Grundlagen der Chemie für Studierende des Maschinenbaus, Prof. Grunwaldt und Prof. Heske

Chemistry for Students of Mechanical Engineering
Studiengang Bachelor

Thursday, 13th March 2014, 14:00-17:00

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 or explain a point, a clear sketch is often sufficient!

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

Conversion from % to mark:

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

Question 1:

(a) What is the difference between an element and a chemical compound? What is the difference between isotopes of the same element? (3P)

An element is composed of atoms all with the same number of protons (atomic number).
A compound contains atoms of more than one element (different numbers of protons).
Isotopes are atoms with the same number of protons, but different numbers of neutrons.

(b) What do the numbers in the nuclide $^{7}_{3}\mathrm{Li}$ tell us? (1P)

The atomic number Z (number of protons in nucleus) = 3. Atomic weight (protons + neutrons) = 7, so number of neutrons = 7-3 = 4.

(c) Give the electronic configurations of sodium (Na) and nitrogen (N), showing clearly how electrons are distributed between orbitals of the same energy.

Na (Z=11): $1s^2 2s^2 2p^6 3s$ N (Z=7): $1s^2 2s^2 2p_x 2p_y 2p_z$

(d) Explain why compounds of the formulae Na_2O and NH_3 form from their respective constituent elements. Give reasons for your answer. (4P)

Na attains inert gas configuration by losing its one valence (forming Na^+).
N reaches inert gas configuration by gaining three electrons (through formation of three covalent bonds.

(e) In the analytical method Atomic Absorption Spectroscopy, the substance to be analysed is first atomised, the atoms are then introduced into a beam of polychromatic light, and the intensity of the transmitted light is measured as a function of wavelength.

What results does one obtain from this? Why can it be used as an analytical method? (1P)

A series of sharp absorption lines, at wavelengths characteristic for the atoms of the elements present is seen. The amount of light absorbed at one of these

wavelengths is proportional to the amount of the element present in the sample.

This method is based on a principle that is important for the description of the electronic structure of atoms. What is this principle? (2P)

That the electrons in an atom can only adopt certain (quantised) energies.

(f) Name the four Quantum Numbers, that determine the energy levels of an electron in an atom. State briefly the significance of each Quantum Number. (4P)

n – principal QN (size of the orbital)
l – auxiliary QN (shape of the orbital)
m – magnetic QN (orientation of the orbital)
s – spin QN (orientation of the electron's spin)

(g) On which physical principle is the separation process Solvent Extraction based? (1P)

The partition of a dissolved substance between two immiscible liquids

Question 2:

(a) What are the oxidation states of the nitrogen atoms in the following compounds: N_2O, N_2, NH_3, NO_2? (2P)

N_2O: +1, N_2: 0, NH_3: -3, NO_2: +4

(b) The formation of ammonia (NH_3) from the elements is an exothermic equilibrium reaction. Give the equation for the reaction, and explain why entropy decreases as the reaction proceeds. Why was it such a great challenge to develop an efficient industrial synthesis of ammonia, for which Carl Bosch obtained the Nobel Prize?

$N_2 + 3\ H_2 \leftrightarrows 2\ NH_3$
The entropy decreases, as there are fewer gas molecules on the right-hand side.
Very high activation energy, so rate of uncatalysed reaction very slow.

In which direction is the equilibrium position shifted, if:

(i) the temperature is increased?
Towards starting materials (i.e. endothermic direction)
(ii) the pressure is increased?
Towards product (NH_3), since fewer gas molecules on this side
Explain your answer, noting that the reaction is exothermic (ΔH = -46 kJ/mol). (6P)

(c) Fritz Haber, who taught in Karlsruhe, discovered in 1909 that the synthesis of ammonia from the elements required the use of a catalyst, and at first used metallic osmium for this.

Why must a catalyst be used?
To reduce the high activation energy and so increase the rate of reaction.
Does this alter the equilibrium position?
No
Osmium is very expensive. What catalyst is now used industrially? (3P)
$Fe_3O_4/Al_2O_3/KOH$

(d) Ammonia, or alternatively urea, can be used to remove polluting substances from waste gases.

Which toxic gases are formed in internal combustion motors?
Unburned hydrocarbons, soot, CO, NO, NO_2

What group of toxic waste gases can be removed using ammonia? Give the reaction equations.

NO, NO_2 (or NO_x)

$6\ NO + 4\ NH_3 \rightarrow 5\ N_2 + 6\ H_2O$

$6\ NO_2 + 8\ NH_3 \rightarrow 7\ N_2 + 12\ H_2O$

Why is urea used instead of ammonia in mobile systems such as car engines?

NH_3 is toxic; urea is easier to handle (6P)

(e) The use of gas-powered motors is being encouraged. What volume (in m^3) of CO_2 is produced by the combustion of 2.24 m³ of methane (in both cases at 273K und 1 bar)? What is the mass of this CO_2 in kg? (C: 12 g mol^{-1}, H: 1 g mol^{-1})

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$ (1mol CH_4 → 1 mol CO_2)

$V(CO_2) = V(CH_4) = 2.24\ m^3$

$2.24\ m^3$ = 2224 litres = 100 mol; $FW(CO_2) = 44\ g\ mol^{-1}$; $m(CO_2) = 100 \times 44g = 4.4$ kg (2P)

(f) What is understood by the "Greenhouse Effect"?

Warming of the atmosphere by absorption of heat emitted from the earth's surface by greenhouse gases and the re-irradiation of some of this heat back to the earth.

Which property of the CO_2 molecule makes it a significant greenhouse gas?

Its strong absorption of infrared radiation (heat) (2P)

Question 3:

(a) According to Brønsted and Lowry, what is understood by acids and bases?

Acids are proton donors; bases are proton acceptors.

Give the reaction equation for the protolysis equlibrium of ethanoic acid (CH_3COOH) in water. State which of the four species involved are acting as acids, and which as bases.

$CH_3COOH + H_2O \leftrightarrows (CH_3COO)- + H_3O^+$

$acid_1$ $base_2$ $base_1$ $acid_2$ (3P)

(b) At room temperature, the solubility product of $PbCl_2$ $L_{PbCl2} = 3.2 \times 10^{-5}$ (mol/l)³. What is the concentration of Pb^{2+} (In mol/l) in a saturated solution of $PbCl_2$ in pure water and what would the concentration of Pb^{2+} be if the water contains 0.1 mol/l chloride?

$[Pb^{2+}][Cl^-]^2 = 3.2 \times 10^{-5}\ (mol\ l^{-1})^3$

In pure water: $[Cl^-] = 2[Pb^{2+}]$

$[Pb^{2+}] \times 4[Pb^{2+}]^2 = 4[Pb^{2+}]^3 = 3.2 \times 10^{-5}\ (mol\ l^{-1})^3$

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

$[Cl^-] = 0.1\ mol^{-1} \rightarrow [Pb^{2+}] \times (0.1)^2 = 3.2 \times 10^{-5}\ (mol\ l^{-1})^3$

$[Pb^{2+}] = 3.2 \times 10^{-3}\ mol\ l^{-1}$

Use these Pb^{2+} concentrations to calculate the solubility of $PbCl_2$ (in g/l) in the two solutions. $M(PbCl_2)$ = 278.2 g/mol (4P)

Pure water: $L_{PbCl2} = (2 \times 10^{-2}) \times 278.2 = 5.564$ g/l

$[Cl^-] = 0.1\ mol^{-1}$: $L_{PbCl2} = (3.2 \times 10^{-3}) \times 278.2 = 0.89$ g/l

(c) Determine the stoichiometric coefficients for the "Thermite" redox reaction:

[**1**] Fe_2O_3 + [**2**] Al → [**2**] Fe + [**1**] Al_2O_3

Which substance is acting as a reducing agent, and which as an oxidising agent?

Reductant: Al; oxidant: Fe_2O_3 (3P)

What is the potential (in volts) of a Co/Zn Daniell cell, if 1 molar solutions of cobalt(II) sulphate and zinc(II) sulphate are used? What are the redox half-reactions? (n.b. standard reduction potentials are listed on the last page of the Klausur).

$Zn \rightarrow Zn^{2+} + 2\ e^-$ (Oxidation)
$Co^{2+} + 2\ e^- \rightarrow Co$ (Reduktion)
$E^o = -0{,}28 - (-0{,}76)\ V = 0{,}48\ V$

Will the potential of this Galvanic cell increase or decrease, if the concentration of Co^{2+} is decreased? What is the equation that can be used to calculate this (give either the equation itself or its name)?

$E_{cell} = E^o + (RT/zF)\ ln\{[ox]/[red]\}$ = Nernst equation
In the cell, $[ox] = [Co^{2+}]$.
If $[Co^{2+}]$ decreases, E_{cell} will decrease (5P)

Two glass beakers each contain a piece of tin metal (Sn). One beaker is then filled with a 1 mol/l solution of $CuSO_4$, the other with a 1 mol/l solution of $FeSO_4$. In each case, use the table of Standard Reduction Potentials on the last page to explain whether you expect a chemical reaction to take place.

$Sn + Cu^{2+} \rightarrow Sn^{2+} + Cu$
$E = E^o(Cu^{2+}/Cu) – E^o(Sn^{2+}/Sn) = +0.34 – (-0.14) = + 0.44\ V > 0$.
Reaction will take place, metallic Cu will be deposited
$Sn + Fe^{2+} \rightarrow Sn^{2+} + Fe$
$E = E^o(Fe^{2+}/Fe) – E^o(Sn^{2+}/Sn) = -0.41 – (-0.14) = - 0.27\ V < 0$.
No reaction (2P)

(f) Give the equations for the two redox half-reactions that take place when a lead accumulator (car battery) is discharged.

$Pb + SO_4^{2-} \rightarrow PbSO_4 + 2\ e^-$
$PbO_2 + SO_4^{2-} + 4\ H_3O^+ + 2\ e^- \rightarrow PbSO_4 + 6\ H_2O$

What happens when the accumulator is recharged?

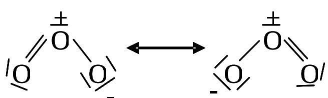
Reactions are reversed (3P)

Question 4:

(a) Give the name of an industrial method for the production of hydrogen from hydrocarbons. Give the corresponding reaction equation(s). (2P)

Steam reforming (partial or autothermal oxidation also OK)
$C_nH_m + n\ H_2O \rightarrow n\ CO + (n+ m/2)\ H_2$

(b) Draw the Lewis-structure for the ozone (O_3) molecule, and give the reaction equation for the formation of ozone. (2P)



$O_2(g) \rightarrow 2O(g)$ (high T or UV irradiation)
$O(g) + O_2(g) \rightarrow O_3(g)$

(c) State three industrially-important properties of metals. (3P)

Three from: ***electrical conductance***
thermal conductivity
ductility
high tensile strength
high melting point

(d) What is understood by Passivation? (1P)

The formation of a thin stable layer of metal oxide on the surface of a metal, that protects it from further oxidation.

(e) State a property of aluminium that makes it an important industrial material.

Low density or passivation

The main raw material for the production of aluminium is the ore bauxite, which is a mixture of Al_2O_3 and Fe_2O_3.

What are the four principal steps in the production of aluminium from bauxite? Give the equations for the reactions that take place in each stage. (6P)

(i) Reaction with aqueous NaOH at 200 ºC and separation of Fe_2O_3 by filtration:

$Al_2O_{3(s)} + Fe_2O_{3(s)} + 3H_2O + 2NaOH \rightarrow 2Na^+ + 2[Al(OH)_4]^-_{(aq)} + Fe_2O_{3(s)}$

(ii) Re-precipitation by acidification:

$[Al(OH)_4]^-_{(aq)} + H^+ \rightarrow Al(OH)_3\downarrow + H_2O$ ***Solid $Al(OH)_3$ isolated by filtration.***

(iii) Calcination:

$2Al(OH)_3 \rightarrow Al_2O_3 + 3H_2O$ ***(1000 ºC)***

(iv) Smelting flux electrolysis in molten cryolite at 900 ºC:

Cathode: $Al^{3+} + 3e^- \rightarrow Al_{(l)}$

Anode: e.g. $O^{2-} + C \rightarrow CO + 2e^-$

(f) Most of the sulphur that is needed for the production of sulphuric acid is obtained from the processing of mineral oil or natural gas.

Which sulphur-containing compound is obtained in this way? Which process is used to obtain sulphur from this compound? Give the reaction equations.

H_2S.

Claus Process: $2 H_2S + 3 O_2 \rightarrow 2 SO_2 + 2 H_2O$ ***and*** $SO_2 + 2 H_2S \rightarrow 3 S + 2 H_2O$

Give the equations of the reactions that take place during the industrial production of sulphuric acid from sulphur.

$S + O_2 \rightarrow SO_2$,

$2 SO_2 + O_2 \rightleftarrows 2 SO_3$

$SO_3 + H_2O \rightarrow H_2SO_4$ (5P)

(g) In a Blast Furnace, partial oxidation of coke results in formation of the reducing agent CO. This is also involved in the Boudouard equilibrium, by which finely-divided carbon is formed which dissolves in the liquid iron.

Give the reaction equation for the Boudouard equilibrium.

$CO_2 + C \leftrightarrows 2 CO$

What disadvantageous effect does this dissolved carbon have on the "pig iron"?

It becomes brittle

Give the name of a process that is used to reduce this carbon content during the production of steel.

Air-refining (3P)

(h) What is understood by corrosion

Destruction of materials via redox reactions

and what is a local element?

Contact between two metals of different electronegativity (or a more noble and a less noble metal) in the presence of a conducting electrolyte, leading to bimetallic corrosion. (2P)

(i) Give two methods for protecting metals from corrosion.

Coatings (paint, plastic, enamel)
Sacrificial electrodes (Mg or Zn)
Passivation (either natural: Zn, Al, or through addition of e.g. Cr)
Electroplating or galvanisation (2P)

(j) Give the equations of the reactions that take place when iron rusts in moist air.

$Fe(s) \rightarrow Fe^{2+}(aq) + 2 e^-$

$O_2(g) + 2 H_2O + 4 e^- \rightarrow 4 OH^-(aq)$

$Fe^{2+}(aq) + 2 OH^-(aq) \rightarrow Fe(OH)_2(s)$

($Fe + \frac{1}{2} O_2 + H_2O \rightarrow Fe(OH)_2$ ***also OK***)

Then $2 Fe(OH)_2(s) + \frac{1}{2} O_2 \rightarrow Fe_2O_3(s) + H_2O$ (4P)

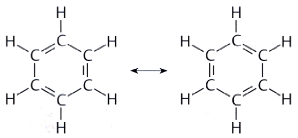
Question 5:

(a) What is the hybridisation of carbon atoms involved in single, double and triple bonds, respectively? In each case, what is the three-dimensional geometry of the bonds to the central carbon atom? (3P)

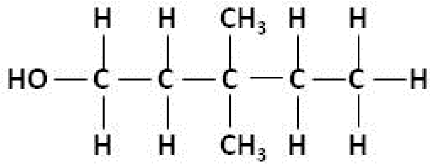
Single bonds: sp^3 hybridisation, tetrahedral geometry with bond angles ca. 109^o
Double bond: sp^2 hybridisation, trigonal planar geometry with bond angles ca. 120^o
Triple bonds: sp hybridisation, linear geometry with bond angle ca. 180^o

(b) Give three structural characteristics of the benzene molecule, and draw the Lewis-structures of the two mesomeric structures. What is the hybridisation of the carbon atoms? (3P)

3 from: planar hexagon of C atoms, all C-C bonds equal length, bond angles 120^o, 6 delocalised π-molecular orbitals.
Hybridisation: sp^2

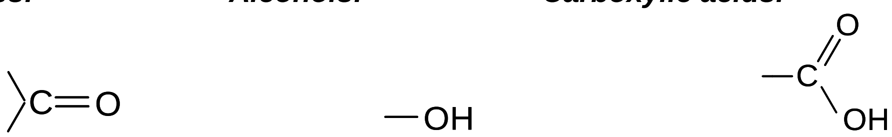


(c) Give the Lewis-structure of the 3,3-dimethylpentan-1-ol molecule. (2P)



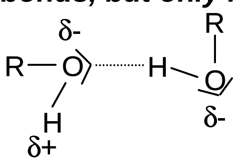
(d) Draw the Lewis-structures of the characteristic functional groups of ketones, alcohols and carboxylic acids. (3P)

Ketones: ***Alcohols:*** ***Carboxylic acids:***



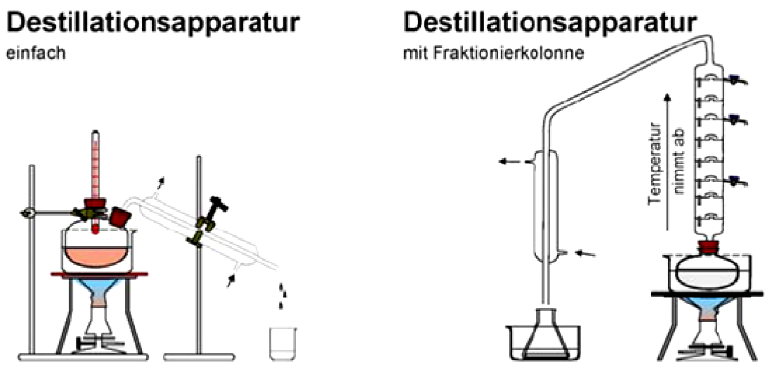
(e) Explain why an alcohol has a much higher boiling point than the corresponding alkane with the same number of carbon atoms. Why is ethane hydrophobic, whereas ethanol is hydrophilic? (2P)

Higher boiling point: -OH groups of alcohol form intermolecular hydrogen bonds, but only much weaker Van der Waals forces between alkane molecules



Ethanol molecules can form H-bonds to surrounding water molecules; ethane cannot.

(f) Describe using a simple sketch the difference between a simple distillation and distillation using a fractionating column. (2P)



A sketch that clearly illustrates the difference is enough!

(g) Which pollutants are formed when heavy heating oil is burned with an excess of air in a power station? (5P)

NO, NO_2 (or NO_x), CO, soot, SO_2, ash

Name the process, by which the nitrogen oxides can be removed from the flue gases. Which reagent is used?

Selective Catalytic Reduction (SCR). Ammonia (NH_3) (n.b. in power stations NH_3 is used rather than urea)

Periodic table

Key:

1	Atomic number, Z
H	Element symbol
1.008	Relative atomic mass, A_r

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 **H** 1.008																	2 **He** 4.00
3 **Li** 6.94	4 **Be** 9.01											5 **B** 10.81	6 **C** 12.01	7 **N** 14.01	8 **O** 16.00	9 **F** 19.00	10 **Ne** 20.18
11 **Na** 22.99	12 **Mg** 24.31											13 **Al** 26.98	14 **Si** 28.09	15 **P** 30.97	16 **S** 32.06	17 **Cl** 35.45	18 **Ar** 39.95
19 **K** 39.10	20 **Ca** 40.08	21 **Sc** 44.96	22 **Ti** 47.90	23 **V** 50.94	24 **Cr** 52.01	25 **Mn** 54.94	26 **Fe** 55.85	27 **Co** 58.93	28 **Ni** 58.69	29 **Cu** 63.54	30 **Zn** 65.37	31 **Ga** 69.72	32 **Ge** 72.59	33 **As** 74.92	34 **Se** 78.96	35 **Br** 79.91	36 **Kr** 83.80
37 **Rb** 85.47	38 **Sr** 87.62	39 **Y** 88.91	40 **Zr** 91.22	41 **Nb** 92.91	42 **Mo** 95.94	43 **Tc** 98.91	44 **Ru** 101.07	45 **Rh** 102.91	46 **Pd** 106.4	47 **Ag** 107.87	48 **Cd** 112.40	49 **In** 114.82	50 **Sn** 118.71	51 **Sb** 121.75	52 **Te** 127.60	53 **I** 126.90	54 **Xe** 131.30
55 **Cs** 132.91	56 **Ba** 137.34	**La–Lu**	72 **Hf** 178.49	73 **Ta** 180.95	74 **W** 183.85	75 **Re** 186.2	76 **Os** 190.2	77 **Ir** 192.2	78 **Pt** 195.08	79 **Au** 196.97	80 **Hg** 200.59	81 **Tl** 204.37	82 **Pb** 207.19	83 **Bi** 208.98	84 **Po** 210	85 **At** 210	86 **Rn** 222
87 **Fr** 223	88 **Ra** 226.03	**Ac–Lr**	104 **Unq**	105 **Unp**	106 **Unh**	107 **Uns**	108 **Uno**	109 **Une**									

Lanthanoids	57 **La** 138.91	58 **Ce** 140.12	59 **Pr** 140.91	60 **Nd** 144.24	61 **Pm** 146.92	62 **Sm** 150.35	63 **Eu** 151.96	64 **Gd** 157.25	65 **Tb** 158.92	66 **Dy** 162.50	67 **Ho** 164.93	68 **Er** 167.26	69 **Tm** 168.93	70 **Yb** 173.04	71 **Lu** 174.97
Actinoids	89 **Ac** 227.03	90 **Th** 232.04	91 **Pa** 231.04	92 **U** 238.03	93 **Np** 237.05	94 **Pu** 239.05	95 **Am** 241.06	96 **Cm** 244.07	97 **Bk** 249.08	98 **Cf** 252.08	99 **Es** 252.09	100 **Fm** 257.10	101 **Md** 258.10	102 **No** 259	103 **Lr** 262

Reduzierte Form	⇌ Oxidierte Form	$+z\,e^-$	Standardpotential $E°$ in V
Li	⇌ Li^+	+ e^-	−3,04
K	⇌ K^+	+ e^-	−2,92
Ba	⇌ Ba^{2+}	$+2\,e^-$	−2,90
Ca	⇌ Ca^{2+}	$+2\,e^-$	−2,87
Na	⇌ Na^+	+ e^-	−2,71
Mg	⇌ Mg^{2+}	$+2\,e^-$	−2,36
Al	⇌ Al^{3+}	$+3\,e^-$	−1,68
Mn	⇌ Mn^{2+}	$+2\,e^-$	−1,19
Zn	⇌ Zn^{2+}	$+2\,e^-$	−0,76
Cr	⇌ Cr^{3+}	$+3\,e^-$	−0,74
S^{2-}	⇌ S	$+2\,e^-$	−0,48
Fe	⇌ Fe^{2+}	$+2\,e^-$	−0,41
Cd	⇌ Cd^{2+}	$+2\,e^-$	−0,40
Co	⇌ Co^{2+}	$+2\,e^-$	−0,28
Sn	⇌ Sn^{2+}	$+2\,e^-$	−0,14
Pb	⇌ Pb^{2+}	$+2\,e^-$	−0,13
Fe	⇌ Fe^{3+}	$+3\,e^-$	−0,036
$H_2 + 2\,H_2O$	⇌ $2\,H_3O^+$	$+2\,e^-$	0
Sn^{2+}	⇌ Sn^{4+}	$+2\,e^-$	+0,15
Cu^+	⇌ Cu^{2+}	+ e^-	+0,15
$SO_2 + 6\,H_2O$	⇌ $SO_4^{2-} + 4\,H_3O^+$	$+2\,e^-$	+0,17
Cu	⇌ Cu^{2+}	$+2\,e^-$	+0,34
Cu	⇌ Cu^+	+ e^-	+0,52
$2\,I^-$	⇌ I_2	$+2\,e^-$	+0,54
$H_2O_2 + 2\,H_2O$	⇌ $O_2 + 2\,H_3O^+$	$+2\,e^-$	+0,68
Fe^{2+}	⇌ Fe^{3+}	+ e^-	+0,77
Ag	⇌ Ag^+	+ e^-	+0,80
Hg	⇌ Hg^{2+}	$+2\,e^-$	+0,85
$NO + 6\,H_2O$	⇌ $NO_3^- + 4\,H_3O^+$	$+3\,e^-$	+0,96
$2\,Br^-$	⇌ Br_2	$+2\,e^-$	+1,07
$6\,H_2O$	⇌ $O_2 + 4\,H_3O^+$	$+4\,e^-$	+1,23
$2\,Cr^{3+} + 21\,H_2O$	⇌ $Cr_2O_7^{2-} + 14\,H_3O^+$	$+6\,e^-$	+1,33
$2\,Cl^-$	⇌ Cl_2	$+2\,e^-$	+1,36
$Pb^{2+} + 6\,H_2O$	⇌ $PbO_2 + 4\,H_3O^+$	$+2\,e^-$	+1,46
Au	⇌ Au^{3+}	$+3\,e^-$	+1,50
$Mn^{2+} + 12\,H_2O$	⇌ $MnO_4^- + 8\,H_3O^+$	$+5\,e^-$	+1,51
$3\,H_2O + O_2$	⇌ $O_3 + 2\,H_3O^+$	$+2\,e^-$	+2,07
$2\,F^-$	⇌ F_2	$+2\,e^-$	+2,87