Selfassessment MSc Chemistry, University of Bonn

With the following tasks/questions you can check if the knowledge you acquired during your Bachelor's studies meets the requirements for successful studying in our Master's programme.

Please note: The topics dealt with in the tasks/questions are not exhaustive by far. It only serves to give you an impression of what is required already in the modules of the first semester of our Master's programme.

If you find out that you are not acquainted with a larger part of the topics dealt with in the tasks/questions you will most probably not be able to be successful in our Master's programme.

General Chemistry

Stoichiometry

The qualitative analysis of an unknown compound has shown that it only contains iron and sulfur. 299.9 mg of the compound are dissolved in a mixture of hydrochloric acid and H_2O_2. From the resulting solution 1167 mg of a fine white precipitate is obtained with $BaCl_2$ solution.

Calculate the formula (Fe_mS_n) of the iron sulphide.

($M(Fe) = 55.845$ g mol^{-1}, $M(S) = 32.06$ g mol^{-1}, $M(H) = 1.008$ g mol^{-1}, $M(O) = 15.999$ g mol^{-1}, $M(Ba) = 137.327$ g mol^{-1}, $M(Cl) = 35.45$ g mol^{-1})

Ideal Gas Law

Calculate the density of chlorine gas at 25 °C and ambient pressure (1013 hPa) using the ideal gas law. Give the value in g/cm^3. ($M(Cl) = 35.45$ g/mol, $R = 8.31446$ J/(mol K))

Structure of the Electron Shell

Which of the following statements on the structure of the electron shell are correct?

a) The Schrödinger equation can be solved exactly only for the hydrogen atom (and other atomic systems with only one electron in the shell).

b) For multiple electron systems, solutions of the Schrödinger equations can be obtained by neglecting the electron-electron interaction and replacing it by shielding (reduction of the effective charge of the nucleus by the "cloud" of the other electrons).

c) The multiple electron wave functions of many electron atoms can be well approximated by the sum of one-electron wave functions.

d) The one-electron wave functions used to build up multiple electron wave functions are similar to the exact wave functions of the hydrogen atom.

e) The electrons in the shell of an atom are characterised by four quantum numbers.

f) The maximum of the magnetic quantum number m_l in the N shell (principal quantum number $n = 4$) is $5 (n + 1)$.

g) The Aufbau principle states that, starting from the hydrogen atom, the ground states of the atoms can be obtained by inserting an additional electron into the energetically lowest, not fully occupied atomic orbital for every additional proton in the nucleus.

h) Hund's rule states that two electrons in an atom cannot match in all four quantum numbers.

i) For open shell systems, it is more appropriate to treat the electron shell in the form of terms rather than in configurations.

Ionisation Energy, Electron Affinity, Electronegativity

Which of the following statements are correct?

a) The electron affinity is the energy released when a neutral atom A in the gas phase accepts an electron to become the ion A^-.

b) The concept of electronegativity was first established by Robert Mulliken.

c) Linus Pauling's definition of the electronegativity is based on the observation that the mean of the bond dissociation energies of homoatomic bonds (A–A and B–B) is lower than that of the respective heteroatomic bond (A–B).

d) The first ionisation energy increases monotonously within a period.

e) The electronegativity decreases monotonously within a main group.

f) The first ionisation energy of Xe is lower than the IE of F, Cl, O and N, respectively.

g) The element with the highest electron affinity is fluorine.

Ionic compounds, lattice energy, Madelung constants

Which of the following statements are correct?

a) The Madelung constant of an AB compound is the factor by which the ionic lattice is electrostatically better than an ionic AB molecule with the same A–B distance as in the lattice.

b) The coordination polyhedra in ionic compounds are typically highly symmetric.

c) The lattice energy of an ionic AB compound is defined as the energy released in the following reaction: $A^+(g) + B^-(g) \rightarrow AB(s)$

d) In the series of the typical AB structure types sphalerite, rock salt, and cesium chloride, the Madelung constant decreases by about 5 % from sphalerite to rock salt and from rock salt to cesium chloride, respectively.

e) The main binding force in ionic compounds consists of the energy gain when pairing the spins of two formerly separate electrons in one orbital.

Lewis formula, Mesomerism

Draw three different Lewis formulas of the thiocyanate ion (also known as rhodanide) and discuss their importance for the real structure.

VSEPR Theory

Which structure do the following molecules/molecular ions have?

ICl_4^-, SF_4, XeF_4, $SiCl_4$, $SbCl_4^-$, $GaCl_4^-$

ClF_3, BF_3, NF_3, $TeCl_3^+$, ClO_3^-, CO_3^{2-}

MO diagrams of diatomic molecules X_2

The MO diagrams of the diatomic molecules of the elements of the second row are similar to one of the two diagrams shown.
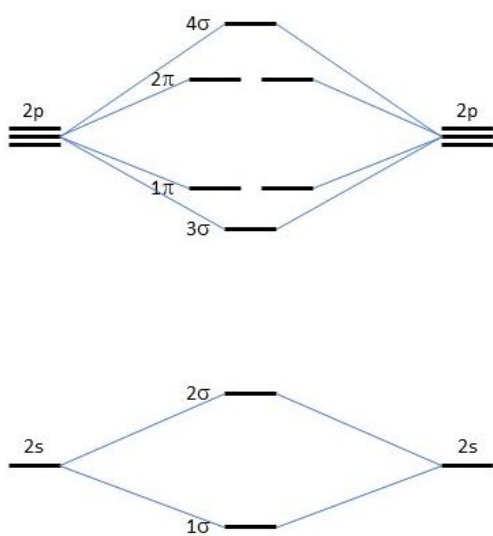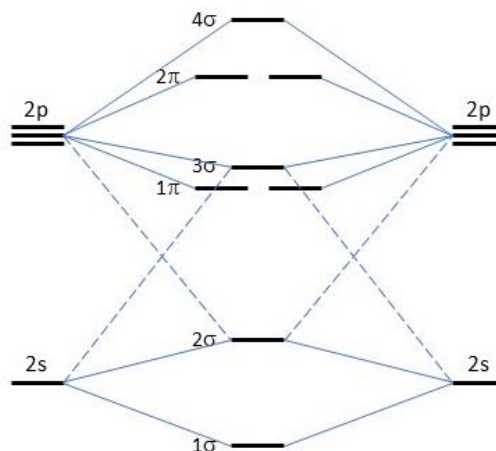

Diagram A   Diagram B

Which of the following statements are correct?

a) The 3σ orbitals of both diagrams have binding character.

b) Diagram A is valid for the elements N, O and F, respectively.

c) Diagram B is valid for the lighter elements of the second row because of the smaller energy gap between 2s and 2p atomic orbitals which leads to extensive mixing between the σ_s^* (2σ) and the σ_p (3σ) orbitals of diagram A.

d) Filling in the electrons for O_2 shows that the unpaired electrons of O_2 possess antibinding character.

e) The bond length in O_2^+ should be shorter than in O_2.

f) The B_2 molecule is diamagnetic.

g) The two lowest excited states of O_2 are both diamagnetic.

h) The π bonds in N_2 are stronger than the σ bond.

Hess's law

The disproportionation of carbon monoxide is the famous Boudouard reaction:

1. Enter the correct stoichiometric coefficents:

   __ CO = __ C + __ CO_2

2. The standard enthalpies of formation of carbon monoxide and carbon dioxide are $\Delta H_f(CO)$ = -111 kJ/mol and $\Delta H_f(CO_2)$ = -394 kJ/mol, respectively. Calculate the standard reaction enthalpy of the Boudouard reaction.

3. Which of the following statements are correct?

   a) When increasing the pressure, the Boudouard equilibrium shifts to the CO_2 side.

   b) When increasing the temperature, the Boudouard equilibrium shifts to the CO_2 side.

   c) At room temperature, the reaction rate is neglectable so that CO becomes metastable.

   d) At room temperature, the equilibrium amount of CO is neglectable.

Acids and bases, buffers

200 mL of a solution of disodium oxalate (c = 0.50 mol L^{-1}) are mixed with 30 mL of hydrochloric acid (2.0 mol L^{-1}). Calculate the pH of the resulting solution.

(pK_{a1} ($H_2C_2O_4$) = 1.23, pK_{a2} ($H_2C_2O_4$) = 4.19)

Acid base titration

The diagram shows the pH vs $V(NaOH)$ diagram of the titration of a solution of a weak acid. The concentration of the used NaOH solution is $c(NaOH) = 0.100$ mol L^{-1}.

Acid-Base-Titration
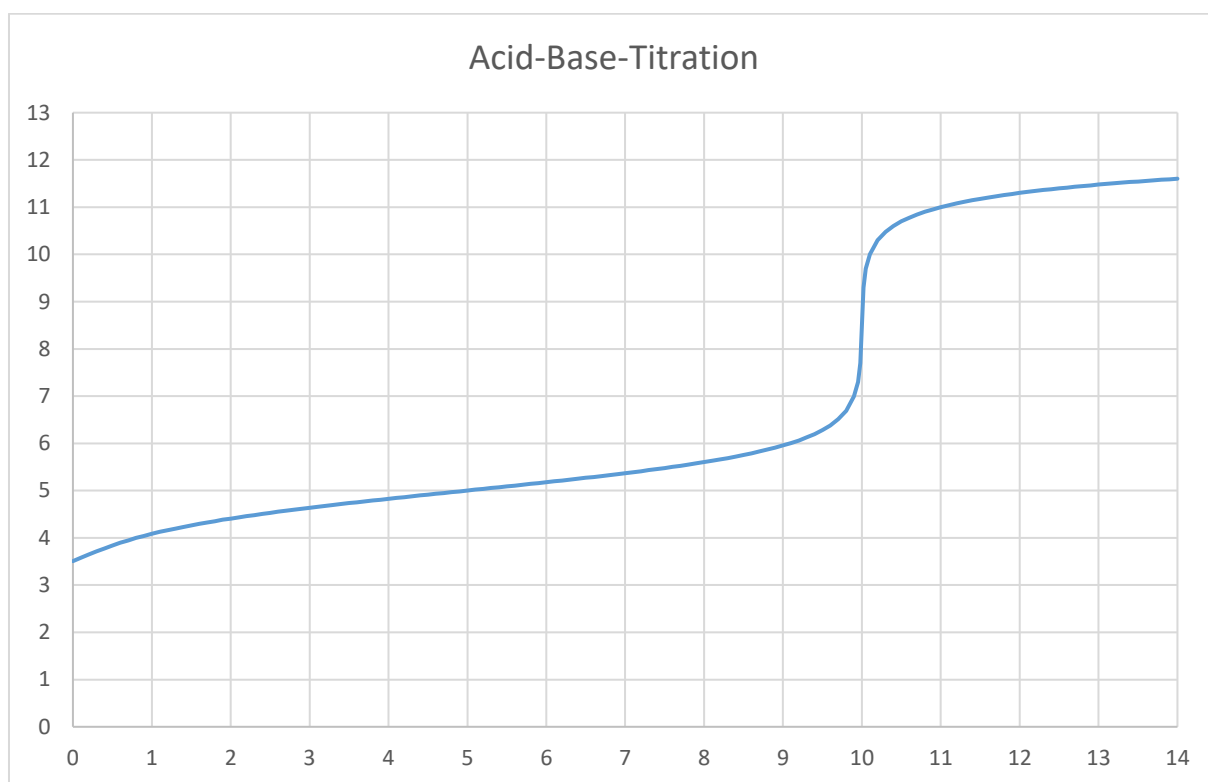
Which amount of the weak acid did the solution contain (in mmol)?

What is the pK_a value of the weak acid?

Ligand exchange reactions

Ligand exchange reactions are an important reaction type (in aqueous solution).

Which of the following statements are correct?

a) In ligand exchange reactions of the type $[M(H_2O)_6]^{n+} + 6\,L = [ML_6]^{n+} + 6\,H_2O$, the ligand exchange takes place step by step. Therefore, also mixed complexes $[M(H_2O)_{6-m}L_m]^{n+}$ are present in the equilibrium even if only in low concentrations.

b) The higher stability of complexes of multidentate ligands compared to similar monodentate ligands is mainly an enthalpic effect due to the particular stability of the usually formed five- or six-membered rings.

c) The formation of blue $[Cu(NH_3)_4]^{2+}$ on adding ammonia to an aqueous solution of $CuSO_4$ is an example for a reaction in which a rather soft cation (Cu^{2+}) forms a stable complex with a soft ligand.

d) The indicators in complexometric titrations (e. g. with EDTA) are multidentate ligands which form stable complexes with the analysed cation. At the endpoint of the

titration, they are displaced by the titration ligand. The endpoint detection is possible since the indicator shows different colours in free form and when bound in the complex.

e) The formation of stable complexes to prevent undesired side reactions is called "hiding" (e.g. hiding Fe^{3+} by addition of HPO_4^{2-} yielding stable $[Fe(HPO_4)_3]^{3-}$).

Solubility product

The solubility product of $PbBr_2$ is $4 \cdot 10^{-6}$ mol^3 L^{-3}. Calculate the concentrations of Pb^{2+} ions and Br^- ions in a saturated solution of $PbBr_2$ in pure water.

Balancing redox reactions

Balance the following redox reactions:

__ BiO_3^- + __ MnO_2 + __ H^+ -> __ Bi^{3+} + __ MnO_4^- + __ H_2O

__ $Fe(OH)_3$ + __ Cl_2 + __ OH^- -> __ FeO_4^{2-} + __ Cl^- + __ H_2O
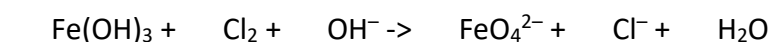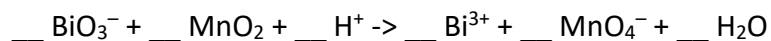
All these tasks of the General Chemistry section address knowledge or skills that are absolutely essential. If you have detected larger gaps in this part you can omit the rest of the selfassessment. Your chemical education will not be sufficient to study successfully in our Master's programme.

Inorganic Chemistry

Technical Processes

The following list contains some important technical processes. Which substances are produced in these processes?

- Haber-Bosch process
- (Double) Contact process
- Frasch process
- Ostwald process
- (Olin) Raschig process
- Anthraquinone process
- Downs process
- Chloralkali process

Chemistry of boron

Which of the following statements on the chemistry of boron are correct?

a) B_{12}-Cluster are typical for the structures of elemental boron.
b) The molecular structures of boron hydrides B_mH_n can be rationalized with the Dewar rules.
c) A characteristic feature of boron hydrides is the occurrence of two-electron-multiple-center bonds.
d) In aqueous solution, boric acid $B(OH)_3$ is a weak acid similar to acetic acid. Reaction with hydroxide yields the $BO(OH)_2^-$ ion.
e) The electron deficiency of the boron atom in BF_3 is partially compensated by π-donation from nonbonding electron pairs of the fluorine ligands.
f) BCl_3 consists of dimeric molecules B_2Cl_6 (two edge-sharing BCl_4 tetrahedra).
g) BH_3 consists of dimeric molecules B_2H_6 (two edge-sharing BH_4 tetrahedra).
h) Many boron compounds (e.g. BF_3) undergo addition reactions with Lewis bases to obtain an electron octet at the boron atom.

Low spin/High spin complexes

Which of the following complexes are diamagnetic, which paramagnetic?

- $[Fe(H_2O)_6]^{2+}$
- $[Co(NH_3)_6]^{3+}$
- $[Fe(CN)_6]^{4-}$
- $[PdCl_4]^{2-}$

- $[CoCl_4]^{2-}$
- $[RhCl_6]^{3-}$
- $[Ni(CN)_4]^{2-}$

Magnetic properties are an important part of transition metal chemistry. In mononuclear complex compounds the metal atoms are completely separated from each other. Therefore, these compounds usually exhibit the most basic magnetic properties, diamagnetism or paramagnetism. In most cases, it can be predicted from the sum formula of the complex under consideration. This requires an understanding of some essential concepts in transition metal chemistry, e. g. structures of complexes (mainly octahedral, tetrahedral and square-planar), splitting of d-orbitals in various environments (ligand field theory), the spectrochemical series, the differences between $3d$-, $4d$- and $5d$-transition metals.

σ-/π-Donor-/Acceptor Ligands

Which of the following statements on complexes of d transition metals are correct?

a) π donor ligands like chloride exhibit low ligand fields in octahedral complexes.
b) The strength of the ligand fields in tetrahedral complexes are about three quarter of those in octahedral complexes (same ligands, similar metal ion).
c) Low spin complexes of $3d$ transition metals are only formed with π acceptor ligands.
d) The ligand field in similar complexes increases when going from $3d$ to $4d$ to $5d$ transition metals.
e) High spin complexes of $5d$ transition metals are rare.
f) π acceptor ligands are especially useful for the stabilization of high oxidation states of the d transition metals.

Metal Carbonyls

Which of the following statements on metal carbonyls are correct?

a) A versatile analytical method to probe the strength of the C–O bond of the bonded carbon monoxide ligand is Raman spectroscopy.
b) Metal carbonyls $M_m(CO)_n$ of group 7 and 9 metals are always multinuclear.
c) The only paramagnetic metal carbonyl $M(CO)_n$ is $V(CO)_6$.
d) The C–O stretching vibration in metal carbonyls lies at lower wave numbers than in free CO.
e) The C–O bond is strengthened by π backdonation in metal carbonyls.

f) The direct reaction of the (finely divided) metal with CO gas is the standard procedure to obtain metal carbonyls.

g) Preparation of metal carbonyls by reduction of a metal salt or oxide in the presence of CO often requires high pressure (up to 300 atm).

h) The carbon atom of the coordinated CO ligand is susceptible to nucleophilic attack (e. g. Hieber base reaction).

i) Bridging CO ligands in multinuclear metal carbonyls can be identified by the lower frequency of their C–O stretching vibration as measured by IR spectroscopy.

The substance class of metal carbonyls is extensively dealt with in the Advanced Inorganic Chemistry course of our Bachelor's program. Comprehension of the bonding situation in metal carbonyls is the basis for discussing other metal organic complexes, e. g. those important in catalysis. Dealing with metal carbonyls deepens the knowledge about MO theory of complex compounds, about how analytical methods help to gain insight into the electronic and geometric structure of molecules, and about synthetic methods in modern inorganic chemistry.

Metallocenes and Bis(arene) complexes

Which of the following statements are correct?

a) The d-orbitals of the metal atoms in $Fe(C_5H_5)_2$ or $Cr(C_6H_6)_2$ are split in two sets (twofold degenerate at lower energy, threefold degenerate at higher energy).

b) The standard method for the synthesis of metallocenes $M(C_5H_5)_2$ is the direct reaction between the metal M and cyclopentadiene.

c) The C_5H_5 moieties of ferrocene are apt to undergo electrophilic substitution reactions.

d) In metallocenes $M(C_5H_5)_2$ the energy difference of the staggered and the eclipsed conformation of the rings is very small (few kJ/mol)

e) Cobaltocene is a strongly reducing compound.

f) The $M–C$ bond length in metallocenes $M(C_5H_5)_2$ shortens along the series M = V, Cr, Mn, Fe, Co, Ni.

g) Bis(benzene) vanadium is a strongly reducing compound.

Metallocenes and bis(arene) complexes are important model compounds in transition metal coordination chemistry. They are extensively dealt with in the Advanced Inorganic Chemistry course of our Bachelor's program. Various concepts of organometallic and coordination chemistry can be studied using these examples, e. g. MO theory of d transition metal

complexes, typical synthetic routes to organometallic compounds, redox behavior of coordination compounds (18 electron rule).

All these concepts are used in the mandatory Inorganic Chemistry course of our Master's program.

Close packed spheres, octahedral and tetrahedral holes

The concept of close packed spheres is of great importance for the description of structures of inorganic solids. Which of the following statements are correct?

a) Sodium chloride can be described as a cubic close packing (ccp) of chloride ions, all octahedral holes filled with sodium ions.

b) Spinel ($MgAl_2O_4$) can be described as cubic close packed oxygen anions with one half of the octahedral holes filled by Mg^{2+} and one quarter of the tetrahedral holes filled by Al^{3+}.

c) The hcp (hexagonal close packing) analogue to the NaCl structure type is the NiAs structure type.

d) Both the sphalerite and the wurtzite structure consist of close packed anions with one half of the tetrahedral holes filled with cations.

e) Perowskite ($CaTiO_3$) can be seen as a cubic close packing of oxygen anions, one third of the octahedral holes filled with Ca^{2+}, another third with Ti^{4+}.

f) Fluorite (CaF_2) consists of a hcp of Ca^{2+} ions with all tetrahedral holes filled with F^-.

The concept of close packing of atoms and (partially) filling the octahedral and/or tetrahedral holes with atoms of another element is a key concept for describing and understanding the 3D-structures of inorganic solid state compounds, especially of alloys and predominantly ionic compounds. This concept is introduced in the Advanced Inorganic Chemistry course of our Bachelor's program and used extensively in the mandatory inorganic chemistry modules of our Master's program.
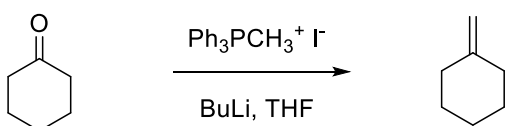
Organic Chemistry

Name reactions

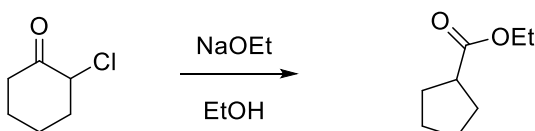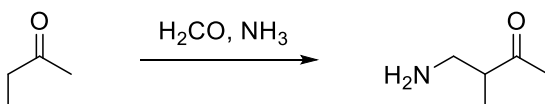How are the following reactions named?

a)
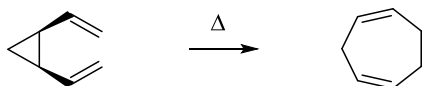
b)

c)

d)

Many reactions in Organic Chemistry are named by the chemist(s) who invented or established the method. Many of these reactions are dealt with in the Organic Chemistry modules of our Bachelor's program. Often also the mechanisms of the reactions are discussed, especially if this is important for the regio- or stereoselectivity of a reaction. Please note: The four reactions above serve only as examples representing a large number of name reactions you should be acquainted with when entering the mandatory Organic Chemistry module of our Master's program.

Diels Alder reaction

Please mark the correct answers for the reaction shown below.
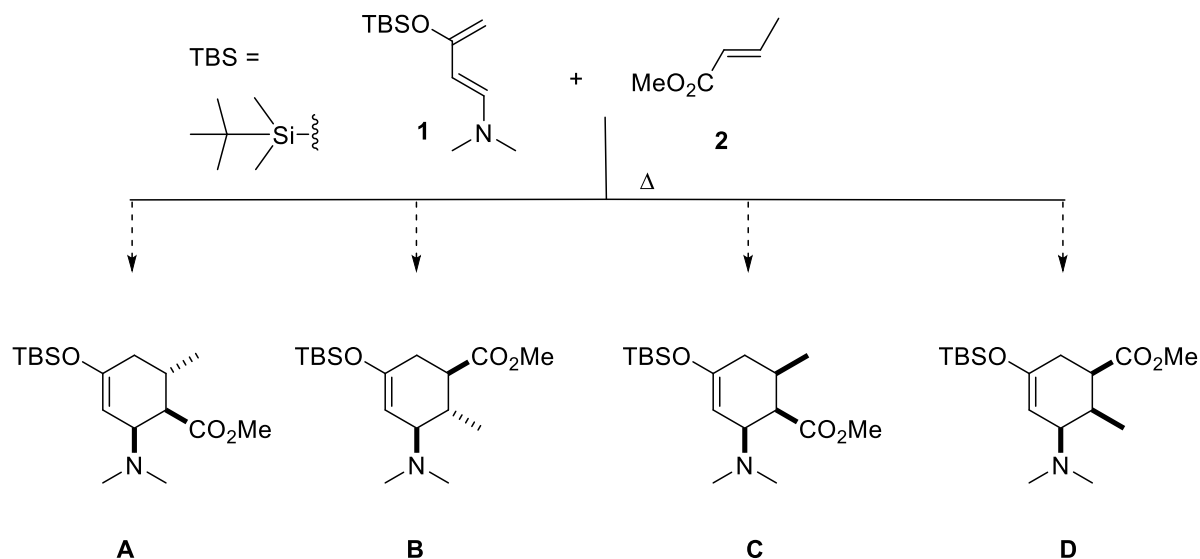
Which main product do you expect ?   A ☐   B ☐   C ☐   D ☐

Please consider the following statements:

(1) A pericyclic reaction is shown.   True ☐   False ☐

(2) The diene reacts via an s-trans conformation.   True ☐   False ☐

(3) The reaction is enantioselective.   True ☐   False ☐

(4) The reaction may be accelerated by Lewis acids.   True ☐   False ☐

(5) The reation proceeds suprafacially with respect to both reaction partners. True ☐   False ☐

(6) Application of the frontier orbital theory relies

on key interactions of the LUMO of **1** and the HOMO of **2**.   True ☐   False ☐

Pericyclic reactions like Diels-Alder reactions are extensively dealt with during the Advanced Organic Chemistry module of our Bachelor's programme. Important topics are the stereochemistry of these reactions, thermal vs photochemical reactions, and considerations of frontier orbitals.

Transition states and stereochemistry

Please mark the correct answers for the reaction shown below.
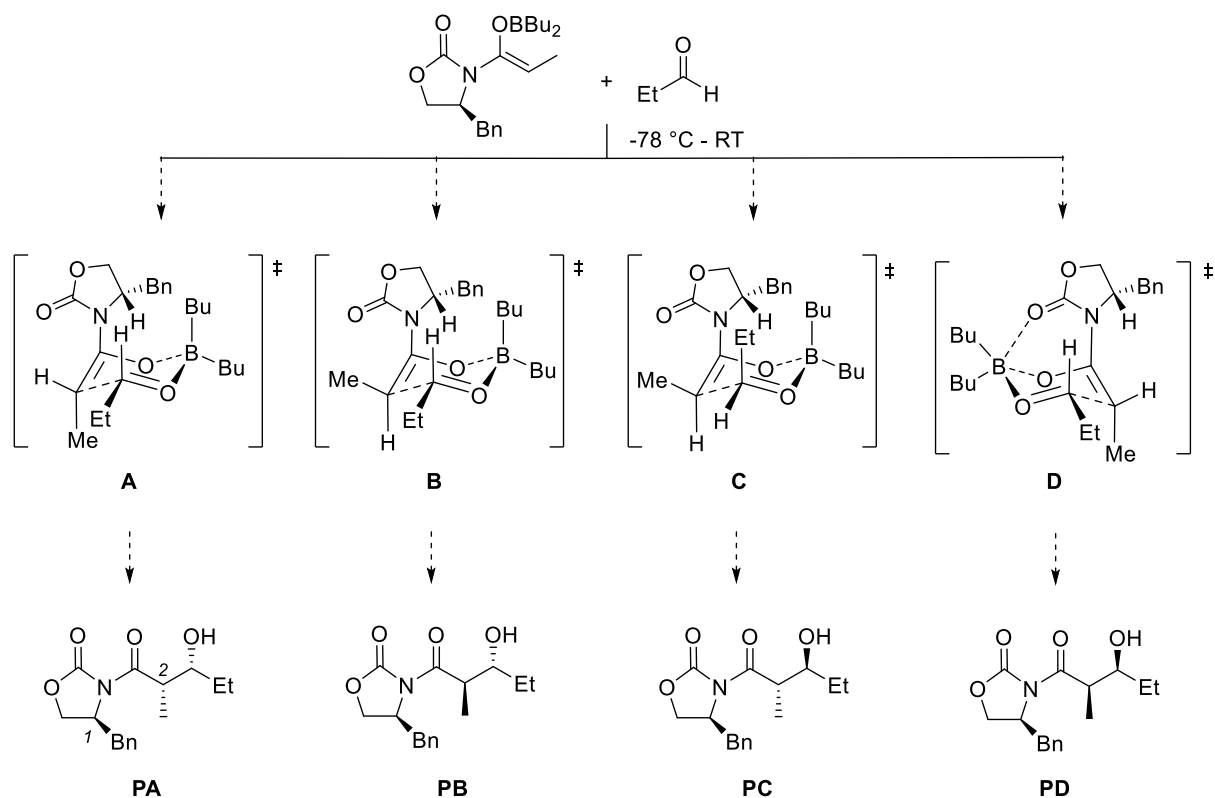
Which of the transition states **A-D** is most relevant?   **A** ☐   **B** ☐   **C** ☐   **D** ☐

Which of the shown transition states **A-D**, if it would be relevant, would lead to the given products **PA-PD**? Multiple answers may be correct.

A ☐   **B** ☐   **C** ☐   **D** ☐

The configurations at atoms 1 and 2 of compound **PA** may be designated as:

(R,R) ☐   (R,S) ☐   (S,R) ☐   (S,S) ☐

Another important subject of the Advanced Organic Chemistry module consists of reactions of metalorganic reagents which proceed via six-membered cyclic transition states. Especially the understanding of the stereochemical implications of six-membered cyclic transition states is needed in the Master's programme. Students in our Master course should also be very familiar with Cahn-Ingold-Prelog nomenclature of compounds containing stereogenic elements.
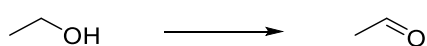
Biochemistry

Please select the correct cofactor(s) for the following enzymatic reactions. Multiple answers may be correct.
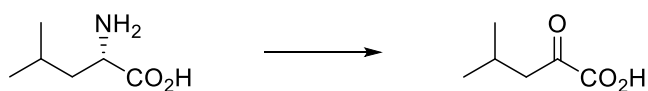
a)   biotin

b)   thiamine diphosphate (TPP)

c)   pyridoxal phosphate (PLP)

d)   adenosine triphosphate (ATP)

e)   NADPH
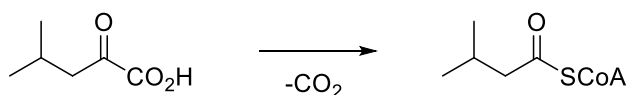
a)   thiamine diphosphate (TPP)

b)   lipoic acid

c)   biotin

d)   coenzyme A

e)   FAD

a)   pyridoxal phosphate (PLP)

b)   S-adenosylmethionine (SAM)

c) NAD^+

d)   coenzyme A

e)   tetrahydrofolate

Biochemical / enzymatic reactions, cofactors, and metabolic pathways are extensively discussed in our Bachelor's biochemistry program. Basic knowledge is necessary for our Organic Chemistry courses in the Master's program.

Physical Chemistry

Extensive and intensive Quantities

Which of the following physical quantities are extensive, which are intensive properties?

a) Pressure p
b) Volume V
c) Density ρ
d) Molar heat capacity C_p/C_V
e) Amount of substance n
f) Mass m
g) Temperature T
h) Joule-Thomson coefficient μ

Van der Waals equation

The van der Waals equation can be given in the following form:

$$\left(p + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

Which of the following statements are correct?

a) The van der Waals equation is an extension of the ideal gas law which accounts for attractive interactions between gas phase particles and for the finite size of them.
b) The behaviour of real gases is well described by the van der Waals equation for temperatures above the critical temperature.
c) For high temperatures van der Waals isotherms coincide with ideal gas isotherms.
d) The parameter b is connected with the volume of the particles.
e) The critical constants are functions of the van der Waals parameters a and b.
f) For T < Tc, the derivative of the van der Waals equation has two zeroes.

Clausius-Clapeyron relation

Which of the following statements on the Clausius Clapeyron relation are correct?

a) The Clausius-Clapeyron relation specifies the temperature dependence of the vapour pressure of a pure liquid or solid substance.
b) The Clausius-Clapeyron relation is exact for all pure substances between the melting point and the critical temperature.
c) For deriving the Clausius-Clapeyron relation from the Clapeyron equation, the gas has to be treated as an ideal gas.

d) For deriving the Clausius-Clapeyron relation from the Clapeyron equation, the molar volume of the condensed phase has to be neglected.

e) By aid of the Clausius-Clapeyron relation, the enthalpy of vaporization can be received from the boiling points of a substance at different pressures.

f) Since sublimation enthalpies are generally larger than vaporisation enthalpies, it can be deduced from the Clausius-Clapeyron relation that the slope of the sublimation pressure curve is larger than the slope of the vapor pressure curve near the intersection of both (the triple point).

Temperature-composition diagrams

The diagram shows the liquid/gas part of the phase diagram of a simple two component system at ambient pressure. The diagram shows the boiling temperature and the dew temperature as a function of the mole fraction of component B (all temperatures in K).
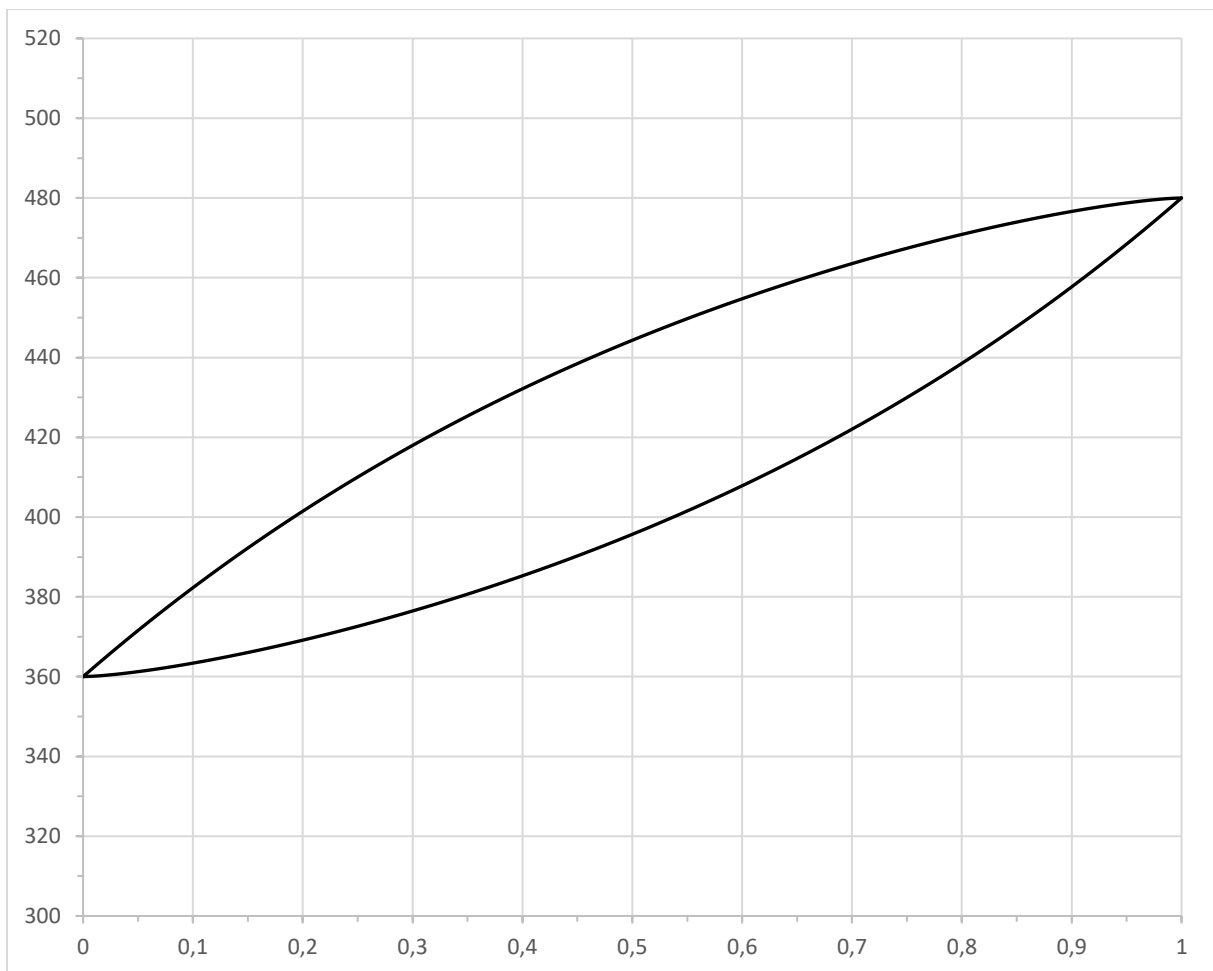
Boiling temperature and dew temperature of A/B-mixtures as a function of the mole fraction of B

Extract the boiling points of the following liquids from the diagram:

a) pure compound A
b) pure compound B
c) A:B = 1:1 mixture
d) A:B = 1:3 mixture

Give the approximate composition of the gas phase over a boiling 1:1 mixture.

Which of the following statements on temperature-composition diagrams of two compound mixtures are correct?

a) If there is a miscibility gap in the liquid phase, there will also be a miscibility gap in the gas phase.
b) In systems with a high boiling azeotrope, distillation will lead to a point where the remaining liquid does not change in composition.
c) The boiling point of a high boiling azeotrope is higher than the boiling points of both pure compounds.
d) In systems with a low boiling azeotrope the composition of the distillate is always nearer to the azeotrope composition than to the composition of the liquid mixture.
e) The boiling point of a mixture of two immiscible liquids is always lower than the boiling points of both pure liquids.

Laws of Thermodynamics

Which of the following statements on the laws of thermodynamics are correct?

a) Spontaneous change is always connected to an overall increase of entropy.
b) Adiabatic processes are always reversible because there is no change in entropy.
c) Reversible adiabatic expansion of an ideal gas leads to a decrease of the internal energy of the gas.
d) The standard molar entropy of all elements in their most stable modification is by definition $0 \text{ J K}^{-1} \text{ mol}^{-1}$ at 298 K.
e) If the entropy decreases in a spontaneous reaction it must be exothermic.

Integrated rate laws

Which of the following statements on integrated rate laws are correct?

a) The half-life $t_{\frac{1}{2}}$ of a substance A that reacts to some products by a first order reaction is independent of the concentration of A.

b) The steady-state approximation simplifies the determination of integrated rate laws of multi-step reactions by assuming the concentrations of all intermediates being constant.

c) The rate constant of a reaction of second order has the unit mol $L^{-1} s^{-1}$.

d) The order of an elementary reaction is the same as its molecularity.

e) If the order of a reaction differs from the sum of the stoichiometric coefficients of the reactants the mechanism must consist of more than one step.

f) The determination of rate laws consists of solving differential equations containing the concentration of a substance *A* and its rate of decrease (reactant) or increase (product).

Infrared and RAMAN Spectroscopy

Which of the following statements on the vibration-rotation spectra (IR and RAMAN) of gaseous diatomic molecules are correct?

a) Homoatomic molecules do not show any IR absorptions.

b) Heteroatomic molecules do not yield RAMAN spectra.

c) The lines of the Q branch are very close so that they usually cannot be resolved. Any splitting is due to slightly different rotational constants of the two vibrational levels involved.

d) IR spectra of diamagnetic molecules *AB* do not show the Q branch.

e) The lines in the P branch of the IR spectra belong to transitions with $v \to v+1$ and $\Delta J = -1$.

f) The anharmonicity of the vibration results in decreasing distances of adjacent lines with increasing *J* in the R branch.

g) The lines in the vibration-rotation RAMAN spectra stem from transitions with $\Delta v = 2$ and $\Delta J = 1$.

h) The O branch of the vibration-rotation RAMAN spectrum is detected only at the Stokes side, the S branch only at the anti-Stokes side of the spectrum.

Electronic transitions

Which of the following statements on electronic transitions are correct?

a) Electronic transitions are allowed only between states of the same parity (Laporte rule).

b) The Franck-Condon principle states that the most intensive transition is the one from the vibrational ground state of the initial electronic state to the first excited vibrational state of the final electronic state ($\Delta v = +1$).

c) The separation of vibrational lines in electronic absorption spectra contain information about the vibrations of the excited state.

d) Fluorescence occurs when the excited electronic states of an irradiated substance undergo nearly immediate transition to the ground state by spontaneous emission.

e) Fluorescence spectra are displaced to lower wavelengths compared to the corresponding absorption spectra.

f) Intersystem crossing is a mechanism by which a system can change the multiplicity without emission of radiation during the relaxation of an excited electronic state.

g) The precondition for phosphorescence is trapping in an excited electronic state of a multiplicity different from that of the ground state. Spontaneous emission is then spin-forbidden.

h) The main principle of laser action is the depletion of an excited electronic state by a chain reaction of stimulated emission.

i) The probability of a system undergoing a transition between two states by absorption (e. g. ground state G to excited state X) is twice the probability of the corresponding transition by stimulated emission (e. g. excited state X to ground state G).

j) The main advantage of a four level laser is that pumping always results in a population inversion of the states of the laser transition.

Basics of Electrochemistry

Which of the following statements are correct?

a) The Nernst equation relates the thermodynamic potential of a redox reaction with the equilibrium constant of this reaction.

b) In redox reactions, electrons are transferred from the species with the higher potential to the species with the lower potential.

c) The Gibbs energy (ΔG^0) of an electrochemical cell relates exponentially to the cell potential (ΔE^0).

These questions/tasks should give you an impression on the depth with which these topics are dealt with in our Bachelor's program. The most important subjects of our Physical Chemistry education are:

- Thermodynamics
- Kinetics
- Statistical Thermodynamics
- Spectroscopy

Thorough knowledge on these topics is needed throughout the whole Master's program.

Quantum Chemistry

Hamilton operator, Schrödinger equation, wave functions

Which of the following statements on the Hamiltonian and the time-independent Schrödinger equation are correct?

a) Solving the Schrödinger equation means finding the eigenvalues and eigenfunctions of the Hamiltonian.
b) The Hamilton operator is the quantum mechanical operator associated with the kinetic energy of a particle.
c) The Schrödinger equation is a differential equation.
d) There are only few systems for which the Schrödinger equation can be solved analytically, amongst these the particle in a box, the harmonic oscillator and the hydrogen atom.
e) Since wave functions have to be normalized their value cannot exceed ± 1.
f) The value of a wave function at some point is proportional to the probability to find the particle at this specific point.
g) The wave functions can be used to calculate the expectation value of any property of the described quantum mechanical object by using the corresponding operator.
h) If an operator is used to calculate an expectation value of an eigenfunction of that operator the result will be a discreet eigenvalue.
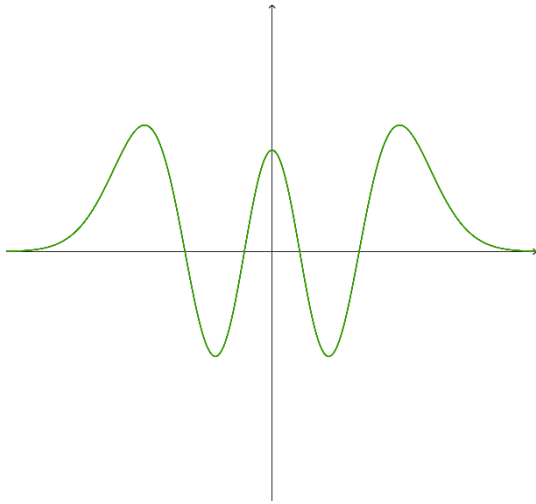
Harmonic Oscillator

Assign the correct quantum number v for the wave functions of the harmonic oscillator depicted in the following diagrams.
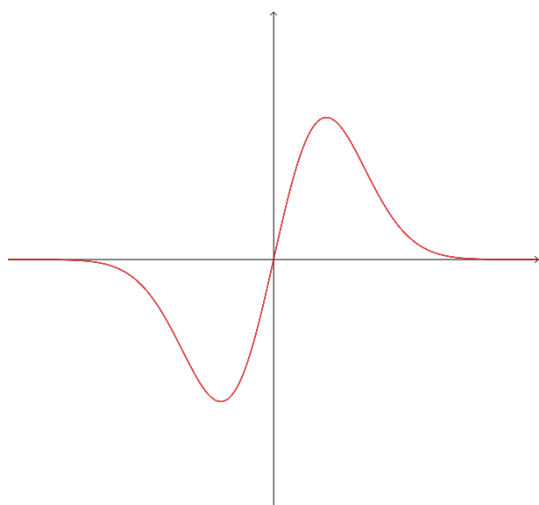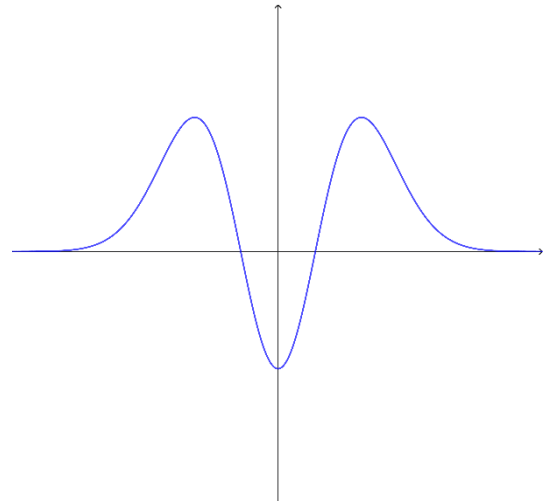

Wave function A
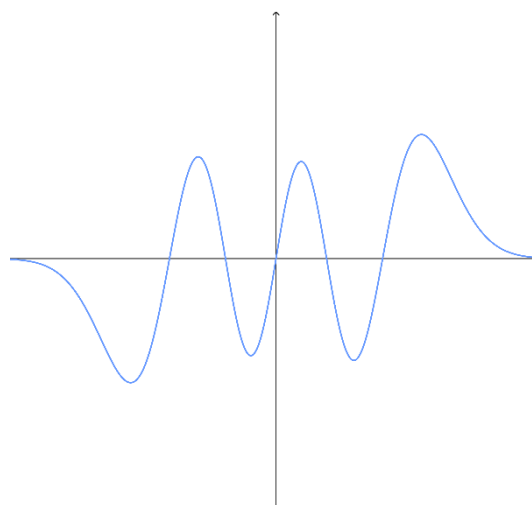
Wave function B

Wave function C

Wave function D

Which of the following statements on the harmonic oscillator are correct?

a) The characteristic potential of the harmonic oscillator is parabolic.
b) The distance between two adjacent energy levels of the harmonic oscillator is proportional to the vibration quantum number v of the upper level.
c) The energy of the ground state of the harmonic oscillator ($v = 0$) equals the minimum of the potential.
d) For every v, there is a non-zero probability to find the oscillating particle outside the potential well.
e) The kinetic and the potential energy of a harmonic oscillator are related by $E_{kin} = \frac{1}{2} E_{pot}$.

Hydrogen atom

Which of the following statements on the solutions of the Schrödinger equation for the hydrogen atom are correct?

a) The wave functions depend on the three quantum numbers n, l and m.
b) To obtain wave functions that obey the Pauli exclusion principle the solutions of the Schrödinger equation have to be multiplied by a spin function (spin up or spin down).
c) The energy of the electron in a hydrogen atom depends on the principal quantum number n and on the angular momentum quantum number l.
d) The wave functions of the hydrogen atom are the sum of a radial function and an angular wave function.
e) The radial part of the wave functions changes sign n times (n: principal quantum number).

The main goal of the modules dealing with Quantum Chemistry in our Bachelor's program is the introduction of some basic concepts of Quantum Mechanics like wave-particle duality, Hamilton operator, Schrödinger equation (eigenvalue problem, matrix form, quantum numbers). This is done using simple examples like the particle in a box or the harmonic oscillator. The solutions of the Schrödinger equation for the hydrogen atom are discussed in detail. A thorough understanding of the physical background and the calculation techniques is required for the mandatory Quantum Chemistry course of our Master's program.

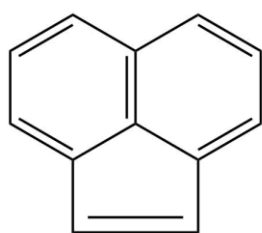## QM treatment of molecules, Born-Oppenheimer approximation

Which of the following statements on the quantum mechanical description of molecules are correct?

a) Since the nuclei are much heavier and thus much slower than the electrons it is possible to separate the nuclear motion from the electronic motion (Born-Oppenheimer approximation).

b) The Schrödinger equations for molecules are generally solvable only by approximation methods.

c) The electronic structure of molecules is often described in the form of molecular orbitals. The main difference to atomic orbitals is that these MOs are not subject to the Pauli principle.

d) A common way to "construct" molecular orbitals is the linear combination of atomic orbitals (LCAO method). For homonuclear diatomic molecules (e. g. N_2) the formed MOs all consist either of a (normalized) sum or difference of two equal AOs of the two atoms.

e) The "construction" of MOs by the LCAO method is simplified by the use of symmetry. MOs can only be formed by AOs (or symmetry adapted linear combinations of AOs) of the same irreducible representation.
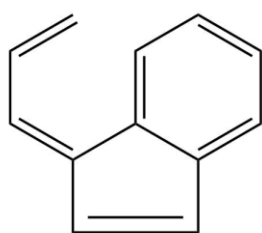
Hückel Method

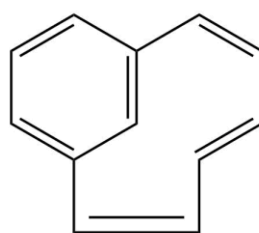Which of the molecules below is described by the Hückel matrix given in the table?

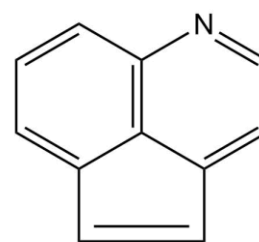|	1	2	3	4	5	6	7	8	9	10	11	12
1	0	1	0	0	0	0	0	0	0	0	0	0
2	1	0	1	0	0	0	0	0	0	0	0	0
3	0	1	0	1	0	0	0	0	0	0	0	0
4	0	0	1	0	1	0	0	1	0	0	0	0
5	0	0	0	1	0	1	0	0	0	0	0	0
6	0	0	0	0	1	0	1	0	0	0	0	0
7	0	0	0	0	0	1	0	1	0	0	0	1
8	0	0	0	1	0	0	1	0	1	0	0	0
9	0	0	0	0	0	0	0	1	0	1	0	0
10	0	0	0	0	0	0	0	0	1	0	1	0
11	0	0	0	0	0	0	0	0	0	1	0	1
12	0	0	0	0	0	0	1	0	0	0	1	0

A　　　　　　B　　　　　　C　　　　　　D

The quantum mechanical treatment of many electron systems (atoms, molecules) requires approximation methods. Some basic concepts are dealt with in our Bachelor's program, e. g. the Born-Oppenheimer approximation and the Pauli principle. An easy semiempirical method to describe molecules with extended π-systems is the Hückel method. These concepts and methods are required to understand the advanced methods introduced in the mandatory Quantum Chemistry course of our Master's program.

Mathematics

Differentiation

Assign the correct derivative(s) of the following functions. (More than one derivative function may be correct.)

a) $f(x) = x^3 - 2x^2 + \frac{1}{x}$ $(x \in \mathbb{R}\backslash\{0\})$

$f'(x) = 3x^2 - 4x + \dfrac{1}{x^2}$

$f'(x) = 2x^2 - 2x - \dfrac{1}{x^2}$

$f'(x) = 3x^2 - 4x - \dfrac{1}{x^2}$

$f'^{(x)} = 3x^4 - 4x^3 + \ln(x)$

b) $g(x) = \frac{x^2 - 2x + 1}{3x - 2}$ $(x \in \mathbb{R}\backslash\{\frac{2}{3}\})$

$g'(x) = \dfrac{2x - 2}{3}$

$g'(x) = \dfrac{3x^2 - 4x + 1}{(3x - 2)^2}$

$g'(x) = \dfrac{3x^2 + 4x - 1}{(3x - 2)^2}$

$g'(x) = \dfrac{6x^2 - 4x + 2}{9x^2 - 6x + 4}$

$g'(x) = \dfrac{2x - 2}{3x - 2} + \dfrac{3x^2 + 6x - 1}{9x^2 - 12x + 4}$

$g'(x) = \dfrac{2x - 2}{3x - 2} - \dfrac{3x^2 - 6x + 3}{9x^2 - 12x + 4}$

c) $h(x) = (x^2 + 3ax + 2)e^{ax^2 + x}$ $(x, a \in \mathbb{R})$ (a is a parameter)

$h'(x) = [2ax^3 + (3a^2 + 1)x^2 + (5a + 2)x + 3a + 2]e^{ax^2 + x}$

$h'(x) = (2ax)(2x + 3a)e^{ax^2 + x}$

$h'(x) = (2x + 3a)e^{2ax + 1}$

$h'(x) = [2ax^3 + (6a^2 + 1)x^2 + (7a + 2)x + 3a + 2]e^{ax^2 + x}$

$h'(x) = (2x + 3a)e^{ax^2 + x} + (x^2 + 3ax + 2)(2ax + 1)e^{ax^2 + x}$

$h'(x) = 2x + 3a + (2ax + 1)e^{2ax + 1}$

Indefinite Integration

Assign the correct indefinite integrals to the following functions. (More than one function may be correct.)

a) $f(x) = x^3 - 2x^2 + \frac{1}{x}$

$$F(x) = \frac{1}{4}x^4 - \frac{2}{3}x^3 + \ln(x)$$

$$F(x) = \frac{1}{3}x^4 - x^3 + \ln|x|$$

$$F(x) = \frac{1}{3}x^4 - x^3 + \ln(x)$$

$$F(x) = \frac{1}{4}x^4 - \frac{2}{3}x^3 + \ln|x|$$

b) $f(x) = \sin(x) \cdot \cos(x)$

$$F(x) = -\frac{1}{2}\sin^2(x)$$

$$F(x) = \frac{1}{2}\sin^2(x)$$

$$F(x) = -\frac{1}{2}\cos^2(x)$$

$$F(x) = \frac{1}{2}\cos^2(x)$$

$$F(x) = \frac{1}{4}\sin^2(x) - \frac{1}{4}\cos^2(x)$$

$$F(x) = -\sin(x) \cdot \cos(x)$$

c) $f(x) = \frac{2x-1}{(x-4)^2}$

$$F(x) = 2\ln|x - 4| - \frac{7}{x - 4}$$

$$F(x) = 2\ln|x - 4| + \frac{7}{x - 4}$$

$$F(x) = 2\ln|x - 4| - \frac{2x - 1}{x - 4}$$

$$F(x) = 2\ln|x - 4| - \frac{2x + 1}{x - 4}$$

$$F(x) = \ln(x - 4)^2 - \frac{7}{x - 4}$$

$$F(x) = \ln(x - 4)^2 + \frac{7}{x - 4}$$

$$F(x) = \frac{x^2 - x}{x - 4}$$

$$F(x) = \frac{2}{(x-4)^3}$$

Curve sketching

Consider the function f with $f(x) = \frac{x^3 - 6x^2 - x + 30}{x^2 - 1}$

Which of the following statements on f are correct?

a) f possesses zeroes at $x = 2$, $x = -3$ and $x = -5$.

b) f possesses definition gaps at $x = 1$ and $x = -1$.

c) The definition gap at $x = 1$ is removable.

d) For $x \to \infty$, f approaches the straight line with $g(x) = x - 6$ from above.

e) For $x < -1$, f possesses an inverse function.

f) f possesses two inflection points.

Plotting functions

Use a software of your choice to plot the function f with $f(x) = (x^3 - x^2 - 6x + 18)e^{-\left(\frac{x}{4}\right)^2}$.
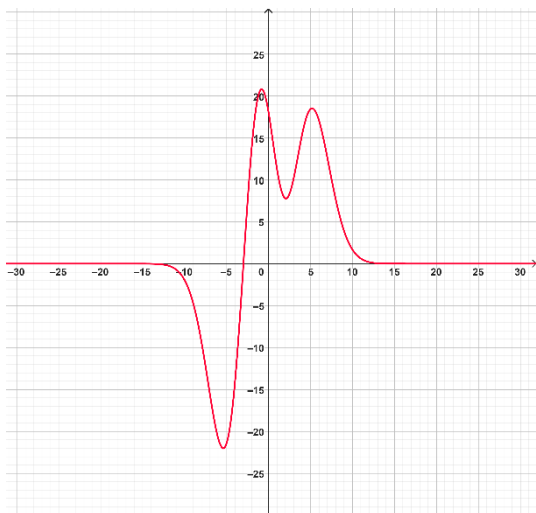
Which of the following diagrams shows a plot of f?
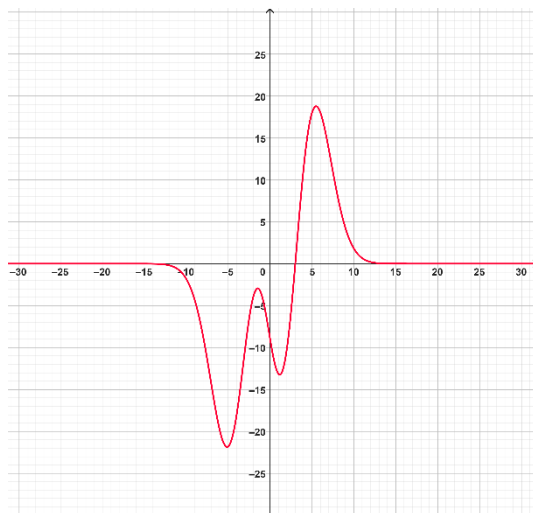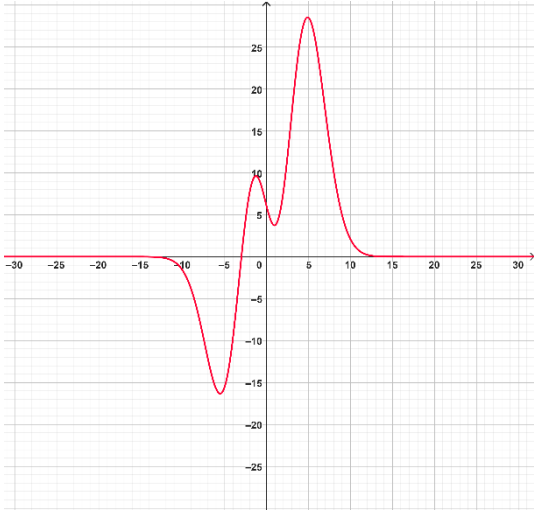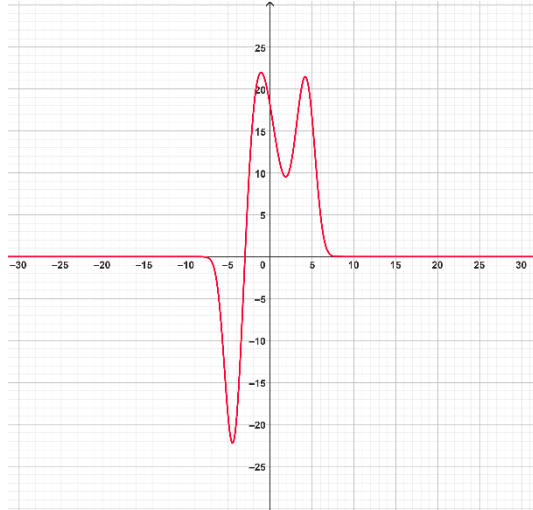

Diagram A

Diagram B

Diagram C

Diagram D

Taylor series

The first six terms of the Taylor expansion of the function g with $g(x) = \sin(2x)$ at the position $x = \pi/4$ are:

$$g(x) = a + b\left(x - \frac{\pi}{4}\right) + c\left(x - \frac{\pi}{4}\right)^2 + d\left(x - \frac{\pi}{4}\right)^3 + e\left(x - \frac{\pi}{4}\right)^4 + f\left(x - \frac{\pi}{4}\right)^5$$

Calculate the coefficients a to f. Enter them as decimal numbers with two decimal places.

Matrices and Determinants

Consider the matrix $A = \begin{pmatrix} 3 & 2 \\ 7 & 5 \end{pmatrix}$.

a) What is the determinant $\begin{vmatrix} 3 & 2 \\ 7 & 5 \end{vmatrix}$ of A?

b) What is the trace of A?

c) What is the transpose A^T of A $\left(A^T = \begin{pmatrix} a & b \\ c & d \end{pmatrix}\right)$?

d) What is the inverse matrix A^{-1} of A $\left(A^{-1} = \begin{pmatrix} e & f \\ g & h \end{pmatrix}\right)$?

e) What is the characteristic polynomial of A?

f) What are the eigenvalues of A?

Exact Differentials

Which of the following differentials are exact?

a) $df = (6x + y)dx + (x + 4y)dy$

b) $dg = \sin(3x^2 + 2y^3)\left(9y^2 dx + 4x dy\right)$

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c) $dh = (6x^2y^4)dx + (8x^3y^3)dy$

d) $dk = -e^{-(x^2+y^3)}(2x\,dx + 3y^2\,dy)$

Lagrange multiplier

At which points does the function f with $f(x,y) = x \cdot y$ have a maximum under the constraint $4x^2 + y^2 = 4$?

Reduction of a reducible representations

The representation of a C_{3v} object yields the characters 4 (E), 1 (2 C_3), and 2 (3 σ_v). To which irreducible representations can this representation be reduced?

Character table C_{3v}

C_{3v}	E	2 C_3	3 σ_v
A_1	1	1	1
A_2	1	1	−1
E	2	−1	0

A thorough mathematical education is absolutely necessary to follow the lectures, especially in the fields of Physical and Theoretical Chemistry.

Please note that the above list is not exhaustive by far. The following calculation techniques are required (at least):

- Functions, Derivatives, Integrals
- Complex numbers
- Sequences and Series
- Taylor Series
- Functions of multiple variables
- Lagrange Multipliers
- Differential equations
- Vectors, Matrices, Determinants
- Eigenvalues and Eigenfunctions
- Fourier Transform

Lab Experience

Technical Skills

Were the following tasks/procedures part of your technical education during your Bachelor's programme? Did you perform it on your own? Was it demonstrated? Or was it only discussed in theory?

- Keeping a lab journal
- Preparation of an experimental protocol
- Qualitative analyses (detection of anions, cations, group precipitations, separation of cations)
- Titrations (Acid-Base-T., Redox-T.)
- Gravimetric analyses
- (Organic) reactions in ground glass apparatus (heating under reflux, using a dripping funnel, reactions under cooling, …)
- Distillation under atmospheric pressure
- Distillation under reduced pressure
- Separation of a solvent by using a rotary evaporator
- Working with solids, liquids and gases under inert conditions
- Drying of solvents
- Solid state reactions at high temperatures and/or in (salt) melts
- Conduction of physical/physicochemical experiments with preinstalled experimental devices (calorimetric measurements, recording of spectra, …)

The technical education during the Bachelor's programme Chemistry at the University of Bonn comprises all of these tasks/procedures. Everything is done by the students on their own, mostly individually. Some experiments are conducted and evaluated in teams of two or three students.

These skills are a prerequisite for the practical courses of the Master's program.

Analytical Knowledge

Were the following analytical methods taught in your Bachelor's studies? Did you perform the measurements and analyze the data on your own? Did you get data to analyze without performing the measurement? Or were the basics of the method taught without details on the analysis of experimental data?

- NMR spectroscopy
- IR spectroscopy
- Raman spectroscopy

- UV/vis spectroscopy
- mass spectrometry
- X-ray powder diffraction

All of these methods are taught in our Bachelor's program. In most cases, the measurements are not performed by the students themselves, but there is a demonstration of the measurement devices. For all these methods, the students get measurement data to analyze themselves.

Knowledge of the fundamentals and the areas of application of these analytical methods is a prerequisite for the mandatory modules of the Master's program.