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 is 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!

BCl_3
$SiCl_4$
PF_5
SO_2
ClF_3
$Ni(CO)_4$
$[Ni(CN)_4]^{2-}$
$SbCl_5$
SbF_6^-
XeF_2
XeF_4
XeF_6
$XeOF_2$
$XeOF_4$
XeO_2F_2

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? Also sketch the MO diagrams for the molecular species!

8) To which point group belongs the Sombrero galaxy (M104, NGC 4594)? Many celestial objects have approximately K_h symmetry. Discuss a reason for this finding and 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!

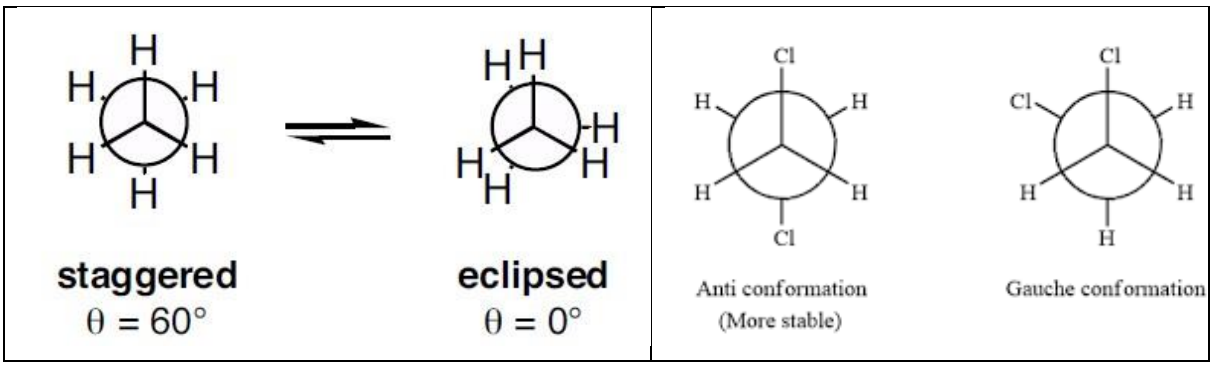
11) Name an atomic and a molecular transition, which are important for microwave/ radioastronomy!

12) Explain the roles of interstellar dust for astrochemistry! Please also explain the interstellar dust-grain model!

Chapter 3: Point Groups and Group Theory

13) Please write down all symmetry elements of the following molecules!
a) NH_3
b) Acetone
c) Cis-Dimethyl cyclopentane
d) Ethandiol
e) Propadiene
f) Methane

14) Determine the point groups for
a) Ethane (staggered conformation)
b) Ethane (eclipsed conformation)
c) Chloroethane (staggered conformation)
d) 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) H-C≡C-F
c) H-C≡C-CH_3
d) H-C≡C-CH_2Cl
e) H-C≡C-Ph (Ph = phenyl)!

17) Determine the point groups for
a) Naphtalene
b) 1,8-Dichloronaphtalene
c) 1,5-Dichloronaphtalene
d) 1,2-Dichloronaphtalene!

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^+

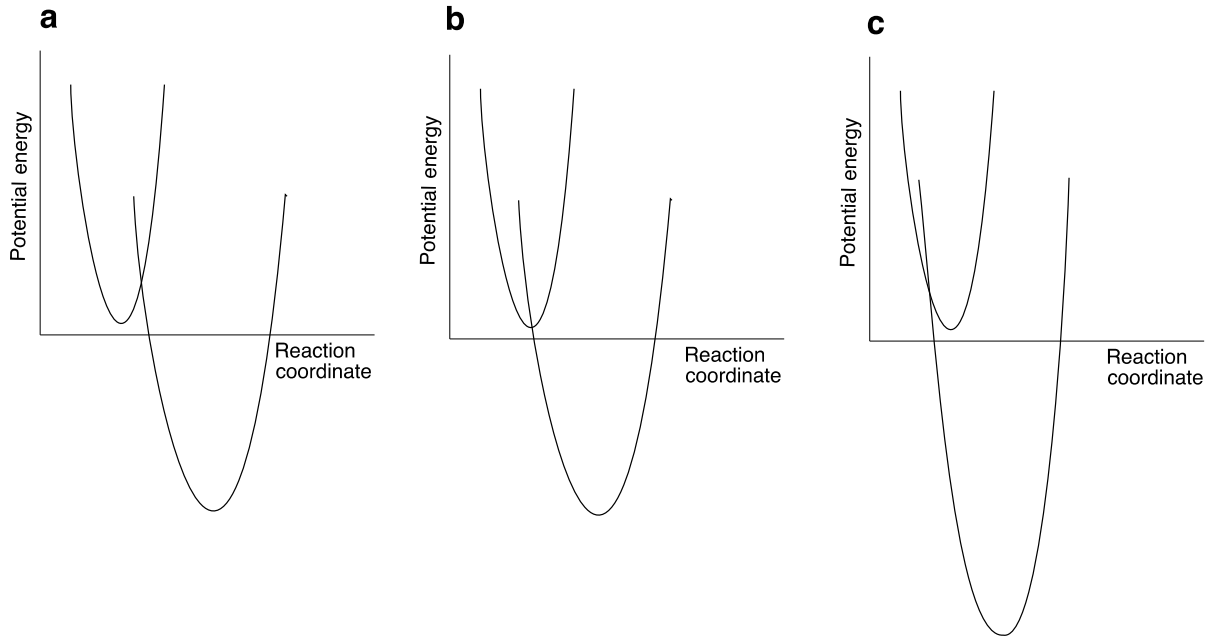
27) On the basis of molecular orbitals, predict the weakest bond, and provide a brief explanation.
a. P_2, S_2, Cl_2
b. S_2^+, S_2, S_2^-
c. NO^-, NO, NO^+

28) Although the peroxide ion, O_2^{2-}, and the acetylide ion, C_22-, 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-}!

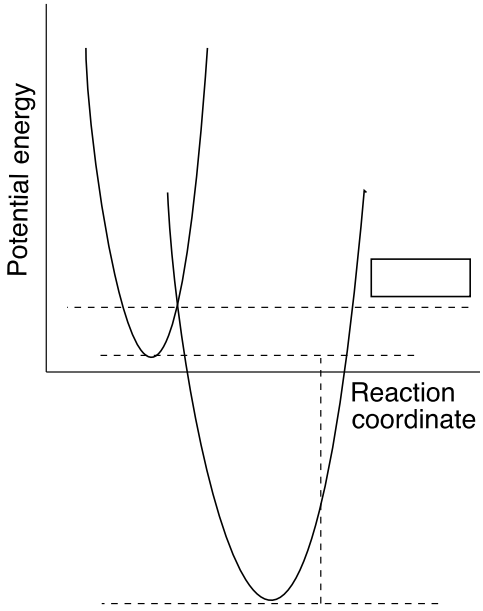
Chapter 5: Markus Theory

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?
a. Resonance
b. Induction
c. Reaction rates
d. 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!
a) H
b) O
c) Ti^{3+}
d) Ce^{3+}

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 d^n (high-spin) configurations?
a) d^1
b) d^2
c) d^3
d) d^4
e) d^6
f) d^7
g) d^8
h) d^9
i) d^0 or d^{10}

42) How many 3d microstates and energy levels do you expect for ions with the electron configuration $[Ar]3d^n$?

43) How many 4f microstates and energy levels do you expect for ions with the electron configuration $[Xe]4f^n$?

44) Explain the origin of optical transitions of Cu^{2+} in the blue pigments Han or Egyptian blue as well as in blue copper proteins!

45) Transition metal ions with d^2 or d^8 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 ^2E 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+}
k) Ni^{2+}

Chapter 9: Lanthanides and Actinides

55) Ce^{3+} activated inorganic materials are widely applied as color converters in LEDs and as scintillators in CT, SPECT, and PET scanners. Sketch the energy level diagram of Ce^{3+} in YBO_3 (D_{3d} symmetry) and in $Y_2(CN_2)_3$ (C_2 symmetry) and discuss the observed PL spectra!

56) Eu^{3+} activated luminescent materials are widely applied as red emitter in light sources and RGB displays, while the emission spectrum is a sensitive function of the crystallographic sites where Eu^{3+} is located.

a) Please determine the space group and the crystallographic Eu sites of the following Eu^{3+} activated luminescent materials by the aid of literature!
Ba_2MgWO_6:Eu
$InBO_3$:Eu
YVO_4:Eu
$Y_3Al_5O_{12}$:Eu
LaOCl:Eu
YBO_3:Eu
$LaPO_4$:Eu
Y_2O_3:Eu

b) Predict the number of observed emission lines due to the 4f4f-transitions according to $^5D_0 - {}^7F_J$ on the basis of the local symmetry of Eu^{3+} sites of the above listed materials! Use the following table and explain why mostly much more lines are observed!

Point symmetry of Eu^{3+} site	$^5D_0$ - $^7F_0$ (ed)	$^5D_0$ - $^7F_1$ (md)	$^5D_0$ - $^7F_2$ (ed)	$^5D_0$ - $^7F_3$ (md)	$^5D_0$ - $^7F_4$ (ed)
O_h	None	T_{1g}	None	T_{1g}	None
D_{3d}	None	A_1, E	None	A_1, E	None
D_{3h}	None	A'_2, E''	E'	A'_2, E''	A''_2, 2E
D_{2d}	None	A_2, E	B_2, E	A_2, 2E	B_2, 2E
D_3	None	A_2, E	2E	$2A_2$, 2E	A_2, 3E
C_{4v}	A_1	A_2, E	A_1, E, 2B	A_2, 2E, B', B''	$2A_1$, A_2, 2E, B', B''
C_{3v}	A_1	A_2, 2E	A_1, 2E	$2A_2$, 2E	$2A_1$, 3E
C_3	A	A, E	A, 2E	3A, 2E	3A, 3E
C_{2v}	A_1	A_2, B_1, B_2	$2A_1$, B_1, B_2	$2A_2$, $2B_1$, $2B_2$	$3A_1$, $2B_1$, $2B_2$
C_2	A	3A	5A	7A	9A

C_1	A	3A	5A	7A	9A

ed = electrical dipole transitions
md = magnetic dipole transitions

57) Assign Mullikan symbols to the seven types of f-orbitals

58) Explain the terms “Lanthanide contraction” and “Oddo-Harkins rule”!

59) Which trivalent lanthanide ion is useful as a green color filter and why?

60) The most stable oxidation state of all Ln elements is +III. However, the reduction potential becomes less reductive from La to Lu. Explain this finding!

61) Actinides also appear in much higher oxidation states as observed for lanthanides. Explain this observation!

62) The uranyl cation $[UO_2]^{2+}$ is an efficient sensitizer for Eu^{3+} and Mn^{4+} ions. Sketch a simplified energy level diagram to illustrate the energy flow in the following compounds!
a) $K_4(UO_2)Eu_2(Ge_2O_7)_2$
b) $K_3(UO_2)F_5:Mn^{4+}$

Chapter 10: Lanthanides and Actinides

63) Radiation therapy is applied for cancer therapy in more than 50% of the cases.
a) Name three ways to reduce the side effects of radiation therapy!
b) Sketch the energy flow pathway in the UV-C scintillator $LuPO_4:Pr^{3+},Nd^{3+}$
c) Propose further co.-dopants to obtain a UV-C scintillator that can be used for imaging too.

64) Diagnostic markers are widely applied to localize infected tissue. Name two contrast agents each for
a) MRT imaging
b) Optical imaging

65) Niels Bohr calculated the speed of the 1s electron in a H atom in the ground state to 1/137 of the speed of light in vacuum, which is known as fine structure constant α.
a) Derive the fine structure constant from the equilibrium between $F_{el.}$ and $F_{centrifugal}$!
b) Calculate the relativistic mass of the H-atom w.r.t. the rest mass of the H-atom!
c) Calculate the radial velocity and mass of a 1s electron in the Uranium atom (Z = 92) by using the following equations!

$\langle v_r \rangle \approx \left(Z/137\right) \cdot c$	$\mathbf{m_{rel}} = \frac{\mathbf{m_0}}{\sqrt{(1 - (v/c)^2)}}$

66) Discuss the relativistic effect on the body color of the noble metals Cu, Ag, and Au!