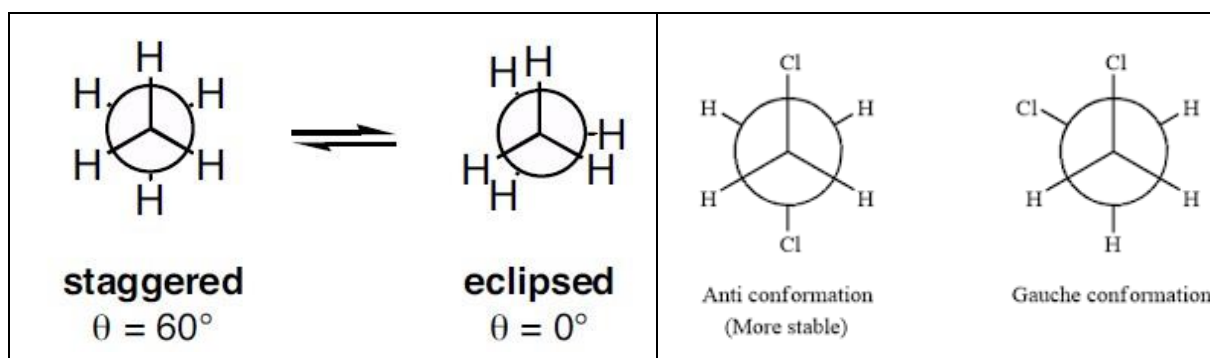
- 4) What structures do you expect for the ozone molecule and the ozonide anion O_3^- ?
- 5) Name isoelectronic diatomic molecules or ions with 12, 13, 14, or 15 electrons in total!
- 6) Mention some selected roles of inorganic chemistry for the following disciplines!
 - a) Astrochemistry
 - b) Geochemistry
 - c) Atmospheric Chemistry
 - d) Biochemistry
 - e) Medicine
 - f) Pharmacy
 - g) Toxicology

Chapter 2: Astro and Cosmochemistry

- 7) Which "H" species do you expect in the interstellar medium (ISM) of the milky way and other galaxies?
- 8) To which point group belongs the Sombrero galaxy (M104, NGC 4594)? Many celestial objects have K_h symmetry. Discuss mechanisms for the breaking of such high symmetry!
- 9) Name eight gas-phase interstellar acid-base pairs!
- 10) Speculate about the reaction product of acetylene with water in the ISM! Discuss the isomerization of the primary product as well!
- 11) Name an atomic and a molecular transition, which are important for microwave/radioastronomy!
- 12) Explain the roles of interstellar dust for astrochemistry!

Chapter 3: Point Groups and Group Theory

- 13) Please write down all symmetry elements of the following molecules!
- NH_3
 - Acetone
 - Dimethylcyclopentane
 - Ethandiol
 - Propadiene
 - Methane
- 14) Determine the point groups for
- Ethane (staggered conformation)
 - Ethane (eclipsed conformation)
 - Chloroethane (staggered conformation)
 - 1,2-Dichloroethane (staggered anti-conformation)!



- 15) Determine the point groups for

- a) Ethylene
- b) Chloroethylene
- c) The possible isomers of dichloroethylene!

16) Determine the point groups for

- a) Acetylene
- b) $\text{H-C}\equiv\text{C-F}$
- c) $\text{H-C}\equiv\text{C-CH}_3$
- d) $\text{H-C}\equiv\text{C-CH}_2\text{Cl}$
- e) $\text{H-C}\equiv\text{C-Ph}$ (Ph = phenyl)!

17) Determine the point groups for

- a) Naphthalene
- b) 1,8-Dichloronaphthalene
- c) 1,5-Dichloronaphthalene
- d) 1,2-Dichloronaphthalene!

18) The water molecule has C_{2v} symmetry! Which characters does the p_x orbital have and which is the name of the representation?

Chapter 4: MO Theory

19) The azide ion N_3^- is isoelectronic with NO_2^+ and N_2O . From hybrid orbitals construct a bonding model and give your expectation for the bonding angles.

20) What is a σ -, a π -, a δ -, and a 2-electron-3-center-bond?

21) Do you expect a Mg_2 molecule to exist?

22) What behavior with respect to the bond lengths do you anticipate for the cations O_2^+ and B_2^+ in comparison to the uncharged molecules?

23) Construct the MO diagram for the following molecules, which can occur in the interstellar medium (ISM)!

- H_2
- H_2^+
- H_3
- H_3^+

Why is H_2 more stable than H_3 ?
What is meant by HI in astrophysics?

24) Sketch a MO diagram for HF and HCl (please account for differences in electronegativity and energy levels)!

25) The acetylide ion C_2^{2-} is present for an example in CaC_2 , which used to have great importance for the generation of acetylene. Nowadays, CaC_2 is predominantly an intermediate in the synthesis of Calcium cyanamide $CaCN_2$, an important fertilizer.

- Reproduce the electronic structure of the acetylide ion!
- Which hybrid orbitals may be utilized in the description according to the VB method?
- In terms of the MO method create its correlation diagram!
- What is the bond order for both methods?
- Is the ion diamagnetic or paramagnetic?
- What are the HOMO and LUMO composed of?
- Discuss the capability of the C_2^{2-} ions to coordinate to transition metals (compare σ -donor and π -acceptor bonds of CO!)

26) On the basis of molecular orbitals, predict the shortest bond, and provide a brief explanation!

- a) Li_2^+ , Li_2
- b) F_2^+ , F_2
- c) He_2^+ , HHe^+ , H_2^+

27) On the basis of molecular orbitals, predict the weakest bond, and provide a brief explanation.

- a. P_2 , S_2 , Cl_2
- b. S_2^+ , S_2 , S_2^-
- c. NO^- , NO , NO^+

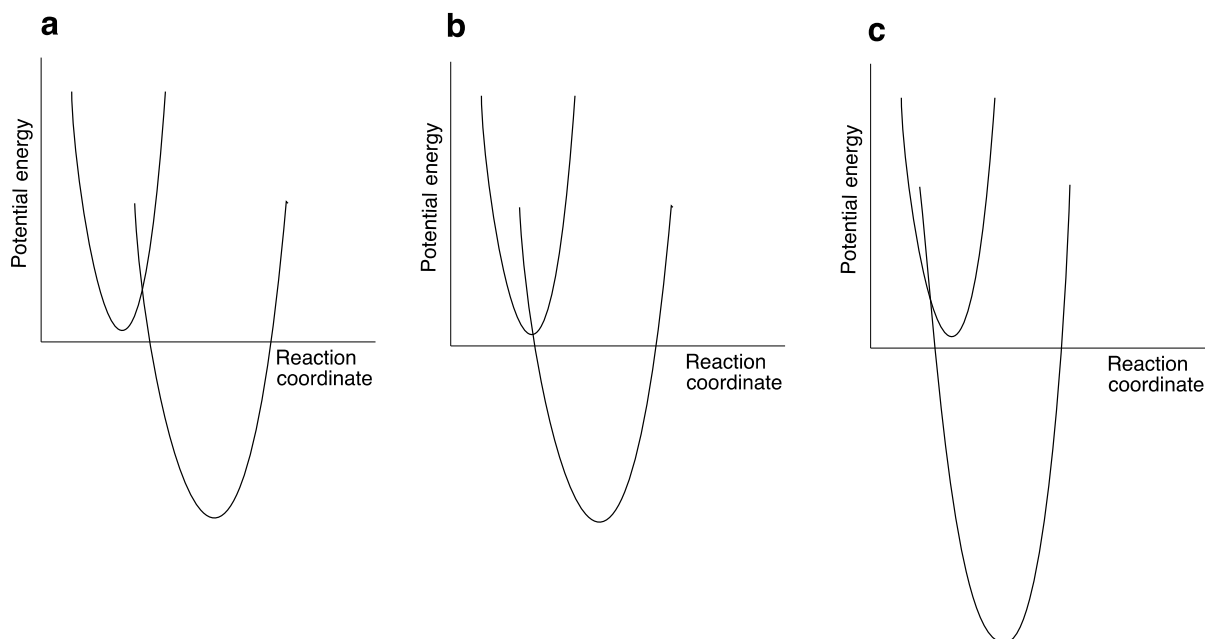
28) Although the peroxide ion, O_2^{2-} , and the acetylide ion, C_2^{2-} , have long been known, the diazenide ion N_2^{2-} has only been prepared much more recently. By comparison with the other diatomic species, predict the bond order, bond distance, and number of unpaired electrons for N_2^{2-} !

Chapter 5: Marcus Theory

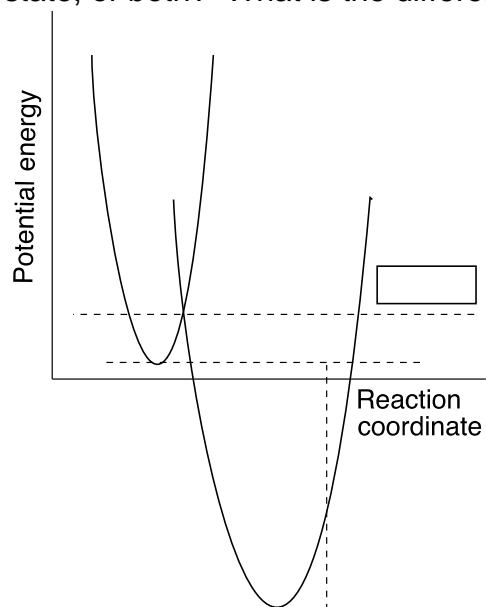
29) What does Marcus theory describe that transition state theory doesn't?

- a) Quantum tunneling
- b) Electron transfer reactions
- c) Transition state energies
- d) All of the above

30) Which pair of potential curves would you expect to result in the reaction with the fastest rate?



31) Does the box on the diagram below represent the intrinsic barrier, the transition state, or both? What is the difference between the two?



32) Marcus cross relation relates what values?

- Resonance
- Induction
- Reaction rates
- All of the above

33) Name an example for an inner-sphere and an outer-sphere reaction!

34) Explain the role of the Jahn-Teller effect for the reaction rate of outer-sphere redox reactions!

35) What is meant by the Robin-Day-Classification of intervalent complexes?

Chapter 6: Intervalence Complexes

- 36) Define the term intervalence electron transfer!
- 37) Sketch the Creutz-Taube complex ion and classify it according to the Robin and Day classification!

Chapter 7: Spectroscopy of Inorganic Compounds

- 38) Sketch the energy level diagrams for the following atoms in the gas phase! Consider all contributions to the splitting of energy levels!
- H
 - O
 - Ti³⁺
 - Ce³⁺
- 39) Explain the role of symmetry for the selection rules for electric dipole transitions!
- 40) What kind of optical transitions do you expect in transition metal complexes?
- 41) How many d-d bands do you expect for octahedrally coordinated transition metal ions with the following dⁿ (high-spin) configurations?
- d¹
 - d²
 - d³
 - d⁴
 - d⁶
 - d⁷
 - d⁸
 - d⁹
 - d⁰ or d¹⁰
- 42) How many 3d microstates and energy levels do you expect for ions with the electron configuration [Ar]3dⁿ?
- 43) How many 4f microstates and energy levels do you expect for ions with the electron configuration [Xe]4fⁿ?
- 44) Explain the origin of optical transitions of Cu²⁺ in the blue pigments Han or Egyptian blue as well as in blue copper proteins!
- 45) Transition metal ions with d² or d⁸ configuration show 3 absorption bands due to d-d transitions. Please explain the origin of these transitions by the respective Tanabe-Sugano diagram for octahedral coordination.

46) Mn^{4+} has a low to moderate absorption cross-section, it is a strong oxidizer, and shows strong photoluminescence in crystalline environments.

a) Explain the origin of the weak absorption of Mn^{4+} compounds and show a way to enhance the absorption strength!

b) Explain the shift of oxidation power by changing the alkalinity or acidity of the chemical surrounding

c) Discuss the shift of the ${}^2\text{E}$ emission lines of Mn^{4+} as function of the covalent character of the Mn^{4+} to ligand bonds!

Chapter 8: Catalysis in Inorganic Chemistry

47) Explain the roles of transition metals in catalysis! Please also name an example for a catalytical process relying either on (coordinated) metal ions, metalorganic compounds, metal salts, or metal particles!

48) Name some catalytical processes in biochemistry, which require the presence of metal ions!

49) Name the requirements on inorganic photocatalysts for photocatalytic water splitting!

50) Explain ways to avoid the generation of detonating gas during water splitting!

51) A good photocatalyst must offer a high mobility of charge carrier in the conduction band! Explain this finding and discuss in view of the suitability of luminescent materials for photocatalysis!

52) Sketch the working principle of the Grätzel cell and compare the different steps to photosynthesis in autotrophic organisms!

53) Explain ways for the sensitization of inorganic photocatalysts to use visible light!

54) Discuss potential roles of the following metal ions for catalytical reactions!

a) Ti^{4+}

b) V^{5+}

c) Fe^{2+}

d) Mn^{4+}

e) Co^{2+}

f) Cu^{2+}

g) Zn^{2+}

h) Ce^{3+}

i) Pr^{3+}

j) Lu^{3+}