Grundlagen der Chemie für Studierende des Maschinenbaus, Prof. Dr. Meier

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:

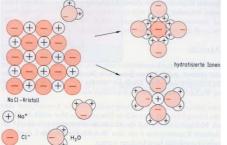
a) What do the Pauli Principle and Hund's Rules tell us?

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 deAscribe 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 *I* (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
 1s² 2s² 2^{p6} 3s² 3^{p3} Also OK: [Ne] 3s² 3p³
- 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 → simliar/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 Gibb's free energy of reaction. $\Delta_R H = \sum v_i \cdot \Delta H_f^0 \text{ (products)} - \sum v_i \cdot \Delta H_f^0 \text{ (reactants)}$ $\Delta_R S = \sum v_i \cdot \Delta S_f^0 \text{ (products)} - \sum v_i \cdot \Delta S_f^0 \text{ (reactants)}$ then either $\Delta_R G = \sum v_i \cdot \Delta G_f^0 \text{ (products)} - \sum v_i \cdot \Delta G_f^0 \text{ (reactants)}$ or $\Delta_R G = \Delta_R H - T \Delta_R S$
- c) Explain in terms of Gibbs free energy why NH₄Cl 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: $\Delta G = \Delta H - T \cdot \Delta S < 0$, when $T \cdot \Delta S > \Delta H$
- 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 PbCl₂ at room temperature is 3.2×10⁻⁵ (mol/l)³. What is the concentration of Pb²⁺ in a saturated aqueous solution of PbCl₂, and what is the new concentration of Pb²⁺ when the chloride concentration is increased to 0.1 mol/l?

(i) Pure water:

- 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-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; LiAIH₄: -I; KCIO₄: +VII
- j) Fill in the stochiometric coefficients to balance the following redox reactions
 - 1. [1] Cu + [1] SO₄²⁻ + [4] H⁺ \rightarrow [1] Cu²⁺ + [1] SO₂ + [2] H₂O
 - 2. [3] $Fe_2O_3 + [1] CO \rightarrow [2] Fe_3O_4 + [1] CO_2$
- 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: $2 H_2 + 4 H_2O \rightarrow 4 H_3O^+ + 4 e^-$ (oxidation) Cathode: $O_2 + 4 H_3O^+ + 4 e^- \rightarrow 6 H_2O$ (reduction)

All conditions standard: $P(O_2) = P(H_2) = 1$ bar; $[H_3O^+] = 1$ mol/l, so use standard reduction potentials from list at end of exam paper: $E^0(2 H_3O^+ + 2 e^- \rightarrow H_2 + 2 H_2O) = 0 V$ (by definition: hydrogen electrode!)

 $E^{0}(O_{2} + 4 H_{3}O^{+} + 4 e^{-} \rightarrow 6 H_{2}O) = +1.23 V$ 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"
 O₂ + NO₂ ______ Sonne, λ<420 nm → NO + O₃
- 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!

$$\begin{array}{l} H_2S+O_2\rightarrow SO_2+H_2O\\ SO_2+2\,H_2S\rightarrow 3\,S+2\,H_2O\\ (\text{solid S easier to transport than gaseous SO}_2!)\\ S+O_2\rightarrow SO_2\\ 2\,SO_2+O_2\leftrightarrows 2\,SO_3\\ SO_3+H_2SO_4\rightarrow H_2S_2O_7\\ H_2S_2O_7+H_2O\rightarrow 2\,H_2SO_4 \end{array}$$

In the production of sulphuric acid, the formation of SO_3 is an exothermic equilibrium reaction. What is the effect of raising the reaction temperature on the maximum yield of SO_3 ?

The yield goes down

What measures are taken to increase the degree of conversion?

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Use of a catalyst to reduce the working temperature
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Cooling of the gas mixture in the reactor between runs over the catalyst Excess of O_2

Removal of SO₂ as it forms

Calculate the amount of SO₂ (in kg) emitted when 32 tonnes of sulphur are converted to H_2SO_4 . 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 S + O₂ \rightarrow SO₂ mol (SO₂) = mol (S) = m(S)/*M*(S) = 3.2×10^7 g / 32 g mol⁻¹ = 10^6 mol Mol (SO₂) emitted = 0.005×10^6 mol = 5×10^3 mol Mass of SO₂ emitted = $(5 \times 10^3) \times M(SO_2) = (5 \times 10^3)$ mol × 64 g mol⁻¹ = 3.2×10^5 g = 320 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: Al₂O₃ + Fe₂O₃ + 3H₂O + 2NaOH $\xrightarrow{1.\text{Erwärmen}, 2.\text{Filtrieren}(-\text{Fe}_2\text{O}_3)} 2 \text{Na}^+ + 2[\text{Al}(\text{OH})_4]^-$ Reprecipitation of Al(OH)₃: $[Al(OH)_4]^- + H^+ \rightarrow Al(OH)_3 \downarrow + H_2O \xrightarrow{\text{Filtrieren}} Al(OH)_3$ Calcination of Al(OH)₃: $2 \text{Al}(\text{OH})_3 \xrightarrow{\text{Heat}} Al_2\text{O}_3 + 3 \text{H}_2\text{O}$ Smelting Flux Electrolysis: Al₂O₃ $\xrightarrow{\text{Flussmittel}(\text{Na}_3\text{AlF}_6),900^{\circ}\text{C}} Al^{3+} + 3O^{2-}$ Cathode: $Al^{3+} + 3e^- \rightarrow Al$ Anode: $2O^{2-} \rightarrow O_2 + 4e^- \text{ or } O^{2-} + C \rightarrow CO + 2e^- \text{ or } 2O^{2-} + C \rightarrow CO_2 + 4e^-$

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

 $CO_2 + C \leftrightarrows 2 CO$ 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.

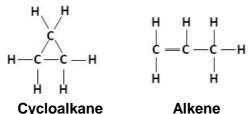
Decarburisation (oxygen lance) or Electrosteel process

- h) What is meant by corrosion
 Destruction of a material through chemical reactions

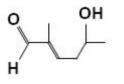
 and by a local element
 When two metals of different electrode potentials (or electronegativity) are in
 physical contact, and the point of contact is exposed to an electrolyte solution
- i) State two important methods for protection from corrosion **Protective coating (paint, enamel, galvanising), passivation, sacrificial electrode**

Section 4:

a) Two organic compounds have the sum formula C₃H₆.
 Give the Lewis structures for both compounds. To which classes of organic compounds do each of these molecules belong?



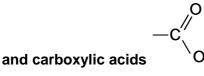
b) Give the Lewis structure for the molecule 2-methyl-5-hydroxyhex-2-enal.



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

$$_{\mathsf{ketones}}
angle_{\mathsf{C}=\mathsf{O}}$$

alcohols -OH



d) Give the reaction equations for the industrial productions of methanol: CO + 2H₂ $\xrightarrow{380^{\circ}C; p > 200 \text{ bar}}$ CH₃OH ethanol: C₂H₄ + H₂O $\xrightarrow{H_2SO_4}$ C₂H₅OH

and ethanoic (acetic) acid: $CH_3OH + CO \rightarrow CH_3COOH$

- 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: sp³, tetrahedral Double bonds: sp², 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

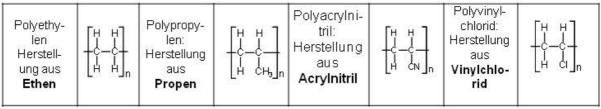
Initiation:	$Br_2 \rightarrow 2 Br_1$
Propagation:	$H-CH_3 + Br \bullet \rightarrow \bullet CH_3 + HBr$
	$\bullet CH_3 + Br_2 \rightarrow BrCH_3 + Br \bullet$
Termination:	2 $Br \bullet \rightarrow Br_2$
	•CH ₃ + Br• \rightarrow BrCH ₃
	$2 \bullet \mathbf{CH}_3 \to \mathbf{C_2H_6}$

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?

(3P)

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?



(In English add an "e" to the name of each monomer!) What type of polymerisation reaction is involved? Radical polymerisation

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17 VIIA	F 9 18.998403 4.0 1- Fluor	CI 17 35.453 3.0 1- Chlor	Br 35 79.904 2.8 1- Brom	 53 126.90447 2.5 1- Iod	At 85 209.9871 2.2 1- Astat	20ut1130uq 114up 115uh 116ux 1170uo 11 292 - 289 - 292 Ununtrium Ununpentium Ununbertium Ununoctium Ununoctium		
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Li	≓ Li+	+ e ⁻	-3,04
К	$\rightleftharpoons K^+$	+ e ⁻	-2.92
Ba	$\Rightarrow Ba^{2+}$	+2e ⁻	-2,90
Ca	\rightleftharpoons Ca ²⁺	+2e ⁻	-2,87
Na	\Rightarrow Na ⁺	+ e ⁻	-2,71
Mg	$\Rightarrow Mg^{2+}$	+2e ⁻	-2,36
Al	$\Rightarrow Al^{3+}$	+3e ⁻	-1,68
Mn	\Rightarrow Mn ²⁺	+2e ⁻	-1,19
Zn	$\Rightarrow Zn^{2+}$	+2e ⁻	-0.76
Cr	\Rightarrow Cr ³⁺	+3e ⁻	-0,74
S ²⁻	≓ S	$+2e^{-}$	-0,48
Fe	\Rightarrow Fe ²⁺	$+2e^{-}$	-0,41
Cd	\Rightarrow Cd ²⁺	$+2e^{-}$	-0,40
Co	$\rightleftharpoons \mathrm{Co}^{2+}$	$+2e^{-}$	-0.28
Sn	\Rightarrow Sn ²⁺	+2e-	-0,14
Pb	$\Rightarrow Pb^{2+}$	+2e ⁻	-0,13
Fe	\Rightarrow Fe ³⁺	$+3e^{-}$	-0,036
$H_{2} + 2 H_{2}O$	$\Rightarrow 2 H_3 O^+$	+2e ⁻	0
Sn ²⁺	\Rightarrow Sn ⁴⁺	+2e ⁻	+0,15
Cu ⁺	\Rightarrow Cu ²⁺	+ e ⁻	+0.15
$SO_2 + 6H_2O$	\Rightarrow SO ₄ ²⁻ + 4H ₃ O ⁺	+2e ⁻	+0,17
Cu	$\rightleftharpoons Cu^{2+}$	+2e ⁻	+0,34
Cu	\rightleftharpoons Cu ⁺	+ e ⁻	+0,52
21-	\rightleftharpoons I ₂	$+2e^{-}$	+0,54
$H_2O_2 + 2H_2O$	$\Rightarrow O_2 + 2H_3O^+$	$+2e^{-}$	+0,68
Fe ²⁺	\Rightarrow Fe ³⁺	+ e ⁻	+0,77
Ag	$\Rightarrow Ag^+$	+ e ⁻	+0,80
Hg	\Rightarrow Hg ²⁺	$+2e^{-}$	+0,85
$NO + 6H_2O$	$\Rightarrow NO_3^- + 4H_3O^+$	+3e-	+0.96
2Br ⁻	\rightleftharpoons Br ₂	+2e ⁻	+1,07
6H2O	$\Rightarrow O_2 + 4 H_3O^+$	+4e ⁻	+1,23
$2 Cr^{3+} + 21 H_2O$	$\Rightarrow Cr_2O_7^{2-} + 14 H_3O^+$	+6e ⁻	+1,33
2 Cl-	\Rightarrow Cl ₂	+2e ⁻	+1,36
$Pb^{2+} + 6H_2O$	$\Rightarrow PbO_2 + 4H_3O^+$	+2e ⁻	+1,46
Au	$\Rightarrow Au^{3+}$	+3e ⁻	+1,50
$Mn^{2+} + 12 H_2O$	\Rightarrow MnO ₄ ⁻ + 8H ₃ O ⁺	+5e ⁻	+1.51
$3 H_2 O + O_2$	$\Rightarrow O_3 + 2H_3O^+$	+2e ⁻	+2,07
2F ⁻	\Rightarrow F ₂	$+2e^{-}$	+2.87