

**Prüfung in Chemie
für Studierende des Maschinenbaus und des Lehramts an
Gymnasien**

Monday, 1st October 2012, 10:00-13:00

No unauthorised resources (e.g. lecture notes, textbooks etc.) may be used during the examination. Any attempt to use such unauthorised resources will be considered as cheating, and will lead to immediate exclusion from the examination and a mark of 5,0.

Foreign students may use a dictionary (mother tongue – English) but this may not contain any handwritten notes. The use of a calculator is **not** permitted.

Numerical answers that are given without showing any working or explanation will receive no marks.

In general, short answers with keywords will be sufficient; long essays are not necessary! To illustrate a point, a sketch will be sufficient, provided it clarifies the point!

The maximum number of points for each question is given in parentheses.

| | | | | | | | | | | |
|--------|-------|-------|-------|-------|-------|-------|-------|-------|-------|--------|
| 0-49,5 | 50-54 | 55-59 | 60-64 | 65-70 | 71-75 | 76-80 | 81-85 | 86-90 | 91-95 | 96-100 |
| 5,0 | 4,0 | 3,7 | 3,3 | 3,0 | 2,7 | 2,3 | 2,0 | 1,7 | 1,3 | 1,0 |

Section 1:

- a) What do the Pauli Principle and Hund's Rules tell us?

No two electrons in the same atom can have all four quantum numbers the same – any orbital can contain at most two electrons with antiparallel spins ($s = +\frac{1}{2}, -\frac{1}{2}$). When orbitals have the same energy, they will accept one electron each; only when they all have one electron will they start to accept their second electrons.

- b) What are the four quantum numbers that describe the energy levels of electrons in an atom? Briefly describe the significance of each quantum number.

Principal QN n (defines the shell or energy of the orbital), Auxiliary QN l (defines the shape of the orbital), Magnetic QN m (defines the orientation of the orbital in space), Spin QN s (orientation of the spins of the electrons in the orbital).

- c) Give the electron configuration of the phosphorus (P) atom
 $1s^2 2s^2 2p^6 3s^2 3p^3$ Also OK: **$[\text{Ne}] 3s^2 3p^3$**

- d) What is understood by electronegativity?

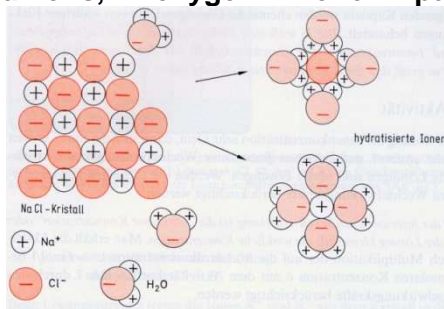
The ability of an atom within a molecule to attract the electrons in the surrounding bonds to itself.

- e) Give the three-dimensional geometries of the CO_2 , SF_6 , CH_4 und H_2O molecules
 CO_2 : linear; SF_6 : octahedral; CH_4 : tetrahedral; H_2O : bent

- f) Which of the molecules in question e) have a non-zero dipole moment? **H_2O**

- g) What interactions between ions and water molecules compensate for the loss of lattice energy when an ionic salt is dissolved?

Dipolar interactions between ions and water molecules: hydrogen bonds to anions, oxygen lone pairs of water molecules to cations:



- h) Write down the ideal gas equation $PV = nRT$
- i) Give two important properties of metals. **Ductility, electrical conductivity, thermal conductivity etc.**
- j) What is the common characteristic of the elements in a Group of the Periodic Table? **They have the same number of valence electrons → similar/related chemical properties**

Section 2:

- a) What does Hess's Law tell us?

That the enthalpy change of a reaction does not depend on the path taken.

- b) Give the equations used to calculate enthalpy of reaction, entropy of reaction and Gibbs free energy of reaction.

$$\Delta_R H = \sum v_i \cdot \Delta H_f^0 (\text{products}) - \sum v_i \cdot \Delta H_f^0 (\text{reactants})$$

$$\Delta_R S = \sum v_i \cdot \Delta S_f^0 (\text{products}) - \sum v_i \cdot \Delta S_f^0 (\text{reactants})$$

$$\text{then either } \Delta_R G = \sum v_i \cdot \Delta G_f^0 (\text{products}) - \sum v_i \cdot \Delta G_f^0 (\text{reactants})$$

$$\text{or } \Delta_R G = \Delta_R H - T\Delta_R S$$

- c) Explain in terms of Gibbs free energy why NH_4Cl dissolves spontaneously in water, even though this process is endothermic

The positive enthalpy change is (over)compensated by the positive entropy change, when T is high enough:

$$\Delta G = \Delta H - T\Delta S < 0, \text{ when } T\Delta S > \Delta H$$

- d) What does Le Chatelier's Principle tell us?

If a change in conditions is imposed on a system in chemical equilibrium, the equilibrium position will change so as to counteract the change.

What is the effect of raising the temperature on the equilibrium position of an endothermic reaction

Eq. position will move in endothermic direction to reduce the temperature – towards products

and how does increasing the pressure affect the equilibrium position of a gas-phase reaction in which the number of molecules decreases as the reaction proceeds?

Eq. will shift towards the side of the reaction with fewer gas molecules to reduce the pressure – towards products

- e) The solubility product of PbCl_2 at room temperature is $3.2 \times 10^{-5} (\text{mol/l})^3$.

What is the concentration of Pb^{2+} in a saturated aqueous solution of PbCl_2 , and what is the new concentration of Pb^{2+} when the chloride concentration is increased to 0.1 mol/l?

(i) Pure water:

$$[\text{Pb}^{2+}] \cdot [\text{Cl}^-]^2 = 3.2 \cdot 10^{-5} (\text{mol/l})^3$$

$$[\text{Cl}^-] = 2 \cdot [\text{Pb}^{2+}] \Leftrightarrow$$

$$[\text{Pb}^{2+}] \cdot 4[\text{Pb}^{2+}]^2 = 4[\text{Pb}^{2+}]^3 = 3.2 \cdot 10^{-5} (\text{mol/l})^3$$

$$[\text{Pb}^{2+}] = (8 \cdot 10^{-6})^{1/3} \text{ mol/l} = 2 \cdot 10^{-2} \text{ mol/l}$$

(ii) $[\text{Cl}^-] = 0.1 \text{ mol l}^{-1}$:

$$[\text{Pb}^{2+}] \cdot 10^{-2} (\text{mol/l})^2 = 3.2 \cdot 10^{-5} (\text{mol/l})^3$$

$$[\text{Pb}^{2+}] = 3.2 \cdot 10^{-3} \text{ mol/l}$$

- f) What is meant by rate of reaction,

The rate of change with time of the concentration of one of the reactants $d[A]/dt$ and by the order of a reaction?

If $d[A]/dt = k[A]^x[B]^y$, then the order of the reaction with respect to A is x, and the overall order is x + y

- g) Give the equation that describes the effect of temperature on the rate of a chemical reaction.

$$k(T) = A \cdot \exp(-E_a/RT)$$

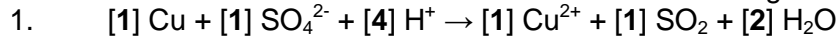
h) What is understood by oxidation and reduction?

Oxidation is the loss of electron(s) from an atom during a reaction, reduction is the gain of electron(s)

i) What is the oxidation state of the elements in bold type in the following compounds?

HNO₃: +V, Na₃VO₄: +V; LiAlH₄: -I; KClO₄: +VII

j) Fill in the stoichiometric coefficients to balance the following redox reactions



k) What is the potential of a Galvanic fuel cell which runs using hydrogen and oxygen gases, when the hydrogen and oxygen are each introduced at a pressure of 1 bar, and the pH = 0? What are the half reactions that take place?

Anode: 2 H₂ + 4 H₂O → 4 H₃O⁺ + 4 e⁻ (oxidation)

Cathode: O₂ + 4 H₃O⁺ + 4 e⁻ → 6 H₂O (reduction)

All conditions standard: P(O₂) = P(H₂) = 1 bar; [H₃O⁺] = 1 mol/l, so use standard reduction potentials from list at end of exam paper:

E⁰(2 H₃O⁺ + 2 e⁻ → H₂ + 2 H₂O) = 0 V (by definition: hydrogen electrode!)

E⁰(O₂ + 4 H₃O⁺ + 4 e⁻ → 6 H₂O) = +1.23 V

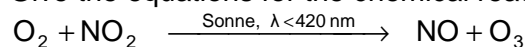
E = E(red) - E(ox) = 1.23 - 0 = +1,23 V

Section 3:

- a) What is "Los Angeles Smog" (also known as "Summer-Smog")?

Ozone (O₃) –containing smog

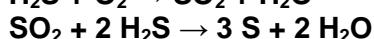
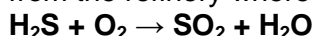
Give the equations for the chemical reactions that result in "Los Angeles Smog"



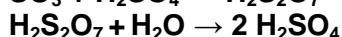
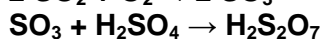
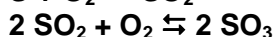
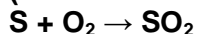
- b) Most of the sulphur used in Germany for the production of sulphuric acid comes from the processing of mineral oil and natural gas. In the form of which compound is most of this sulphur found?

H₂S

Give the reaction equations of the processes by which this chemical is converted into sulphuric acid. You can assume that the sulphuric acid plant is a long distance away from the refinery where the oil or gas is processed!



(solid S easier to transport than gaseous SO₂!)



In the production of sulphuric acid, the formation of SO₃ is an exothermic equilibrium reaction. What is the effect of raising the reaction temperature on the maximum yield of SO₃?

The yield goes down

What measures are taken to increase the degree of conversion?

Use of a catalyst to reduce the working temperature

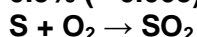
Cooling of the gas mixture in the reactor between runs over the catalyst

Excess of O₂

Removal of SO₂ as it forms

Calculate the amount of SO₂ (in kg) emitted when 32 tonnes of sulphur are converted to H₂SO₄. Assume that all the equations proceed quantitatively, except for the conversion of SO₂ to SO₃, which is only 99.5% complete.

0.5% (= 0.005) of the SO₂ formed is lost to the atmosphere

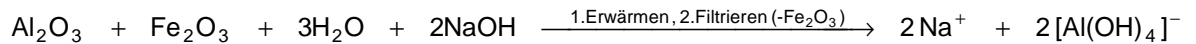
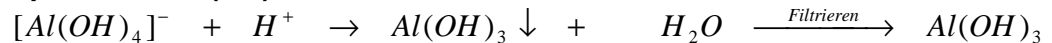
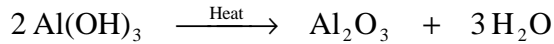
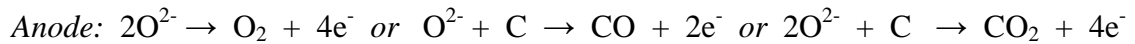
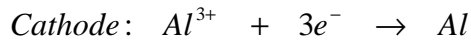
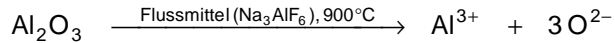


$$\text{mol}(\text{SO}_2) = \text{mol}(\text{S}) = m(\text{S})/M(\text{S}) = 3.2 \times 10^7 \text{ g} / 32 \text{ g mol}^{-1} = 10^6 \text{ mol}$$

$$\text{Mol}(\text{SO}_2) \text{ emitted} = 0.005 \times 10^6 \text{ mol} = 5 \times 10^3 \text{ mol}$$

$$\text{Mass of SO}_2 \text{ emitted} = (5 \times 10^3) \times M(\text{SO}_2) = (5 \times 10^3) \text{ mol} \times 64 \text{ g mol}^{-1} \\ = 3.2 \times 10^5 \text{ g} = 320 \text{ kg}$$

- c) State a property of iron that is made use of in its industrial applications.
High melting point, ductility, high tensile strength, magnetisable)
- d) Why is limestone (CaCO₃) used as an additive in the Blast Furnace process?
Si and/or P impurities in the iron ore react with CaO (formed from CaCO₃) to form slag.
- e) Give the equations for the reactions that take place in the Blast Furnace, in which the limestone or a substance formed from the limestone takes part.
CaO formed in situ from limestone: CaCO₃ → CaO + CO₂
CaO(s) + SiO₂(s) → CaSiO₃ and/or
3 CaO + 2 P₂O₅ → Ca₃(PO₄)₂
- f) Bauxite is an important raw material in the production of aluminium, and is usually a mixture of Al₂O₃ und Fe₂O₃.
What are the four important stages in the formation of metallic aluminium from this raw material? Give the equations for the chemical reactions that take place

Dissolution of the Al₂O₃:**Reprecipitation of Al(OH)₃:****Calcination of Al(OH)₃:****Smelting Flux Electrolysis:**

- g) In the Blast Furnace, carbon is formed via the Boudouard reaction. Give the reaction equation for this equilibrium reaction.



What negative effect does dissolved carbon have on the properties of the raw („pig“) iron?

It becomes brittle

Give the name of a process which is used during steel production to reduce the content of carbon in the raw iron.

Decarburisation (oxygen lance) or Electrosteel process

- h) What is meant by corrosion

Destruction of a material through chemical reactions

and by a local element

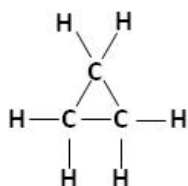
When two metals of different electrode potentials (or electronegativity) are in physical contact, and the point of contact is exposed to an electrolyte solution

- i) State two important methods for protection from corrosion

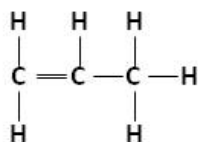
Protective coating (paint, enamel, galvanising), passivation, sacrificial electrode

Section 4:

- a) Two organic compounds have the sum formula C_3H_6 .
Give the Lewis structures for both compounds. To which classes of organic compounds do each of these molecules belong?

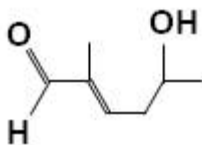


Cycloalkane

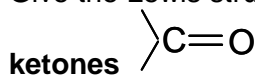


Alkene

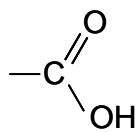
- b) Give the Lewis structure for the molecule 2-methyl-5-hydroxyhex-2-enal.



- c) Give the Lewis structures of the characteristic functional groups of



and carboxylic acids



- d) Give the reaction equations for the industrial productions of
methanol: $\text{CO} + 2\text{H}_2 \xrightarrow{380^\circ\text{C}; p > 200 \text{ bar}} \text{CH}_3\text{OH}$
ethanol: $\text{C}_2\text{H}_4 + \text{H}_2\text{O} \xrightarrow{\text{H}_2\text{SO}_4} \text{C}_2\text{H}_5\text{OH}$

and ethanoic (acetic) acid: $\text{CH}_3\text{OH} + \text{CO} \rightarrow \text{CH}_3\text{COOH}$

- e) What is the hybridisation of the carbon atoms in single, double and triple bonds?
What are the 3-D geometries of the bonds around such carbon atoms?

Single bonds: sp^3 , tetrahedral

Double bonds: sp^2 , trigonal planar

Triple bonds: sp , linear

- f) Describe the mechanism of a radical chain reaction, using the formation of CH_3Br from CH_4 and Br_2 as an example

Initiation: $\text{Br}_2 \rightarrow 2 \text{Br}\cdot$

Propagation: $\text{H-CH}_3 + \text{Br}\cdot \rightarrow \cdot\text{CH}_3 + \text{HBr}$

$\cdot\text{CH}_3 + \text{Br}_2 \rightarrow \text{BrCH}_3 + \text{Br}\cdot$

Termination: $2 \text{Br}\cdot \rightarrow \text{Br}_2$

$\cdot\text{CH}_3 + \text{Br}\cdot \rightarrow \text{BrCH}_3$

$2 \cdot\text{CH}_3 \rightarrow \text{C}_2\text{H}_6$

(3P)

- g) What is understood by the term macromolecule
A molecule of very high molecular weight, usually built up from smaller chemical building blocks (either similar or different)
and what is polymerisation?

The chemical linkage of small molecules (monomers - usually organic molecules) into high molecular weight polymers

- h) Give the structural formulas of the repeating units in polyethylene, polypropene, polyvinylchloride and polyacrylonitrile. From which monomers are these polymers produced?

| | | | | | | | |
|--|--|---|---|---|---|---|---|
| Polyethy- len Herstell- ung aus Ethen | $\left[\begin{array}{cc} \text{H} & \text{H} \\ & \\ -\text{C} & - & \text{C}- \\ & \\ \text{H} & \text{H} \end{array} \right]_n$ | Polypropy- len: Herstellung aus Propen | $\left[\begin{array}{cc} \text{H} & \text{H} \\ & \\ -\text{C} & - & \text{C}- \\ & \\ \text{H} & \text{CH}_3 \end{array} \right]_n$ | Polyacrylni- tril: Herstellung aus Acrylnitril | $\left[\begin{array}{cc} \text{H} & \text{H} \\ & \\ -\text{C} & - & \text{C}- \\ & \\ \text{H} & \text{CN} \end{array} \right]_n$ | Polyvinyl- chlorid: Herstellung aus Vinylchlorid | $\left[\begin{array}{cc} \text{H} & \text{H} \\ & \\ -\text{C} & - & \text{C}- \\ & \\ \text{H} & \text{Cl} \end{array} \right]_n$ |
|--|--|---|---|---|---|---|---|

(In English add an "e" to the name of each monomer!)

What type of polymerisation reaction is involved?

Radical polymerisation

| Reduzierte Form | \rightleftharpoons Oxidierte Form | $+ z e^-$ | Standardpotential E° in V |
|--|--|-----------|-------------------------------------|
| Li | $\rightleftharpoons \text{Li}^+$ | $+ e^-$ | -3,04 |
| K | $\rightleftharpoons \text{K}^+$ | $+ e^-$ | -2,92 |
| Ba | $\rightleftharpoons \text{Ba}^{2+}$ | $+ 2e^-$ | -2,90 |
| Ca | $\rightleftharpoons \text{Ca}^{2+}$ | $+ 2e^-$ | -2,87 |
| Na | $\rightleftharpoons \text{Na}^+$ | $+ e^-$ | -2,71 |
| Mg | $\rightleftharpoons \text{Mg}^{2+}$ | $+ 2e^-$ | -2,36 |
| Al | $\rightleftharpoons \text{Al}^{3+}$ | $+ 3e^-$ | -1,68 |
| Mn | $\rightleftharpoons \text{Mn}^{2+}$ | $+ 2e^-$ | -1,19 |
| Zn | $\rightleftharpoons \text{Zn}^{2+}$ | $+ 2e^-$ | -0,76 |
| Cr | $\rightleftharpoons \text{Cr}^{3+}$ | $+ 3e^-$ | -0,74 |
| S^{2-} | $\rightleftharpoons \text{S}$ | $+ 2e^-$ | -0,48 |
| Fe | $\rightleftharpoons \text{Fe}^{2+}$ | $+ 2e^-$ | -0,41 |
| Cd | $\rightleftharpoons \text{Cd}^{2+}$ | $+ 2e^-$ | -0,40 |
| Co | $\rightleftharpoons \text{Co}^{2+}$ | $+ 2e^-$ | -0,28 |
| Sn | $\rightleftharpoons \text{Sn}^{2+}$ | $+ 2e^-$ | -0,14 |
| Pb | $\rightleftharpoons \text{Pb}^{2+}$ | $+ 2e^-$ | -0,13 |
| Fe | $\rightleftharpoons \text{Fe}^{3+}$ | $+ 3e^-$ | -0,036 |
| $\text{H}_2 + 2\text{H}_2\text{O}$ | $\rightleftharpoons 2\text{H}_3\text{O}^+$ | $+ 2e^-$ | 0 |
| Sn^{2+} | $\rightleftharpoons \text{Sn}^{4+}$ | $+ 2e^-$ | +0,15 |
| Cu^+ | $\rightleftharpoons \text{Cu}^{2+}$ | $+ e^-$ | +0,15 |
| $\text{SO}_2 + 6\text{H}_2\text{O}$ | $\rightleftharpoons \text{SO}_4^{2-} + 4\text{H}_3\text{O}^+$ | $+ 2e^-$ | +0,17 |
| Cu | $\rightleftharpoons \text{Cu}^{2+}$ | $+ 2e^-$ | +0,34 |
| Cu | $\rightleftharpoons \text{Cu}^+$ | $+ e^-$ | +0,52 |
| 2I^- | $\rightleftharpoons \text{I}_2$ | $+ 2e^-$ | +0,54 |
| $\text{H}_2\text{O}_2 + 2\text{H}_2\text{O}$ | $\rightleftharpoons \text{O}_2 + 2\text{H}_3\text{O}^+$ | $+ 2e^-$ | +0,68 |
| Fe^{2+} | $\rightleftharpoons \text{Fe}^{3+}$ | $+ e^-$ | +0,77 |
| Ag | $\rightleftharpoons \text{Ag}^+$ | $+ e^-$ | +0,80 |
| Hg | $\rightleftharpoons \text{Hg}^{2+}$ | $+ 2e^-$ | +0,85 |
| $\text{NO} + 6\text{H}_2\text{O}$ | $\rightleftharpoons \text{NO}_3^- + 4\text{H}_3\text{O}^+$ | $+ 3e^-$ | +0,96 |
| 2Br^- | $\rightleftharpoons \text{Br}_2$ | $+ 2e^-$ | +1,07 |
| $6\text{H}_2\text{O}$ | $\rightleftharpoons \text{O}_2 + 4\text{H}_3\text{O}^+$ | $+ 4e^-$ | +1,23 |
| $2\text{Cr}^{3+} + 21\text{H}_2\text{O}$ | $\rightleftharpoons \text{Cr}_2\text{O}_7^{2-} + 14\text{H}_3\text{O}^+$ | $+ 6e^-$ | +1,33 |
| 2Cl^- | $\rightleftharpoons \text{Cl}_2$ | $+ 2e^-$ | +1,36 |
| $\text{Pb}^{2+} + 6\text{H}_2\text{O}$ | $\rightleftharpoons \text{PbO}_2 + 4\text{H}_3\text{O}^+$ | $+ 2e^-$ | +1,46 |
| Au | $\rightleftharpoons \text{Au}^{3+}$ | $+ 3e^-$ | +1,50 |
| $\text{Mn}^{2+} + 12\text{H}_2\text{O}$ | $\rightleftharpoons \text{MnO}_4^- + 8\text{H}_3\text{O}^+$ | $+ 5e^-$ | +1,51 |
| $3\text{H}_2\text{O} + \text{O}_2$ | $\rightleftharpoons \text{O}_3 + 2\text{H}_3\text{O}^+$ | $+ 2e^-$ | +2,07 |
| 2F^- | $\rightleftharpoons \text{F}_2$ | $+ 2e^-$ | +2,87 |