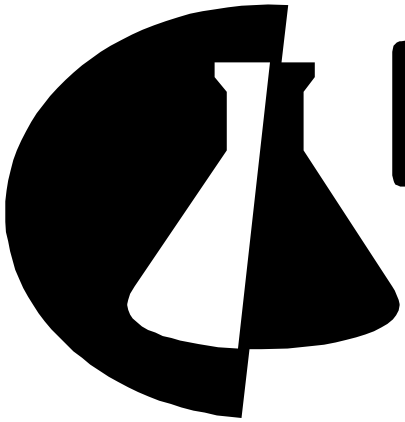

38. International Chemistry Olympiad Korea 2006

National German competition and IChO

Volume 12

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Volume 12

Preface

To become a member of the German IChO-team you have to be successful in four rounds of a national competition.

The problems to be solved in the 1st round are sent to all highschools. To solve the problems the students may use all resources available, e.g. textbooks etc.

All those students who solve about 70% of the tasks correctly will receive the problems of the 2nd round, which are to be solved in the same way as mentioned above. These problems are the most difficult ones in the whole competition.

The top 60 of the participants of the 2nd round are invited to the 3rd round, a one-week chemistry camp. Besides lectures, excursions to chemical plants or universities and cultural events there are two written theoretical tests of 5 hours each.

The top 15 of the 3rd round are the participants of the 4th round, a one-week practical training. There are two written five-hour tests - one theoretical and one practical - under the same conditions as at the IChO. Here the team is selected.

Responsible for organic questions: Dr. Wolfgang Bünder

Responsible for all other questions: Wolfgang Hampe

Responsible for the practical test: Dr. Wolfgang Bünder

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Part 1

The problem set of the four rounds

First Round (homework)

Problem 1-1 Correct Indications in a Catalog?

In catalogs of chemicals you find concentrated sulfuric acid, 95 -98 % solution. On the bottle shipped to a school is written ”1 L = 1.84 kg”.
To find out the real concentration a student dilutes 5 mL of it to 500 mL. Then he takes five samples of 10.00 mL each and titrates with standardized sodium-hydroxide solution (c(NaOH) = 0.1760 mol/L):

sample	1	2	3	4	5
V(NaOH) in mL	20.15	19.65	21.30	20.40	20.35

a) Calculate the concentration (mol/L) in the 500 mL solution.
b) What is the mass percentage of the original sulfuric acid?
c) Calculate the mole fraction of sulfuric acid in the original solution.

Problem 1-2 Production of Aluminium

You cannot imagine modern everyday life without aluminium.
Raw material for the production of aluminium is bauxite which contains aluminium oxide.

a) Name at least three advantages of aluminium as a substance compared to iron. Give disadvantages too.
Specify the approximate percentage of Al_2O_3 in bauxite, name deposits of bauxite which are actually exploited. Explain the origin of the name “bauxite“.

To produce aluminium aluminium oxide (corundum) has to be seperated from bauxite. Afterwards a fused salt electrolysis is made of a solution of corundum in cryolite. The temperature of the melt is about 970 °C, a current of 130 kA is used with an efficiency of 95% and a voltage of 5 to 7 V.

b) Describe the actually used process of seperation of aluminium oxide. Use reaction equations.

c) Give the formula of corundum and the reason why it is employed.
Write equations for primary and as the case may be secondary reactions at the anode and the cathode. Give a total reaction equation which includes the secondary reactions too.

d) Calculate the energy (in kWh), the mass of bauxite (which contains % of mass of Al_2O_3) and the mass of the anode material graphite to produce 1 t of aluminium.
Assume 5.0 V as voltage of the electrolysis and again a current efficiency of 95%.

The thermodynamical data of the table below are approxomately valid for 970 °C. They shall be used for the calculations in e).

	$Al_{(l)}$	$O_{2(g)}$	$Al_2O_{3(s)}$
$\Delta_f H$ in kJ/mol at 970 °C	48	38	- 1610
S in J/(K·mol) at 970 °C	78	238	98

Using the free enthalpie of the process $2\ Al_2O_3 \longrightarrow 4\ Al\ +\ 3\ O_2$ you approximately determine the voltage theoretically necessary for the electrolysis to give aluminium and oxygen. (As a matter of fact a higher voltage is needed.)

e) Calculate the theoretical voltage of the fused salt electrolysis.

f) Give the reason why aluminium can not be produced from an acidic aqueous solution of Al^{3+}-ions.

For the given chemical reactions the temperature dependence of ΔG is known:

$4\ Al\ +\ 3\ O_2 \rightleftarrows 2\ Al_2O_3$ $\quad \Delta G_1 = (-\ 3351.4 + 0.6264 \cdot T/K)\ kJmol^{-1}$ $\quad (T > 933\ K)$

$2\ C\ +\ O_2 \rightleftarrows 2\ CO$ $\quad \Delta G_2 = (-\ 221.06 - 0.17872 \cdot T/K)\ kJmol^{-1}$

$C\ +\ O_2 \rightleftarrows CO_2$ $\quad \Delta G_3 = (-\ 393.51 - 0.00286 \cdot T/K)\ kJmol^{-1}$

g) Calculate the minimum temperature above which the reduction of Al_2O_3 by carbon is theoretically possible. (Actually it is not possible because of the formation of Al_4C_3)

Problem 1-3 An Experiment to Do by Yourself

10 mL of a solution of Fe^{3+} and 30 mL of a solution of SCN^- are mixed. Both solutions have equal concentrations otherwise the effect cannot be seen.
Observation 1: A red solution forms.

10 mL of the red solution are filled up with water to 100 mL.
Observation 2: The colour of the solution turns to brown.

To one part of this diluted solution solid iron(III) chloride is added.
Observation 3: The colour changes to red.

To another part of the diluted solution ammonium thiocyanate is added.
Observation 4: The colour changes to red.

a) Interpret the four observations.

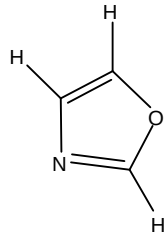
b) Why do the explanations of the observations 3 and 4 support the explanation of observation 2?

Problem 1-4 Substitution with Obstacles

Find an optimal way to synthesize 1-bromo-3-Chlorobenzene. Use only reactions with high yield.
Starting material for the synthesis is 1-chlorobenzene.
Account for the individuel steps of the synthesis.

Problem 1-5 Aromatic Heterocyclic Compounds

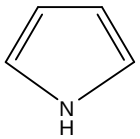
Oxazole is an aromatic heterocyclic compound with a five membered ring:



Oxazole

a) Draw the ring with its p orbitals and the orbitals with free electron pairs.
Explain why oxazole is aromatic.

b) Compare the alkalinity (acceptance of protons) between oxazole and pyrrole.



Pyrrole

Which of the N atoms in oxazole or in pyrrole is more alkalic?
Justify your decision using orbital images of oxazole and pyrrole.

Second Round (homework)

Problem 2-1: Chromium and Chromate

1. The redox couple chromium(III)/dichromate ($E°(Cr^{3+}|Cr_2O_7^{2-}) = +1.380$ V) is often used in analytical chemistry.

a) *Write the reaction equation for this redox system and check whether a solution of chromium(III)/ dichromate ($c(Cr^{3+})=c(Cr_2O_7^{2-})=1$ mol/L) is able to release elemental iodine from a neutral solution which contains iodide ($E(I^-|I_2) = E°(I^-|I_2) = +0.54$ V).*

The intense yellow colour of the chromate ions and the intense orange colour of the dichromate ions are often used to detect chromium. In an important preliminary test chromium(III) oxide is molten together with potassium nitrate and soda. In aqueous solutions reactions with hydrogen peroxide, sodium peroxodisulfate or elemental bromine are common to identify Cr(III).

b) *Write balanced equations of these four reactions. What is the role of potassium nitrate and sodium carbonate in the melting process?*

According to the standard potential of bromide/bromine ($E°(Br^-|Br_2) = + 1.065$ V) the reaction of chromiun(III) ions with bromine should not be suitable as a detection test.

c) *Why is it still possible to use bromine as a detecting agent? Refer your answer to the standard potential $E°(Br^-|Br_2)$. Show your calculations.*

In some detecting reactions the presence of certain compounds cause an interference, e.g. if you use hydrogen peroxide bromide and iodide ions must not be present, whereas using bromine there must not be an excess of Mn^{2+} ions.

d) *Account for these interferences.*

Another detection reaction for chromium is the reaction of dichromate with hydrogen peroxide. If it is positive an intense blue colour appears.
The reaction equation is

$$Cr_2O_7^{2-} + 4\ H_2O_2 + 2\ H^+ \longrightarrow 2\ CrO_5 + 5\ H_2O$$

e) *What is reduced during this reaction, what is oxidized? Allocate oxidation numbers.*

2. Magnetic measurements are an important method to determine the oxidation states of metal ions. You can measure the magnetic susceptibility and hence determine the magnetic moment. On the other hand you can calculate the relative magnetic moment μ - especially for centres of metals of the first transition series - by $\mu = \sqrt{n \cdot (n+2)}$ (n = number of unpaired electrons). Comparing these two values you may find the formal oxidations state.
An octahedral cyanide-containing complex of chromium, soluble in water, is able to

reduce other compounds. Its magnetic properties are determined by the number of unpaired electrons which are assumed not to interfere with each other (spin-only complex).

It shows the following susceptibility χ depending on temperature:

Temperature in K	Susceptibility in cm^3 / g
10	$2.74 \cdot 10^{-4}$
20	$1.37 \cdot 10^{-4}$
30	$9.15 \cdot 10^{-5}$
40	$6.86 \cdot 10^{-5}$
50	$5.49 \cdot 10^{-5}$
60	$4.57 \cdot 10^{-5}$
70	$3.92 \cdot 10^{-5}$
80	$3.43 \cdot 10^{-5}$
90	$3.05 \cdot 10^{-5}$
100	$2.74 \cdot 10^{-5}$
110	$2.49 \cdot 10^{-5}$
120	$2.29 \cdot 10^{-5}$
130	$2.11 \cdot 10^{-5}$

Temperature in K	Susceptibility in cm^3 / g
140	$1.96 \cdot 10^{-5}$
150	$1.83 \cdot 10^{-5}$
160	$1.71 \cdot 10^{-5}$
170	$1.61 \cdot 10^{-5}$
180	$1.52 \cdot 10^{-5}$
190	$1.44 \cdot 10^{-5}$
200	$1.37 \cdot 10^{-5}$
210	$1.31 \cdot 10^{-5}$
220	$1.25 \cdot 10^{-5}$
230	$1.19 \cdot 10^{-5}$
240	$1.14 \cdot 10^{-5}$
250	$1.10 \cdot 10^{-5}$
260	$1.06 \cdot 10^{-5}$

f) Plot the magnetic susceptibility as a function of temperature.

The magnetic property of this complex follows Curies Law $\chi = \frac{C}{T}$.

g) Determine the Curie constant C of this complex.

The relative magnetic moment in terms of the Bohr magneton is

$$\mu = \frac{\sqrt{3 \cdot R \cdot C \cdot M}}{N_A \cdot 9.274 \cdot 10^{-21} \text{erg} \cdot \text{Oersted}^{-1}}$$

$R = 8.314 \cdot 10^7 \text{ erg} \cdot K^{-1} \cdot \text{mol}^{-1}$

$M = 364.49 \text{ g} \cdot \text{mol}^{-1}$ $\quad N_A = 6.022 \cdot 10^{23} \cdot \text{mol}^{-1}$

$1 \text{ erg} = 1 \text{ g} \cdot \text{cm}^2 \cdot \text{s}^{-2}$ $\quad 1 \text{ Oersted} = 1 \text{ cm}^{-½} \cdot \text{g}^{½} \cdot \text{s}^{-1}$

h) Calculate the magnetic moment of the complex in Bohr magnetons (BM).

Hint: Magnetic measurements and calculations are conducted in the CGS-unit system with the basic units centimetre (cm), gram (g) and second (s). It is still used as all values of magnetic moments given in literature would have to change if you use SI units.

i) What ist the oxidation state of chromium in the complex?

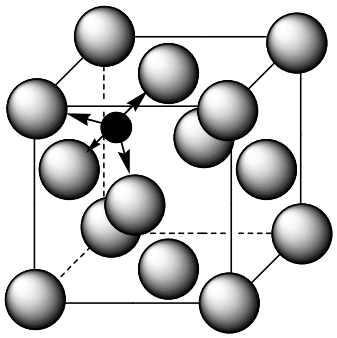
If you replace cyanide ions by ammonium molecules the complex shows paramagnetism.

j) Which magnetic moment (in BM) do you expect after the exchange of ligands for this complex. Account for your decision.

Problem 2-2 Spinels

In a narrower sense spinels are mixed oxides of the type $M(II)M'(III)_2O_4$ (M, M´ = metal cations), which owe their name to the so called "spinel" $MgAl_2O_4$.
The basis of their crystal lattices forms a cubic face-centred closed packing of oxide ions. In this packing there are cavities of different sizes, octahedral and tetrahedral holes. The following figure shows the position of a tetrahedral hole.

Fig.1 Cubic face-centred close packing with tetrahedral hole



In spinels M^{2+} ions occupy tetrahedral , M'^{3+} ions octahedral holes.

a) Draw one octahedral hole in a plot like fig. 1. Mark the centres of all the other octahedral holes.

b) Calculate the percentage of occupied tetrahedral and octahedral holes respectively of the spinel $CoAl_2O_4$.

The unit cell of a spinel lattice consists of eight cubes shown in fig. 1. At a certain temperature T the edge of the unit cell of $CoAl_2O_4$ has a length of 912 pm. Thereby directly neighbouring spheres of oxide ions touch each other.

c) Calculate the density of this compound at the temperature T.

d) Determine the maximal radius which the spherical M^{2+} ions and the spherical M'^{3+} ions may have in order to fit in the corresponding holes of this unit cell.

Besides the cubic face-centred packing of the oxide ions it depends on the ratio of cations and anions whether a compound is assigned to the spinels or not. This ratio has to be 3:4. These conditions provided even compounds with oxidation numbers of the metal ions diverging from +II und +III are assigned to spinels.

e) Which oxidation numbers may the metal ions in the spinel $SnCo_2O_4$ exhibit?

It is possible to determine the oxidation states of the metals in $SnCo_2O_4$ by measuring the paramagnetism.

f) Give the number of unpaired electrons per formula for all cases mentioned in e). Take also the possibility into account that not Sn^{n+}- but Co^{m+}-ions occupy the tetrahedral holes.

A spinel X shows a compositon of 43,9% O, 18,5% Al as well as 37,6% of other metal ions (mass percentage in each case)

g) Determine the other metal ions in the spinel X.

In a test the amount of M in MAl_2O_4 shall be found by an experimental redox titration. The students found the results of the preparatory experiment:

mL	0	1	2	3	4	5	6	7	8	9	10	10.5	11	11.5	12
E	0.60	0.71	0.73	0.75	0.76	0.77	0.77	0.78	0.79	0.81	0.83	0.85	1.20	1.47	1.51

Knowing from their lessons that only ions of Sn, Fe, Co, Ti, Mn und Cu have to be considered they are able to find out which kind of ions they will face in the test. On the sheet of paper found was not written what the meaning of ‚mL' and ‚E' should be but the students know from former instructions that ‚mL' means the volume of the added titrant (oxidizing or reducing agent) and ‚E' the potential of the solution.

h) Determine M. Find from the data above and by calculation how many electrons per ion M are released or absorbed.

Aufgabe 2-3 Physical Chemistry

There are 64.4 g of a mixture of NO_2 and N_2O_4 in a vessel (V = 15 L). The temperature is constantly held at 300 K.

a) Calculate the pressure in the vessel when the equilibrium NO_2/N_2O_4 has established.

In another vessel there was at the beginning a mixture of NO_2 and N_2O_4 in equilibrium under a pressure of 3.00 bar. The temperature is constantly 350 K all the time.
A valve of the vessel is defective. This leads to a decline in pressure which is proportional to the pressure in the vessel and amounts to 0.1 % s^{-1}.

b) Determine the partial pressure of NO_2 as a function of time and plot this function from t=0 h to t=1 h.

c) Determine the mole fraction of NO_2 in the vessel as a function of time and plot this function in the same time interval as in b).

d) Explain why the graphs proceed with a different trend.

Data of ΔH_f^0 and S_f^0 under standard conditions (p = 1 .0000·10^5 Pa (!), T = 298 K)

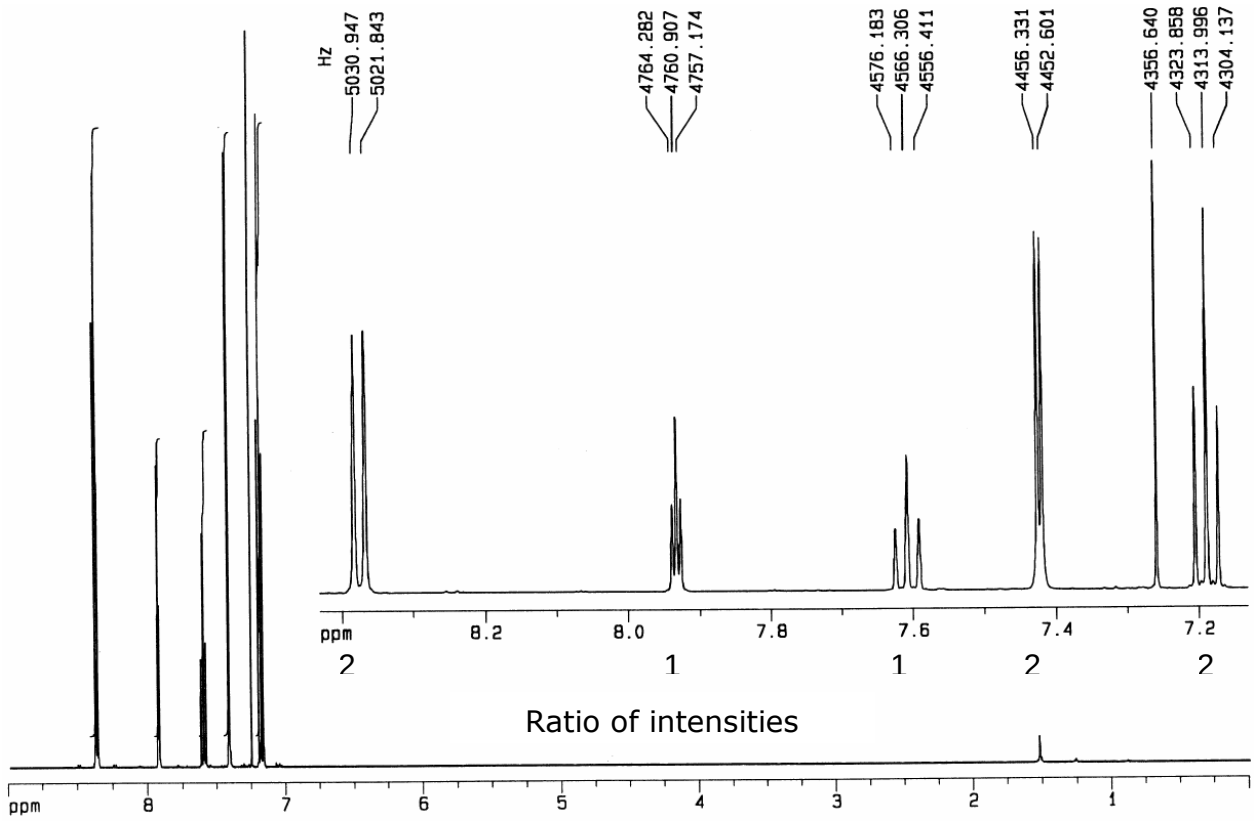
	ΔH_f^0 in kJ	S_f^0 in $JK^{-1}mol^{-1}$	Cp in $JK^{-1}mol^{-1}$
NO_2	33 .20	240 .1	37 .2
N_2O_4	9 .16	304 .3	77 .8

Hints:
Take for granted that NO_2 and N_2O_4 are ideal gases.
In a) take the values of 298 K for ΔH^0_f und S^0_f at T = 300 K.
In b) and c) the dependence of ΔH^0_f und S^0_f on temperature has to be taken into account.
In b) assume for simplification that the gas expands into a vacuum.

Problem 2-4: Structure and Reaction of an Organic Compound

Compound **D** naturally occurs in terms of manifold derivates. Essential oils (e.g. camo-mile oil) which are valued for their anti-inflammatory impact embody some of the deri-vates of **D**. **D** is a blue hydrocarbon, soluble not in water but in strong mineral acids. The dipole moment amounts to 1.08 Debye, unexpected high for a hydrocarbon. The elementary analysis shows water and carbon dioxid in the mass fraction of 1 : 6,11.

The following image is the ^{1}H-NMR-spectrum of compound **D**:
($CHCl_3$ = contaminant in the solvent $CDCl_3$ gives rise to the peak at 7,26 ppm)



*a) By means of the spectrum you are able to predict a property of the structure of **D** without knowing the exact structure.*
Specify this property of the structure.
*Calculate the ratio n(C):n(H) and the empirical formula of **D**.*

The exact structure of compound **D** is to be determined by classical synthesis.

It starts with 2,4-dinitrochlorobenzene and pyridine. These two compounds form in a nucleophilic substitution a compound **A**. **A** does not contain any chlorine.

A reacts with 2 equivalents dimethylamine eliminating 2,4-dinitroaniline to form an open chain compound **B**.

Next **B** reacts with cyclopentadiene in the presence of sodium methoxide. On basic conditions an additon takes place at first followed by an elimination of dimethylamine to form compound **C** ($C_{12}H_{15}N$).

In a vacuum at 200°C **C** eliminates dimethylamine to form the wanted compound **D**.

*b) Give the structures of the compounds **A** to **D**.*

*c) Map out a feasible reaction mechanism of the reaction of **B** with cyclopentadiene in the presence of sodium methoxide to form **C**.*

The ^{1}H-NMR- spectrum shows doublets and triplets.

*d) Explain how compound **D** generates a doublet and a triplet in the structure of **D.** Mark those carbon atoms that are connected to hydrogen atoms whose signal is a triplet.*

Knowing the structure of **D** you can now understand some of the unusual chemical and physical properties of **D** mentioned in the beginning.

e) Account for the following properties: Dipole moment, insolubility in water, solubility in mineral acids and blue colour.
(Give explanations or models, e.g. resonance structures)

Compound **D** is able to perform a lot of different reactions, for example:

- **D** reacts with tert. butanole in a substitution reaction catalysed by acids to form **F**.
- **D** reacts with Grignard reagents (addition reaction) to form a salt. Conversion with water and oxidation with tetrachloro parabenzochinone leads to an alkyl substituted derivate of compound **D**.

Two products are imaginable. One of them (**G**) occurs when using methyllithium, the other one (**H**) of the two conceivable isomers forms if triphenylmethyl lithium is used.

*f) Draw the structures of **F**, **G** and **H**. What makes the difference when using different compounds of alkyllithium to form **G** and **H** respectively?*

Even transition-metal compounds of **D** are known. If **D** reacts with lithium aluminium hydride followed by treatment with iron(II) chloride a red compound **I** forms, which is a mixture of several stereoisomers.
Precautious hydrogenation of this mixture of isomers leads to only one orange compound **J** ($C_{20}H_{26}Fe$).

*g) Draw the structures of al the isomers of **I** and of **J**.*

Problems for Round 3

Test 1 Berlin and Köln 29. 03. 2006: Problems 3-01 to 3-10

Test 2 Berlin and Köln 31. 03. 2006: Problems 3-11 to 3-20

time	5 hours,
your name	write it on **every** answer sheet,
relevant calculations	write them down in the appropriate boxes, otherwise you will get no points
atomic masses	use only the periodic system given,
constants	use only the values given in the table
answers	only in the appropriate boxes of the answer sheets. n**othing else will be marked**
draft paper	use the back of the pages of the problem booklet**,** but everything written there will not be marked,
problem booklet	you may keep it.

Good Luck

Useful formulas and data

$\Delta G = \Delta H - T \cdot \Delta S$ $\Delta G = - \Delta E \cdot z \cdot F$ $\Delta G = - R \cdot T \cdot \ln K_{th}$

$S^o(T) = S^o(298) + Cp \cdot \ln(T/298)$

$\Delta U_{reaction} = \Delta H_{reaction} + W$ (p,V-work only at constant pressure: $W = - p \cdot \Delta V$)

$K_{th} = K_p \cdot p_o^{-\Delta n}$; $K_{th} = K_c \, (mol/l)^{-\Delta n}$ $\ln (Kp_1/Kp_2) = -\Delta H/R \cdot (T_1^{-1} - T_2^{-1})$

$p \cdot V = n \cdot R \cdot T$

Nernst equation : $E = E_0 + \frac{R \cdot T}{z \cdot F} \cdot \ln (c_{Ox}/c_{Red})$

for metals $c_{Red} = 1$ mol/L

for non-metals $c_{Ox} = 1$ mol/L

rate laws

0. order	c	=	$c_o - k \cdot t$
1. order	c	=	$c_o \cdot e^{-k_1 \cdot t}$
2. order	c^{-1}	=	$k_2 \cdot t + c_o^{-1}$

Arrhenius equation: $k = A \cdot e^{-Ea/(R \cdot T)}$

A pre-exponential factor,
E_a activation energy

Bragg's equation: $n \cdot \lambda = 2a \cdot \sin\vartheta$

Law of Lambert and Beer: $E = \varepsilon \cdot c \cdot d$

ε molar absorption coefficient
d length of the cuvette
c conzentration

Henry's law for dissolving gases in water ($A(g) \rightleftharpoons A(aq)$)

$K_H = \frac{c(A(aq))}{p(A(g))}$ K_H Henry constant

Raoul's law for perfect solutions (mixtures):

$p_A = x_A \cdot p^*_A$

p_A vapor pressure of A in the mixture
x_A mole fraction of A in the mixture
p^*_A vapor pressure of the pure liquid A

$R = 8{,}314$ JK^{-1}mol^{-1} $F = 96485$ Cmol^{-1} $N_A = 6{,}022 \cdot 10^{23}$mol^{-1}

$p_o = 1{,}000 \cdot 10^5$ Pa 1 atm $= 1{,}013 \cdot 10^5$ Pa 1 bar $= 1 \cdot 10^5$ Pa

A periodic table was provided

Third Round, Test 1

Problem 3-1 (multiple choice, more than one answer may be correct)

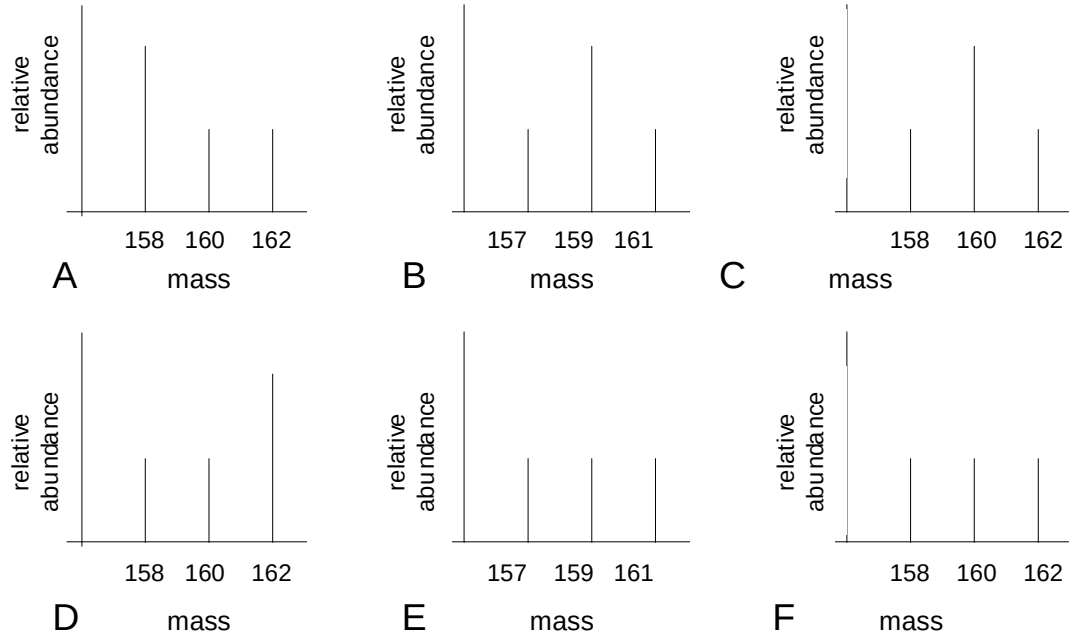
a) Catalysts are substances which

A) change the reaction rate
B) transform a reaction into a spontaneous reaction
C) shift the equilibrium of a reaction towards the products
D) change the activation energy

b) A, B and C are gases which react according to $A + B \rightleftharpoons 2\,C$, $K_p = 3.6$ (5000 K). In a system it can be observed that $p_A = 2.3$ bar, $p_B = 4.0$ bar and $p_C = 3.6$ bar. Which of the following statements is correct?

A) the system is at equilibrium
B) the system is not at equilibrium, A and B react to form C
C) the system is not at equilibrium, C reacts to form A and B
D) the system is at equilibrium, nevertheless a part of A and B reacts to form C
E) the system is at equilibrium, nevertheless a part of C reacts to form A and B

c) The two Br isotopes, ^{79}Br and ^{81}Br, have a natural molar abundance of about 50% each. Which is the expected mass spectrum of the parent cation, Br_2^+?



d) The ions below are isoelectronic. Which of the following sequences is correctly arranged according to their size?

A) $I^- < Te^{2-} < Ba^{2+} < Cs^+$	B) $Ba^{2+} < Te^{2-} < Cs^+ < I^-$	C) $Cs^+ < Ba^{2+} < Te^{2-} < I^-$
D) $Te^{2-} < I^- < Cs^+ < Ba^{2+}$	E) $Ba^{2+} < Cs^+ < I^- < Te^{2-}$	

e) A compound has the molecular formula C_4H_8. How many isomers may exist maximally?

A) 2	B) 3	C) 4	D) 5	E) 6

Problem 3-2: Metals

We are studying the following seven metals:
Aluminium, zinc, silver, calcium, potassium, copper and iron.

a) Which of these metals will "dissolve" in water?
b) Which of the remaining "dissolves" in hydrochloric acid?
c) Which of the those left over from a) evolves hydrogen with a solution of sodium hydroxide?
d) How can you dissolve the metals that have proved to be unreactive previously?

Answer in reaction equations.

There are a solution of lead(II) ions and a solution of copper (II) ions with equal concentrations. Two plates having the same size and mass of an unknown metal Me, which forms Me^{2+} ions, are put into these solutions, one in each.
Copper and lead precipitate on the plates. Later on the plates are removed simultaneously from the solutions, dried and weighed. During these procedures all the precipitated metal remains completely on the plates.
The plate taken out of the lead(II) solution shows an increase of mass of 19%, the other one a decrease of mass of 9,8%, relating to the starting mass of the plates.
Assume that the reaction rate of the precipitation of the metal is the same in both solutions .

e) Determine the unknown metal.

Problem 3-3 Impurities

During a custom control a parcel with heroin ($C_{21}H_{23}O_5N$) was found, however admixed with lactose ($C_{12}H_{22}O_{11}$).
1 g of this mixture was dissolved in water, the solution filled up to 100 mL. This solution had an osmotic pressure of 718 hPa at 25°C.

a) Calculate the composition (mass percentage) of the sample.

Desiccated anhydrous calcium chloride was stored in an improperly closed vessel. Thus it was partially hydrated again. A 150 g sample of this material was completely dissolved in 80 g of hot water, then the solution was cooled down to 20°C. On cooling 74.9 g of $CaCl_2 \cdot 6\ H_2O$ precipitated.
Solubility of calcium chloride at 20°C is 74.5 g of $CaCl_2$/100 g of water.

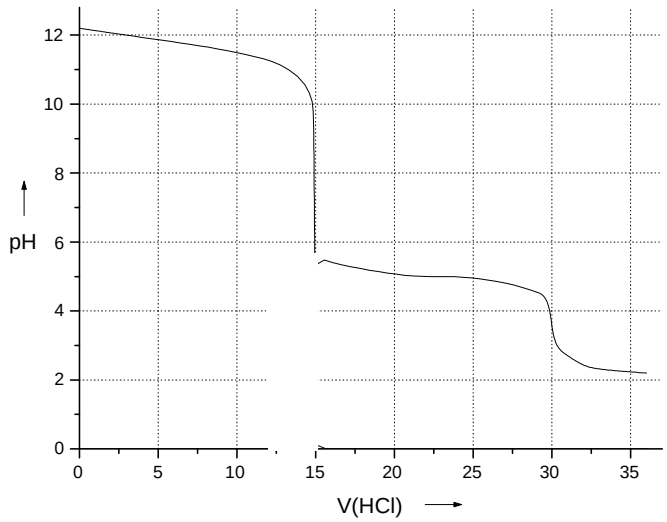
b) Determine the water content of calcium chloride in the 150 g sample (mole of water per 1 mol of $CaCl_2$)

Problem 3-4 Acids

The degree of protolysis in an aquous solution of acetic acid is 85% .

a) Determine the concentration of acetic acid (K_a = 1.74·10^{-5}),) and calculate the pH. How many g of acetic acid had to be dissolved to yield 1 L of this solution?

Sodium propionate was dissolved in a solution of sodium hydroxide and the solution was filled up to 250 mL. It showed a pH value of 12.18. 20 mL of this solution were titrated with hydrochloric acid of unknown concentration. The image below shows the results graphically.



b) Calculate the amount of sodium propionate dissolved (in g).

Problem 3-5 Equilibria

At T = 1000 K and p = 1.000·10^3 hPa (= $p_{standard}$) the degree of dissociation (homolytic dissociation into the elements) of water vapor and hydrogen chloride are 2.48·10^{-7} and 1.10·10^{-5} respectively.

Calculate the equilibrium constant and Gibbs free energy change for the reaction

$$4\ HCl + O_2 \rightleftharpoons 2\ Cl_2 + 2\ H_2O.$$

Problem 3-6 Structures

The valence shell electron pair repulsion theory of Gillespie (VSEPR-model) is an appropriate model to describe the stereochemical structure of molecular compounds.

a) Write down the basic principles of this theory.(One of them shows a relation between the binding electron pair and the electronegativity of the central ion and the ligand respectively.)

b) Using this model draw the possible structures of

CCl_4, $TeCl_4$ and XeF_4

If there exists more than one possible structure, give all of them and indicate, which of them is most likely. Account for your decision.

c) Anwer the questions in b) also for the following molecules

$BeCl_2$, $SnCl_2$, H_2S und XeF_2.

(Remember, there may be more than one structure for a molecule.)

Estimate the bond angles.

d) Phosphorus forms trihalides PX_3 with X = F, Cl, Br, I .

Which is the maximum size of the angle XPX according to the VSEPR-model?

Actually the angles of the trihalides are smaller.

Give the reason.

There is a tendency in the size of the angles from I to F.

Specify this tendency and give the reason for it.

e) With the help of the VSEPR model account for the changes of the following bond angles:

NH_3 107° $\longrightarrow$ PH_3 93,6°

and

PH_3 93,6° $\longrightarrow$ PF_3 96,3°

Problem 3-7 A Ceramic Hard Coating

Boron phosphide is a highly esteemed abrasion-resistant hard coating that is produced in the reaction of boron tribromide and phosphorus tribromide in a hydrogen atmosphere at high temperatures (>750°C). This ceramic material is used as a thin protecting thin on metal surfaces.

a) Give the equation for the formation of boron phosphide.

b) Draw 3-D structures of boron tribromide and phosphorus tribromide. What are the geometrical characteristics?

Boron phosphide crystillises in zinc-blende structure, derived from a cubic-close packed structure of boron atoms with phosphorus atoms located in tetrahedral holes.

c) Draw the structure of boron phosphide.

d) The lattice parameter of the unit cell ist 4,78 Å.

Calculate the density in kg/m^3.

e) Calculate the distance between a boron and a phosphorus particle.*

The Born-Landé formula can be used to calculate the lattice energy:

$$U_{lattice} = - f \cdot \frac{Z_+ \cdot Z_- \cdot M \cdot e^2}{r_+ + r_-}\left(1 - \frac{1}{n}\right) \qquad \text{(U in kJ/mol)}$$

The factor $f \cdot e^2$ amounts to 1390 when r_+ and r_- are given in Å. The Madelung constant M is 1.638 and n = 7. The charges of the ions ,Z^+ and Z^-, have to be inserted as absolute values, as integers.

f) Calculate the lattice energy of boron phosphide.

The rate (r) of formation of boron phosphide depends on the concentration of the reactants as given in the table.

temperature in °C	$c(BBr_3)$ in $molL^{-1}$	$c(PBr_3)$ in $molL^{-1}$	$c(H_2)$ in $molL^{-1}$	r in $mols^{-1}$
800	$2.25 \cdot 10^{-6}$	$9.00 \cdot 10^{-6}$	0.070	$4.60 \cdot 10^{-8}$
800	$4.50 \cdot 10^{-6}$	$9.00 \cdot 10^{-6}$	0.070	$9.20 \cdot 10^{-8}$
800	$9.00 \cdot 10^{-6}$	$9.00 \cdot 10^{-6}$	0.070	$18.4 \cdot 10^{-8}$
800	$2.25 \cdot 10^{-6}$	$2.25 \cdot 10^{-6}$	0.070	$1.15 \cdot 10^{-8}$
800	$2.25 \cdot 10^{-6}$	$4.50 \cdot 10^{-6}$	0.070	$2.30 \cdot 10^{-8}$
800	$2.25 \cdot 10^{-6}$	$9.00 \cdot 10^{-6}$	0.035	$4.60 \cdot 10^{-8}$
880	$2.25 \cdot 10^{-6}$	$9.00 \cdot 10^{-6}$	0.070	$19.6 \cdot 10^{-8}$

g) Determine the rate equation and the order of the reaction.
Calculate the rate constants at 800°C and at 880°C.

h) Calculate the activation energy of the formation of boron phosphide.

* Extract from a formulary concerning a tetrahedron with the edge a:

$V = a^3 \cdot \sqrt{2}/12$ $O = a^2 \cdot \sqrt{3}$ $h = a \cdot \sqrt{6}/3$ $r_{circumcircle} = a \cdot \sqrt{6}/4$ $r_{incircle} = a \cdot \sqrt{6}/12$

Problem 3-8 Determination of a Structure

An organic compound X contains 65.2% (m/m) carbon and 8.75% (m/m) hydrogen and no other element except oxygen.

X is known to be acidic and titration of 43,7 mg of this compound required 23.7 mL of sodium hydroxide solution (c = 0.0100 mol/L) to reach the equivalent point.

The molecular weight of X was determined to be less then 200 g/mol. There are no rings in X.

a) What is the molecular formula of X? What functional groups might be responsible for the acidity of the compound?
Calculate the number of double bonds in X.

Hint: $C_aH_bO_c$ contains $DBE = \frac{2a+2-b}{2}$ double bond equivalents.

The following reactions are known:

- X reacts with hydrogen in the presence of finely divided platinum metal to form a new compound A.
- Further reduction of A with sodium borohydride in ethanol produces substance B.
- Compound B was readily dehydrated upon warming with strong sulfuric acid to form C. C contains a double bond.
- ^{13}C-NMR of C revealed among other features the presence of a methyl group attached to a double bond.

b) What functional groups are consistent with the above reactions?

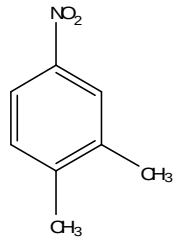
Ozonolysis of C followed by an oxidative work up gave only two fragments, acetic acid and the dicarboxylic acid HOOC-$(CH_2)_6$- COOH.
Similar cleavage of X itself yielded oxalic acid (HOOC-COOH) and a substance E which contained a carboxylic acid group.

c) Deduce the structures of the compounds A, B, C and of compound X.
There are two isomeric foms of X.

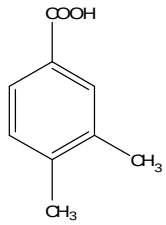
d) Depict the isomers of X. Which kind of isomerism do they show?

Problem 3-9 Synthesis of an Acid

Starting with compound X you get compound Y in high yield performing a multi-step synthesis.
Suggest how this could be done using structures in the reaction steps shown.



compound X



compound Y

Problem 3-10 Chirality of a Compound

The chirality of1-Bromo–3,4-dichlorocyclopentane shall be analysed.

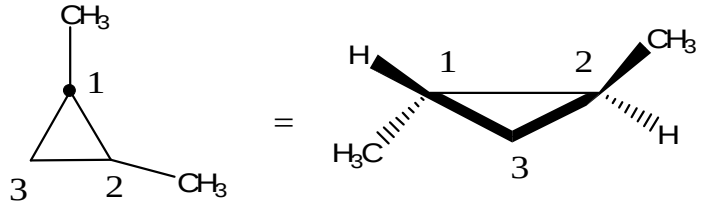
a) *Give the number of stereogenic centres of 1-bromo-3,4-dichlorocyclopentane and the maximum number of stereoisomers you may expect.*

Actually there are less isomers.

b) *Depict all structural formulas of the stereoisomers of 1-bromo-3,4-dichlorocyclopentane and account for the reason that there are less than the maximum number.*
Which of them show optical activity?

Hint for the images: In the picture of a three membered ring the thick point indicates an H atom above the plain of the ring.
If there is not such a point the H atom lies below that plain and therefore the substituent lies above it.

example:



You may use one of these ways of drawing.

Third round, test 2

Problem 3-11

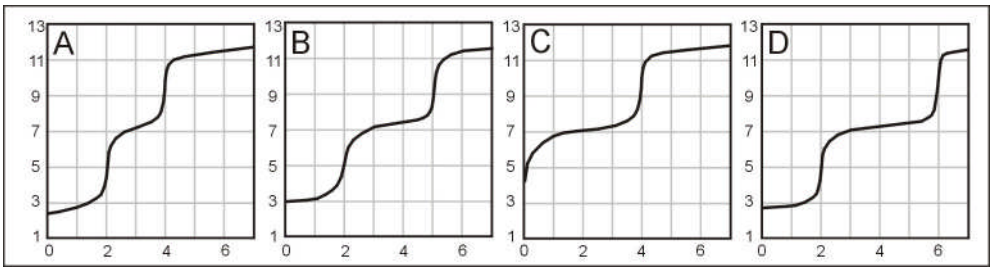
a) Chemical bonding in some species cannot be described by the Lewis model, i.e. assuming that atoms tend to attain nobel-gas configuration by sharing electron pairs. An example of such species is

A) NH^{4+}	B) BF_4^-	C) HF_2^-	D) SO_4^{2-}	E) $S_2O_3^{2-}$

b) Which of the following species has the smallest F - X - F bond angle:

A) BF_4^-	B) CF_2Cl_2	C) BF_3	D) BeF_2

c) Solutions containing H_3PO_4 and/or NaH_2PO_4 are titrated with a strong base. Assign the contents of these solutions to the titration curves (pH vs. volume of titrant) shown in the figure (for H_3PO_4: $pK_1 = 2.1$, $pK_2 = 7.2$, $pK_3 = 12.0$).

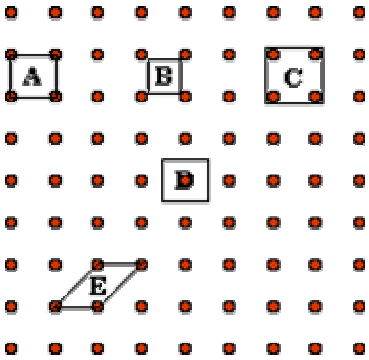


(i) The solution contains H_3PO_4 only

(ii) The solution contains H_3PO_4 and NaH_2PO_4 in the mole ratio 2:1

(iii) The solution contains H_3PO_4 and NaH_2PO_4 in the mole ratio 1:1.

d) Which of the parallelograms in the figure below are unit cells?



e) To 30 mL of a $Ba(OH)_2$ solution (0,10 mol/L) 30 mL of a H_2SO_4 solution are added (0,10 mol/L) . The increase of temperature is ΔT_1. The experiment is repeated with 90 mL of each of the same solutions and the rise in temperature is ΔT_2. Which of the following equation is correct?

A) $\Delta T_2 = \Delta T_1$	B) $\Delta T_2 = 3 \cdot \Delta T_1$	C) $\Delta T_2 = 6 \cdot \Delta T_1$	D) $\Delta T_2 = \frac{1}{3} \cdot \Delta T_1$

Problem 3-12 Acids

Tea-flavouring tablets are sold in packs of 200. The tablets in 1 pack have the weight of 25 g altogether. The tablets consist of citric acid (2-Hydroxy-1,2,3-propanetricarboxylic acid) and other additives.
Tasty tea can be made by dissolving 6 tablets in 1 L of tea. The pH of this solution is 4.2. (Tea leaves and the additives do not contribute to the change in pH-value)

a) Calculate the mass of citric acid in one tablet.
(Take only the first step of protolysis into consideration)

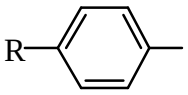
Actually the second step of protolysis plays a certain role and leads to a deviation of about 16% compared with the result of a).

b) Write all the equations which are necessary to calculate the mass of citric acid in one tablet if you include the second step.

A person with a stomach content of 2.30 L drinks two cups of the flavoured tea (320mL)- The original pH of the gastic juice was 2.1 before drinking the tea due to the hydrochloric acid excreted by the stomach. ($K_{a1,\ citric\ acid} = 3.98 \cdot 10^{-6}$, $K_{a2,\ citric\ acid} = 7.24 \cdot 10^{-11}$, $K_{a3,\ citric\ acid} = 6.3 \cdot 10^{-20}$)

c) What is the ratio between the protolysis of the citric acid in the tea and in the stomach?
(You may assume that the content of the stomach increases by drinking two cups of tea, the amount of H_3O^+ ions, however, remains practically constant.)

d) Assign the pK_a values 3.41, 4.01, 4,21, 4.35, 4.46 to the following benzoic acids



H, CH_3, NO_2, OCH_3, Cl

Explain your decisions.

Problem 3-13

Diluted sulphuric acid was dropping on 1 g of a compound A until no further reaction occurred. The products of the reaction were a gas B and a nearly colourless solution of C. After drying the amount of gas was 0.211 L (at 25° and 1.013 hPa) with a weight of 0.38 g.

The solution containing C was diluted to 100 mL. It was treated as follows.

I 50 mL of it were titrated with an acidic solution of potassium permanganate (c = 0.0200 mol/L), consumption 43.15 mL.

II H_2O_2 was added to the nearly colourless solution of C. The colour changed to pale yellow. Further addition of ammonia gives a brown precipitate D.This precipitate was

filtrated off and solved in diluted hydrochloric acid to yield a yellow solution of E. This solution turned to deep red after addition of potassium thiocyanate.

a) Identify A to E.

Show all your calculations and write balanced equations for all reactions.

b) Prove whether really 1 g of A reacted at the beginning. If not please give reasons.

Problem 3-14 Redox Reaction

A solution containing Sn^{2+} ions is titrated potentiometrically with a solution of Fe^{3+} ions at 25°C.

The standard reaction potentials are

$Sn^{4+} + 2\ e^- \rightleftarrows Sn^{2+}$ E° = 0.154 V

$Fe^{3+} + e^- \rightleftarrows Fe^{2+}$ E° = 0.771 V

a) Write the overall reaction equation and calculate the standard free energy change (ΔG°) of it.

b) Determine the equilibrium constant of the reaction.

20 mL of a solution of Sn^{2+} ions (c = 0.10 mol/L) is titrated with a solution of Fe^{3+} ions (c = 0.20 mol/L) . A saturated calomel electrode ($E°_{calomel}$ = 0.242 V) is used as reference electrode.

Calculate the voltage of the cell

c) when 5 mL of the Fe^{3+} solution are added,

d) at the equivalence point (hint: At the equivalence point is $E(Sn^{4+}/Sn^{2+}) = E(Fe^{3+}/Fe^{2+})$),

e) when 30 mL of the Fe^{3+} solution are added.

Problem 3-15 Kinetics

1.00 g of X, a pungent smelling organic liquid, was solved in water and filled up to 100.0 mL. 10.0 mL of this solution were titrated with a solution of potassium hydroxide (c = 0.5000 mol/L). When 43.5 mL of the potassium-hydroxide solution were added the colour of the solution containing phenolphthalein changed from colourless to pink.

a) Determine X.

Under the influence of a concentrated acid S a portion of X disintegrates to form water and a gas.

b) Write the reaction equation. Which acid S is likely to be used?

The following kinetic data of disintegration was obtained at 25°C and $p = 1.013 \cdot 10^5$ Pa:

t in s	0	50	100	150	200	∞
V(Gas) in mL	0	11.6	20.2	26.1	30.4	41.5

c) Calculate the amount of X in the beginning. Which reaction order do you expect? Account for your assumption.

d) Prove your assumption using the given data. Calculate the reaction-rate constant.

The decomposition of nitrosyl chloride between 150°C und 250°C follows a homogeneous reaction of the second order: $2\ NOCl \rightleftarrows 2\ NO + Cl_2$.

The following rate constants were found:

Temperature in °C	150	170	190	210	230
k (in $L \cdot mol^{-1} \cdot s^{-1}$) /$10^3$	3.65	12.9	43.0	123	370

e) Determine the activation energy of the reaction (preferably graphically).

Problem 3-16 UV-Spectroscopy

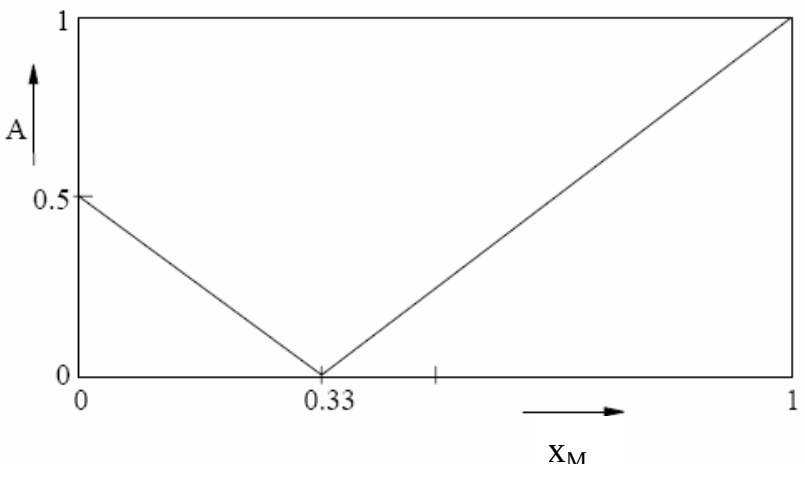
Using the law of Lambert and Beer you can use UV-spectrometry to determine the concentration of a substance in a solution. In doing so the absorption A ($A = {}^{10}\log (I_o/I)$) is measured.

Here the maximal and the minimal concentration of ferroin in a solution will be looked at by using a spectrometer at $\lambda = 512$ nm ($\varepsilon = 10500\ L mol^{-1} cm^{-1}$).

a) Calculate the lowest concentration of ferroin that can be determined in a 1 cm cuvet, if a 2% difference in light intensity still can be measured.

b) Calculate the highest concentration of ferroin that can be determined in a 1cm cuvet, if at least 2% of the incident light must reach the detector.

The composition of a complex between a metal M and a ligand L can also be determined. In this method the sum of concentrations of M and L is constant while their ratio is varied (Job's methode). The following graph of absorbance vs. mol fraction for a complex is given, whereby the mol fraction $x_M = c_M/(c_M + c_L)$ is varied (measurement at 552 nm).



c) Determine the composition of the complex.

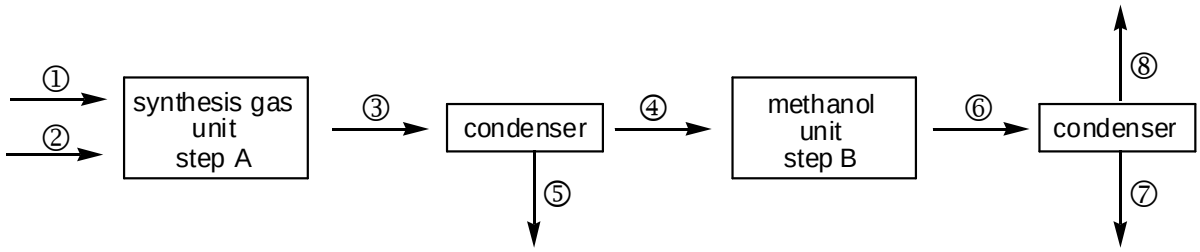
d) Which compound absorbs at x_M = 0, which at x_M = 1?
Show how you derive your answer.

e) Calculate the ratio of absorption coefficients of M and L.

f) Calculate the percentage of the incident light that has been transmitted through the solutions at x_M = 0 and at x_M =1, respectively.

Problem 3-17 An Industrial Process

Methanol is produced in large amounts from synthesis gas, a mixture of carbon monoxide and hydrogen, whereas synthesis gas is made von methane, a main component of natural gas, and water vapor.
The continuous process of the methanol synthesis is schematically shown in the figure below.
In step A synthesis gas is produced, in step B methanol.



Stream ① consists of methane at a pressure of 250.0 kPa and a temperature of 25.0°C, stream ② consists of water vapor under a pressure of 200.0 kPa and a temperature of 100,0°C.
The flows of stream ① and ② are 55,0 m^3/s and 150,0 m^3/s respectively.
Sream ③ leaving the synthesis gas unit is a mixture of synthesis gas and an excess of one reactant, which condenses at ≈ 25.0°C and is lead off via stream ⑤. Methanol is synthesised in step B.
Stream ⑥ contains methanol and the excess of one reactant. In the following unit methanol condenses at 25°C and is lead off in stream ⑦.
$\rho(CH_3OH)$ (l) = 0.791 g·mL^{-1}.

Assumptions: All gases are perfect, total conversion in steps A and B, complete seperation in the condensers.

a) Give the reaction equation of step A and of step B.

b) After step A and after step B there is an excess of one reactant. Which and how much of it is it in each case?

c) Calculate the flows in m^3/s (at 25°C and 101.3 kPa) of the following streams

(i) ⑤ *ii)* ⑦ *iii)* ⑧

Actually there is not a complete conversion in step B. The factory is designed in such a way that 2/3 of the CO is converted to methanol. In stream ④ the flow of CO is 1500 mol/s besides the associated amount of hydrogen (these values do not correspond to the data above).

d) Calculate the flow of CO, H_2 and methanol in stream ⑥ in mol/s.

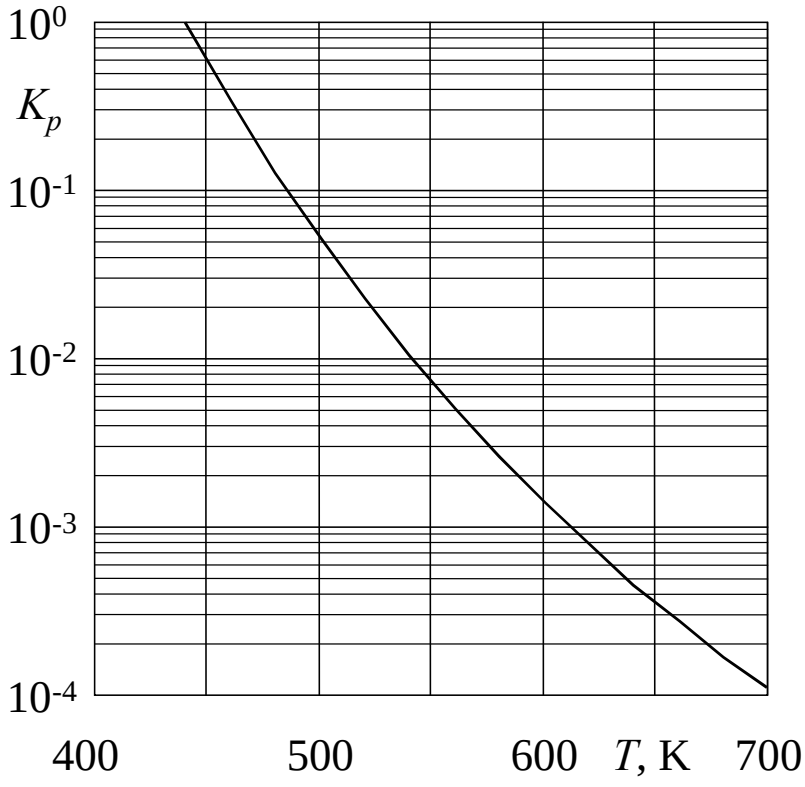
In stream ⑥ all species are gases. The total pressure 10 MPa.

e) Calculate the partial pressures in MPa of CO, H_2 and CH_3OH in stream ⑥.

When the methanol reactor is large enough the reaction goes to equilibrium. The partial pressures in stream ⑥ obey the equation:

$$K_p = \frac{p(CH_3OH)\cdot p_0^2}{p(CO)\cdot p^2(H_2)}$$

wherein p_0 is a constant (0.1 MPa) and K_p is a function of temperature as is shown in the figure below (the vertical scale is logarithmic).



f) Calculate K_p and ascertain the temperature T at which the reaction must be operated to achieve this equilibrium.

Aufgabe 3-18 Second Substituion

Toluen (Methylbenzene) is treated with a mixture of nitric acid and sulfuric acid.

a) Which compound(s) do you expect to be main product(s) of monosubstitution? Write the structural formula(s) of the compound(s).

b) Justify your decision by showing all intermediate stages and comparing their energies. What is the influence of the methyl group?

Phenol (hydroxybenzene) is treated with a mixture of nitric acid and sulfuric acid.

c) Which compound(s) do you expect to be main product(s) of monosubstitution? Write the structural formula(s) of the compound(s).

d) Justify your decision by showing all intermediate stages and comparing their energies. What is the influence of the OH group?

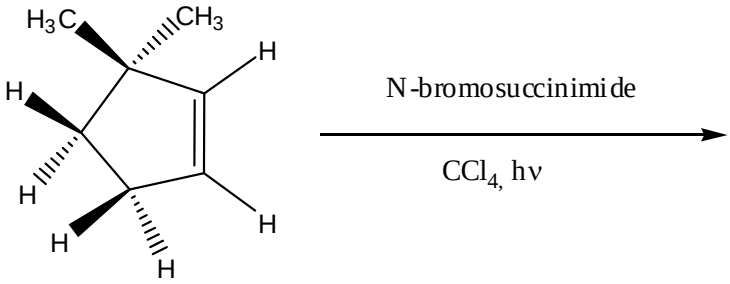
The substitution of p-methylphenol leads to 2-brom-4-methylphenol as main product.

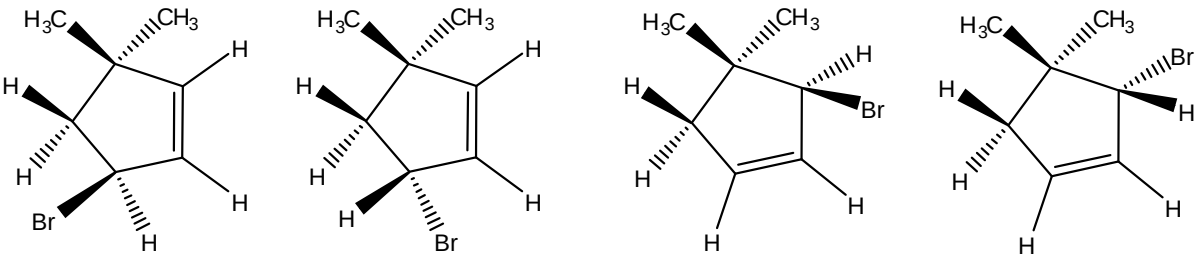
e) Give reasons for the formation of this bromo-compound.

Problem 3-19 Bromation of an Allyl Compound

The bromation with N-bromsuccinimide follows a free-radical mechanism.
Is this reaction carried out with a cyclic compound with allylic structure, the C=C -double bond persists and the appropriate products of bromation form.

The folowing reaction was performed:





I II III IV

a) Give a mechanism for the formation of these four compounds.

The exlplanation shjould include

- the formation and structure of the radical parent compound
- a reason for the stability of this radical structure
- the formation of the compounds I - IV from this structure.

b) Which kinds of isomerism do you find between the compounds?
Assign to each pair of compounds the approppriate kind of isomerism.

Problem 3-20 Reaction of an Organic Compound

2,3,5 Trimethylhept – 3- ene (compound A) reacts with a diluted solution of permanganate to form compound B. The reaction of B with periodic acid (HIO_4) leads to two products C and D with the same molecular formula ($C_5H_{10}O$).

Compound C shows a positive Tollens' reaction test. This test is negative when carried out with D, but D shows a positive iodoform test.

Compound D forms a yellow residue with 2,4-dinitrophenylhydrazine. Both compounds, C and D, form a pure hydrocarbon E when brought together with zinc amalgm and hydrochloric acid.

a) Give the structural formulas and the names of the compounds A to E.

Write down the equations of the reactions which lead to the compounds B,C,D and E. Give also the equations of the reactions with Tollens' reagent ($[Ag(NH_3)_2]^+$) and with 2,4 dinitrophenylhydrazine.

b) Which of the compounds shows optical activity? Mark the stereogenic centres with an asterix (*).

The compounds C and D can be formed directly from A.

c) Show this reaction with all its intermediates.

Fourth round (theoretical problems)

Problem 4-1

Radiotherapy involves the targetting of sites of active cell division by radionuclides to induce cell death. On the other hand nuclear imaging employs radioisotopes to reveal metabolic details of an organ. One such technique involves determination of a patient's blood volume. Three radiopharmaceutical compounds are available. Thy contain, respectively, the radioisotopes ^{71}Zn ($t_{1/2}$ = 2.4 minutes), ^{67}Ga ($t_{1/2}$ = 78.25 hours) and ^{68}Ge ($t_{1/2}$ = 287 days), each with an activity of $7.0 \cdot 10^7$ Bq/mL.

a) Calculate (for each pharmaceutical)

(i) the activity (in Bq/mL) after ¾ of an hour have elapsed and

(ii) the activity after ¾ of an hour and after dilution of 10mL of the pharmaceutical to 25 L

The modes of decay for these three isotopes are β-particle emission (^{71}Zn) and electron capture (^{67}Ga and ^{68}Ge).

b) What are the products of these decay processes?

10.25 mg of Ga, containing $5.0 \cdot 10^{-5}$ % (mol/mol) ^{67}Ga at the moment of synthesis, react completely to form gallium citrate ($GaC_6H_5O_6 \cdot 3H_2O$). Following syntheses the citrate sample is dissolved in 100mL of water. Eight hours after syntheses 1 mL of the solution is administered intravenously to a patient, and one hour later a 1 mL blood sample is taken from the patient. This blood sample has an activity of 165,6 Bq/mL.

c) Calculate the blood volume of this patient.

(1 Bq (Becquerel) = 1 decay/second)

Problem 4-2

In the construction industry limestone is used in great amounts as raw material. The technical process of lime burning is known since ancient times.
In this process the partial pressure of CO_2 ,$p(CO_2)$, depends on temperature:

T in K	800	900	1000	1100	1200	1300
$p(CO_2)$ in hPa	0.50	10.0	112	800	4050	16100

a) Calculate ΔG of the decomposition of calcium carbonate at each of the temperatures given.

b) Calculate the change of enthalpy ΔH° and the change of entropy ΔS°. Due to the reaction equation it is possible to predict the algebraic signof ΔS°. State the reason.

c) Above which temperature (in °C) is the reaction spontaneous (be exact upto 10°C)

Standard pressure $p_0 = 1.000 \cdot 10^5$ Pa
for simplification: ΔH and ΔS independent of temperature

Problem 4-3 Electrochemistry and Solibility Products

Given a solution A of silver nitrate and lead nitrate in water with $c(AgNO_3) = 0.050\ mol \cdot L^{-1}$ and $c(Pb(NO_3)_2) = 0.100\ mol \cdot L^{-1}$.

a) Calculate the pH of the solution.

10 mL of a solution of potassium iodid ($c = 0.250\ mol \cdot L^{-1}$) and nitric acid (($c = 0.200\ mol \cdot L^{-1}$) are added to 10 mL of solution A to form 20 mL of solution B with a sediment. Together with a silver electrode half cell 1 is generated.
Solution C is made by dissolving of $0.010\ mol \cdot L^{-1}$ silver nitrate and $0.040\ mol \cdot L^{-1}$ potassium thiocyanate. Together with a silver electrode half cell 2 is generated.
Both half cells are connected with a salt bridge to form an electrochemical cell.

b) Calculate the voltage of the cell, E_{cell} at 25°C (= 298 K).

c) Write the total cell reaction and calculate the eqilibrium constant of this reaction.

A small amount of sodium hydroxide is added to solution B.

d) How does the voltage change? Discuss two different cases depending on the amount of sodium hydroxide added.

Iron(III)-nitrate is added to solution C.

e) Explain how the voltage of the cell changes.

Data:

$Ag^+ + H_2O \rightleftharpoons AgOH + H^+ \qquad K_1 = 10^{-11.70}$

$Pb^{2+} + H_2O \rightleftharpoons PbOH^+ + H^+ \qquad K_2 = 10^{-7.80}$

$pK_{sp}(AgI) = 16 \qquad pK_{sp}(PbI_2) = 7.86 \qquad pK_{sp}(AgSCN) = 12 \qquad E°(Ag^+/Ag) = 0.799\ V$

Many elements e.g. vanadium form ions with different oxidation states. The standdard potentials are found in tables:

$V^{3+} + e^- \rightleftharpoons V^{2+} \qquad E° = -0.255\ V$

$VO^{2+} + 2\ H^+ + e^- \rightleftharpoons V^{3+} + H_2O \qquad E° = 0.377\ V$

$VO_2^+ + 2\ H^+ + e^- \rightleftharpoons VO^{2+} + H_2O \qquad E° = 1.00\ V$

$V(OH)_4^+ + 2\ H^+ + e^- \rightleftharpoons VO^{2+} + 3\ H_2O \qquad E° = 1.00\ V$

$V(OH)_4^+ + 4\ H^+ + 5\ e^- \rightleftharpoons V + 4\ H_2O \qquad E° = -0.25\ V$

f) Calculate $\Delta G°$ for the reaction $V^{2+} + H_2 \rightleftharpoons V + 2\ H^+$

Problem 4-4 Michaelis-Menten Mechanism

In some cases steady state approximation is used in the calculation of kinetics. The steady state approximation assumes that during the major part of the reaction the concentration of all reactive intermediates are constant and small.
An example are biochemical reactions of the type

$$S + E \underset{k_2}{\overset{k_1}{\rightleftharpoons}} ES \xrightarrow{k_3} P + E$$

S = substrate (e.g. penicillin) E = enzyme (e.g. β-lactamase)
ES = enzym-substrat-complex P = product.

It is assumed that the pre-equilibrium reaction is installed very quickly, so that the reverse reaction can be neglected and that the concentration of S is much larger than that of E.

a) Show that these assumptions lead to the equation

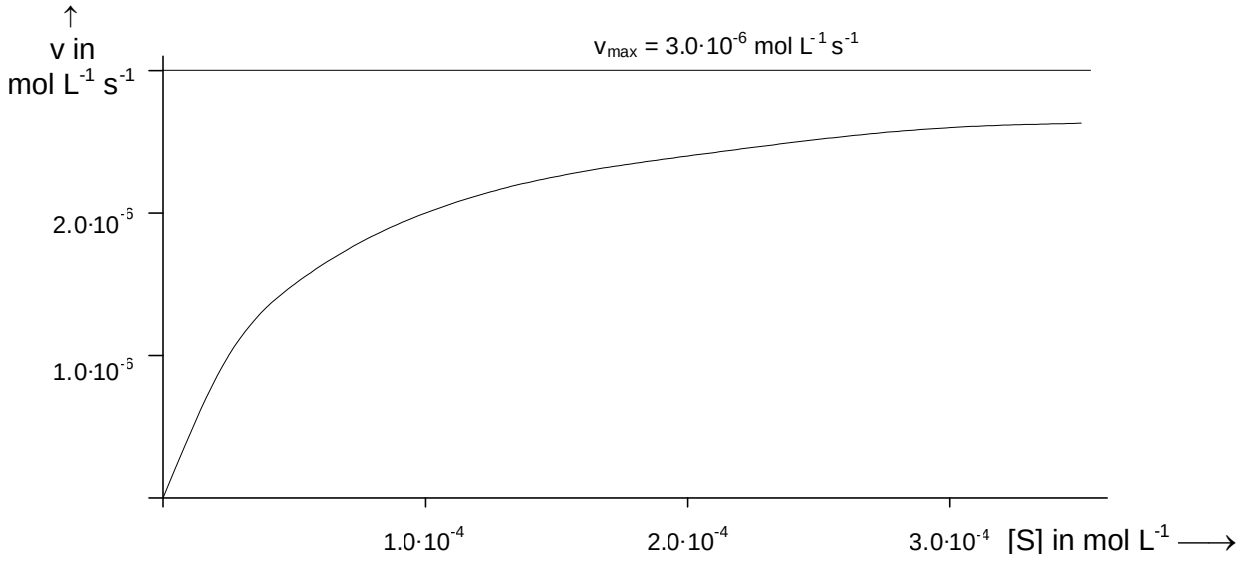
$[ES] = \frac{[E]_{total} \cdot [S]}{K_M + [S]}$ *with the Michaelis constant* $K_M = \frac{k_2 + k_3}{k_1}$

$[E]_{total}$ = total concentration of enzyme ([E] + [ES])

b) Account for the fact that the maximum reaction rate is $(d[P]/dt)_{max} = v_{max} = k_3 \cdot [E]_{total}$.

c) Derive from a) and b) the Michaelis-Menten equation $v = \frac{v_{max} \cdot [S]}{K_M + [S]}$.

d) Read K_M from the plot (v = f([S]) below. Where can you read this value, explain your decision.



Often you find the Lineweaver-Burk plot $\frac{1}{v} = f(\frac{1}{[S]})$.

e) Show that $\frac{1}{v} = \frac{K_M}{v_{max}} \cdot \frac{1}{[S]} + \frac{1}{v_{max}}$.

In an experiment with the enzyme concentration $E_{total} = 1.0 \cdot 10^{-9}$ mol L^{-1} the initial rate is measured for several different initial concentrations of S:

$[S]_0 \cdot 10^6$ in mol L^{-1}	3.0	5.0	10	20
$v_0 \cdot 10^5$ in mol L^{-1} min^{-1}	1.06	1.55	2.37	3.21

f) Draw a Lineweaver-Burk plot and determine the Michaelis constante K_M and the reaction rate constant k_3.

In another enuymatic reaction the Michaelis constante is $K_M = 1.5 \cdot 10^{-5}$ mol·L^{-1}. The initial concentration of the substrate is $3 \cdot 10^{-5}$ mol·L^{-1}.

g) Calculate the fraction (f_{ES}) of enzyme molecules, which bind to the substrate.

The catalytic efficiency of an enzyme is given by the catalytic constant k_{kat} (turnover number). This number tells you the amount of substrate molecules which form the product per time unit, if the total amount of enzyme is bound to the substrate.
The enzyme pepsin (M = 41977 g·mol^{-1}) cleaves the peptid bonding of proteins . In 10 mL of a solution 10^{-9} g pepsin were dissolved. The maximum reaction rate was measured:
$v_{max} = 7.15 \cdot 10^{-11}$ mol·L^{-1}·min^{-1}.

h) Calculate the tunrover number of pepsin in s^{-1}.

Problem 4-5

A solution of potassium permanganate was standardised by titration with a solution of sodium oxalate. The average of several experiments is: weighed portion 0.1702 g pure sodium oxalate dissolved in water and 26.70 mL of permanganate solution needed to titrate up to the equivlance point.

a) Write the reaction equation and determine the concentration of the permanganate solution.

A sample of 0.2250 g contains a mixure of iron and iron(III)-oxide. This sample is dissoluted completely and then treated with a saturated solution of SO_2 in water. The excess of SO_2 is removed by adding acid and boiling.
In a following titration with the solution of potassium permanganate (from a)) 37.50 mL are used.

b) Write the equations of all reactions involved and calculate the mass ratio (%) of iron and iron(III)-oxide in the sample.

A sample of steel contains ~ 10% nickel and ~ 70% iron. 0.200 g are dissolved completely in acid and diluted to 200 mL. Iron is precipitated as iron(III)-hydroxide, which is ignited to constant weight.

c) *Calculate the range of pH, in which the precipitation of iron(III)-hydroxide has to be performed for a quantitative determination of iron without any interference by nickel. After precipitation a maximum of* 0.1% of iron may stay in the solution.

Solubility products $K_{sp}(Fe(OH)_3) = 4 \cdot 10^{-38}$ $K_{sp}(Ni(OH)_2) = 6 \cdot 10^{-16}$

Problem 4-6

Mesurements in the exosphere above 700 km show a gas density of $1.0 \cdot 10^6$ molecules/cm^3 and a temperature of about 1200 K. In this region the mean free path of a molecule exeeds 13000 km, the diameter of the earth.

a) *Calculate the medial pressure in the height of 700 km.*

In a good vacuum on the earth you can reach a pressure of 10^{-9} mm Hg at T = 298 K. This specification is unusual and not according to SI-units. “Pressure of 1 mm Hg“ is the pressure of a 1 mm column of mercury on the base area.

b) *Convert the pressure in the vacuum to the unit pascal.*

c) *Calculate the number of gas molecules/cm^3 in such a vacuum at 25°C and compare with the result of a).*

Assume that the particles mentioned above are hydrogen atoms.

d) Calculate the mean speed ($\sqrt{\frac{8 \cdot R \cdot T}{\pi \cdot M}}$) of these hydrogen atoms under both conditions and compare.

At low temperatures hydogen atoms meeting each other form molecules. You shall compare how often hydrogen atoms in intergalactic space (1 hydrogen atom/m^3 at T = 2.7 K) and in a vacuum on earth ($40 \cdot 10^{15}$ hydrogen atoms/m^3 at a temperature at which their mean speed is 2400 m/s) collide.

Consider for this purpose the so called collision cylinder. This is a cylinder swept out by a hydrogen atom in one second calculated by multiplying the cross sectional area, $\pi \cdot d^2 \cdot \sqrt{2}$, by its speed (d = diameter of a hydrogen atom = $1 \cdot 10^{-8}$ cm).

The number of particles of this cylinder leads to the number of collisions per second.

e) *Calculate under both conditions the collision frequency and and the mean free path i.e. the average distance a hydrogen atom covers until it meets another one.*

Data : $\rho(Hg) = 13.55$ g/cm^3 $g = 9.81$ m/s^2

Problem 4-7

Gout comprises a number of diseases which are designated by repeated attacks of arthritis (inflammation of joints) and by formation of kidney stones.
Precondition for the appearance of gout is a concentration of uric acid (HUr) and urate (Ur^-) in blood far to high. Arthritis is created by cristals of sodium urate in the joint fluid.

In this connection the following equilibria play a decisive role:

$HUr\ (aq) + H_2O\ (l) \rightleftharpoons Ur^-\ (aq) + H_3O^+\ (aq)$ $\quad pK = 5.4$ at 37°C

$Ur^-\ (aq) + Na^+\ (aq) \rightleftharpoons NaUr\ (s)$

At 37°C 8.0 mmol sodium urate are soluble in 1.0 L of water.

a) Calculate the solubility product of sodium urate. Neglect the protolysis of urate.

In blood serum (pH = 7.4; 37°C) is $c(Na^+)$ = 130 mmol/L.

b) Calculate the maximum feasable concentration of urate in serum, at which no sodium urate precipitates.

The solubility product depends on temperature. It is known that pains caused by gout usually appear at first in toes and fingers.

c) Indicate the dependency of K_{sp} on temperature.

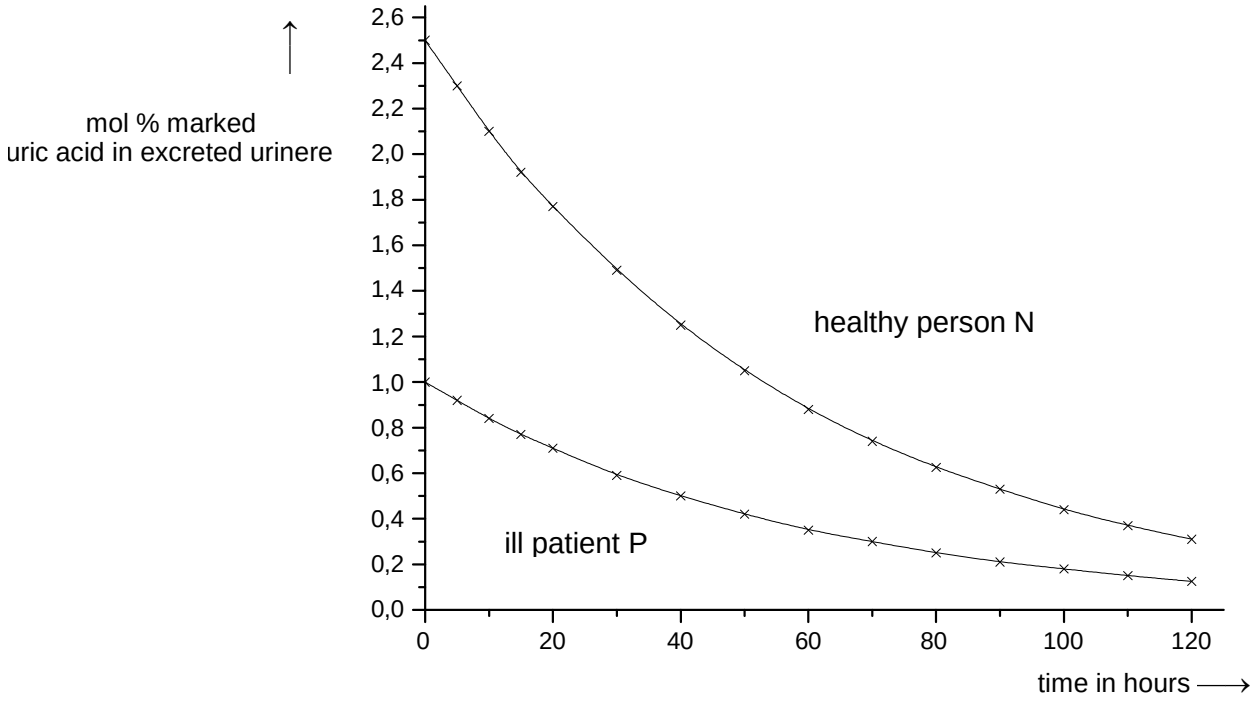
The solubility of uric acid in water at 37°C is 0.5 mmol/L.

d) If there is no precipitation of sodium urate, show by calculation that uric acid will not precipitate either i.e. arthristis cannot be caused by sole precipitation of uric acid. Assume that only HUr and Ur^- are responsible for the pH-value.

Often stones consisting of cristals of uric acid are found in kidneys of patients. The reason is a far too high concentration of (uric acid + urate) in the urine of these patients in connection with a low (but normal) pH of the urine (pH = 5 to 6).

e) Calculate the pH at which stones of uric acid can form in the urine of a patient Assume a concentration of (uric acid + urate) of 2.0 mmol/L.

Reason for too much uric acid and urate at gout patients can be both, an increase of production of uric acid and/or a decrease of excretion of uric acid.
In an experiment 20 mg of radioactive marked uric acid are injected intravenously. It mixes quickly and evenly with the uric acid in the body, both are excreted in the urine. In the urine the total amount of excreted uric acid is measured.
The following plot shows the results of an ill patient P and a healthy person N.



f) Calculate the mass of uric acid in the body of the patient P and in the body of the person P before the injection of the sample of 20 mg. Use the data of the plot.

g) Derive from the plot that the process of excretion in both cases follows a rate law of first order. Calculate the rate constants.

Problem 4-8 Aldol Reactions

If two aldehydes or ketones react the products formed are called „aldol" („β-hydroxyaldehyde") or „β-hydroxyketone" respectively. The aldol reaction takes place in a basic surrounding and is reversible.

Example: Two molecules of acetaldehyde are in equilibrium with 3-hydroxybutanal.

(Remark: Don't bother with stereoisomers when asked for reaction products)

a) Which product forms in an aldol reaction of propanal? Write the reaction mechanism and give the name of the product.

b) Comment on the reaction mechanism of an aldol reaction of RCH_2CHO as an example. To do this respond to the following questions:

- *Which function has the base in the aldol reaction?*
- *Which is the electrophilic and which the nucleophilic reactant in this aldol reaction?*
- *Which precondition of a carbonyl compound is necessary to form the nucleophilic part in the course of reaction?*

Formaldehyde and acetaldehyde react in a simple aldol reaction. Two products form.

c) Give the formulas of these two products. Why do only two but not four products form?

If acetaldehyde (pK_s~17) and 2,4-pentadione (pK_s~9) react in an aldol reaction mainly one product forms.

d) Give the reaction mechanism of the formation of this favoured product. Account for the preference of this product.

The compound 2,5-hexadione performs under mild conditions in the presence of a base an intramolecular aldol reaction. Two products form.

e) Show the course of reactions which lead to these products by giving the respective intermediate steps.
One of the products is more stable. Account for the reason.

Problem 4-9 Sugars

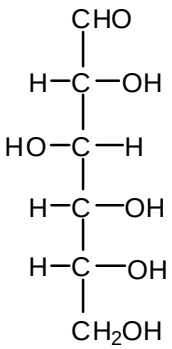
D-Glucose has the following structure in Fischer projection.

a) Give the structure of L-glucose in Fischer projection.

b) How many stereogenic centres has L-glucose (open chain)?
Which kind of stereoisormers are D- and L-glucose

c) Draw the structure of D-glucose (α-D-glucose, pyranose form) and L-glucose (β-L-glucose, pyranose form) as Haworth projection (ring with oxygen atom at the upper right)

d) Draw the structures of α-D-glucopyranose, β-D-glucopyranose and β-L-glucopyranose) in chair representation.
Label the substituents with an a for axial and e for equatorial position.
Explain which of these compounds is (are) especially stable.



D-Glucose

e) β-D-glucopyranose reacts with an excess of acetic anhydride (basic surrounding).
Which compound forms?
Draw the Haworth projection of the product.
To which class of compounds does the product belong?

f) β-D-glucopyranose react with an excess of alkyl halides (e.g. CH_3I) in the presence of silver oxide.
Which compound forms?
Draw the Haworth projection of the product.
To which class of compounds does the product belong?

g) After the reaction of β-D-glucopyranose with one equivalent of methanol (catalysed by an acid) a compound forms that does not show mutarotation any longer.

Draw the Haworth projection of this product. Give the reasons why the product does not show mutarotation.

To which class of compounds does the product belong?

Problem 4-10 Determination of a structure by Spectroscopic Data

Compound A has the empirical formula $(C_2H_4O)_n$.
The structure of a is analised by spectroscopic methods.
The following data are acquired:

A) The base peak M^+ in the mass spectrum is found at m/z = 88
B) The IR spectrum of A shows a strong band at 1730cm^{-1} and further bands between 2850cm^{-1} and 2930cm^{-1}.
C) Spectrum I shows the 1H-NMR spectrum of A.

a) Which is the molecular formula of A?

b) Determine possible functional groups of A.

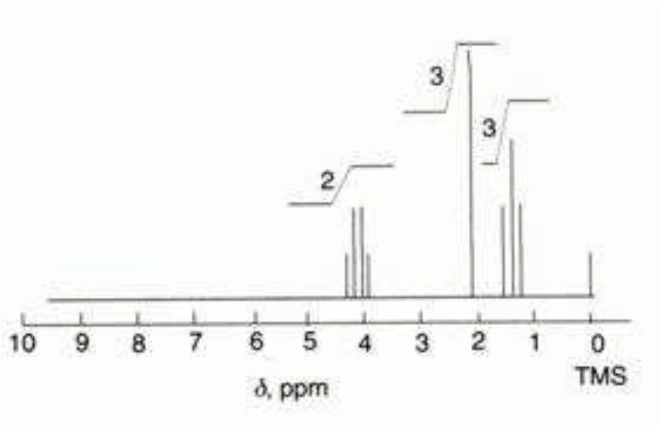
c) Which is the physical base of an IR spectrum? (maximum of 5 sentences)

d) Make a proposal of the structure of A.

Thereto:

- *Assign the different peaks or groups of peaks to different protons or groups of protons in your proposal.*
- *Determine the respective number of protons for each peak or group of peaks.*
- *Account for your proposal by interpreting the different couplings.*

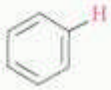
1H-NMR-Spectrum of A

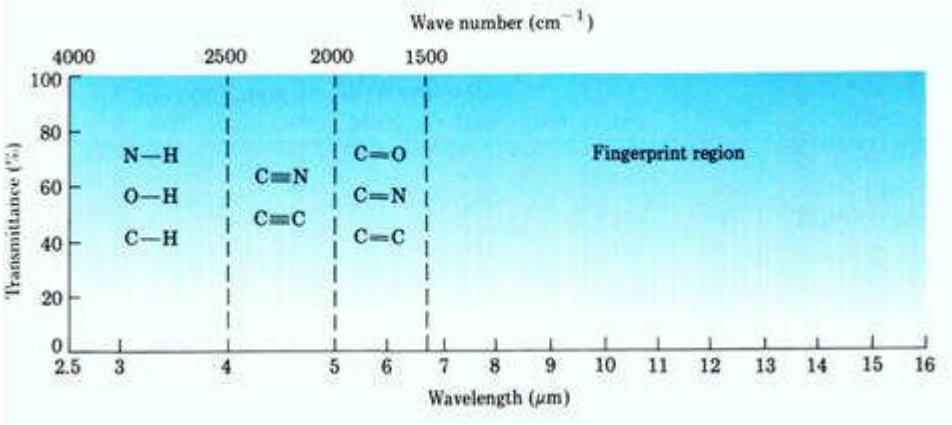


Correlation of ^1H Chemical Shift with Environment

Type of proton	*Formula*	*Chemical shift (δ)*
Reference peak	$(CH_3)_4Si$	0
Saturated primary	$-CH_3$	0.7–1.3
Saturated secondary	$-CH_2-$	1.2–1.4
Saturated tertiary	$-\overset{|}{C}-H$	1.4–1.7
Allylic primary	$C=C-CH_3$	1.6–1.9
Methyl ketones	$-\overset{O}{\overset{\|\|}{C}}-CH_3$	2.1–2.4
Aromatic methyl	$Ar-CH_3$	2.5–2.7
Alkyl chloride	$Cl-\overset{|}{C}-H$	3.0–4.0
Alkyl bromide	$Br-\overset{|}{C}-H$	2.5–4.0
Alkyl iodide	$I-\overset{|}{C}-H$	2.0–4.0
Alcohol, ether	$-O-\overset{|}{C}-H$	3.3–4.0
Alkynyl	$-C\equiv C-H$	2.5–2.7
Vinylic	$C=C-H$	5.0–6.5
Aromatic	$Ar-H$	6.5–8.0
Aldehyde	$-\overset{O}{\overset{\|\|}{C}}-H$	9.7–10.0
Carboxylic acid	$-\overset{O}{\overset{\|\|}{C}}-O-H$	11.0–12.0
Alcohol	$-\overset{|}{C}-O-H$	Extremely variable (2.5–5.0)

Regions of the ^1H NMR Spectrum

Region (δ)	*Proton type*	*Comments*
0–1.5	$-\overset{|}{C}-\overset{|}{C}-H$	Protons on carbon next to saturated centers absorb in this region. Thus, the alkane portions of most organic molecules show complex absorption here.
1.5–2.5	$=\overset{|}{C}-\overset{|}{C}-H$	Protons on carbon next to unsaturated centers (allylic, benzylic, next to carbonyl) show characteristic absorptions in this region, just downfield from other alkane resonance.
2.5–4.5	$X-\overset{|}{C}-H$	Protons on carbon next to electronegative atoms (halogen, O, N) are deshielded because of the electron-withdrawing ability of these atoms. Thus, the protons absorb in this midfield region.
4.5–6.5	$C=C\overset{H}{}$	Protons on double-bond carbons (vinylic protons) are strongly deshielded by the neighboring pi bond and therefore absorb in this characteristic downfield region.
6.5–8.0		Protons on aromatic rings (aryl protons) are strongly deshielded by the pi orbitals of the ring and absorb in this characteristic low-field range.



Fourth round (practical problems)

Problem 4-11

Quantitative Determination of a Solution of Different Salts by Titration

A Problem

You get a solution of magnesium chloride and calcium chloride. The concentrations c of these salts have to be determined (c in mol/L). To perform this there a differnet possibilities at your disposal. You have to choose from

Titration of the cations with a solution of EDTA (c = 0.100 mol/L) using Erio T as indicator.

Seperation of the cations by precipitation of calcium oxalate.

Oxidimetric titration of an oxalate with a solution of potassium permanganate (c = 0,020 mol/L).

Determination of chloride concentration by Mohr titration.

B Procedures

Titration with EDTA

Fill the volumetric flask up to 250 mL. Take a sample, add 5 mL of buffer solution and a small amount of water. Before starting the titration add a spaturla-tipfull of indicator (as trituration NaCl: Erio T = 100 : 1).

Titrate with the solution of EDTA (c = 0.100 ml/L).

Seperation of magnesium ions and calcium ions

Add 6 ml of diluted HCl to a sample and dilute with about 100 mL of water. After adding solution of NH_3 until the sample shows a slightly basic reaction heat it to boiling and add hot solution of $(NH_4)_2$-oxalate slowly in small amounts until there is no more precipitation. After boiling for 15 minutes the precipitate is filtered off

Then, the precipitate is washed 5x with small amounts of hot solution of $(NH_4)_2$ (c=0.01 mol/L) (small!) and then 1x carefully with a small amount of warm water.

The precipitate is dissolved in warm sulfuric acid (3 parts of H_2O with 1 part of conc. H_2SO_4) and diltuted with 50 mL of water.

Oxidimetric titration of oxalate with a solution of $KMnO_4$ (c = 0.020 mol/L)

The acidic solution of oxalate is heated up to 60 – 80°C and then titrated with the solution of potassium permanganate. At the equivalence point a weak pink colour can be observed for several minutes.

Determination of chloride concentration by Mohr titration

The sample has to be neutralised to pH = 7. Add about 2 mL of a solution of potassium dichromate (w = 5 %).

Titrate with a solution of $AgNO_3$ (c = 0.100 mol/L) until a dark yelllow colour occurs.

C Questions

Choose at least three titrimetric methods to determine the concentrations of both salts. Therefor

1. *Characterise the principle of your titration in keywords.*
2. *Give the equation of the reaction which you use as basis for your calculation.*
3. *Write down for each titration*
    - *the volume of the sample (taken from the 250 mL volumetric flask),*
    - *consumption of standard solution in mL,*
    - *consumption taken for calculation (account for your choice),*
    - *calculations of the concentrations of cations and anions in mol/L.*
4. *Comment about and critical valuation of your results.*

Problem 4-12
Preparation of Hydrazones to Identify Aldehydes and Ketones

Hydrazines react with aldehydes and ketones to form hydrazones. Hydrazones form derivates with different metlting points. These can be used to identify unknown aldehydes and ketones.

The two test tubes in front of you contain an aldehyde or a ketone each.

Identify the compounds in the test tubes by forming the respective hydrazone and measuring the melting point.

Chemicals:

2 beakers with 2,4-dinitrophenyl hydrazine dissolved in methanol
2 test tubes (1 and 2), each with an unknown aldehyde or ketone
conc. sulfuric acid, ethanol, dem. water, Tollens reagent,
solution of sodium hydroxide, conc. ammonia, Schiff's reagent

A: Preparation of the hydrazone

In each of the two given beakers there are 200 mg of 2,4-dinitrophenyl hydrazine dissolved in 5 mL of methanol. **(Wear gloves!)**

Add dropwise and slowly as much conc. sulfuric acid until all 2,4-dinitrophenyl hydrazine is dissolved completely (mix accurately).

Take a sample of 5 mL from test tube 1 and test tube 2 with the unknown compounds and add it to the yellow solution.

If there is no precipitation after 5 minutes add about 10 mL of sulfuric acid (c = 0.5 mol/L).

The crystals formed are filtered off by suction, the product of test tube 2 is recrystallized in ethanol (heating plate), again fiiltered off by suction, washed with a small amount of water and dried on the air. The product of test tube 1 is only washed with a small amount of water and dried on the air.

Question

1. *Give the equation of the reaction of 2,4-dinitropheny lhydrazine with acetone as an example.*

B) Identifcation of aldehyde and ketone

While the crystals are drying other reactions are used to idenfy whether in the respective test tubes are aldehydes or ketones.

The identification is to be performed with Tollens reagent and Schiff's reagent.

Reaction with Tollens reagent:

5 mL of a solution of silver nitrate are filled in an absolutely clean test tube. Solution of ammonia is added until the white precipitate is dissolved. Afterwards a pellet of sodium hydroxide is added.

To this solution two drops of the unknown compound are given. The test tube is heated for a short time in a water bath up to 60 - 70°C.

Reaction with Schiff's reagent:

Two drops of the organic compound are added to 2 mL of Schiff's reagent and shaken well.

Questions

2. *Determine the kind of carbonyl compounds in the test tubes.*
3. *Measure the melting points of the hydrazones.*
4. Which aldehyde or which ketone contains test tube 1 and test tube 2 respectively

Table 1

Chosen Aldehydes / Ketones	Intervals of melting of the respecive 2,4-dinitrophenyl hydrazones in °C
Crotonaldehyde	**190 - 195**
Formaldehyde	**160 - 166**
Propionaldehyde	**150 - 155**
Chloral	**127 - 131**
Heptanal	**100 - 108**
Ethyl methyl ketone	**110 - 117**
Isopropyl methyl ketone	**120 - 123**
Methyl propyl ketone	**138 - 144**
Diethyl ketone	**150 - 156**
Cyclohexanone	**158 - 162**

Part 2

The answers to the problems of the four rounds

The solutions are more detailed than expected from the pupils. That may facilitate their comprehension in case of mistakes.

Answers Round 1

Solution to problem 1-1

a) $2\ H_3O^+ + SO_4^{2-} + 2\ OH^- \rightleftarrows 4\ H_2O + SO_4^{2-}$

$c(NaOH)\cdot V(NaOH) = 2\cdot c(H_2SO_4)\cdot V(H_2SO_4)$

$0.1760\ mol/L \cdot 20.37\ mL = 2\cdot c(H_2SO_4)\cdot 10.00\ mL$

$c(H_2SO_4) = 0.1793\ mol/L$

b) $n = 0.5000\ L \cdot 0.1792\ mol/L = 0.0896\ mol\ H_2SO_4$, 1 liter contains 17.93 mol H_2SO_4.

$m(H_2SO_4) = 1759\ g$, $100\% \cdot 1759/1840 =$ **95.6%**

c) 1 L of sulphuric acid contains 1759 g of H_2SO_4 (17.93 mol) and 81 g of H_2O (4.50 mol)

$$\mathbf{x} = \frac{17.93}{17.93+4.00} \mathbf{= 0.799}$$

Solution to problem 1-2

a) Advantages:

- Low density, alloys have nearly the same stability as steel, suitable for vehicle construction
- corrosion restistant,
- low melting point, easy deformable, easy to roll out to form plastic films for wrapping,
- good electrical conductance (2/3 of copper),
- high combustion heat, appropriate to use in explosives and fire crackers.

Disadvantages:

- high consumption of energy at production,
- accurate flue gas cleaning necessary otherwise hydrogen fluoride and dust of other fluorides will escape during production and damage to the environment.

Percentage of Al_2O_3 in bauxite: 50 - 75 mass %.

Bauxite is exploited in Australia, Guinea, Jamaica, Brasil, France, Hungary, USA, Guayana, Northern China.

It was called after the first place it was found, Le Baux (southern France).

b) Principally the solubility of amphoteric $Al(OH)_3$ in bases is used to seperate it from $Fe(OH)_3$, which does not have this property.

Bauxite is mixed with sodium-hydroxide solution (35%) at 170 to 180° C under high pressure. Under these conditions a soluble aluminium complex and insoluble iron hydroxide form:

$$Al_2O_{3\,(s)} + 3\,H_2O_{(l)} \longrightarrow 2\,Al(OH)_{3\,(s)}$$
$$Al(OH)_{3\,(s)} + OH^- \rightleftarrows [Al(OH)_4]^- \qquad (1)$$
$$Fe_2O_{3\,(s)} + 3\,H_2O_{(l)} \longrightarrow 2\,Fe(OH)_{3\,(s)}$$

$Fe(OH)_{3\,(s)}$ is filtered off. The solution is diluted and seed crystals of Al_2O_3 are added. By dilution the equilibrium (1) moves to the left. Sometimes this effect is supported by inducing CO_2:

$$(CO_2 + OH^- \rightleftarrows HCO_3^-)$$
$$Al(OH)_4]^- \longrightarrow OH^- + Al(OH)_{3\,(s)}$$

$Al(OH)_3$ is transformed into Al_2O_3 by heating:

$$2\,Al(OH)_{3\,(s)} \longrightarrow Al_2O_{3\,(s)} + 3\,H_2O_{(g)}$$

c) Cryolyte (Na_3AlF_6) has a low melting point (~ 1000° C) compared with aluminium oxide (~ 2050° C). For practical reasons the electrolysis is performed in a solution of Al_2O_3 in liquid cryolite. In such a solution a melting point of ~ 950° C is achieved.

Reactions: in the melt $Al_2O_3 \longrightarrow 2\,Al^{3+} + 3\,O^{2-}$

at the cathode $Al^{3+} + 3\,e^- \longrightarrow Al$

at the anode $2\,O^{2-} \longrightarrow O_2 + 4\,e^-$

$$O_2 + 2\,C \longrightarrow 2\,CO$$

Total reaction: $2\,Al_2O_3 + 6\,C \longrightarrow 4\,Al + 6\,CO$

(besides carbon monoxide CO_2, COF_2, C_2F_4 and other gases form in smaller amounts)

$Q = I \cdot t$ $\quad Q = 130 \cdot 10^3\ A \cdot 366 \cdot 24 \cdot 3600\ s \cdot 0.95 = 3.905 \cdot 10^{12}$

$Q = n \cdot z \cdot F$ $\quad Q = m/M \cdot 3 \cdot 96485\ As/mol$ $\quad M(Al) = 26.98\ g/mol$

$$\Rightarrow \quad m = \frac{130 \cdot 10^3 \cdot 366 \cdot 24 \cdot 3600 \cdot 0.95 \cdot 26.98}{3 \cdot 96485}\,g \approx \mathbf{364\ t}$$

d) $W = P \cdot t$ and $P = U \cdot I$

$W = U \cdot I \cdot t$ $\quad W = U \cdot Q$ and $Q = n \cdot z \cdot F$

$W = U \cdot n \cdot z \cdot F$ with $U = 5\ V$ $\quad n = (10^6/26{,}98)\ mol$ $\quad z = 3$ $\quad F = 96485\ As/mol$

$W = 5 \cdot 10^6/26.98 \cdot 3 \cdot 96485\ As$ $\quad W \approx 14900\ kWh$

efficiency = 95 % $\quad \Rightarrow \quad$ **$W_{(for\ 1\ t\ Al)}$ = 15700 kWh**

1 t bauxite contains 600 kg $Al_2O_3 = 0.6 \cdot 10^6/101.96\ mol\ Al_2O_3$

to form 1.2·/101,96 · 26.98 t Al = 0.318 t Al. ⇨ $\mathbf{m_{(for\ 1\ t\ Al)}} = 0.318^{-1}$ t

$\mathbf{m_{(for\ 1\ t\ Al)} \approx 3\ t\ bauxite}$.

(In literature you often find 4 t.)

To form 1 mol Al you need 1.5 mol C $\mathbf{m_{(for\ 1\ t\ Al)} \approx 670\ kg\ graphite.}$

e) $2\ Al_2O_3 \longrightarrow 4\ Al + 3\ O_2$

$\Delta_R H$ = [4·48 + 3·38 - 2·(- 1610)] kJ/mol = 3526 kJ/mol

$\Delta_R S$ = [4·78 + 3·238 - 2·98] kJ/(Kmol) = 830 kJ/(K·mol)

$\Delta_R G = \Delta_R H - T\ \Delta_R S$ $\Delta_R G$ = (3526 - 1243· 0.830)kJ/mol = 2494.31 kJ/mol

$\Delta E = - \Delta_R G / (z \cdot F)$ $\Delta E = 2494.31 \cdot 10^3/(12 \cdot 96485)$ V **ΔE = 2.15 V**

f) According to the negative standard potential of aluminium [$E°(Al^{3+}/Al)$ = - 1.66 V] hydrogen is formed at the cathode.

g) Possible reactions

I $2\ Al_2O_3 + 6\ C \longrightarrow 4\ Al + 6\ CO$ with $\Delta G_I = 3 \cdot \Delta G_2 - \Delta G_1$

II $2\ Al_2O_3 + 3\ C \longrightarrow 4\ Al + 3\ CO_2$ with $\Delta G_{II} = 3 \cdot \Delta G_3 - \Delta G_1$

$\Delta G_I < 0$: 3 · (- 221.06 - 0.17872·T_I/K) kJ/mol - (- 3351.4 + 0.6264·T_I/K) kJ/mol < 0

$\Leftrightarrow$ 2688.22 < 1.16256 · T_I T_I > 2313 K

$\Delta G_{II} < 0$: 3 ·(- 393.51 - 0.00286·T_{II}/K) $kJmol^{-1}$ - (- 3351.4 + 0.6264·T_{II}/K) kJ/mol < 0

$\Leftrightarrow$ 2170.87 < 0.63498 · T_{II} T_{II} > 3419 K, at this temperature CO_2 does not form.

T > 2313 K = 2040°C (Actually it is not possible because of the formation of Al_4C_3.)

Solution to problem 1-3

a) <u>Observation 1:</u>

$Fe^{3+}_{(aq)}$ (yellow) + 3 $SCN^-_{(aq)}$ (coulorless) $\rightleftarrows$ $Fe(SCN)_{3\ (aq)}$ (red)

or $[Fe(H_2O)_6]^{3+} + 3\ SCN^- \rightleftarrows Fe[(SCN)_3(H_2O)_3] + 3\ H_20$

Not only $Fe(SCN)_{3\ (aq)}$ is reason for the red colour but also complexes like $Fe[(SCN)_x(H_2O)_{6-x}]^{3-x}$ with x ranging from 1 to 6.

<u>Observation 2:</u>

$K = \dfrac{c_{eq}(Fe(SCN)_3)}{c_{eq}(Fe^{3+}) \cdot c^3_{eq}(SCN^-)}$. Dilution decreases the concentrations from c_{gl} to $c_{gl}/10$.

$$Q = \frac{c_{eq}(Fe(SCN)_3)/10}{[c_{eq}(Fe^{3+})/10]\cdot[c^3_{eq}(SCN^-)]/10^3} = K\cdot 1000.$$

To reach equilibrium again, the numerator of Q will decrease and the denominator will increase by decompositon of $Fe(SCN)_{3\,(aq)}$ to result in showing the brown colour of a solution of Fe^{3+}.

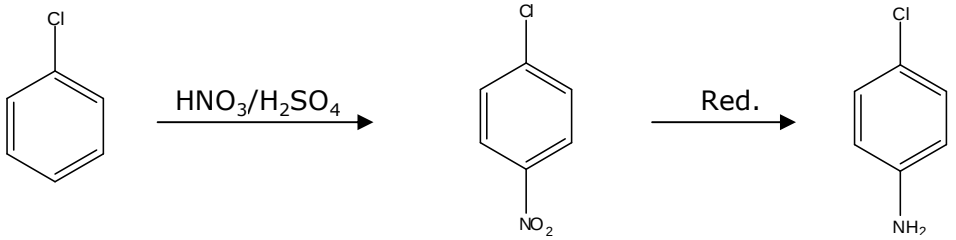
Observations 3 and 4:

By adding the solid material the concentration of a reactant increases and more product forms. Thus the solution shows again the red colour of a $Fe(SCN)_3$ solution.

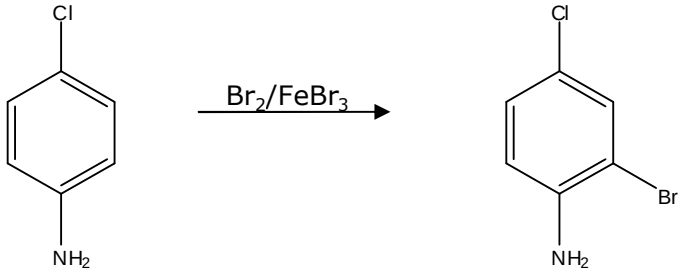
b) Observations 3 and 4 show that observation 2 is not due to an effect of dilution as someone may use a an explanation.

Solution to problem 1-4

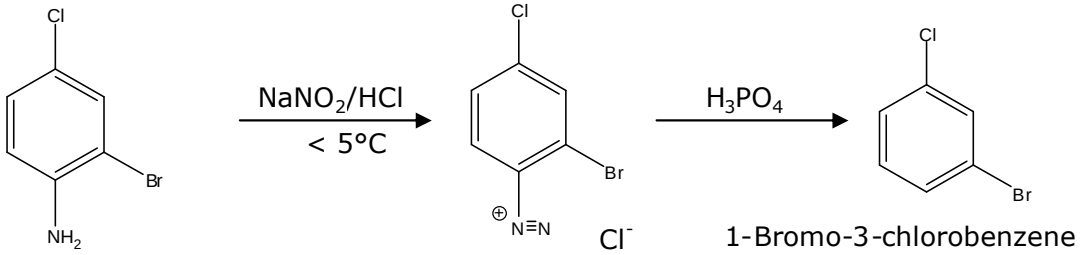
Substituents like Cl show an ortho and para directing effect. Therefore in the beginning an additional substituent is inserted in p position.
In this case you choose a strongly activating substituent, e.g. NH_2:



Secondly bromine is inserted in ortho-position of the additional substituent (NH_2):



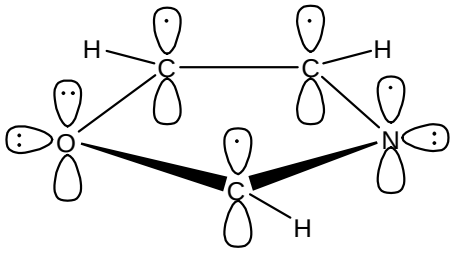
the addtional substituent (NH_2) is removed



1-Bromo-3-chlorobenzene

Solution to problem 1-5

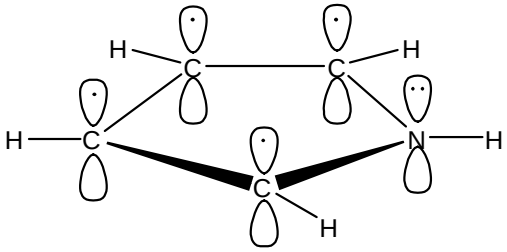
a)



Oxazole is aromatic because it

- is cyclic,
- is planar,
- has a conjugated π-elektron system,
- fulfills Hückel's rule to contain 4n + 2 (with n = 1) electrons.

b) π-elektron system of pyrrole:



In pyrrole the free electron pair of the N Atom is part of the π-elektron system. Adding of a proton to this free electron pair leads to a loss of aromaticity of pyrrole. On the other side the N atom of oxazole possesses a free electron pair which is not part of the π-elektrone system. Therefore the addition of a proton is not accompanied by a loss of aromaticity.

Thus the N atom of oxazole is more basic.

Answers round 2

Solution to problem 2-1

1.

a) $Cr_2O_7^{2-} + 14\ H^+ + 6\ e^- \quad \rightleftarrows \quad 7\ H_2O + 2\ Cr^{3+}$

Potential of the given chromium(III)/dichromate solution at pH = 7:

$$E = 1{,}38\ V + \frac{R \cdot T}{6 \cdot F} \cdot \ln \frac{c(Cr_2O_7^{2-}) \cdot c(H^+)^{14}}{c(Cr^{3+})^2} \qquad E = 1{,}38\ V + \frac{8{,}314 \cdot 298}{6 \cdot 96485} V \cdot \ln (10^{-7})^{14}$$

$E = 0{,}414\ V$

That does not suffice to set free iodine from a solution which contains iodide.

b) <u>Reaction with potassium nitrate/soda:</u>

$Cr_2O_3 + 3\ KNO_3 + 2\ Na_2CO_3 \longrightarrow 2\ Na_2CrO_4 + 2\ CO_2 + 3\ KNO_2$

<u>Reaction with hydogenperoxide:</u>

$2\ Cr^{3+} + 3\ H_2O_2 + 10\ OH^- \longrightarrow 2\ CrO_4^{2-} + 8\ H_2O$ or

$2\ Cr^{3+} + 3\ H_2O_2 + H_2O \longrightarrow Cr_2O_7^{2-} + 8\ H^+$

<u>Reaction with sodium peroxodisulfate:</u>

$2\ Cr^{3+} + 3\ Na_2S_2O_8 + 16\ OH^- \longrightarrow 2\ CrO_4^{2-} + 6\ SO_4^{2-} + 6\ Na^+ + 8\ H_2O$ or

$2\ Cr^{3+} + 3\ Na_2S_2O_8 + 7\ H_2O \longrightarrow Cr_2O_7^{2-} + 6\ SO_4^{2-} + 6\ Na^+ + 14\ H^+$

<u>Reaction with bromine:</u>

$2\ Cr^{3+} + 3\ Br_2 + 16\ OH^- \longrightarrow 2\ CrO_4^{2-} + 6\ Br^- + 8\ H_2O$ or

$2\ Cr^{3+} + 3\ Br_2 + 7\ H_2O \longrightarrow Cr_2O_7^{2-} + 6\ Br^- + 14\ H^+$

Potassium nitrate is used as an oxidizing agent, soda (sodium carbonate) lowers the melting point of the mixture.

c) The oxidation of chromium(III) to chromium(VI) depends on the pH-value. Thus you have to find a pH value with the potential of ($Cr^{3+}|Cr_2O_7^{2-}$) being smaller than the standard potential of the system ($Br^-|Br_2$).

$$1.065 > 1.38 + \frac{8.314 \cdot 298}{6 \cdot 96485} \cdot \ln c(H^+)^{14} \quad \Leftrightarrow \quad -73.60 > \ln c(H^+)^{14}$$

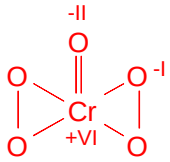
$$\sqrt[14]{e^{-73.60}} = 5.21 \cdot 10^{-3} > c(H^+) \qquad 2.28 < pH$$

At pH > 2.28 it is possible to oxidize chromium(III) by using bromine.

d) Hydrogenperoxide oxidizes halides too. Elemental bromine or iodine would form. Both are coloured and complicate the detection of chromium.

Manganese(II) is oxidized by bromine to form the violet permangante ion, which may cover the characteristic colouring of the chromate.

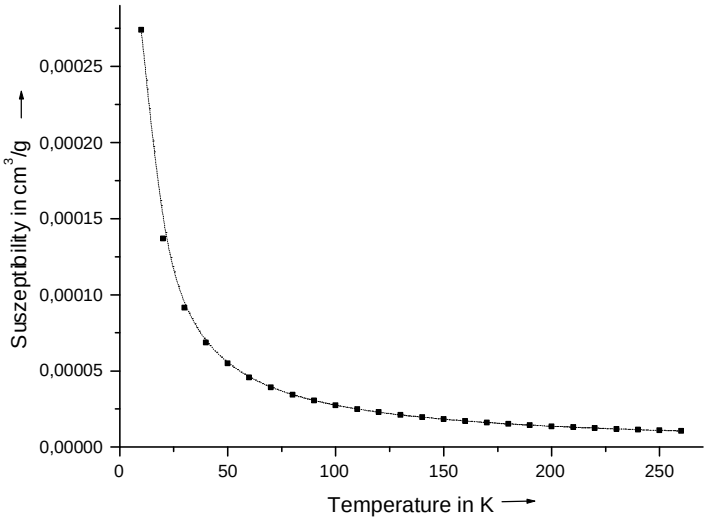
e) There is no change of the oxidation state, no reduction and no oxidation takes place. Hydrogenperoxide becomes attached to the chromium centre as a peroxide dianion.



$$\overset{+VI,-II}{Cr_2O_7^{2-}} + 4\ H_2O_2 + 2\ H^+ \rightarrow 2\ \overset{+I,-I}{CrO_5} + 5\ \overset{+I\ +VI,-II,-I}{H_2O}$$

$$\overset{+I,-II}{H_2O}$$

f)



g) C = T·χ Inserting different pairs leads to **C = 2,74·10^{-3} cm^3 K g^{-1}** as mean value**.**

h) $\mu = \frac{\sqrt{3 \cdot 8.314 \cdot 10^7\,\mathrm{erg \cdot K^{-1} \cdot mol^{-1}} \cdot 0.00274\,\mathrm{cm^3 \cdot K \cdot g^{-1}} \cdot 364.49\,\mathrm{g \cdot mol^{-1}}}}{6.022 \cdot 10^{23}\,\mathrm{mol^{-1}} \cdot 9.274 \cdot 10^{-21}\,\mathrm{erg \cdot Oersted^{-1}}}$

μ = 2.83

The magnetic moment equals 2.83 BM.

i) Comparing μ = 2,83 with the value from $\mu = \sqrt{n \cdot (n+2)}$ (n = number of unpaired electrons)you get n = 2.

2 unpaired electrons may occur for Cr(IV) (d^2-system) or for Cr(II) (d^4-system) in a low-spin complex.

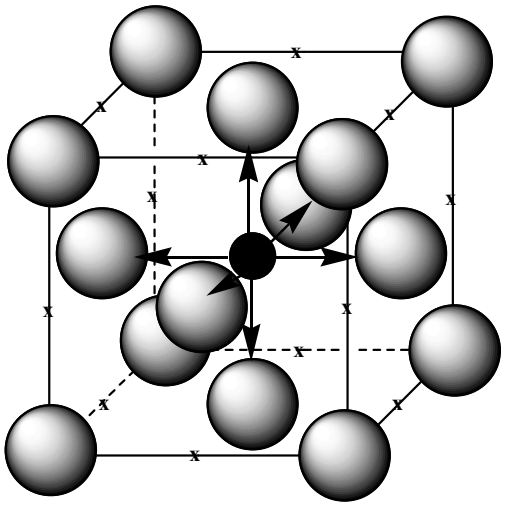
Cr(IV) is not existent in this case as it has no reducing properties, furthermore it is not stable in an aquous solution.

Chromium is existent in the (formal) oxidation state+2.

j) With ammonium as ligands instead of cyanide the complex changes from low-spin to high-spin. Thus there are four unpaired electrons and the expected relative magnetic moment is $\mu = \sqrt{4\cdot(4+2)}$, **μ = 4.90.**

Solution to problem 2-2

a) x = centres of octahedral holes



b) $8\cdot1/8 + 6\cdot½ = 4$ oxide ions per cube ⇨ 1 formula unit $CoAl_2O_4$ per cube

$12\cdot1/4 + 1 = 4$ octahedral holes for 2 Al^{3+} ions **50%**

8 tetrahedral holes for 1 Co^{2+} ion **12.5%**

c) Length of the edge of the unit cell = 912 pm ⇨ length of the cube = 456 pm

$V_{cube} = (4.56\cdot10^{-10}m)^3$

mass of particles (Co + 2 Al + 4 O) in that cube

$m = [(58.93 + 2\cdot26.98 + 4\cdot16.00)/N_A]$ g

$\rho = m/V \qquad \rho = \dfrac{176.89\ g\cdot mol^{-1}}{6.022\cdot10^{23}\ mol^{-1}\cdot(4.56\cdot10^{-10}m)^3} = 3097904\ g/m^3$

ρ = 3.1 g/cm^3

d) $r(M^{2+})$ = radius of the circumcircle of the tetrahedron - radius of the oxide ion

$4\cdot r(O^{2-})$ = length of a diagonal of the plane = $456\cdot\sqrt{2}$ pm

$r(O^{2-})$ = 114· $\sqrt{2}$ pm = 161.22 pm

length of the edge of the tetrahedron a = 2· $r(O^{2-})$ = 322.44 pm

radius of the circumcircle of the tetrahedron r = a· $\sqrt{6}$ /4 = 197.45 pm

$r(M^{2+})$ = r - $r(O^{2-})$ **$r(M^{2+})$ = 36.23 pm**

$r(M'^{3+})$ = [edge length of the cube - 2 · $r(O^{2-})$] / 2

$r(M'^{3+})$ = [456 pm - 322.44 pm] / 2 **$r(M'^{3+})$ = 66.78 pm**

e) Sn(**II**)Co(**III**)$_2O_4$ und Sn(**IV**)**Co**(**II**)$_2O_4$

($Sn(0)Co(IV)_2O_4$ shows a very unfavourable oxidation state of Co, so this is an unlikely possibility)

f) $Sn(II)Co(III)_2O_4$: Sn: 0 unpaired electrons

Co: 0 unpaired electrons in case of low-spin octahedron,
4 unpaired electrons in case of high-spin octahedron,
2 unpaired electrons in case of low-spin tetrahedron,
4 unpaired electrons in case of high-spin tetrahedron,
thus: 0, (6,) 8 possible
(6 drops out as for the same ligand the octahedron splitting is far larger than the tetrahedron splitting and thus the coexistence of high-spin octahedron and low-spin tetrahedron is impossible)

$Sn(IV)Co(II)_2O_4$: Sn: 0 unpaired electrons

Co: 1 unpaired electron in case of low-spin octahedron,
3 unpaired electrons in case of high-spin octahedron,
3 unpaired electrons in case of tetrahedron (you cannot distinguish between high- and low-spin because the number of unpaired electrons is equal)
thus: 2, 4, 6 possible

g) 43.9 % O: 43.9 / 16 = 2.74375

18.5 % Al: 18.5 / 26.98 = 0.68569 37.6 % remainder

⇨ n(Al) : n(O) = 1 : 4 compound $MM'AlO_4$

37.6 % (M + M')

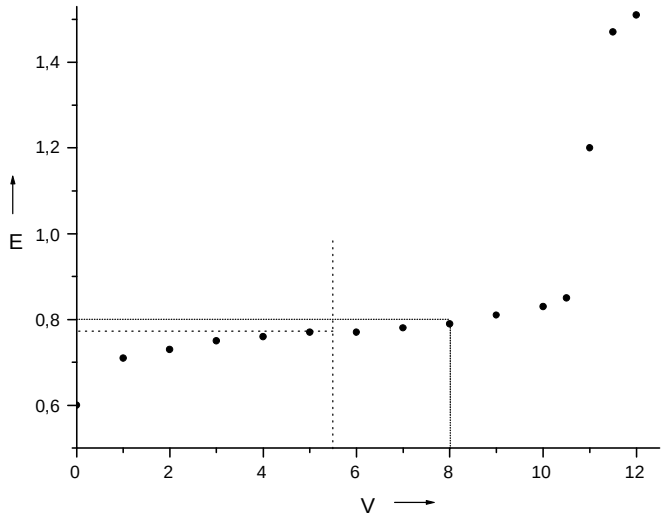
for the sum x of the atom masses of M and M' you find

18.5 / 26.98 = 37.6 $g \cdot mol^{-1}$ / x x = 54.84 $g \cdot mol^{-1}$

M	M'	Σ	
M (27.41) =	M' (27.41)	54.84	no solution for M = M'
Li (6.94)	Ti (47.88)	54.82	possible
Be (9.01)	Sc (44.96)	53.97	deviation to large, no solution
Na (22.99)	S (32.07)	55.06	sulphur is not a metal, no solution
Mg (24.31)	P (30.97)	55.28	phosphorus is not a metal, no solution
Al (26.98)	Si (28.09)	55.07	the percentage of Al would not be correct, no solution

X = $LiTiAlO_4$

h) $E = E° + \frac{R \cdot T}{n \cdot F} \cdot \ln \frac{c_{Ox}}{c_{Red}}$.



From the image: equivalence point at 11

at V = 5.5 is $c_{Ox} = c_{Red}$ and thus E = E° ⇨ E° = 0.77 V = E°(Fe^{2+}/Fe^{3+})

As the function is rising, c_{Ox} is rising during the titration, so in the original solution you find **Fe^{2+}**.

If $\ln(c_{Ox}/c_{Red}) = 1$ then $c_{Ox}/c_{Red} = e$ and you can calculate n:

c_{Ox}/c_{Red} = V / (11 mL - V) V = e·(11 mL - V) V = 8.04 mL ≈ 8 mL

E(V=8 mL) = 0.79 V

0.79 V = 0.77V + (8.314·298 $Jmol^{-1}$)/(n·96485 $C \cdot mol^{-1}$)⇨ n = 1.28

n has to be an integer **n = 1**

Solution to problem 2-3

a) The total pressure depends on the equilibrium, so you have to calculate the equilibrium constant first.

$2\ NO_2 \rightleftarrows N_2O_4$ $\quad \Delta H = (9160 - 2\cdot 33200)\ Jmol^{-1} = -57240\ Jmol^{-1}$

$\Delta S = (304.3 - 2\cdot 240.1)\ JK^{-1}mol^{-1} = -175.9\ JK^{-1}mol^{-1}$

$\Delta G = (-57240 + 300\cdot 175.9)\ Jmol^{-1} = -4470\ kJmol^{-1}$

$\ln K = -\Delta G/RT \quad \ln K = 4470/8.314\cdot 300 \quad K = 6.00$

This K is dimensionless and stands for the term

$$K = \frac{p(N_2O_4)/p_{standard}}{p^2(NO_2)/p^2_{standard}}$$

⇨ $Kp = K/p_{standard} \quad Kp = 6.00\cdot 10^{-5}\ Pa^{-1}$

(Standard pressure $p_0 = 1{,}0000\cdot 10^5$ Pa set by IUPAC)

You may start your calculation of the equilibrium with any composition of the mixture of NO_2 and N_2O_4, e.g. you can assume that only NO_2 exists in the beginning: $n(NO_2) = 64.4g/46.0\ gmol^{-1} = 1.40$ mol

	$2\ NO_2$	$\rightleftarrows$	N_2O_4
Amount of substance in equilibrium:	(1.40 - 2x)mol		x mol

total amount of substance in equilibrium: $n_{total} = (1.40 - x)mol$

partial pressures in equilibrium: $p(NO_2) = (n(NO_2)/n_{total})\cdot p_{total}$

$p(N_2O_4) = (n(N_2O_4)/n_{total})\cdot p_{total}$

$$Kp = \frac{p(N_2O_4)}{p^2(NO_2)}$$

$$6.00\cdot 10^{-5}\ Pa^{-1} = \frac{n(N_2O_4)\cdot n_{total}}{n^2(NO_2)\cdot p_{total}} \quad \text{and} \quad p_{total} = n_{total}\cdot R\cdot T/V$$

$$6.00\cdot 10^{-5} = \frac{x\cdot(1.40-x)}{(1.40-2x)^2}\cdot\frac{15\cdot 10^{-3}}{(1.40-x)\cdot 8.314\cdot 300}$$

⇨ $x^2 + x\cdot\frac{1}{4}\cdot(-5.6 - 15/(18\cdot 8.314)) + \frac{1}{4}\cdot 1.4^2 = 0$

⇨ $x_1 = 0.846$ (not relevant because of $1.40 - 2x < 0$) $\quad x_2 = 0.579$

⇨ $n(N_2O_4) = 0.579$ mol $\quad n(NO_2) = 0.241$ mol $\quad n_{total} = 0.821$ mol

$p_{total} = (0.821 \cdot 8.314 \cdot 300 / 15\cdot 10^{-3})\ Pa = 136.516\ Pa$ $\quad \mathbf{p_{total} \approx 1.37\ bar}$

b) As the pressure decreases the position of the equivalence changes. Thus the partial pressure does not decrease in the same way as the total pressure. The equilibrium composition has to be taken into account.

The decline of the total pressure follows the same law as the radioactive decay:

$p_{gesamt} = p_{0,\,total} \cdot e^{-kt}$ with $k = 0.001\ s^{-1}$

Determination of the equilibrium constant:

$\Delta H = \Delta H_{products} - \Delta H_{reactants} + (Cp_{products} - Cp_{reactants}) \cdot \Delta T$

$\Delta H = -57240\ Jmol^{-1} + (77.8 - 2 \cdot 37.2) \cdot 52\ Jmol^{-1} = -57063\ Jmol^{-1}$

$\Delta S = \Delta S_{products} - \Delta S_{reactants} + (Cp_{products} - Cp_{reactants}) \cdot \ln(T_2/T_1)$

$\Delta S = -175.9\ JK^{-1}mol^{-1} + (77.8 - 2 \cdot 37.2)\ JK^{-1}mol^{-1} \cdot \ln(350/298) = -175.35 JK^{-1}mol^{-1}$

$\Delta G = -57063\ Jmol^{-1} - 350\ K \cdot (-175.35\ JK^{-1}mol^{-1}) = 4310\ Jmol^{-1}$

$\ln K = -4310/(8.314 \cdot 350)$ $K = 0.227$ $Kp = 2.27 \cdot 10^{-6}\ Pa^{-1}$

$Kp = \frac{p(N_2O_4)}{p^2(NO_2)}$ and $p(N_2O_4) + p(NO_2) = p_{total}$ with $p_{total} = p_{0,\,total} \cdot e^{-0.001/s \cdot t}$

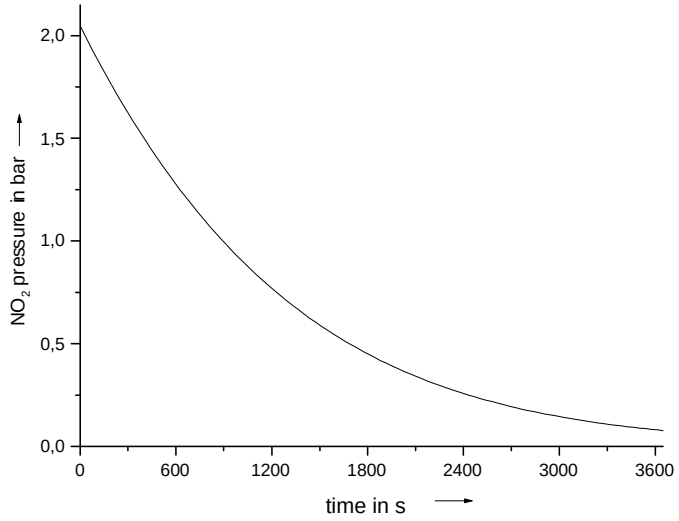
$p(N_2O_4) + p(NO_2) = p_{0,\,gesamt} \cdot e^{-0.001/s \cdot t}$

$$Kp = \frac{3.00 \cdot 10^5 Pa \cdot e^{-0.001\ s^{-1} \cdot t} - p(NO_2)}{p^2(NO_2)}$$

$p^2(NO_2) + p(NO_2) \cdot Kp^{-1} - (3.00 \cdot 10^5\ Pa \cdot e^{-0.001/s \cdot t}) \cdot Kp^{-1} = 0$

$$\mathbf{p(NO_2)} = -\frac{1}{2 \cdot Kp} + \sqrt{\frac{1}{4 \cdot Kp^2} + \frac{3.00 \cdot 10^5 Pa \cdot e^{-0.001\ s^{-1} \cdot t}}{Kp}} \quad \text{or}$$

$$\mathbf{p(NO_2) = [-220 \cdot 10^3 + \sqrt{4.85 \cdot 10^{10} + 1.32 \cdot 10^{11} \cdot e^{-0.001\ s^{-1} \cdot t}}\ ]\ Pa} \qquad (0)$$



c) Molar fraction $x = p(NO_2) / p_{total}$

(1) $\mathbf{x =} \left(-\frac{1}{2 \cdot Kp} + \sqrt{\frac{1}{4 \cdot Kp^2} + \frac{3.00 \cdot 10^5 Pa \cdot e^{-0.001\ s^{-1} \cdot t}}{Kp}}\right) / (3.00 \cdot 10^5\ Pa \cdot e^{-0.001/s \cdot t})$

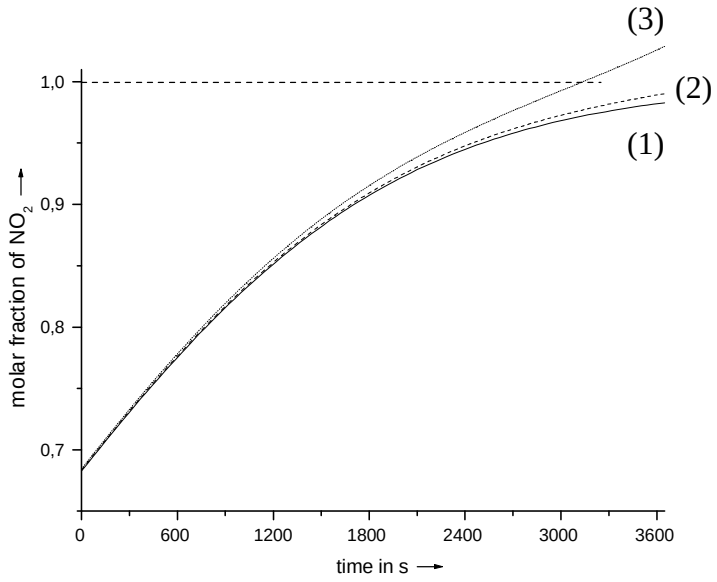
or $Kp = 2.27 \cdot 10^{-6}\ Pa^{-1}$ inserted and rounded with three significant figures:

(2) $\mathbf{x =} \frac{-0.734 + \sqrt{0.539 + 1.47 \cdot e^{-0.001\ s^{-1} \cdot t}}}{e^{-0.001\ s^{-1} t}}$

(Function (1) reacts very sensitive on rounding. The graphs of (1) and (2) hardly differ in the time interval asked for but already at t > 4000 s the graph of (2) exceeds the value 1, what cannot apply to a mole fraction.
If you use equation (0) to determine the function of the molar fraction you get an equation similar to (2):

(3) $x = \frac{-0.733 + \sqrt{0.539 + 1.47 \cdot e^{-0.001\ s^{-1} \cdot t}}}{e^{-0.001\ s^{-1} \cdot t}}$

The course of the plot (3) shows even in the time interval asked for that the molar fraction becomes > 1.)

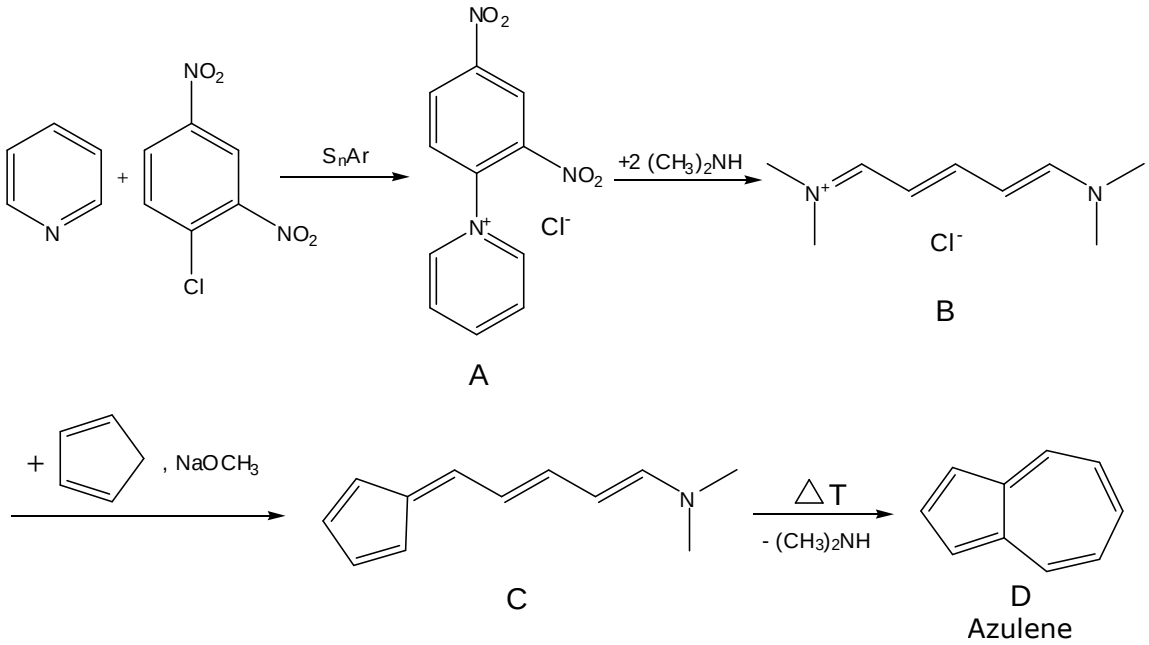


d) Decrease of total pressure leads to decrease of partial pressure of NO_2 as shown in the plot b).
But if the total pressure decreases the composition of the equivalent changes to the side of a higher number of particles (principle of Le Chatelier), thus the formation of NO_2 is favoured and the mole fraction of NO_2 increases according to plot in c).

Solution to problem 2-4

a) As there are signals only in the range from 7 ppm to 8,5 ppm in the ^{1}H-NMR spectrum **D** is an aromatic compound.
n (C) : n (H) = 5:4

b) Due to the NMR spectrum five different kinds of protons exist. Thus the empirical formula of **D** is likely to be $C_{10}H_8$.
Two compounds come into consideration, naphthaline and azulene. Naphthaline is dropped out because of the spectrum and the given properties (dipole moment, blue colour). So **D** should be azulene.
The classical Hafner syntheses confirms this assumption:



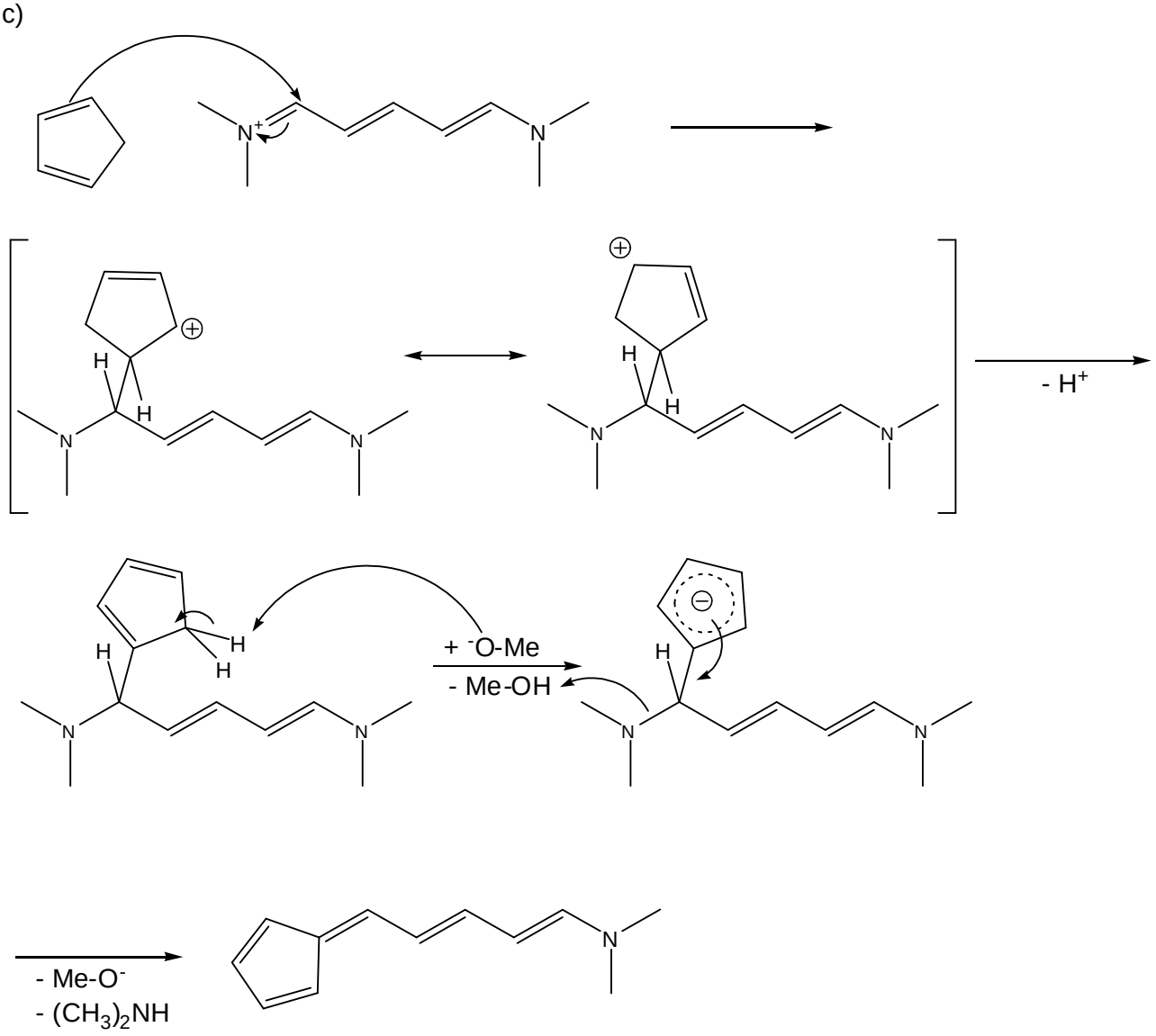
Comment: Pyridine is used as C5 module which can be condensed with cyclopentadiene to form azulene. In a first step pyridine is transferred into a reactive pyridinium salt by reaction with 2,4-dinitrochlorobenzene (nucleophilic substitution).

Through this the pyridine system is activated to undergo a nucleophilic process to open the ring by dimethylamine. At first base **B** arises.

B condenses in a basic surrounding with cyclopentadiene to yield fulvene **C**.

On heating **C** eliminates dimethylamine and cyclises to form azulen **D**.

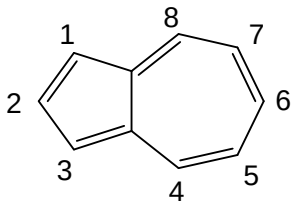
c)



Comment: The reaction of **B** with cyclopentadiene can be described analogous to a kind of Mannich reaction as an addition of the iminium salt to the double bond of cyclopentadiene. Under the influence of sodium methoxide the intermediate formed expels dimthylamine (E1cb-reaction) to give fulvene **C**.

The reaction can also be described as an attack of the deprotonated cyclopentadienide anion on the iminium ion (= analogon of a carbonyl compound). Another deprotonation of cyclopentadiene in the product of the addition reaction leads in an E1cb-elimination to fulvene **C** as shown above.

d)

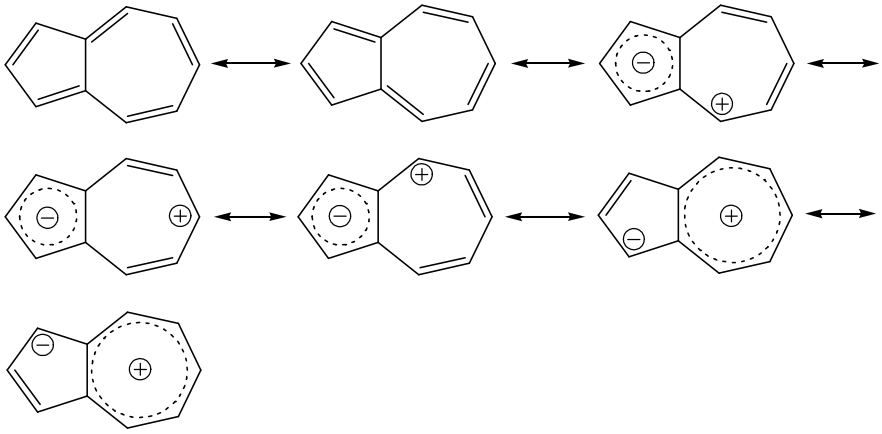


Doublet is due to the coupling of an ^{1}H nucleus to only one proton at a neighbouring C atom.

Triplet is due to the coupling of an ^{1}H nucleus to exactly two protons at neighbouring C atoms.

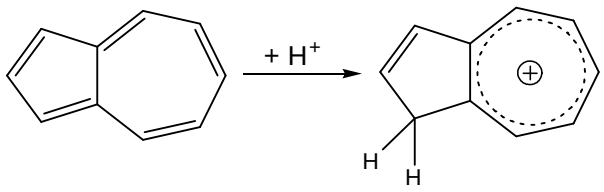
H atoms at the C atoms 2, 5, 6 and 7 can be considered to give rise to triplets.

e)

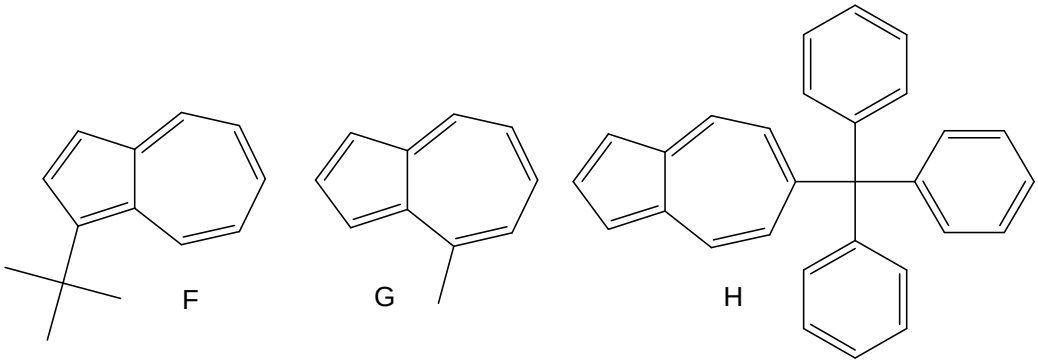


These resonance structures account for the blue colour, the aromatic character and the dipole moment, which is unusually high for a hydrocarbon.

Obviously the dipole moment of **D** is small compared with other compounds soluble in water. Thus azulene in insoluble in water but soluble in strong acids because the molecule can be protonated relative easily. In this case not the whole aromatic system is destroyed and the positive charge is well delocalised. This protonated form solves well in water (see image next page).



f) Structure of **F**, **G** and **H**:



Comment

Compound **F** forms in an elctrophilic substitution. The tert. butylcation which forms from acid and tert. butanole attacks azulene in position 1 and 3 respectively (see the last two resonance structures in e)).

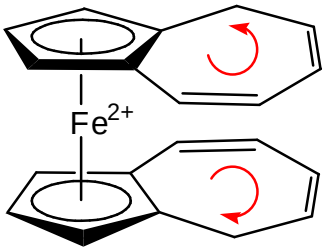
The overall reaction to **G** und **H** is a nucleophilic substitution. The process can be looked at as an addition-elimination process:

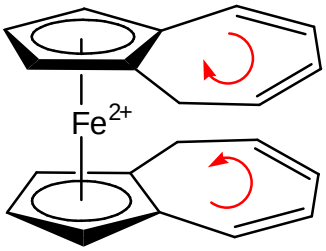
At first an addition of the nucleophilic alkyl group takes place resulting in the formation of a salt. To restore the aromatic system a hydride ion should be eliminated which is done on detour by oxidation (= elimination of a proton and two electrons instead of elimination of a hydride ion).

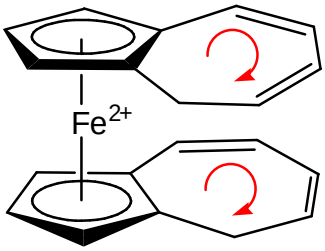
The nucleophilic attack should take place at position 4 (8) and 6 respectively, the attack in position 4 (8) is more likely. With small substituents to insert the product substituted in position 4 will occur.

Having a greater volume as e.g. the triphenylmethyl group the substitution will take place at position 6 due to sterical intramolecular interaction especially to the H atom at C3.

g) Structure of **I**







Pair of Enantiomers

Meso Compound

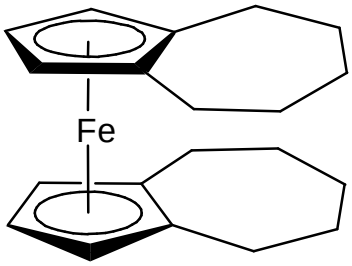
Comment

Again the nucleophile (in this case hydride) attacks in position 4 (8) as shown above. (An attack in position 6 would not lead to a mixture of stereoisomers.)

A cyclopentadienide salt is formed which reacts to the ferrocen derivate **I**.

There exist three stereoisomers of **I** according to the position of the remaining two double bonds: a pair of enantiomers and a meso compound.

Structure of **J**



Answers Round 3 Test 1

Solution to problem 3-1

a) A and D b) B c) C d) E e) E

Solution to problem 3-2

a) $Ca + 2\ H_2O \longrightarrow Ca^{2+} + 2\ OH^- + H_2$

$2\ K + 2\ H_2O \longrightarrow 2\ K^+ + 2\ OH^- + H_2$

b) $2\ Al + 6\ H_3O^+ \longrightarrow 2\ Al^{3+} + 6\ H_2O + 3\ H_2$

$Zn + 2\ H_3O^+ \longrightarrow Zn^{2+} + 2\ H_2O + H_2$

$Fe + 2\ H_3O^+ \longrightarrow Fe^{2+} + 2\ H_2O + H_2$

c) $2\ Al + 6\ H_2O + 2\ OH^- \longrightarrow 2\ [Al(OH)_4]^- + 3\ H_2$

$Zn + 2\ H_2O + 2\ OH^- \longrightarrow [Zn(OH)_4]^{2-} + H_2$

d) $3\ Ag + HNO_3 + 3\ H_3O^+ \longrightarrow 3\ Ag^+ + NO + 5\ H_2O$

$3\ Cu + 2\ HNO_3 + 6\ H_3O^+ \longrightarrow 3\ Cu^{2+} + 2\ NO + 10\ H_2O$

e) n(Me) = n(Cu) = n(Pb) M(Me) = x

$Me + Pb^{2+} \longrightarrow Me^{2+} + Pb$ 100 g ⟶ 119g

$Me + Cu^{2+} \longrightarrow Me^{2+} + Cu$ 100 g ⟶ 90,2 g

100 g - n·x + n·207.2 g/mol = 119 g

<u>100 g - n·x + n·63.55 g/mol = 90.2 g</u>

9.8 g + n·63.55 g/mol = - 19 g + n·207.2 g/mol n = 0.2 mol

x = M(Me) = 112.4 g/mol **Me = Cadmium**

Solution to problem 3-3

a) $n_{total} = p \cdot V/R \cdot T$ $n_{total} = 71800 \cdot 100 \cdot 10^{-6}/((8.314 \cdot 298)$ $n_{total} = 2.90 \cdot 10^{-3}$ mol

$M_1 = M(C_{21}H_{23}O_5N) = 369.45$ g/mol $M_2 = M(C_{12}H_{22}O_{11}) = 342.34$ g/mol

$n = m/M$ $n_1 + n_2 = n_{total}$ $m_1 + m_2 = 1$ g

⇨ $(1-m_2)/M_1 + m_2/M_2 = 2.90 \cdot 10^{-3}$ mol **$m_2 = 0.902$ g (90.2 %)**

$m_1 = 0.098$ g (9.8 %)

b) Together with the sample water is brought into the solution. Cristallisation takes water out of the solution.

$M(CaCl_2) = 110.98$ g/mol $M(CaCl_2 \cdot 6\ H_2O) = 219.1$ g/mol

In 74.9 g $CaCl_2 \cdot 6\ H_2O$ (residue) are

74.9 g·110.98/219.1 = 37.94 g $CaCl_2$

total mass - mass of residue = mass of the saturated solution

230.00 g - 74.90 g = 155.10 g

x = mass of $CaCl_2$ y = mass of H_2O in the saturated solution in each case

x + y = 155.10 g 74.5/100 = x/y $\Rightarrow$ y = 88.88 g x = 66.22 g

In 150 g are 66.22 g + 37.94 g = 104.16 g $CaCl_2$ (0.939 mol) and

150 g - 104.16 g = 45.84 g H_2O (2.54 mol) $\Rightarrow$ **≈ 2.7 mol H_2O per 1 mol $CaCl_2$**

Solution to problem 3-4

a) $c(Ac^-) = c_0(HAc)\cdot\alpha$. $c(Ac^-) = c(H_3O^+)$ $K_a = \frac{(c_0\cdot\alpha)^2}{c_0(1-\alpha)\cdot mol/L}$

$1.74\cdot10^{-5} = \frac{c_0\cdot 0{,}1^2}{0{,}9\cdot mol/L}$ **$c_0 = 1.566\cdot10^{-3}$ mol/L**

$c(Ac^-) = c(H_3O^+) = 1.566\cdot10^{-4}$ mol/L **pH = 3.8**

M(HAc) = 60.04 g/mol **m(HAc) = 0.094 g**

b) At pH ≈ 12 the propionate anion (Pr^-) is the only species of propionic acid i.e. all OH^--ions derive from sodium hydroxide $\Rightarrow$ log(c(NaOH)) = - 14 + pH = -1. 82

c(NaOH) = 0.015 mol/L.

Until you reach the first equivalent point (15 mL HCl) exactly these OH^--ions are neutralised $\Rightarrow$ c(NaOH)·V(NaOH) = c(HCl)·V(HCl)

c(HCl) = (20·0.015 mol/L)/15 = 0.02 mol/L

consumption for the titration of Pr^- = 15 mL HCl

$\Rightarrow$ c(NaPr in the parent solution) = 0.015 mol/L

$M(NaC_2H_5COO)$ = 96.09 g/mol **m(NaPr)** = 0.25·96.09·0.015 g = **0.360 g**

Solution to problem 3-5

a) $2\ H_2O \rightleftharpoons 2\ H_2 + O_2$ $K_p' = \frac{p^2(H_2)\cdot p(O_2)}{p^2(H_2O)} = \frac{(p\cdot\alpha_1)^2\cdot 0.5\cdot p\cdot\alpha_1}{p^2\cdot(1-\alpha_1)^2}$

$K_p' = 7.63\cdot10^{-21}\cdot p$

$2\ HCl \rightleftharpoons H_2 + Cl_2$ $K_p'' = \frac{(0.5\cdot\alpha_2)^2}{(1-\alpha_2)^2} = 3.03\cdot10^{-11}$

$4\ HCl + O_2 \rightleftharpoons 2\ Cl_2 + 2\ H_2O$ $K_p = \frac{p^2(H_2O)\cdot p^2(Cl_2)}{p(O_2)\cdot p^4(HCl)}$

$K_p = \frac{p^2(H_2O)}{p(O_2)\cdot p^2(H_2)}\cdot\frac{p^2(H_2)\cdot p^2(Cl_2)}{\cdot p^4(HCl)}$ = $K_p''^2/K_p'$ $K_p = 0.12\cdot p^{-1}$

$K = K_p\cdot p_0$ **K = 0.12** (as $p = p_0$)

$\Delta G = - R\cdot T\cdot \ln K$ $\Delta G = - 8.314\ JK^{-1}mol^{-1}\cdot 1000\ K\cdot \ln 0.12$ **$\Delta G = 17.6\ kJmol^{-1}$**

Solution to problem 3-6

a) (i) The electron pairs are situated in a way that their distance is at a maximum.

(ii) A non-binding electron pair requires more space than a binding one.

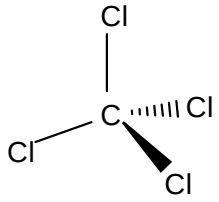
(iii) The size of a binding electron

declines with increasing electronegativity of the ligands

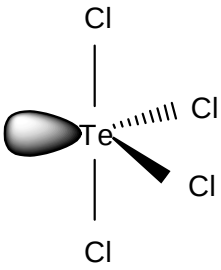
declines with declining electronegativity of the central atom

(iv) The two pairs of a double bond require more space than the pair of an single bond.

b)

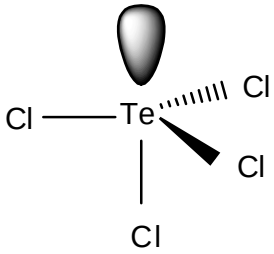


CCl_4

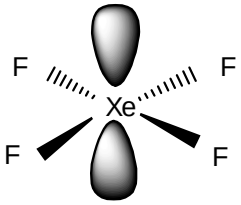


(more stable)

or



$TeCl_4$



(more stable)

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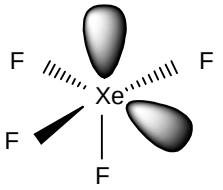
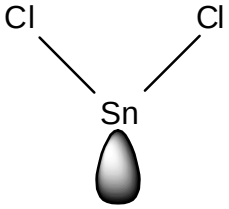


XeF_4

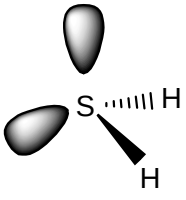
c) $BeCl_2$ Cl — Be — Cl angle = 180°

$SnCl_2$

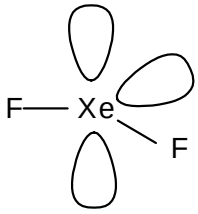


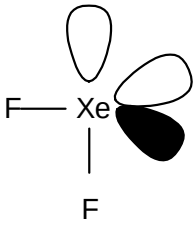
angle ≤120°

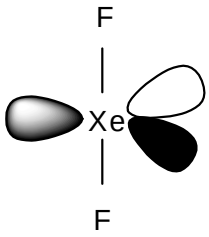
H_2S



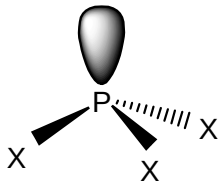
angle ≤109.5°

XeF_2 

or 

or 

favoured
angle 180°

d) 

Maximal angle according to VSEPR: 109.5°.
Actually the angle is smaller. The free electron pair needs more space and pushes the binding electron pairs downwards so the angles between the substituents become smaller.

Trend I→ F: The angle becomes smaller (102°, 101.5°, 100.3°, 97.9°).

Reason: Increasing electronegativity of the substituents.

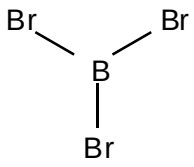
The space at the central atom occupied by the binding electron pairs decreases the more they are attracted to the substituents. Thus it is easier for the free electron pair to enforce its claim of space.

e) NH_3/PH_3 (107°/93.6°)
As the electronegativity decreases from N to P the binding pairs need less space an the central atom and are easier to push away by the free pair.

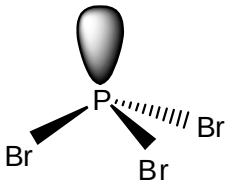
PH_3/PF_3 (93.6°/96.3°)
The angle increases though the EN of F is larger than that of H. Phosphorus possesses empty orbitals which can undergo resonance with the free electron pairs of the fluorine. Thus all bonds are partial double bonds. As double bonds need more space than single bonds (in PH_3), the binding electrons at P can not be pushed away as easily.

Solution to problem 3-7

a) $BBr_3 + PBr_3 + 3\,H_2 \longrightarrow BP + 6\,HBr$

b) 

trigonal planar

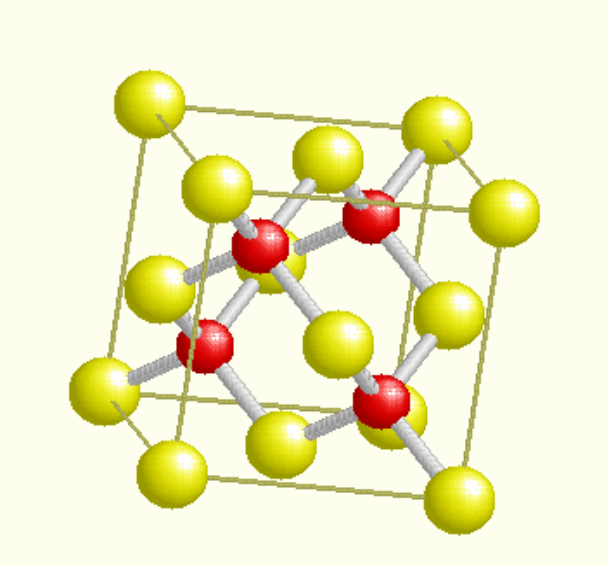


trigonal pyramidal

c)

outside: boron
inside: phosphorus

(the thick lines do not represent bonds but clarify the tetrahedral holes)



d) One unit cell contains 4 BP units

$\rho = m/V$ $\quad m = 4 \cdot M(BP)/N_A$ $\quad V = (4.78\ Å)^3$

$$\rho = \frac{4 \cdot 41{,}78 \cdot 10^{-3}\ kg/mol}{6{,}022 \cdot 10^{23}\ mol^{-1} \cdot (4{,}78 \cdot 10^{-10} m)^3}$$

ρ = 2541 kg/m^3

e) The distance B-P is equal to a quarter of space diagonal

distance B-P = 4.78 Å $\cdot \sqrt{3}$ /4 = 2.070 Å

or

Distance B-P is equal to the radius of circumcircle $r_{circumcircle}$ of the tetrahedron, the basic edge of the tetrahedron is equal to half of the plane diagonal of the elementara unit.

a/2 = 4.78 Å $\cdot \sqrt{2}$ /2 distance B-P = 4.78 Å $\cdot \sqrt{3}$ /4 **distance B-P = 2.070 Å**

f) $U_{lattice} = - \frac{3 \cdot 3 \cdot 1.638 \cdot 1390}{2.070}\left(1 - \frac{1}{7}\right)$ J/mol **$U_{lattice}$ = - 8485 kJ/mol**

g) $r = k \cdot c(BBr_3)^n \cdot c(PBr_3)^m \cdot c(H_2)^p$

From the data given : n = 1. m = 1. p = 0 **$r = k \cdot c(BBr_3) \cdot c(PBr_3)$**

overall order = 2

$k_{800} = 4.60 \cdot 10^{-8}/(2.25 \cdot 10^{-6} \cdot 9 \cdot 10^{-6})$ **k_{800} = 2272 (mol/L)$^{-1}$s^{-1}**

k_{880} = 9679 (mol/L)$^{-1}$s^{-1}

h) $k = A \cdot e^{-Ea/(R \cdot T)}$ $\quad \ln(k_{800}/k_{880}) = - E_a/(R \cdot 1073\ K) + E_a/(R \cdot 1153\ K)$

$E_a = R \cdot \ln(k_{800}/k_{880})/(1/1153 - 1/1073)$ **E_a = 186 kJ/mol**

Solution to problem 3-8

a) n (C) : n (H) : n (O) = (65.2/12.01) : (8.75/1.007) : (26.05/16)
n (C) : n (H) : n (O) = 5.43 : 8.69 : 1.63 = 3.33 : 5.33 : 1 = 10 : 16 : 3
M ($C_{10}H_{16}O_3$) = 184.13 g/mol ⇒ **X = $C_{10}H_{16}O_3$**.

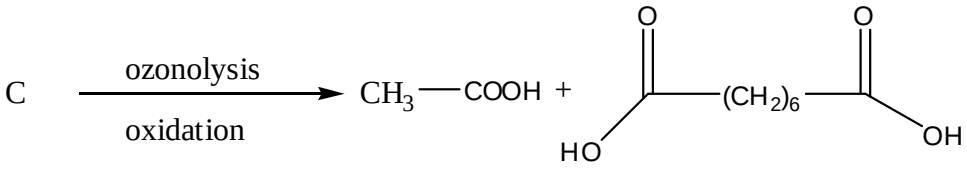
Assumption: one COOH-group is responsible for the acidity.
Titration shows: amount of acid groups n = 0.237 mmol
⇒ M = 184 g/mol. Just 1 **COOH-group in X**.

$$DBE = \frac{2a+2-b}{2} = 3$$

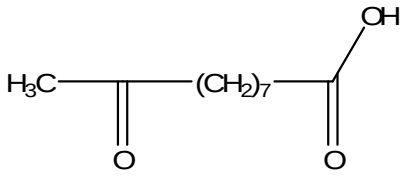
X contains **3 double bonds**, one of them in the COOH-group.

b) B is a secondary alcohol with a **OH-group**.
A is a ketone with a carbonyl group **(-C=O)**.

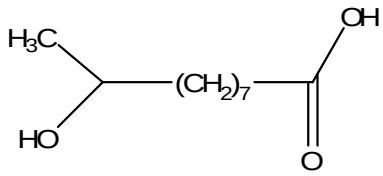
c)



Compound C: CH_3 - CH = CH - $(CH_2)_6$ - COOH



A

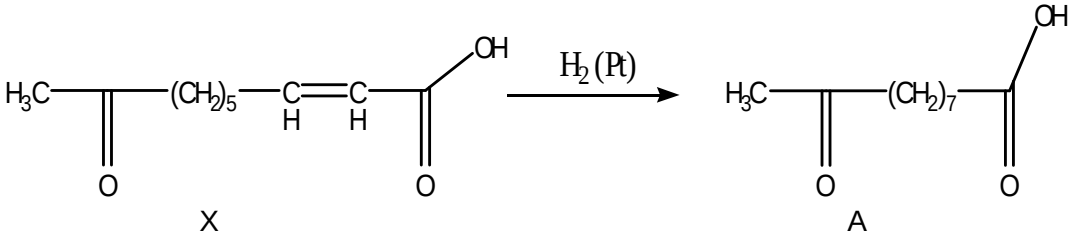


B

If you get oxalic acid from the ozonolysis of X then X must have the structure

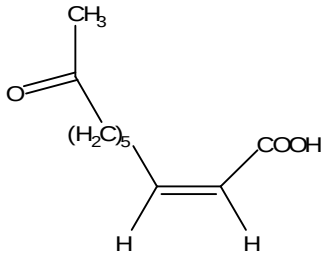
R_1 - HC = CH - COOH .

⇒

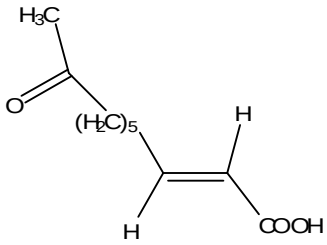


X A

d) **Z,E- isomerism**

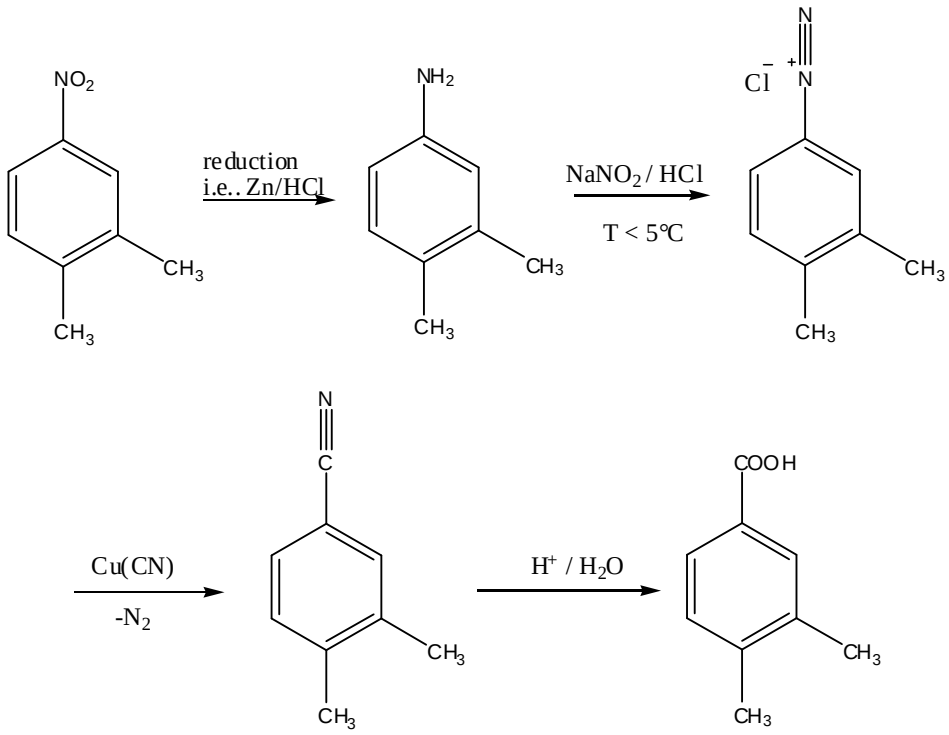


Z-compound
(cis)

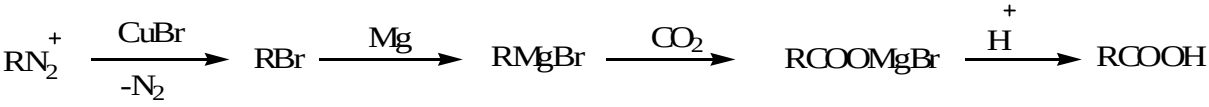


E-compound
(trans)

Solution to problem 3-9



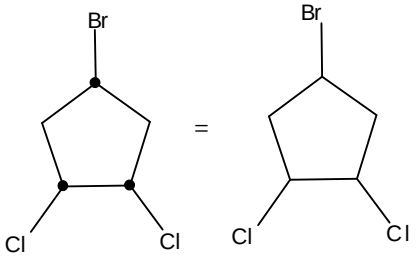
Another possibility:



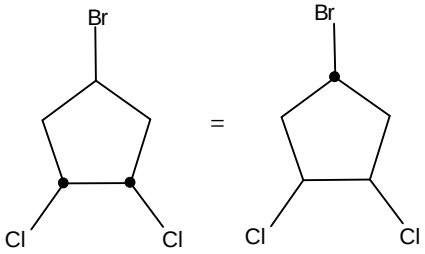
Solution to problem 3-10

a) $2^3 = 8$

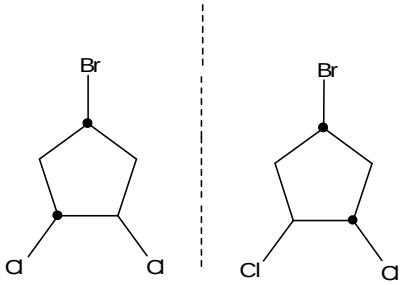
b) Stereoisomers



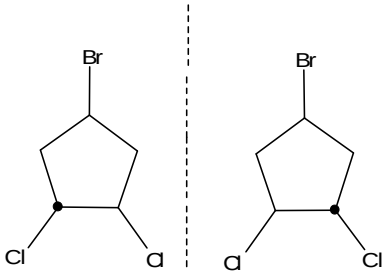
meso-compound (optically inactive)



meso-compound (optically inactive)



enantiomers
(optically active)



enatiomers
(optically active)

Answers Round 3 Test 2

Solution to problem 3-11

a) C b) C c) (i) A (ii) B (iii) D d) A, D und E e) A

Solution to problem 3-12

a) $m = m(H_3Cit \text{ in 6 tablets})/6 = n_0 (H_3Cit \text{ in 6 tablets}) \cdot M(H_3Cit)/6$

$c_0(H_3Cit) = n_0 (H_3Cit \text{ in 6 tablets})/L$ $M(H_3Cit) = 192.14$ g/mol

$K_{a1.\ citirc\ acid} = \frac{c(H_2Cit^-) \cdot c(H_3O^+)}{c(H_3Cit)}$ with $c(H_2Cit^-) = c(H_3O^+)$

and $c(H_3Cit) = c_0(H_3Cit) - c(H_2Cit^-)$

$\Rightarrow\ 7.1 \cdot 10^{-4} = \frac{10^{-8.4}\,mol/L}{c_0(H_3Cit) - 10^{-4.2}\,mol/L} \Rightarrow\ c_0(H_3Cit) = 6.87 \cdot 10^{-5}$ mol/L

$m = 6.87 \cdot 10^{-5} \cdot 192.12$ g /6 **$m = 2.2 \cdot 10^{-3}$ g citric acid/tablet**

b) $m = c_0(H_3Cit) \cdot M(H_3Cit)/6$ $m = c_0(H_3Cit) \cdot (192.14\ g/mol)/6$

$c_0(H_3Cit) = c(H_3Cit) + c(H_2Cit^-) + c(HCit^{2-})$

$K_{a1.\ citric\ acid} = \frac{c(H_2Cit^-) \cdot c(H_3O^+)}{c(H_3Cit)}$ $7.1 \cdot 10^{-4} = \frac{c(H_2Cit^-) \cdot 10^{-4.2}}{c(H_3Cit)}$

$K_{a2.\ citric\ acid} = \frac{c(HCit^{2-}) \cdot c(H_3O^+)}{c(H_2Cit^-)}$ $1.68 \cdot 10^{-5} = \frac{c(HCit^{2-}) \cdot 10^{-4.2}}{c(H_2Cit^-)}$

$c(H_3O^+) = c(H_2Cit^-) + 2 \cdot c(HCit^{2-})$ $10^{-4.2}$ mol/L $= c(H_2Cit^-) + 2 \cdot c(HCit^{2-})$

c) $m = 3 \cdot 10^{-3}$ g citric acid/tablet

$3 \cdot 10^{-3}\ g = c_0(H_3Cit \text{ in tea}) \cdot 1\ L \cdot (192.14\ g/mol)/6$ $c_0(H_3Cit \text{ in tea}) = 9.37 \cdot 10^{-5}$ mol/L

degree of protolysis in tea $\alpha_1 = c(H_2Cit^-)/\ c_0(H_3Cit) = 10^{-4.1}/9.37 \cdot 10^{-5} = 0.85$

degree of protolysis in the stomach

$V_{1.\ before\ drinking} = 2.30$ L $n_1(H_3O^+) = 2.3\ L \cdot 10^{-2.1}$ mol/L

$V_{2.\ after\ drinking} = 2.62$ L $n_2(H_3O^+) = n_1(H_3O^+)$

$$c_2(H_3O^+) = \frac{2.3 \cdot 10^{-2.1}\,mol}{2.62\ L} = 6.97 \cdot 10^{-3}\,mol/L$$

This is the concentration of H_3O^+-ions, the degree of protolysis of citric acid has to be determined:

$$c_0(H_3Cit \text{ in the stomach}) = \frac{9.37 \cdot 10^{-5}\ mol/L \cdot 0.32\ L}{2.62\ L} = 1.14 \cdot 10^{-5}\ mol/L$$

$$K_{a1.\ citric\ acid} = \frac{c(H_2Cit^-)\cdot c(H_3O^+)}{c(H_3Cit)}$$

$$7.1\cdot10^{-4} = \frac{c(H_2Cit^-)\cdot 6.97\cdot10^{-3}}{1.14\cdot10^{-5}\ mol/L - c(H_2Cit^-)} \quad \Rightarrow \quad c(H_2Cit^-) = 1.05\cdot10^{-6}\ mol/L$$

$\alpha_2 = = 1.05\cdot10^{-6} / 1.14\cdot10^{-5}$ $\quad \alpha_2 = 9.21\cdot10^{-2}$

$$\frac{\alpha_1}{\alpha_2} = \frac{0.85}{9.21\cdot10^{-2}} \approx 9.2$$ **$\alpha_1/\alpha_2 \approx 9.2$**

d) Electron donators as R diminish, electron acceptors increase the acidity.

- most powerful acceptor in this row with a -M and -I effect is **NO_2** $\Rightarrow$ **$pK_a = 3.41$**
- following **Cl** with a -I and a smaller +M effect $\Rightarrow$ **$pK_a = 4.01$**
- most powerfull donator is **OCH_3** with a -I and a strong +M effect $\Rightarrow$ **$pK_a = 4.46$**
- following **CH_3** with a +I effect $\Rightarrow$ **$pK_a = 4.35$**
- without effects is **H** $\Rightarrow$ **$pK_a = 4.21$**

Solution to problem 3-13

a) $p\cdot V = n\cdot R\cdot T$ $\quad n(B) = \frac{101300Pa\cdot0.211\cdot10^{-3}m^3}{8.314JK^{-1}mol^{-1}\cdot298K}$ $\quad n(B) = 8.63\cdot10^{-3}$ mol

$M = m/n$ $\quad M(B) = 0.38\ g / 8.63\cdot10^{-3}\ mol \quad M(B) \approx 44$ g/mol

⇨ $B = CO_2$

A = $FeCO_3$ B = CO_2 C = $FeSO_4$ D = $Fe(OH)_3$ E = $FeCl_3$

Reactions:

$2\ H_3O^+ + SO_4^{2-} + FeCO_3 \longrightarrow Fe^{2+} + SO_4^{2-} + 3\ H_2O + CO_2$

$5\ Fe^{2+} + MnO_4^- + 8\ H_3O^+ \longrightarrow 5\ Fe^{3+} + Mn^{2+} + 12\ H_2O$

$2\ Fe^{2+} + H_2O_2 + 2\ H_3O^+ \longrightarrow 2\ Fe^{3+} + 4\ H_2O$

$Fe^{3+} + 3\ OH^- \longrightarrow Fe(OH)_3$

$Fe(OH)_3 + 3\ H_3O^+ + 4\ Cl^- \longrightarrow FeCl_4^- + 6\ H_2O$

$FeCl_4^- + 3\ SCN^- \longrightarrow Fe(SCN)_3 + 4\ Cl^-$

(instead of $FeCl_4^-$ and $Fe(SCN)_3$ there are other possibilities)

b) weighed portion: $n(FeCO_3) = 1g / 115.86\ gmol^{-1} = 8.631\cdot10^{-3}$ mol

titration: $½ \cdot n(Fe^{2+}) = 5\cdot n(MnO_4^-)$

$n(Fe^{2+}) = 2 \cdot 5 \cdot 0.02\ mol/L \cdot 43.15\cdot10^{-3}\ L = 8.631\cdot10^{-3}$ mol

the total amount reacted

Solution to problem 3-14

a) $Sn^{2+} + 2\ Fe^{3+} \longrightarrow Sn^{4+} + 2\ Fe^{2+}$ mit $\Delta G°$

$\Delta G° = -E°\cdot z\cdot F$ $\quad Sn^{4+} + 2\ e^- \rightleftarrows Sn^{2+}$ $\quad \Delta G_1 = -2\cdot F\cdot 0.154$ V

$Fe^{3+} + e^- \rightleftarrows Fe^{2+}$ $\quad \Delta G_2 = -1\cdot F\cdot 0.771$ V

$\Delta G° = 2\cdot\Delta G_2 - \Delta G_1$ $\quad \Delta G° = -1.234\cdot 96485$ J/mol $\quad$ **$\Delta G° \approx -119$ kJ/mol**

b) $\Delta G = -R\cdot T\cdot \ln K$ $\quad \ln K = -(-119\ \text{kJ/mol}) / (8.314\ \text{JK}^{-1}\text{mol}^{-1}\cdot 298\ \text{K})$

$\ln K = 48.03$ $\quad$ **$K = 7.23\cdot 10^{20}$**

c) The cell consitsts of the calomel electrode (positive potential) and the half cell with the solution to be titrated. $\Rightarrow$ voltage of the cell = $E°_{Kalomel} - E_{Lösung}$

In the solution $c(Sn^{4+})/c(Sn^{2+}) = 1/3$

$E_{solution} = 0.154\ \text{V} + \frac{8{,}314\cdot 298}{2\cdot 96485}\text{V}\cdot\ln(1/3)$ $\quad E_{solution} = 0.140$ V

voltage of the cell $= 0.242$ V $- 0.140$ V $\quad$ **$= 0.102$ V**

d) Voltage of the cell $= E°_{calomel} - E(Fe^{3+}/Fe^{2+})$

$$= 0.242\ \text{V} - \left(0.771\ \text{V} + \frac{R\cdot T}{F}\cdot\ln\frac{c(F^{3+})}{c(Fe^{2+})}\right) \qquad (1)$$

$$K = \frac{c(Sn^{4+})\cdot c^2(Fe^{2+})}{c(Sn^{2+})\cdot c^2(Fe^{3+})}$$

at the equivalence point $c(Sn^{4+}) = 0.5\cdot c(Fe^{2+})$ $\quad$ therefore $0.5\cdot c(Fe^{3+}) = c(Sn^{2+})$

$\Rightarrow K = \frac{\cdot c^3(Fe^{2+})}{c^3(Fe^{3+})}$ $\quad \Rightarrow \frac{c(F^{3+})}{c(Fe^{2+})} = \sqrt[3]{\frac{1}{K}}$ $\quad$ inserted in (1)

voltage of the cell $= 0.242\ \text{V} - \left(0.771\ \text{V} + \frac{R\cdot T}{F}\cdot\ln\sqrt[3]{\frac{1}{7{,}23\cdot 10^{20}}}\right)$ $\quad$ **$= -0.118$ V**

e) Beyond the equivalence point you use $c(Fe^{3+})/c(Fe^{2+})$ to calculate $E_{solution}$

$c(Fe^{3+})/c(Fe^{2+}) = ½$ $\quad E_{solution} = 0.771\ \text{V} + \frac{8{,}314\cdot 298}{96485}\text{V}\cdot\ln 0.5 = 0.753$ V

voltage of the cell $= 0.242$ V $- 0.753$ V $\quad$ **$= -0.511$ V**

Solution to problem 3-15

a) 43.5 mL OH^- solution ⇨ $\quad$ 2.175 mmol OH^- for 0.1 g X $\Rightarrow$ $M(X) = 46$ g/mol

⇨ X = HCOOH, formic acid

b) $HCOOH \longrightarrow H_2O + CO$ $\quad$ S = sulfuric acid, H_2SO_4

c) $n_\infty(CO) = n_0(HCOOH) = \frac{p \cdot V}{R \cdot T} = \frac{101300 \cdot 41{,}5 \cdot 10^{-6}}{8{,}314 \cdot 298}$ mol = $1.70 \cdot 10^{-3}$ mol

supposably of 1. order due to the reaction equation

d) Proving wether the reaction is of 1. order:

$k = \frac{1}{t} \cdot \ln \frac{c_0}{c}$ with $\frac{c_0}{c} = \frac{n_0(HCOOH)}{n_t(HCOOH)} = \frac{1{,}70 \cdot 10^{-3}}{1{,}70 \cdot 10^{-3} - n(CO)}$

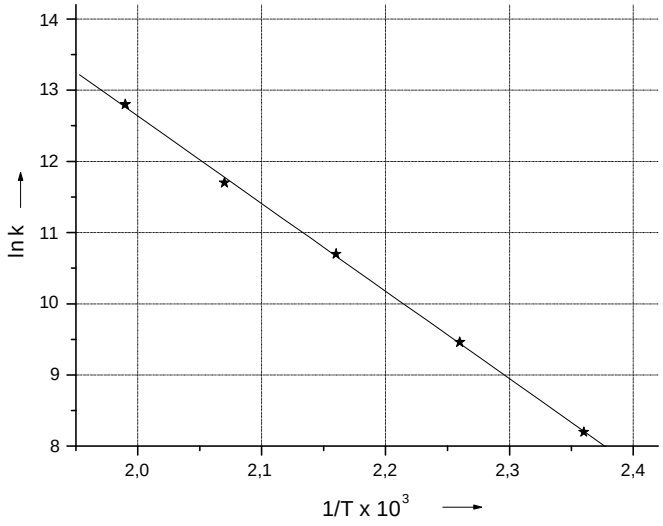
t (in s)	0	50	100	150	200	∞
n_t (in mol)·10^3	1.70	1.23	0.874	0.633	0.457	0
$\ln(c_0/c)$	0	0.324	0.665	0.988	1.31	-
k (in s^{-1})·10^3	-	6.48	6.65	6.59	6.55	-

k is almost constant, q.e.d. $k = 6.57 \cdot 10^{-3}\ s^{-1}$

e) Arrhenius equation $k = A \cdot e^{-\frac{E_a}{R \cdot T}} \Rightarrow \ln k = \ln A - \frac{E_a}{R} \cdot \frac{1}{T}$

plotting ln k as a function of 1/T results in a straight line with the slope $-E_a/R$

1/T (in K^{-1}) · 10^3	2.36	2.26	2.16	2.07	1.99
ln k	8.20	9.46	10.7	11.7	12.8



reading off two points

(1.97/13) und (2.3/9)

$m = -E_a/R$

$-E_a = \frac{13-9}{(1.97-2.30) \cdot 10^{-3} K^{-1}} \cdot R$

E_a = 101 kJ/mol

Solution problem 3-16

a) $I/I_0 = 98/100$

$A = {}^{10}\log (100/98) = 0.00877$ $A = \varepsilon \cdot c \cdot d$

$0.00877 = 10500\ Lmol^{-1}cm^{-1} \cdot c_{min} \cdot 1\ cm$ **$c_{min} = 8.352 \cdot 10^{-7}$ mol/L**

b) $I/I_0 = 2/100 \Rightarrow A = {}^{10}\log (100/2)$ $A = 1.6990$

$1.6990 = 10500\ Lmol^{-1}cm^{-1} \cdot c_{max} \cdot 1\ cm$ **$c_{max} = 1.618 \cdot 10^{-4}$ mol/L**

c) $A(x_M = 0.33) = 0$ (the complex does not absorb) $\Rightarrow 0.33 = c_M/(c_M + c_L)$
$c_L = 2\ c_M$ **ML_2**

d) $x_M = 0 \Rightarrow c_M/(c_M + c_L) = 0 \quad \Rightarrow c_M = 0$ **only L absorbs**
$x_M = 1 \Rightarrow c_M/(c_M + c_L) = 1 \quad \Rightarrow c_L = 0$ **only M absorbs**

e) At $x_M = 0$ and A = 0.5 L has the same concentration as M at $x_M = 1$ and A = 1
$\Rightarrow \varepsilon_L/\varepsilon_M = A_L/A_M = 0.5/1$ **$\varepsilon_M = 2{\cdot}\varepsilon_L$**

f) $x_M = 0$ $0.5 = {}^{10}\log(I_0/I)$ $I/I_0 = 0.32$ **transmission 32 %**
$x_M = 1$ $1 = {}^{10}\log(I_0/I)$ $I/I_0 = 0.10$ **transmission 10 %**

Solution to problem 3-17

a) $CH_4 + H_2O \longrightarrow CO + 3\ H_2$
$CO + 2\ H_2 \longrightarrow CH_3OH$

b) 55.0 m^3/s methane: $p = 250{\cdot}10^3$ Pa. T = 298 K $n = \dfrac{250{\cdot}10^3 Pa{\cdot}55\ m^3}{8.314 JK^{-1}mol^{-1}{\cdot}298K}$

flow of methane $5.55{\cdot}10^3$ mol/s

150.0 m^3/s water vapor: $p = 200{\cdot}10^3$ Pa. T = 423 K $n = \dfrac{200{\cdot}10^3 Pa{\cdot}150 m^3}{8.314 JK^{-1}mol^{-1}{\cdot}423K}$

flow of water vapor $8.53{\cdot}10^3$ mol/s

$\Rightarrow$ excess in stream ③: $(8.53 - 5.55){\cdot}10^3$ mol/s = **$2.98{\cdot}10^3$ mol/s water vapor**

in step A $5.55{\cdot}10^3$ mol/s CO and $3{\cdot}5.55{\cdot}10^3$ mol/s H_2 form

in step B $5.55{\cdot}10^3$ mol/s CO and $2{\cdot}5.55{\cdot}10^3$ mol/s H_2 are consumed

$\Rightarrow$ excess in step ⑥ **$5.55{\cdot}10^3$ mol/s hydrogen (H_2)**

c) i) stream ⑤ water: $2.98{\cdot}10^3$ mol/s $\Rightarrow$ 53.70 kg/s $\Rightarrow$ **53.70 L/s**

ii) stream ⑦ methanol: $5.55{\cdot}10^3$ mol/s CH_4 $\Rightarrow$ $5.55{\cdot}10^3$ mol/s CH_3OH
$\Rightarrow$ 177.9 kg/s CH_3OH $\Rightarrow$ **225 L/s**

iii) stream ⑧ hydrogen: $5.55{\cdot}10^3$ mol/s H_2 at 25°C and 101.3 kPa
$\Rightarrow$ 135.7 m^3/s H_2 $\Rightarrow$ **$135.7{\cdot}10^3$ L/s**

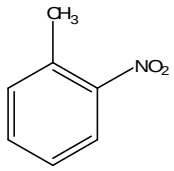
d) 1500 mol/s CH_4 and 4500 mol/s H_2 flow in
$\Rightarrow$ after step 2 in stream ⑥: **1000 mol/s CH_3OH. 500 mol/s CO and 2500 mol/s H_2**

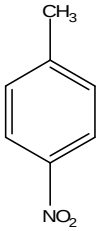
e) $p = p_{total}{\cdot}n_i/n_{total}$ $p_{total} = 10$ MPa $n_{total} = 4000$ mol
p(**CH_3OH**) = 10 MPa · (1000/4000) = **2.50 MPa**
p(**CO**) = 10 MPa · (500/4000) = **1.25 MPa**
p(**H_2**) = 10 MPa · (2500/4000) = **6.25 MPa**

f) $K = 2.50 \cdot (0.1)^2 / (1.25 \cdot 6.25^2)$ $K = 5.12 \cdot 10^{-4}$
read from the diagram **$T \approx 630$ K** (≈ 360°C)

Solution to problem 3-18

a) Main products:

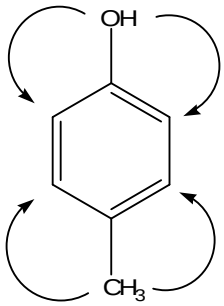
ortho: 

para: 

b) see textbooks

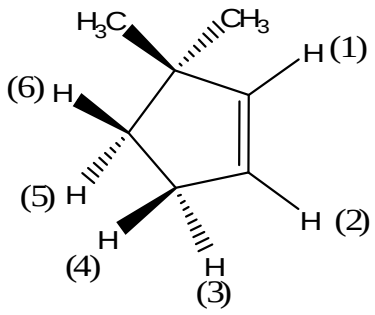
c) ortho- and para- nitrophenol

d) see textbooks

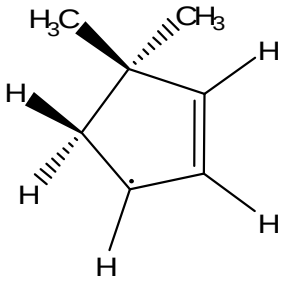
e) 

The OH group as well as the methyl group of the compound are ortho directing. As the +M-effect of the OH group overrules the +I-effect of the methyl group the OH group is ortho directing the bromine to form 2-Brom-4-methylphenol as main product.

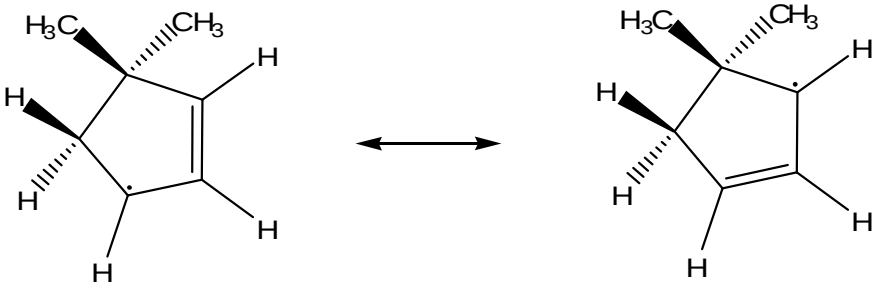
Solution to problem 3-19

a) 

The hydrogen atoms H(3) or H(4) of the starting compound can be split off leading to the following radical:



Due to the adjacent double bound an allyl radical forms stabilised by resonance:

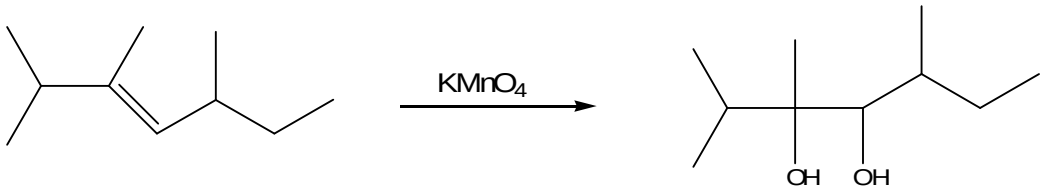


This radical may react at both ends of the allyl system, at each end from „upside“ and „downside“, to form the different compounds I – IV .

b) (I / II) as well as (III / IV) pairs of enantiomers
(I / III), (I / IV), (II / III), (II / IV) pairs of structural isomers

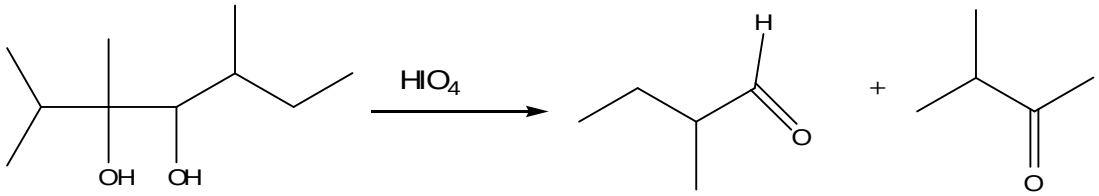
Solution to problem 3-20

a)



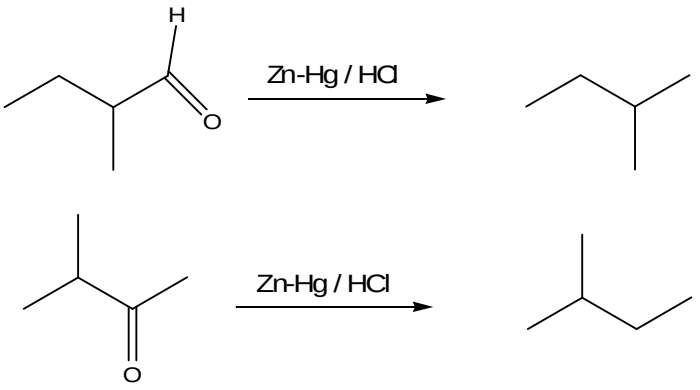
(compound A) (compound B)

2.3.5 - Trimethylheptane – 3.4 – diol



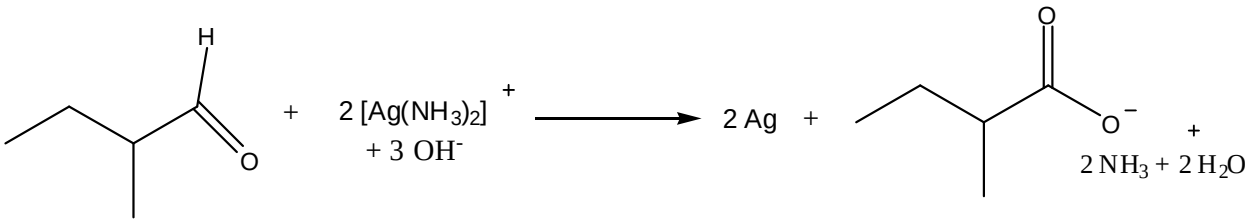
(compound B) (compound C) (compound D)

2-Methylbutanal 3–Methylbutane-2-on



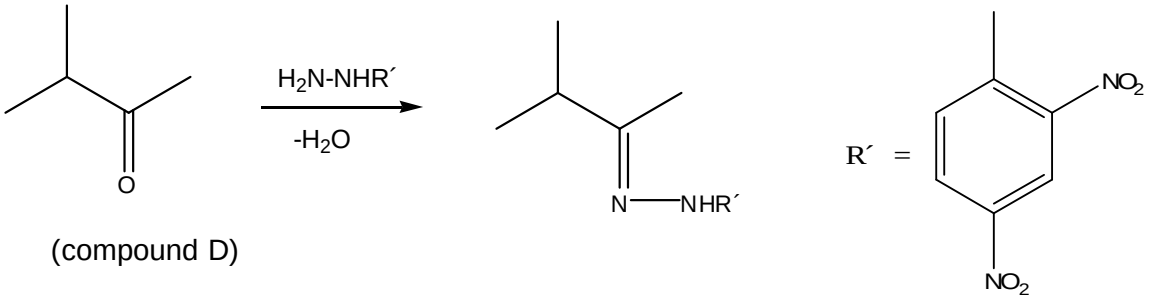
(compound E) 2-Methylbutane

reaction with Tollens reagent (detection of aldehydes)



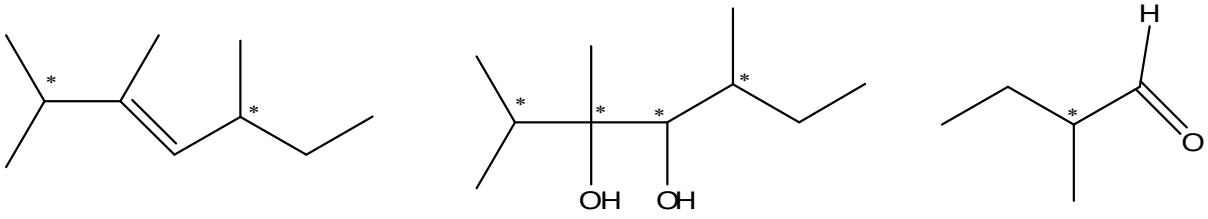
(compound C)

reaction mit 2,4 Dinitrophenylhydrazine (detection of ketons)



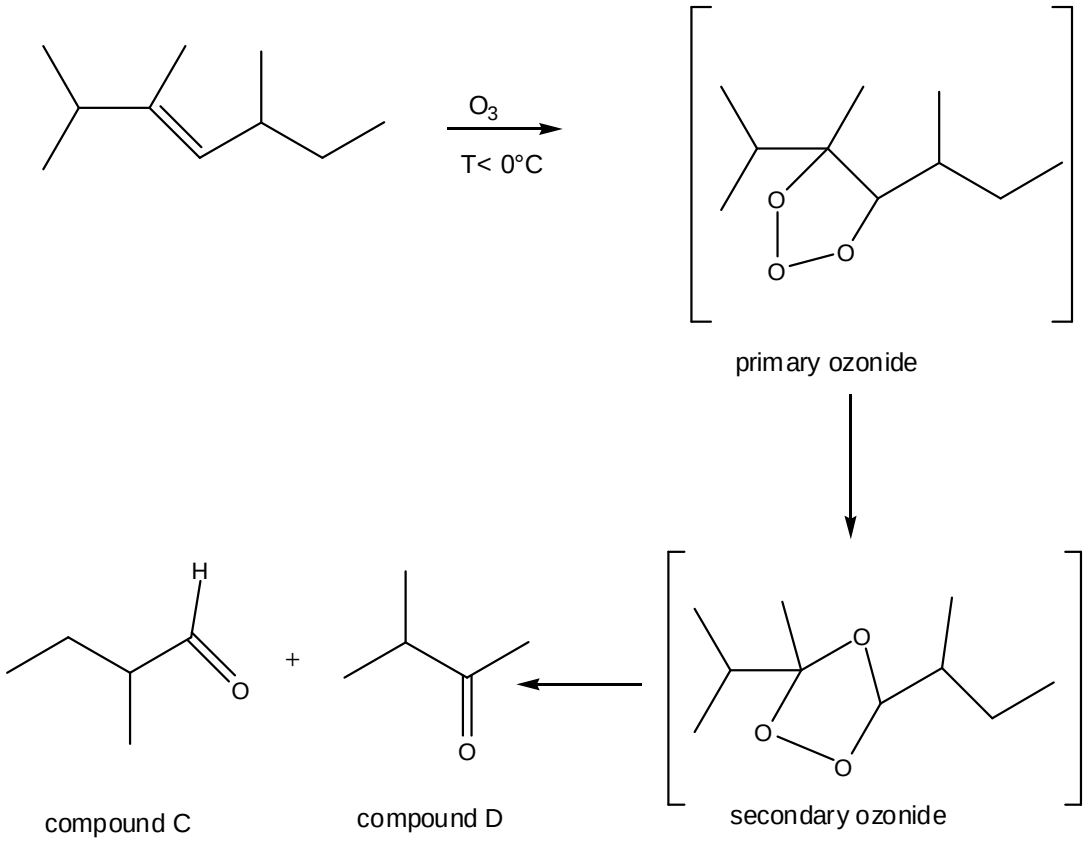
(compound D)

b) optical active compounds



compound A compound B compound C

c)


O3
T< 0°C
primary ozonide
secondary ozonide
compound C
compound D

Answers round 4

Solution to problem 4-1

a) $I_t = I_o \cdot e^{-t \cdot \ln 2 / t_{1/2}}$.

nuclide	I_t in Bq mL^{-1}	I_t after dilution in Bq mL^{-1}
^{71}Zn	$1.59 \cdot 10^2$	0.064
^{67}Ga	$6.95 \cdot 10^7$	$2.78 \cdot 10^4$
^{68}Ge	$7.00 \cdot 10^7$	$2.80 \cdot 10^4$

b) $^{71}_{30}\text{Zn} \longrightarrow {}^{71}_{31}\text{Ga} + {}^{0}_{-1}\text{e} \ (+\gamma)$

$^{67}_{31}\text{Ga} + {}^{0}_{-1}\text{e} \longrightarrow {}^{67}_{30}\text{Zn} \ (+\gamma)$

$^{68}_{32}\text{Ge} + {}^{0}_{-1}\text{e} \longrightarrow {}^{68}_{31}\text{Ga} \ (+\gamma)$

c) n(Ga) = $10.25 \cdot 10^{-3}$ g / 69.72 gmol^{-1} = $1.47 \cdot 10^{-4}$ mol Ga.

n(^{67}Ga) = $1.47 \cdot 10^{-4}$ mol $\cdot$ $5.0 \cdot 10^{-7}$ = $7.35 \cdot 10^{-11}$ mol ^{67}Ga.

z(^{67}Ga) = $4.43 \cdot 10^{13}$ atoms

for radioactive decay of 1. order kinetics the rate of disintegration is

$I_t = k \cdot z_t(^{67}\text{Ga})$. I_t = activity in Bq at time t.

z_t = amount of atoms at time t

$k = \ln 2 / t_{1/2} = 2.461 \cdot 10^{-6}$ s^{-1}

t = 0 s: $I_0 = 2.461 \cdot 10^{-6} \cdot 4.43 \cdot 10^{13}$ Bq/100 mL = $1.090 \cdot 10^6$ Bq/mL

t = 9 h: $I_9 = I_0 \cdot e^{-9 \cdot \ln 2 / 78{,}25}$ $I_9 = 1.006 \cdot 10^6$ Bq/mL

I_{blood} = 165.6 Bq/mL

factor of dilution $I_9 / I_{blood} = 1.006 \cdot 10^6 / 165.6 = 6075$. $\Rightarrow$ **V_{blood} = 6.1 L**

Solution to problem 4-2

a) $CaCO_3 \rightleftharpoons CaO + CO_2$ $K_p = p(CO_2)$

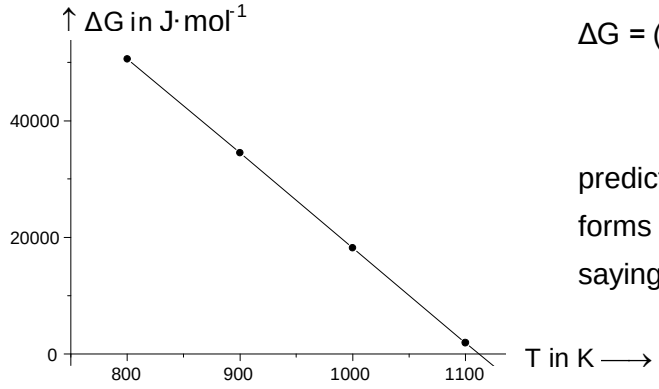
$\Delta G = - R \cdot T \cdot \ln K$ mit $K = Kp/p_0$

T in K	*800*	*900*	*1000*	*1100*	*1200*	*1300*
K_p in Pa	*50*	*1,000*	*11,200*	*80,000*	*405,000*	*1,610,000*
K	*$5 \cdot 10^{-4}$*	*0.01*	*0.112*	*0.8*	*4.050*	*16.1*
ΔG in kJ·mol^{-1}	*50.6*	*34.5*	*18.2*	*2.04*	*- 14.0*	*- 30.0*

b) If the pairs (T, ΔG) found in a) form a straight line and if you assume that ΔH and ΔS are independent of temperature, you find ΔH° and ΔS° as intersection and negative slope respectively of the straight line $\Delta G = \Delta H° - T \cdot \Delta S°$.
Whether a straight line is formed you can prove by a plot or by calculation of the slopes:

T in K	*800*	*900*	*1000*	*1100*	*1200*	*1300*
ΔG in J·mol^{-1}	*50,600*	*34,500*	*18,200*	*2,040*	*- 14,000*	*- 30,000*
m with (800/50,600)	*-*	*- 161.0*	*- 162.0*	*-161.9*	*- 161.5*	*-161.2*

oder



$\Delta G = (- 0.162\ K^{-1} \cdot T + 180)\ kJ \cdot mol^{-1}$

$\Delta S° = 162\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta H° = 180\ kJ \cdot mol^{-1}$

prediction: ΔS° is positive because a gas forms and the number of particles increases, saying the disorder, i.e. entropy, increases.

c) reaction spontaneous ⇔ $\Delta G < 0\ kJ \cdot mol^{-1}$ $\quad - 0.162\ K^{-1} \cdot T + 180 < 0$

$T > 180\ K / 0.162 = 1111\ K$ or 1110 K to be read from the plot

*as of ~ **840°C** the reaction is spontaneous.*

Solution to problem 4-3

a) $Ag^+ + H_2O \rightleftharpoons AgOH + H^+$ $\quad K_1 = 10^{-11.70}$

$Pb^{2+} + H_2O \rightleftharpoons PbOH^+ + H^+$ $\quad K_2 = 10^{-7.80}$

Only the second equilibrium determines the value of pH as $K_2 >> K_1$ ist.

	Pb^{2+} + H_2O ⇌	$PbOH^+$ +	H^+
equilibrium conc. in $mol \cdot L^{-1}$:	0.10 - x	x	x

$\frac{x^2}{0.10-x} = 10^{-7.80} \Rightarrow x = 3.98 \cdot 10^{-5} \Rightarrow$ **pH = 4.40**

b) The concentration of Ag^+ has to be determined in both half cells.

Half cell 1: After unifying both solutions it would be

$c(Ag^+) = 0.025\ mol \cdot L^{-1}$. $c(Pb^{2+}) = 0.050\ mol \cdot L^{-1}$. $c(I^-) = 0.125\ mol \cdot L^{-1}$. $c(H^+) = 0.10\ mol \cdot L^{-1}$

The amount of I^- is equivalent to the amount of Ag^+ and Pb^{2+}, thus AgI and PbI_2 will precipitate completely.

$AgI \rightleftharpoons Ag^+ + I^-$ $\quad K_{sp}(AgI) = 1\cdot10^{-16}$

$PbI_2 \rightleftharpoons Pb^{2+} + 2\ I^-$ $\quad K_{sp}(PbI_2) = 1\cdot10^{-7.86}$

[The formation of $PbOH^+$ can be neglected because of $c(H^+) = 0.10$ mol·L^{-1}:

$Pb^{2+} + H_2O \rightleftharpoons PbOH^+ + H^+$

$\frac{c(PbOH^+)}{c(Pb^{2+})} = \frac{10^{-7.8}}{0.1} = 10^{-6.8} \Rightarrow c(PbOH^+) << c(Pb^{2+})$]

As $K_{sp}(AgI) << K_{sp}(PbI_2)$, only $K_{sp}(PbI_2)$ determines the iodine concentration and thus the concentration of the silver ions.

$x\cdot(2x)^2 = 1\cdot10^{-7.86} \Rightarrow x = 1.51\cdot10^{-3}$ $\quad c(I^-) = 3.02\cdot10^{-3}$ mol·L^{-1}

$c(Ag^+)\cdot3.02\cdot10^{-3}$ mol·L^{-1} $= 10^{-16}$ (mol·L^{-1})^2 $\quad c(Ag^+) = 3.31\cdot10^{-14}$ mol·L^{-1}

Potential of half cell 1 for $Ag^+ + e^- \rightleftharpoons Ag$:

$E_1 = E°(Ag^+/Ag) + R\cdot T/F \cdot \ln c(Ag^+)$ $\quad E_1 = 2\cdot10^{-3}$ V

Half cell 2: AgSCN precipitates:

$Ag^+ + SCN^- \rightleftharpoons AgSCN$ $\quad K_{sp}(AgSCN) = 10^{-12}$

$x \cdot (0.03 + x) = 10^{-12}$ $\quad x = 3.33\cdot10^{-11}$ $\quad c(Ag^+) = 3.33\cdot10^{-11}$ mol·L^{-1}

$E_2 = 0.179$ V

$\Rightarrow \Delta E = E_{cell} = E_2 - E_1$ $\quad$ **$E_{cell} = 0.177$ V**

c) Total cell reaction:

$Ag + I^- \rightleftharpoons AgI + e^-$

$AgSCN + e^- \rightleftharpoons Ag + SCN^-$

$AgSCN + I^- \rightleftharpoons AgI + SCN^-$

$K = \frac{c(SCN^-)}{c(I^-)} = \frac{c(SCN^-)\cdot c(Ag^+)}{c(I^-)\cdot c(Ag^+)}$ $\quad K = \frac{K_{sp}(AgSCN)}{K_{sp}(AgI)} = \frac{10^{-12}}{10^{-16}}$ $\quad$ **$K = 10^4$**

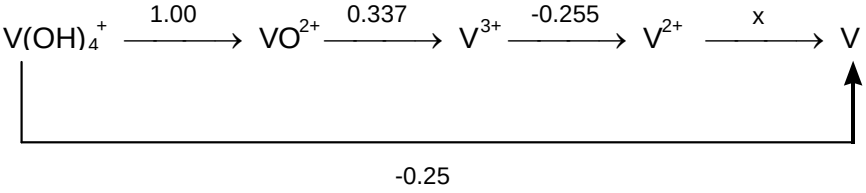
d) Case 1: The amount of NaOH is so small that the acid is not neutralised. Then the formation of $Pb(OH)^+$ doesn't play a role further on, the concentrations of lead, iodine and silver stay constant, **the voltage does not change**.

Case 2: The amount of NaOH added is sufficient to neutralise the acid. Then $Pb(OH)^+$ is formed in a remarkable amount, $c(Pb^{2+})$ decreases , $c(I^-)$ increases and $c(Ag^+)$ decreades. Thus E_1 decreases and **the voltage increases**

e) $Fe^{3+} + SCN^- \longrightarrow FeSCN^{2+} \ldots \longrightarrow Fe(SCN)_2^+ \ldots$
$c(SCN^-)$ decreases, $c(Ag^+)$ increase and for this reason E_2 also. **The voltage increases.**

f) You have to calculate the standard potential E° of $V^{2+} + 2\,e^- \rightleftharpoons V$
because standard potentials refer to a standad hydrogen cell with E° = 0 V.

$\Delta G° = - n \cdot F \cdot E°$ $\quad n = 2$ $\quad E° = ?$



$1.00 + 0.337 - 0.255 + 2 \cdot x = 5 \cdot (- 0.25)$ $\quad x = - 1.17$ $\quad E°(V^{2+}/V) = - 1.17$ V

$\Delta G° = - 2 \cdot 96485 \cdot (- 1.17)$ J $\quad$ **$\Delta G° = 226$ kJ**

Solution to 4-4

a) Steady state: $\frac{d([ES])}{dt} = 0$

$k_1 \cdot [E] \cdot [S] - k_2 \cdot [ES] - k_3 \cdot [ES] = 0$ $\quad [E] = [E]_{total} - [ES]$

$k_1 \cdot ([E]_{total} - [ES]) \cdot [S] = (k_2 + k_3) \cdot [ES]$

$k_1 \cdot [E]_{total} \cdot [S] = (k_2 + k_3 + k_1 \cdot [S]) \cdot [ES]$

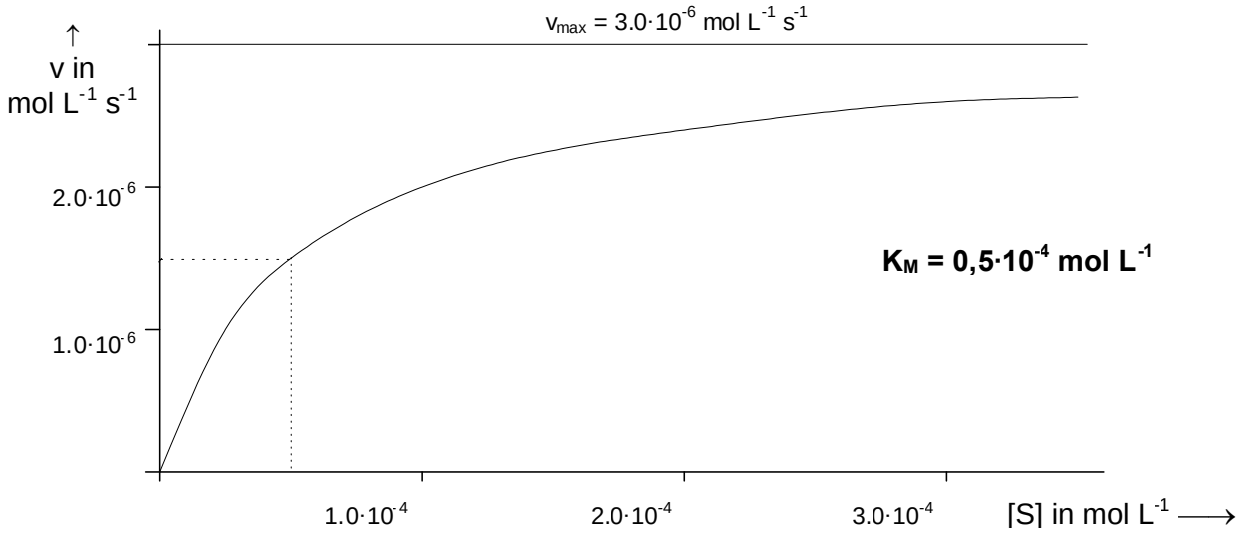
$[ES] = \frac{k_1 \cdot [E]_{total} \cdot [S]}{k_2 + k_3 + k_1 \cdot [S]} \Rightarrow$ **$[ES] = \frac{[E]_{total} \cdot [S]}{K_M + [S]}$**

b) $\frac{d([P])}{dt} = k_3 \cdot [ES]$ $\quad [ES]_{max} = [E]_{total} \Rightarrow$ **$v_{max} = k_3 \cdot [E]_{total}$**

c) $\frac{d([P])}{dt} = k_3 \cdot [ES]$ $\quad$ with a): $[ES] = \frac{[E]_{total} \cdot [S]}{K_M + [S]} \Rightarrow v = k_3 \cdot \frac{[E]_{ttal} \cdot [S]}{K_M + [S]}$

with b): $k_3 \cdot [E]_{total} = v_{max} \Rightarrow$ **$v = \frac{v_{max} \cdot [S]}{K_M + [S]}$**

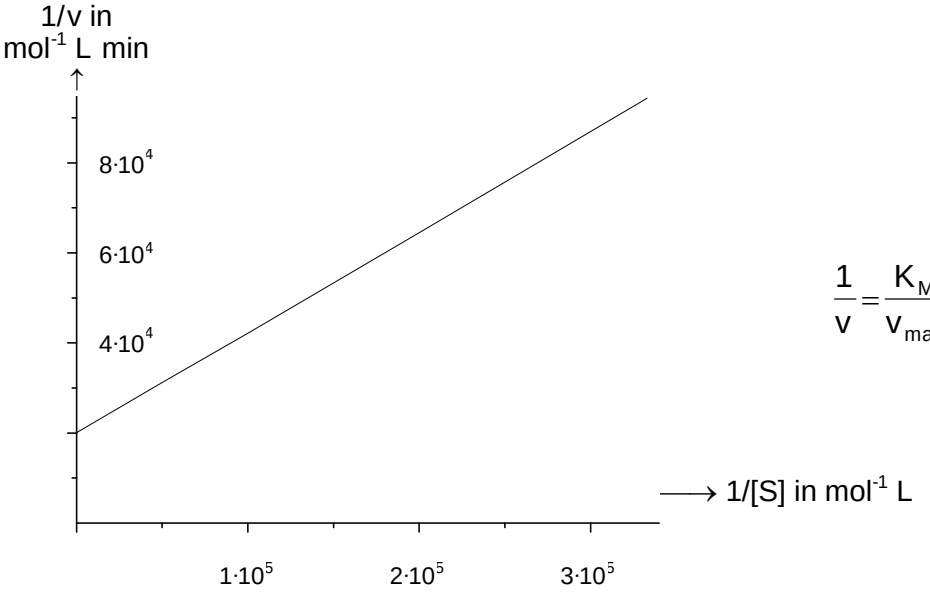
d) With c) $v = ½ \cdot v_{max} \Rightarrow K_M = [S]$,
read the value of [S] at $v = 1.5 \cdot 10^{-6}$ mol L^{-1} s^{-1}



e) with c): $v = \frac{v_{max} \cdot [S]}{K_M + [S]} \Rightarrow \frac{1}{v} = \frac{K_M + [S]}{v_{max} \cdot [S]} \Rightarrow \frac{1}{v} = \frac{K_M}{v_{max}} \cdot \frac{1}{[S]} + \frac{1}{v_{max}}$

f)

$[S]_0 \cdot 10^6$ in mol L^{-1}	$[S]_0^{-1}$ in mol^{-1} L	$v_0 \cdot 10^5$ in mol L^{-1} min^{-1}	v_0^{-1} in mol^{-1} L min
3	3,33·10^5	1,06	9,43·10^4
5	2,00·10^5	1,55	6,45·10^4
10	1,00·10^5	2,37	4,22·10^4
20	0,50·10^5	3,21	3,12·10^4



$$\frac{1}{v} = \frac{K_M}{v_{max}} \cdot \frac{1}{[S]} + \frac{1}{v_{max}} \quad (1)$$

intersection 1/[S] = 0 $\Rightarrow$ $\frac{1}{v_{max}} = 2 \cdot 10^4$ mol^{-1} L min

mit $[E]_{total} = 1{,}0 \cdot 10^{-9}$ mol L^{-1} $\Rightarrow$ [with b)] **$k_3 = 5 \cdot 10^4$ min^{-1}**

with equation (1) for the straight line **$K_M = 1.1 \cdot 10^{-5}$ mol/L**

g) $f_{ES} = \frac{v_0}{v_{max}} = \frac{[S]_0}{K_M + [S]_0}$

$f_{ES} = \frac{3 \cdot 10^{-5} \text{mol} \cdot \text{L}^{-1}}{1.5 \cdot 10^{-5} \text{mol} \cdot \text{L}^{-1} + 3 \cdot 10^{-5} \text{mol} \cdot \text{L}^{-1}}$ **$f_{ES} = 0.67$**

h) $k_{kat} = k_3$ from the equation given in b) $v_{max} = k_3 \cdot [E]_{total}$

$[E]_{total} = \frac{10^{-9} \text{ g}}{0.01 \text{L} \cdot 41977 \text{ g} \cdot \text{mol}^{-1}}$ $= 2.38 \cdot 10^{-12}$ mol$\cdot$L^{-1}

$k_{kat} = \frac{7.15 \cdot 10^{-11} \text{ mol} \cdot \text{L}^{-1} \cdot \text{min}^{-1}}{2.38 \cdot 10^{-12} \text{ mol} \cdot \text{L}^{-1}}$ $= 30$ min^{-1} **$k_{kat} = 0.5$ s^{-1}**

Solution to problem 4-5

a) $2\ MnO_4^- + 5\ C_2O_4^{2-} + 16\ H_3O^+ \longrightarrow 2\ Mn^{2+} + 10\ CO_2 + 24\ H_2O$

$n(C_2O_4^{2-}) = \frac{0.1702 \text{ g}}{M(Na_2C_2O_4)} = \frac{01702 \text{ g}}{134{,}02 \text{ g/mol}}$ $n(C_2O_4^{2-}) = 1.27 \cdot 10^{-3}$ mol

$0.4 \cdot n(C_2O_4^{2-}) = n(MnO_4^-) = c(MnO_4^-) \cdot V(MnO_4^-)$

$c(MnO_4^-) = 0.4 \cdot 1.27 \cdot 10^{-3}$ mol / $26.70 \cdot 10^{-3}$ L **$c(MnO_4^-) = 0.019$ mol/L**

b) $Fe + 2\ H_3O^+ \longrightarrow Fe^{2+} + H_2 + 2\ H_2O$

$Fe_2O_3 + 6\ H_3O^+ \longrightarrow 2\ Fe^{3+} + 9\ H_2O$

$2\ Fe^{3+} + SO_3^{2-} + 3\ H_2O \longrightarrow 2\ Fe^{2+} + SO_4^{2-} + 2\ H_3O^+$

$SO_3^{2-} + 2\ H_3O^+ \longrightarrow SO_2 + 3\ H_2O$

$MnO_4^- + 5\ Fe^{2+} + 8\ H_3O^+ \longrightarrow Mn^{2+} + 5\ Fe^{3+} + 12\ H_2O$

$n(Fe_{total}) = 5 \cdot n(MnO_4^-) = 5 \cdot 0.019$ mol/L $\cdot 37.5 \cdot 10^{-3}$ L $= 3.56 \cdot 10^{-3}$ mol

$n(Fe_{total}) = n(Fe) + 2 \cdot n(Fe_2O_3)$ $n(Fe) = 3.56 \cdot 10^{-3}$ mol $- 2 \cdot n(Fe_2O_3)$

$m_{total} = n(Fe) \cdot M(Fe) + n(Fe_2O_3) \cdot M(Fe_2O_3)$

$0.225 \text{ g} = [3.56 \cdot 10^{-3} \text{ mol} - 2 \cdot n(Fe_2O_3)] \cdot 55.85 \text{ g/mol} + n(Fe_2O_3) \cdot 159.7 \text{ g/mol}$

$n(Fe_2O_3) = 5.45 \cdot 10^{-4}$ mol $m(Fe_2O_3) = 0.087$ g $\Rightarrow$ **38.7 % Fe_2O_3**

61.3 % Fe

c) $c(Ni) = 1.70 \cdot 10^{-3}$ mol/L

no precipitate of $Ni(OH)_2$: $c(OH) \le \sqrt{\frac{6 \cdot 10^{-16}}{1{,}7 \cdot 10^{-3}}}$ mol/L = $5.94 \cdot 10^{-7}$ mol/L

$pH \le 7.7$ (at 7.8 $Ni(OH)_2$ precipitates)

$c(Fe)_{\text{before precipitation}} = 1.25 \cdot 10^{-2}$ mol/L

$c(Fe)_{\text{after precipitation}} \le 1.25 \cdot 10^{-5}$ mol/L

maximum concentration of the solution $1.25 \cdot 10^{-5}$ mol/L:

$$c(OH) \ge \sqrt[3]{\frac{4 \cdot 10^{-38}}{1.25 \cdot 10^{-5}}} \text{ mol/L} = 1.47 \cdot 10^{-11} \text{ mol/L}$$

$pH \ge 3.2$ (at 3.1 error > 0.1%)

precipitation in the range $3.2 \le pH \le 7.7$

Solution to problem 4-6

a) $1.0 \cdot 10^6$ molecules/cm^3 = $1.0 \cdot 10^{12}$ molecules /m^3

$p \cdot V = n \cdot R \cdot T \quad \Rightarrow \quad p = \frac{1{,}0 \cdot 10^{12} \cdot 8{,}314 \cdot 1200}{6{,}022 \cdot 10^{23}}$ Pa **$p = 1.66 \cdot 10^{-8}$ Pa**

b) $p = F/A$ $F = m \cdot g$ $m = V \cdot \rho(Hg) \Rightarrow p = A \cdot h \cdot \rho(Hg) \cdot g$

e.g. $A = 1\ m^2 \Rightarrow p = (1\ m^2 \cdot 10^{-12}\ m \cdot 13.55 \cdot 10^3\ kg/m^3 \cdot 9.81\ m/s^2) / 1\ m^2$

$p = 1.33 \cdot 10^{-7}$ N/m^2 **$p = 1.33 \cdot 10^{-7}$ Pa**

(or 1 mm Hg equals 1 Torr equals $1.013 \cdot 10^5/760$ Pa ect.)

c) Analogous to a) $\frac{1.33 \cdot 10^{-7} \cdot 6{,}022 \cdot 10^{23}}{8.314 \cdot 298}$ molecules /m^3 = $3.23 \cdot 10^{13}$ molecules /m^3

= $3.23 \cdot 10^7$ molecules/cm^3 , 32 times more than in the oxosphere.

d) $\bar{v} = \sqrt{\frac{8 \cdot R \cdot T}{\pi \cdot M}}$ $\bar{v}_{1200} = \sqrt{\frac{8 \cdot 8.314 JK^{-1} mol^{-1} \cdot 1200K}{\pi \cdot 1.008 \cdot 10^{-3} kgmol^{-1}}}$ $\bar{v}_{1200} \approx 5000$ m/s

$\bar{v}_{298} \approx 2500$ m/s $\bar{v}_{1200}$ **:** $\bar{v}_{298}$ **= 2 : 1**

e)

Mean speed $\bar{v}$	
$\bar{v}_1$ = 2400 m/s	$\bar{v}_2 = \sqrt{\frac{8 \cdot 8.314 JK^{-1} mol^{-1} \cdot 2.7K}{\pi \cdot 1.008 \cdot 10^{-3} kgmol^{-1}}}$ = 238 m/s

Volume of collision cylinder = $\pi\cdot(1\cdot10^{-10}\,m)^2\cdot\sqrt{2}\cdot\bar{v}$	
$V_1 = \pi\cdot(1\cdot10^{-10}\,m)^2\cdot\sqrt{2}\cdot2400$ m/s $V_1 = 1.066\cdot10^{-16}\,m^3/s$	$V_2 = 1.057\cdot10^{-17}\,m^3/s$
Density of particles	
$40\cdot10^{15}/m^3$	$1/m^3$
Number of collisions/s = (volume ofcollision cylinder) · (density of particles)	
$z_1 = 1.066\cdot10^{-16}\,m^3/s\cdot40\cdot10^{15}/m^3$ **$z_1 = 4.264$ /s**	**$z_2 = 1.057\cdot10^{-17}$/s**
mean time until first collision = 1/z	
$\bar{t}_1 = 0.235$ s	$\bar{t}_2 = 9.46\cdot10^{16}$ s $\approx 3\cdot10^9$ years
free path = $\bar{t}\cdot\bar{v}$	
free path$_1$ = 564 m	**free path$_2$ = $2.25\cdot10^{19}$ m** **$\approx$ 2400 light years**

Solution to 4-7

a) $K_{sp} = (8\cdot10^{-3}\text{ mol/L})^2 =$ **$6.4\cdot10^{-5}$ (mol/L)^2**

b) $c(Na^+) = 0.130$ mol/L $\Rightarrow$ $c(Ur^-) = 6.4\cdot10^{-5}/0.130$ mol/L = **$4.9\cdot10^{-4}$ mol/L**

c) The lower the temperature the smaller K_{sp} .

d) $pH = pK + \lg\frac{c(Ur^-)}{c(HUr)}$ $\quad pH = 7.4 \Rightarrow 7.4 = 5.4 + \lg\frac{c(Ur^-)}{c(HUr)}$ (1)

If NaUr does not precipitate then $c(Ur^-) \le 4.9\cdot10^{-4}$ mol/L (see b) and with (1)

$c(HUr) \le 4.9\cdot10^{-6}$ mol/L < solubiulity of HUr in water.

e) $pH = 5.4 + \lg\frac{c(Ur^-)}{c(HUr)}$ $\quad c(HUr) + c(Ur^-) = 2\cdot10^{-3}$ mol/L $\quad c(HUr) \ge 0.5\cdot10^{-3}$ mol/L

$\Rightarrow$ $pH \le 5.4 + \lg\frac{1{,}5\cdot10^{-3}}{0{,}5\cdot10^{-3}}$ **$pH \le 5.9$**

f) t = 0 h corresponds to 2.5% of the injected 20 mg. Thus there are 800 mg of uric acid totally in the body of N, before injection **780 mg**

analogous calculation for P **1980 mg**

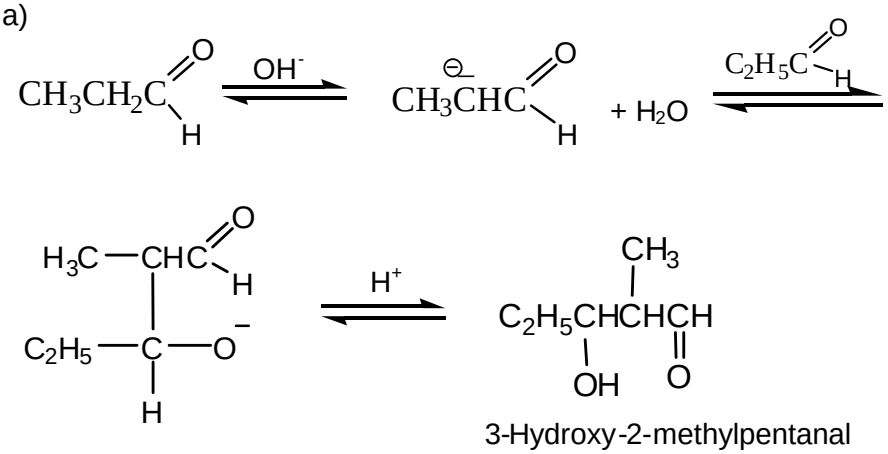
g) The plot shows that the half life in constant in both cases, characteristic for processes of 1. order only

N: half life $t_{1/2} = 40$ hours $\quad k = \ln2/t_{1/2}$ **$k = 1.73\cdot10^{-2}$ h^{-1}**

P: half life $t_{1/2} = 40$ hours $\quad k = \ln2/t_{1/2}$ **$k = 1.73\cdot10^{-2}$ h^{-1}**

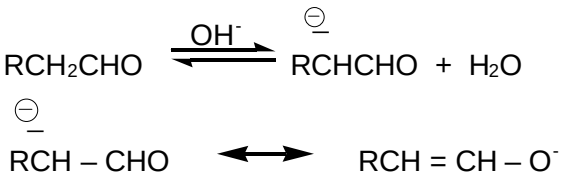
Solution to Problem 4-8

a)

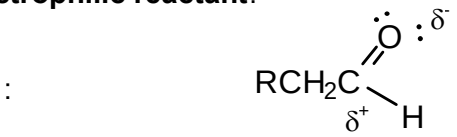


3-Hydroxy-2-methylpentanal

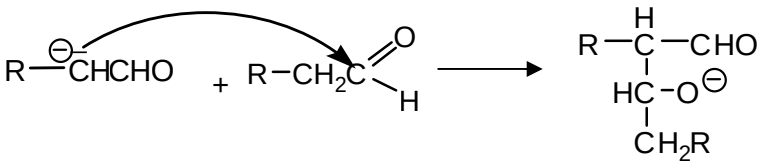
b) The base abstracts the hydroxyl proton to yield a β-keto alkoxide ion which fragments to give one molecule of enolate ion



electrophilic reactant: **nucleophilic reactant**:

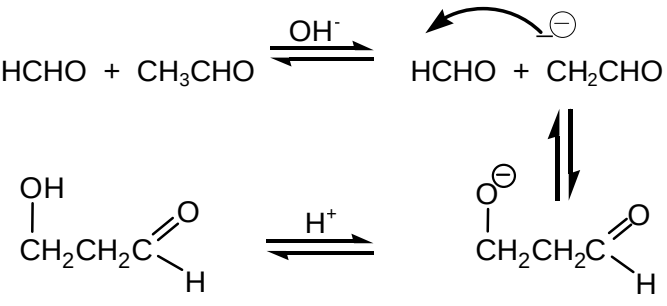


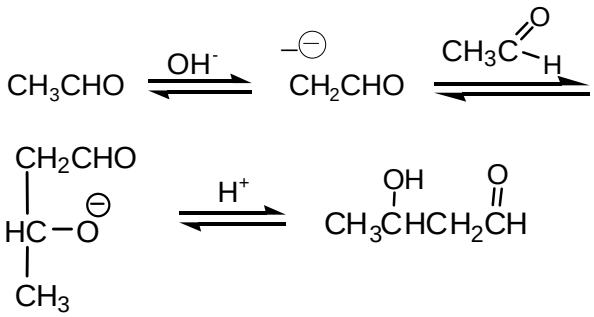
The enolate ion (nucleophil) reacts with the C-atom of the carbonyl group (electrophil)



Precondition ketones or aldehydes with an α-hydrogen atom

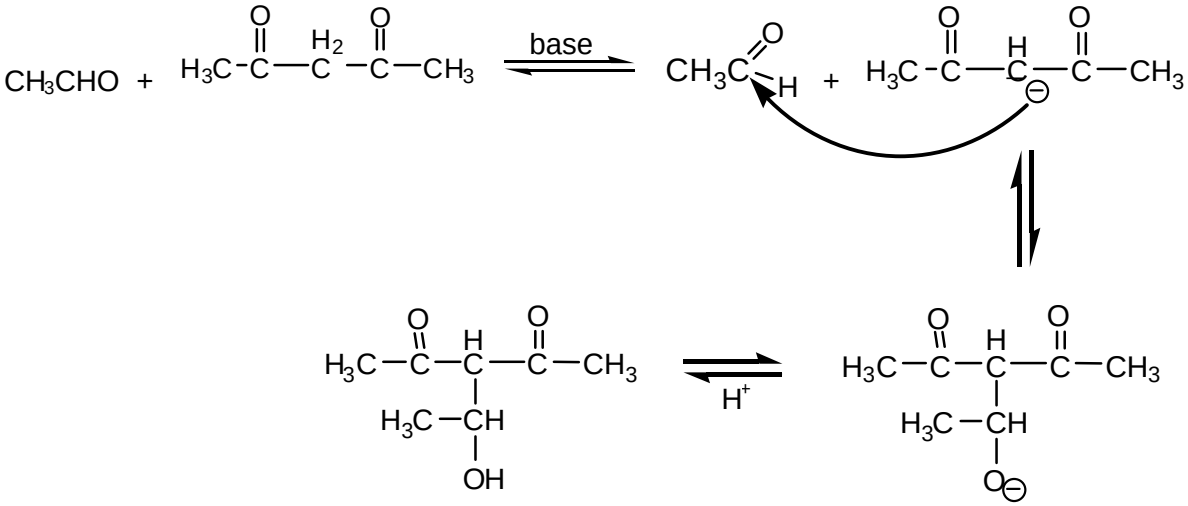
c) 1.



2. 

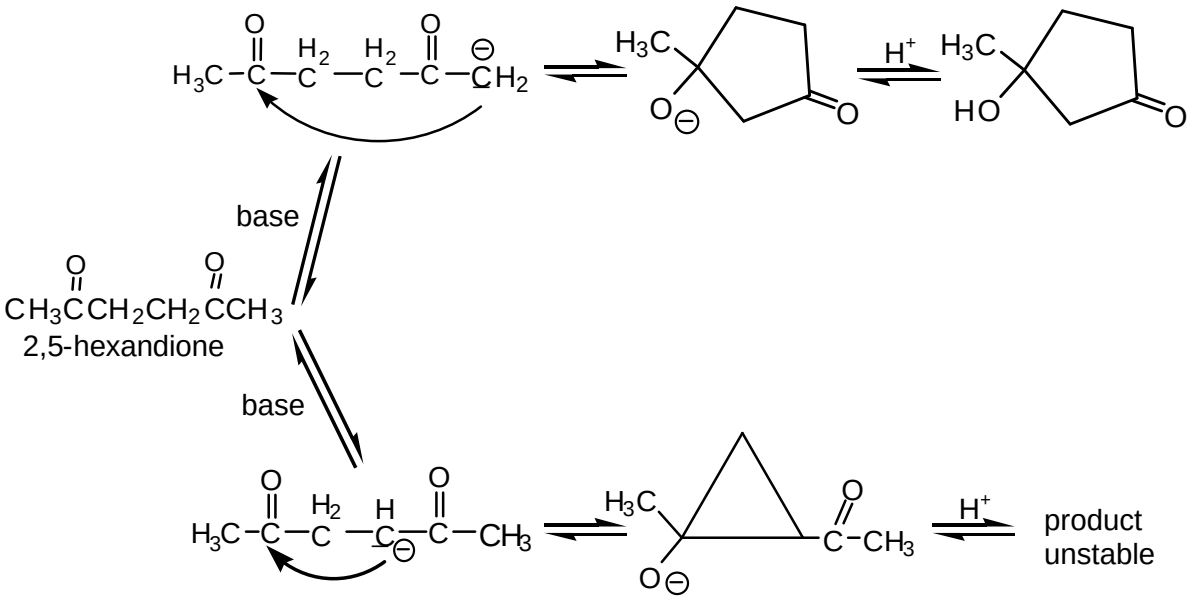
Formaldehyde contains no α-H atom and thus cannot form an enolate ion to condense with itself.

d) Aldol reaction of acetaldehyde and 2,4-pentadione,
favoured reaction:



If one of the carbonyl components (diketone) is unusually acidic and easily transformed into its enolate ion, then a mixed aldol reaction is likely to be successful.

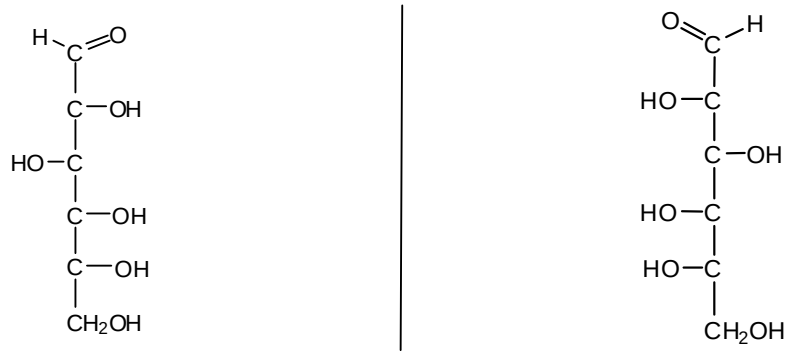
e) Aldol reaction of 2,5-hexadione



The 5-membered ring is more stable than the 3-membered ring according to the great ring strain of the 3-membered ring.

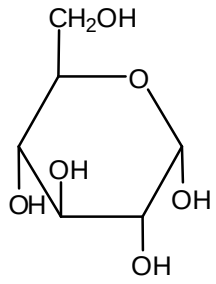
Solution to Problem 4-9

a)

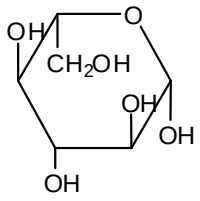


b) There are 4 stereogenic centres in L-glucose. D- and L-glucose are enantiomers.

c)

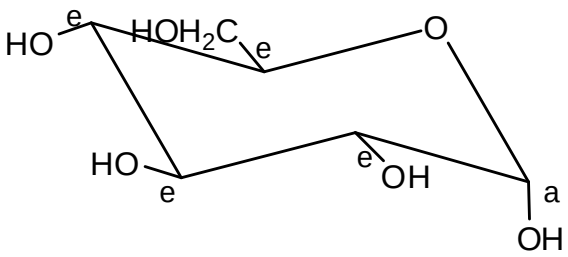


α-D-Glucopyranose

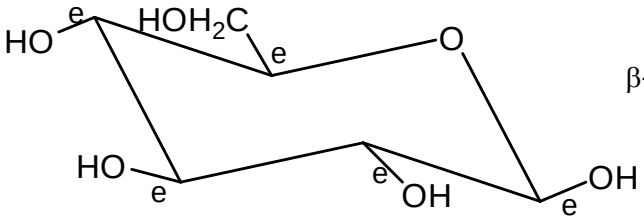


β-L-Glucopyranose

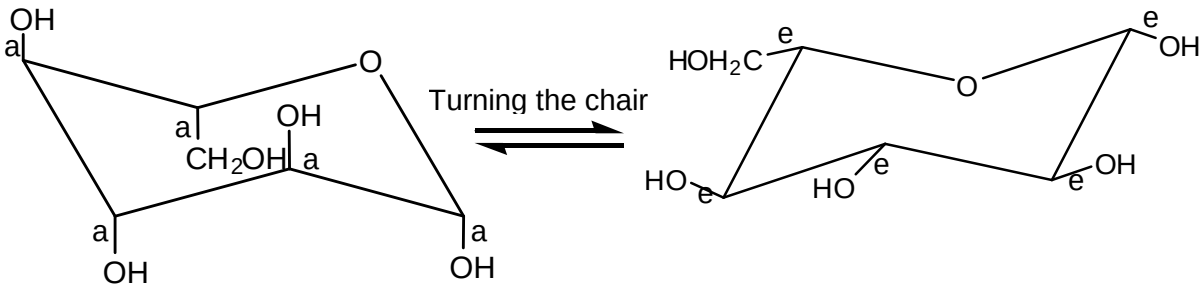
d)



α-D-Glucopyranose



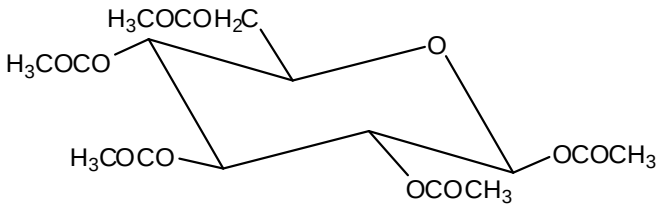
β-D-glucopyranose



β-L-Glucopyranose

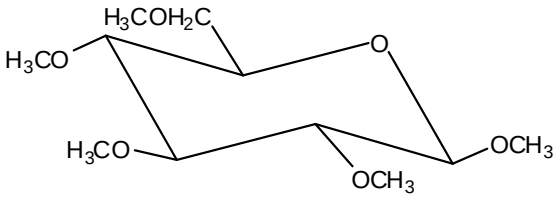
In β-D-glucopyranose and in β-L-Glucopyranose all substituents of the ring are equatorial. Thus these compounds are the least sterically crowded and most stable.

e)



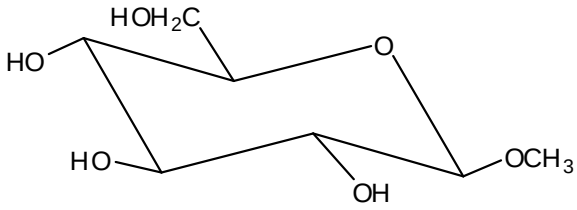
ester

f)



ether

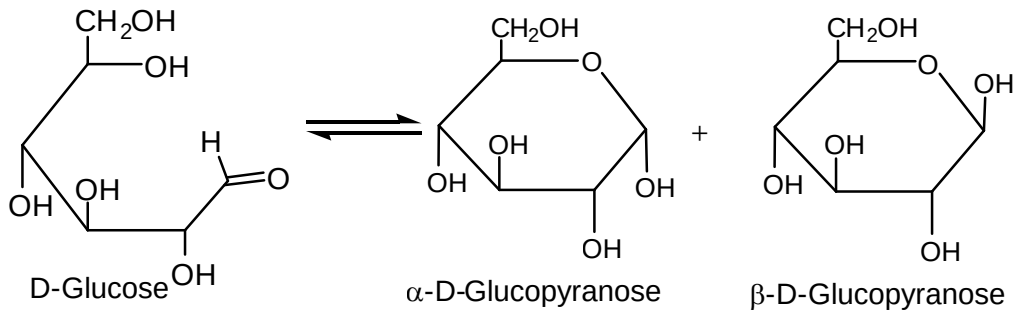
g)



acetal

Mutarotation is to the following equilibrium

open form



As the OH-group in α- or β-position reacted to form the acetal the equilibrium shown above cannot establish via open form.

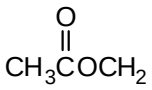
Solution to Problem 4-10

a) $C_4H_8O_2$.

b) Band at 1730cm^{-1} according to carbonyl compound or ester
Band at ~2850cm^{-1} – 2930cm^{-1} according to alkyl group

c) All molecules have a certain amount of energy distributed throughout their structure causing bonds to stretch and bend, atoms to wag and rock, and other molecular vibrations to occur.
The amount of energy is quantised that is a molecule dan stretch, bend,or vibrate only at specific frequencies corresponding to specific energy levels.
When a molecule absorbs infrared radiation the vibrating bond will absorb energy only if the frequency of the light and the vibration are the same.
Since each light frequency absorbed corresponds to a precific molecular motion, we can see what kind of molecular motions a sample has by measuring its infrared spectrum.

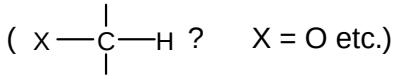
d) Proposal for a structure:



Assingments:

There are three different peaks and peak groups respectively. That is there are three protons or proton groups with different surroundings:

- The singulet at δ = 2.1 ppm leads to an acetyl group (2.1 ppm – 2.4 ppm).
- The triplet at δ = 1.3 ppm indicates a CH_3 group adjacent to a CH_2 group.
- The quartet bei δ = 4.1 ppm is difficult to interprete.



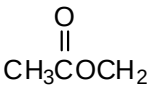
Number of protons:

The total number of H atoms is 8. These 8 protons may be divided in the ratio 2 : 3 : 3. Thus the singulet is a CH_3 group, the triplet another CH_3 group and the quartet a CH_2 group.

Couplings:

.

- The CH_3 group at the carbonyl hydrogen has no further hydrogen to couple with. That results to a singulet.
- The triplet at δ = 1,3 ppm is caused by a terminal CH_3 group which couple with an adjacent CH_2 group.
- The quartet at δ = 4,1ppm arises from the coupling with the three H atoms of the CH_3-Gr..

The structure of A is  (ethylacetate)

Chemistry for Life,
Chemistry for better Life

Theoretical Test

2006. 7. 7
Gyeongsan, Korea

Constants and useful formulas

Gas constant $R = 8.314\ J\ K^{-1}\ mol^{-1}$

Faraday constant $F = 96485\ C\ mol^{-1}$

Use as standard pressure: $p = 1.013 \cdot 10^5\ Pa$

Use as standard temperature: $T = 25°C = 298.15\ K$

Avogadro's number $N_A = 6.022 \cdot 10^{23}\ mol^{-1}$

Planck constant $h = 6.626 \cdot 10^{-34}\ J\ s$

Speed of light $c = 3.00 \cdot 10^8\ m\ s^{-1}$

$\Delta G = \Delta H - T\Delta S$ $\Delta G = -nFE$

$\Delta G^0 = -RT \cdot \ln K$ $\Delta G = \Delta G^0 + RT \cdot \ln Q$ with $Q = \frac{product\ of\ c(products)}{product\ of\ c(reactands)}$

$\Delta H(T_1) = \Delta H^0 + (T_1 - 298.15\ K) \cdot C_p$ (C_p = constant)

Arrhenius equation $k = A \cdot e^{-\frac{E_a}{R \cdot T}}$

Ideal gas law $pV = nRT$

Nernst equation $E = E^0 + \frac{RT}{nF} \cdot \ln \frac{c_{ox}}{c_{red}}$

Beer- Lambert Law $A = \log \frac{P_0}{P} = \varepsilon \cdot c \cdot d$

$V(cylinder) = \pi r^2 h$

$A(sphere) = 4\pi r^2$

$V(sphere) = \frac{4}{3}\pi r^3$

$1\ J = 1\ N\ m$ $1\ N = 1\ kg\ m\ s^{-2}$ $1\ Pa = 1\ N\ m^{-2}$

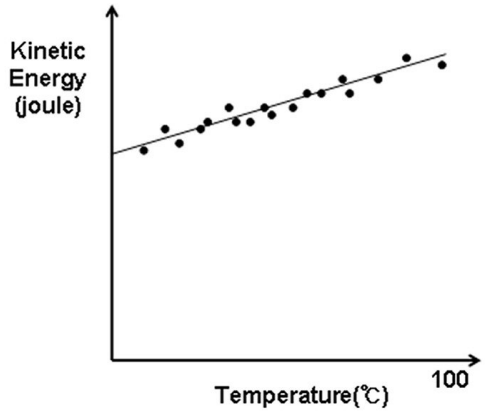
$1\ W = 1\ A\ V = 1\ J\ s^{-1}$ $1\ C = 1\ A\ s$

1. Avogadro's number

Spherical water droplets are dispersed in argon gas. At 27^{o}C, each droplet is 1.0 micrometer in diameter and undergoes collisions with argon. Assume that inter-droplet collisions do not occur. The root-mean-square speed of these droplets was determined to be 0.50 cm/s at 27^{o}C. The density of a water droplet is 1.0 g/cm^{3}.

1-1. Calculate the average kinetic energy ($mv^2/2$) of this droplet at 27^{o}C. The volume of a sphere is given by (4/3) πr^3 where r is the radius.

If the temperature is changed, then droplet size and speed of the droplet will also change. The average kinetic energy of a droplet between 0^{o}C and 100^{o}C as a function of temperature is found to be linear. Assume that it remains linear below 0^{o}C.



At thermal equlibrium, the average kinetic energy is the same irrespective of particle masses (equipartition theorem).
The specific heat capacity, at constant volume, of argon (atomic weight, 40) gas is 0.31 J g^{-1} K^{-1}.

1-2. <u>Calculate</u> Avogadro's number without using the ideal gas law, the gas constant, Boltzmann's constant).

2. Detection of Hydrogen

Hydrogen is prevalent in the universe. Life in the universe is ultimately based on hydrogen.

2-1. There are about 10^{23} stars in the universe. Assume that they are like our sun (radius, 700,000 km; density, 1.4 g/cm^{3}; 3/4 hydrogen and 1/4 helium by mass). *<u>Estimate</u> the number of stellar protons in the universe to one significant figure.*

In the 1920s, Cecilia Payne discovered, by spectral analysis of starlight, that hydrogen is the most abundant element in most stars.

2-2. The electronic transition of a hydrogen atom is governed by $\Delta E(n_i \rightarrow n_f) = -C(1/n_f^2 - 1/n_i^2)$, where m and n are principle quantum numbers, and C is a constant. For detection of the $\Delta E(3 \rightarrow 2)$ transition (656.3 nm in the Balmer series), the electron in the ground state of the hydrogen atom needs to be excited first to the n = 2 state. *Calculate the wavelength (in nm) of the absorption line in the starlight corresponding to the $\Delta E(1 \rightarrow 2)$ transition.*

2-3. According to Wien's law, the wavelength (λ) corresponding to the maximum light intensity emitted from a blackbody at temperature T is given by $\lambda T = 2.9 \times 10^{-3}$ m K. *Calculate the surface temperature of a star whose blackbody radiation has a peak intensity corresponding to the n = 1 → n = 2 excitation of hydrogen.*

The ground state of hydrogen is split into two hyperfine levels due to the interaction between the magnetic moment of the proton and that of the electron. In 1951, Purcell discovered a spectral line at 1420 MHz due to the hyperfine transition of hydrogen in interstellar space.

2-4. Hydrogen in interstellar space cannot be excited electronically by starlight. However, the cosmic background radiation, equivalent to 2.7K, can cause the hyperfine transition.
Calculate the temperature of a blackbody whose peak intensity corresponds to the 1420 MHz transition.

2-5. Wien generated hydrogen ions by discharge of hydrogen gas at a very low pressure and determined the e/m value, which turned out to be the highest among different gases tested. In 1919, Rutherford bombarded nitrogen with alpha-particles and observed emission of a positively charged particle which turned out to be the hydrogen ion observed by Wien. Rutherford named this particle the “proton”.
Fill in the blank.

3. Interstellar Chemistry

Early interstellar chemistry is thought to have been a prelude to life on Earth. Molecules can be formed in space via heterogeneous reactions at the surface of dust particles, often called the interstellar ice grains (IIGs). Imagine the reaction between H and C atoms on the IIG surface that forms CH. The CH product can either desorb from the surface or further react, through surface migration, with adsorbed H atoms to form CH_2, CH_3, etc.
Depending on how energetically a molecule "jumps" from its anchored site, it either leaves the surface permanently (desorption) or returns to a new position at the surface (migration). The rates of desorption and migratory jump follow the Arrhenius formula, $k = A \exp(-E/RT)$, where k is the rate constant for desorption or migratory jump, A the jumping frequency, and E the activation energy for the respective event.

3-1. Desorption of CH from the IIG surface follows first-order kinetics. Calculate the average residence time of CH on the surface at 20 K. Assume that $A = 1 \times 10^{12}$ s^{-1} and $E_{des} = 12$ kJ mol^{-1}.

3-2. Consider the shortest time it would take for one CH unit to move from its initial position to the opposite side of an IIG by successive migratory jumps. Assume that the activation energy for migration (E_{mig}) is 6 kJ mol^{-1}, and the IIG is a sphere with a 0.1 μm radius. Each migratory jump laterally advances the molecule by 0.3 nm. Show work and choose your answer from (a)-(e) below.

(a) $t \leq$ 1 day (b) 10 day $\leq t \leq 10^2$ yr (c) 10^3 yr $\leq t \leq 10^6$ yr

(d) 10^7 yr $\leq t \leq 10^{10}$ yr (e) $t \geq 10^{11}$ yr

3-3. Consider the reaction of CO with H_2 to form H_2CO. The activation energy on a metal catalyst is 20 kJ mol^{-1}, which produces formaldehyde at a rate of 1 molecule/s per site at 300 K. Esitmate the rate of formaldehyde formation per site if the reaction takes place at 20 K.

3-4. Which is a set of all true statements? Circle one.

(a) Most CH species desorb from the IIG surface before encountering other reactants by surface migration.

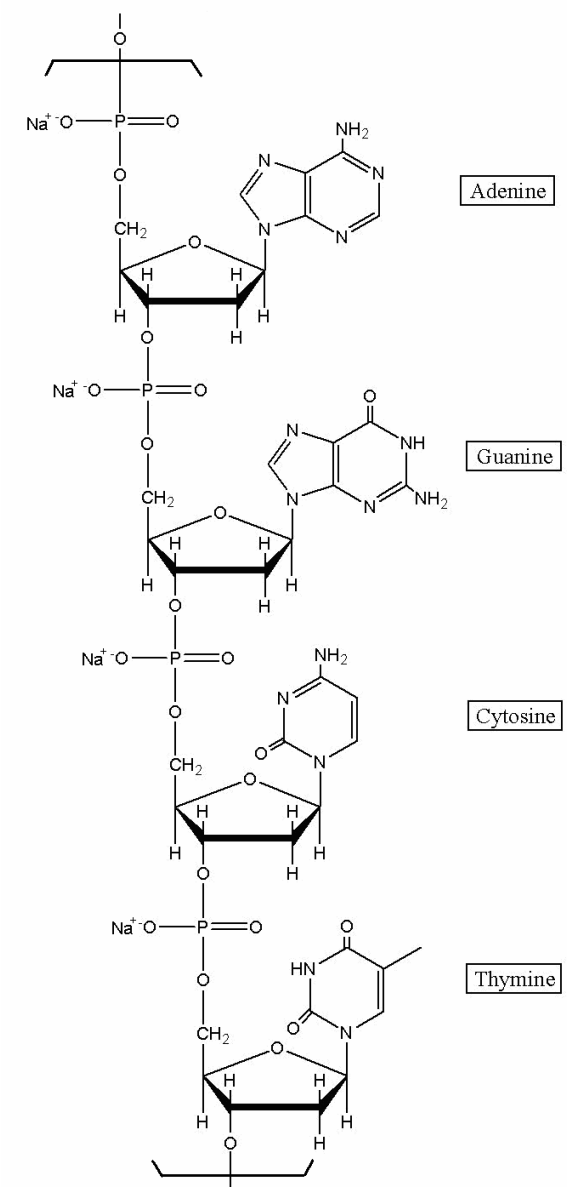
(b) IIGs can assist transformation of simple molecules to more complex ones in interstellar space.

(c) For a reaction on the IIG to occur at an appreciable speed during the age of the Universe (1×10^{10} yr), the reaction energy barrier must be absent or negligible.

(a) (b) (c) (a, b) (a, c) (b, c) (a, b, c)

4. The Chemistry of DNA

4-1. In 1944 Oswald Avery isolated a genetic material and showed, by elemental analysis, that it was a sodium salt of deoxyribonucleic acid. A segment of DNA with formula mass of 1323.72 is shown.



Assuming that equimolar amounts of the four bases are present in DNA, write the number of H atoms per P atom. Calculate, to 3 significant figures, the theoretical weight percentage of H expected upon elemental analysis of DNA.

4-2. Chargaff extracted the separated bases and determined their concentrations by measuring UV absorbance. The Beer-Lambert law was used to obtain the molar concentration. Chargaff discovered the following molar ratio for bases in DNA:

adenine to guanine = 1.43 thymine to cytosine = 1.43

adenine to thymine = 1.02 guanine to cytosine = 1.02

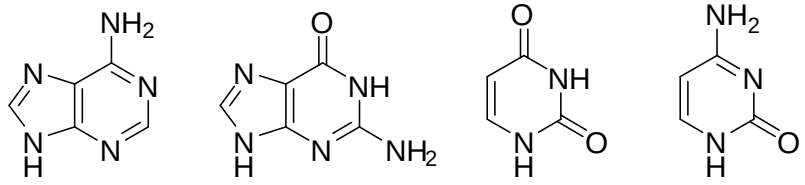
Chargaff's discovery suggested that the bases might exist as pairs in DNA. Watson and Crick mentioned in their celebrated 1953 paper in *Nature*: "It has not escaped our notice

that the specific pairing we have postulated immediately suggests a possible copying mechanism for the genetic material."

Draw structures of the specific pairing found in DNA. Indicate hydrogen bonds. Omit the sugar-phosphate backbone.

4-3. Mutation can occur through base pairings different from the above.
Draw structures of any three alternative base pairs.

4-4. The plausibility of the formation of purine and pyrimidine bases in the prebiotic atmosphere of the Earth from HCN, NH_3, and H_2O has been demonstrated in the laboratory.
Write the minimum number of HCN and H_2O molecules required for formation of the following compounds.



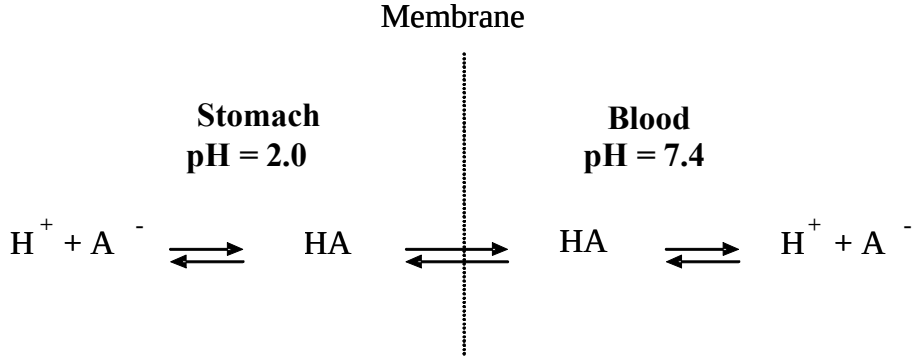
adenine guanine Uracil cytosine

5. Acid-Base Chemistry

5-1. *Calculate $[H^+]$, $[OH^-]$, $[HSO_4^-]$, and $[SO_4^{2-}]$ in a 1.0 x 10^{-7} M solution of sulfuric acid (K_w = 1.0 x 10^{-14}, K_2 = 1.2 x 10^{-2} at 25°C). In your work you may use mass- and charge-balance equations. Answer with two significant figures.*

5-2. *Calculate the volume of 0.80 M NaOH solution that should be added to a 250 mL aqueous solution containing 3.48 mL of concentrated phosphoric acid in order to prepare a pH 7.4 buffer. Answer with three significant figures.* (H_3PO_4 (aq), purity = 85 % wt/wt, density = 1.69 g/mL, FW = 98.00) (pK_1 = 2.15, pK_2 = 7.20, pK_3 = 12.44).

5-3. The efficacy of a drug is greatly dependent on its ability to be absorbed into the blood stream. Acid-base chemistry plays an important role in drug absorption.



Assume that the ionic form (A^-) of a weakly acidic drug does not penetrate the membrane, whereas the neutral form (HA) freely crosses the membrane. Also assume that equilibrium is established so that the concentration of HA is the same on both sides. *Calculate the ratio of the total concentration ([HA] + [A^-]) of aspirin (acetylsalicylic acid, pK = 3.52) in the blood to that in the stomach.*

6. Electrochemistry

Water is a very stable molecule, abundant on earth and essential for life. As such, water was long thought to be a chemical element. However, soon after the invention of a voltaic cell in 1800, Nicholson and Carlyle decomposed water into hydrogen and oxygen by electrolysis.

6-1. Water can be thought of as hydrogen oxidized by oxygen. Thus, hydrogen can be recovered by reduction of water, using an aqueous solution of sodium sulfate, at a platinum electrode connected to the negative terminal of a battery. The solution near the electrode becomes basic.
Write a balanced half-reaction for the reduction of water.

6-2. Water can also be thought of as oxygen reduced by hydrogen. Thus, oxygen can be recovered by oxidation of water at the Pt electrode connected to the positive terminal. Write *a balanced half-reaction for the oxidation of water.*

6-3. When copper is used at both electrodes, gas is generated only at one electrode during the initial stage of electrolysis.
Write the half-reaction at the electrode that does not generate gas.

Another species in solution that can be reduced is sodium ion. The reduction of sodium ion to metallic sodium does not occur in aqueous solution, because water is reduced first. However, as Humphrey Davy discovered in 1807, sodium can be made by electrolysis of fused sodium chloride.

6-4. Based on these observations, connect the half-reactions with the standard reduction potential (in volts).

Reduction of copper ion (Cu^{2+})	+0.340
Reduction of oxygen	- 2.710
Reduction of water	- 0.830
Reduction of sodium ion (Na^+)	0.000
Reduction of hydrogen ion	+1.230

The electrode potential is affected by other reactions taking place around the electrode. The potential of the Cu^{2+}/Cu electrode in a 0.100 M Cu^{2+} solution changes as $Cu(OH)_2$ precipitates. Answer with 3 significant figures for the following problems. The temperature is 25°C. Note that $K_w = 1.00 \times 10^{-14}$ at 25°C.

6-5. Precipitation of $Cu(OH)_2$ begins at pH = 4.84.
Determine the solubility product of $Cu(OH)_2$.

6-6. *Calculate the standard reduction potential for $Cu(OH)_2(s) + 2e^- \rightarrow Cu(s) + 2OH^-$.*

6-7. *Calculate the electrode potential at pH = 1.00.*

Lithium cobalt oxide and specialty carbon are active ingredients for the positive and negative electrodes, respectively, of a rechargeable lithium battery. During the charge/recharge cycles, the following reversible half-reactions occur.

$$LiCoO_2 \rightleftarrows Li_{1-x}CoO_2 + x\,Li^+ + x\,e^-$$

$$C + x\,Li^+ + x\,e^- \rightleftarrows CLi_x$$

The total amount of energy a battery can store is rated in mAh. A battery rated at 1500 mAh can power a device drawing 100 milliamps for 15 hours.

6-8. Graphite has lithium intercalation sites between its layers. Assuming a maximum 6:1 carbon-to-lithium intercalation stoichiometry, *calculate the theoretical charge capacity of 1.00 gram of graphite to intercalate lithium. Answer in mAh/g with 3 significant figures.*

7. Hydrogen Economy

Hydrogen is more energy-dense than carbon, by mass. Thus, historically there has been a move toward fuel with higher hydrogen content: coal → oil → natural gas → hydrogen. Cost-effective production and safe storage of hydrogen are two major hurdles to the successful inauguration of a hydrogen economy.

7-1. Consider hydrogen in a cylinder of 80 MPa at 25 °C. Using the ideal gas law, *estimate the density of hydrogen in the cylinder in kg/m^3.*

7-2. *Calculate the ratio between heat generated when hydrogen is burned and heat generated when the same weight of carbon is burned. The difference comes to a large extent from the fact that the most abundant isotope of hydrogen has no neutron and hydrogen has no inner electron shell. ΔH_f^o [$H_2O(l)$] = -286 kJ/mol, ΔH_f^o [$CO_2(g)$] = -394 kJ/mol.*

7-3. *Calculate the theoretical maximum work produced by the combustion of 1 kg hydrogen (a) from the electric motor using hydrogen fuel cell and (b) from the heat engine working*

between 25 °C and 300 °C. The efficiency (work done/heat absorbed) of an ideal heat engine working between T_{cold} and T_{hot} is given by $[1 - T_{cold}/T_{hot}]$.

$S^{o}_{298}[H_2(g)] = 131$ J/(K mol)

$S^{o}_{298}[O_2(g)] = 205$ J/(K mol)

$S^{o}_{298}[H_2O(l)] = 70$ J/(K mol).

If the fuel cell is working at 1 W and the standard potential difference, how long will the electric motor run at what current?

8. Chemistry of Iron Oxides

The nucleus of iron is the most stable among all elements and, therefore, iron accumulates at the core of massive red giant stars where nucleosynthesis of many elements essential for life (such as C, N, O, P, S, etc.) takes place. As a result, among heavy elements iron is quite abundant in the universe. Iron is also abundant on Earth.

8-1. Development of a technology for reducing iron oxide to iron was a key step in human civilization. Key reactions taking place in the blast furnace are summarized below.

$C(s) + O_2(g) \rightarrow CO_2(g)$ $\Delta H^\circ = -393.51$ kJ(/mol) ----- ①

$CO_2(g) + C(s) \rightarrow 2CO(g)$ $\Delta H^\circ = 172.46$ kJ(/mol) ----- ②

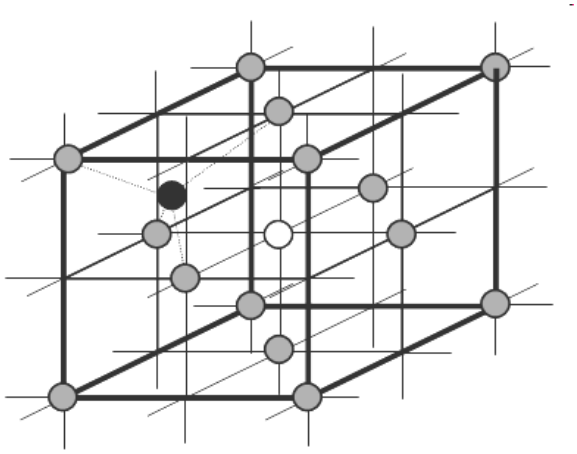
$Fe_2O_3(s) + CO(g) \rightarrow Fe(s) + CO_2(g)$ $\Delta H^\circ =$? ---------- ③

8-1-1. *<u>Indicate</u> the reducing agent in each reaction.*

8-1-2. *<u>Balance</u> reaction ③ and <u>calculate</u> the equilibrium constant of reaction ③ at 1200 °C.* ($\Delta H_f^\circ(Fe_2O_3(s)) = -824.2$ kJ/mol, S°(J/mol/K): $Fe(s) = 27.28$, $Fe_2O_3(s) = 87.40$, $C(s) = 5.74$, $CO(g) = 197.674$, $CO_2(g) = 213.74$)

8-2. In the manufacture of celadon pottery, Fe_2O_3 is partially reduced in a charcoal kiln to mixed oxides of Fe_3O_4 and FeO. The amount of the different oxides seems to be related to the “mystic” color of celadon ceramics.

Fe_3O_4 (magnetite) itself is a mixed oxide containing Fe^{2+} and Fe^{3+} ions and belongs to a group of compounds with a general formula of AB_2O_4. The oxide ions form a face-centered cubic array. The figure shows the array of oxygens (gray circles) and representative sites for divalent A and trivalent B cations. The dark circle represents a tetrahedral site and the white circle an octahedral site.



8-2-1. *How many available octahedral sites for iron ions are there in one AB_2O_4 unit? Certain sites are shared by neighboring units.*

AB_2O_4 can adopt a normal- or an inverse-spinel structure. In normal-spinel structure, two B ions occupy two of the octahedral sites and one A occupies one of the tetrahedral sites. In an inverse-spinel structure, one of the two B ions occupies a tetrahedral site. The other B ion and the one A ion occupy octahedral sites.

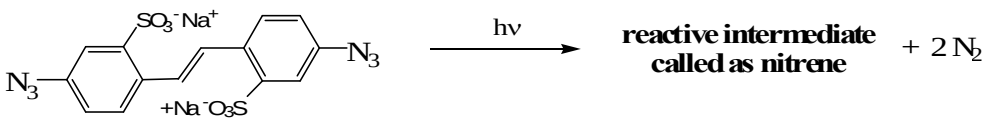
8-2-2. *What percentage of available tetrahedral sites is occupied by either Fe^{2+} or Fe^{3+} ion in Fe_3O_4?*

8-2-3 *Fe_3O_4 has an inverse-spinel structure. Draw the crystal field splitting pattern of Fe^{2+} and fill out the electrons. The electron pairing energy is greater than the octahedral field splitting.*

9. Photolithographic process

Photolithography is a process used in semiconductor device fabrication to transfer a pattern from a photomask to the surface of a substrate. In a typical photolithography process, light is projected, through a mask that defines a particular circuitry, onto a silicon wafer coated with a thin layer of photoresist.

9-1. The earliest photoresists were based on the photochemistry that generates a reactive intermediates from bis(aryl azide). Patterning becomes possible through the cross-linking reaction of the nitrenes generated from the azides.



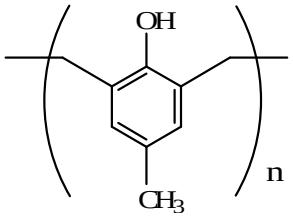
Bis(aryl azide)

9-1-1. <u>Draw</u> two possible Lewis structures of CH_3-N_3, the simplest compound having the same active functional group of bis(aryl azide). Assign formal charges.

9-1-2. <u>Draw</u> the Lewis structure of nitrene expected from CH_3-N_3.

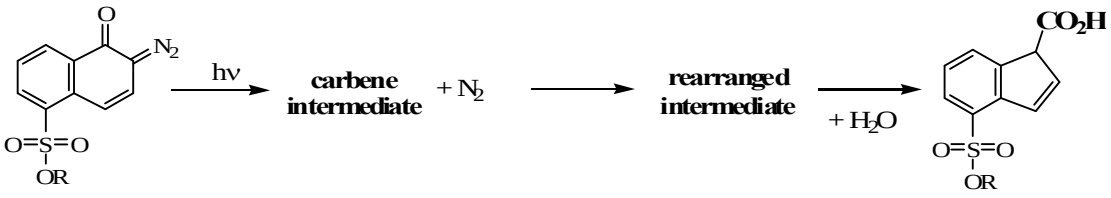
9-1-3. <u>Draw</u> the structures for two possible products, when this nitrene from CH_3-N_3 reacts with ethylene gas (CH_2CH_2).

9-2. Photoresists consisting of Novolak polymers, utilizes acid to change their solubility. The acid component can be produced photochemically from diazonaphthaquinone. In fact, "Novolaks" have been the representative "positive" photoresists of the modern microelectronic revolution.



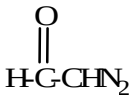
Novolak

When irradiated, diazonaphthaquinone undergoes photochemical decomposition followed by rearrangement eventually producing a carboxylic acid.



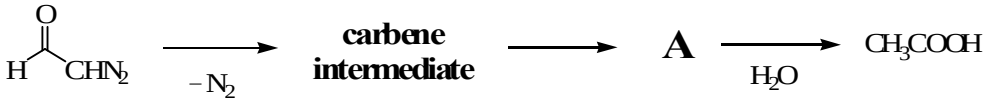
Diazonahpthaquinone derivative

9-2-1. <u>Draw</u> three Lewis structures of diazoacetaldehyde (see below), the simplest compound having the same active functional group of diazonaphthaquinone. Indicate formal charges.

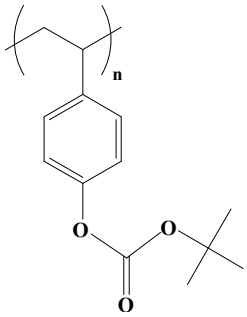


diazoacetaldehyde

9-2-2. <u>Draw</u> a Lewis structure of the rearranged intermediate, A (see below), generated from diazoacetaldehyde after losing N_2. A satisfies Lewis' octet rule and reacts with water to form acetic acid, CH_3CO_2H.

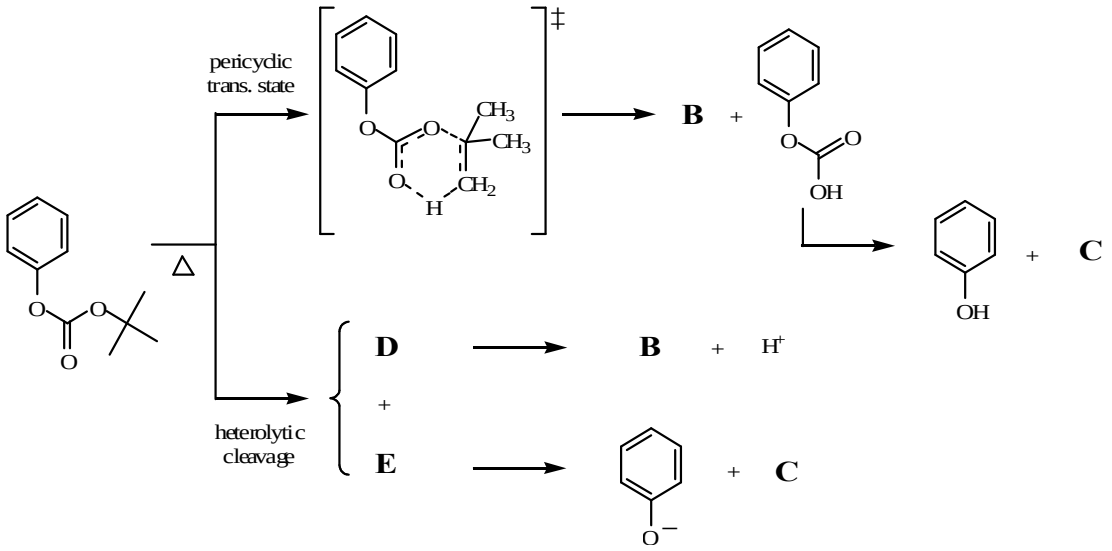


9-3. Advanced photoresists were invented in 1982 based on chemical amplification. The most popular chemical amplification for positive-tone involves the acid catalyzed deprotection of poly(*p*-hydroxystyrene) resin protected by various acid-sensitive protecting groups such as *t*-butyloxycarbonyl (*t*-BOC).

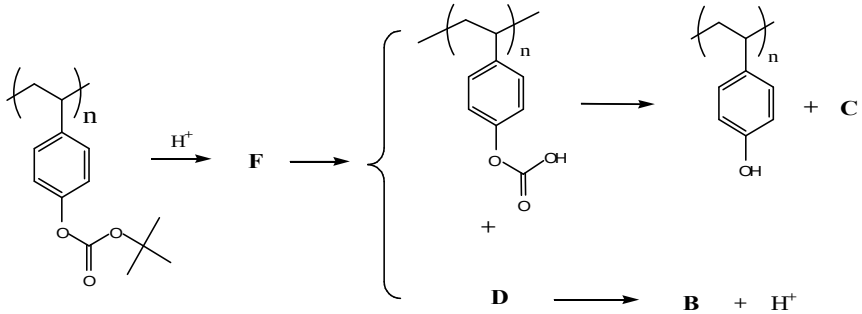


The thermal decomposition of carbonate ester itself normally occurs well above 150°C.

9-3-1. Two plausible mechanisms have been suggested for this decomposition reaction having relatively high activation energy. Draw expected intermediates and products from this reaction.



9-3-2. In the presence of a trace amount of acid, the reaction temperature can be reduced to below 100°C. Draw expected intermediate F from the following chemical amplification process based on using t-BOC.



10. Natural Products – Structural Analysis

Licorice (Glycyrrhizia. Uralensis) Licorice Root

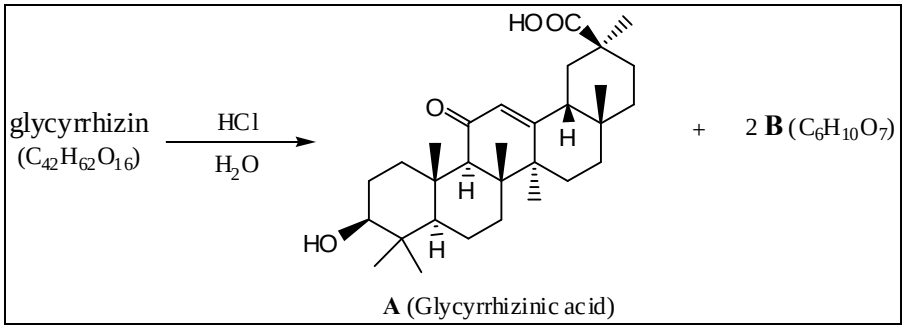
The flavor extracted from the licorice root is 50 – 150 times sweeter than table sugar.

The most important and abundant compound responsible for the sweetness and medicinal effects of licorice is *glycyrrhizin* ($C_{42}H_{62}O_{16}$).

Glycyrrhizin requires three equivalents of NaOH to effect neutralization.

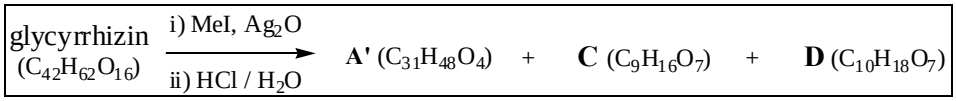
``When *glycyrrhizin* was subjected to acid hydrolysis, *Glycyrrhizinic acid* (**A** ($C_{30}H_{46}O_4$)) and **B** ($C_6H_{10}O_7$) were obtained in a 1:2 molar ratio (figure 1).

Figure 1.



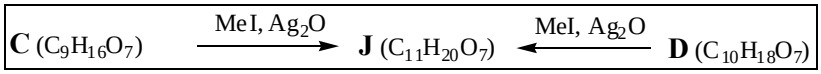
When *glycyrrhizin* was methylated with methyl iodide (MeI) at every possible site before hydrolysis, hydrolysis produced **A'** (methyl glycyrrhizinate), **C** and **D** (figure 2). B, C and D exist as mixtures of anomers.

Figure 2.



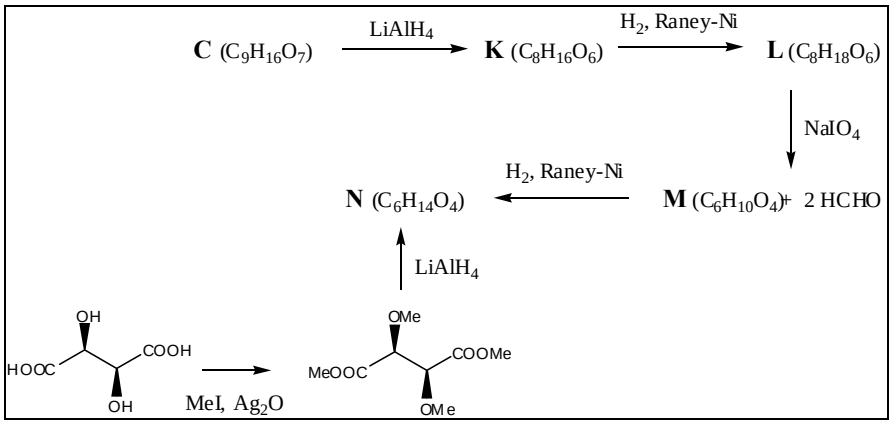
Methylation of **C** and **D** with MeI produced the same isomeric mixture of compounds, **J** (figure 3.)

Figure 3.



C was reduced with $LiAlH_4$ to give **K**, and **L** was produced by the reduction of **K**. Oxidative cleavage of vicinal diol of **L** with $NaIO_4$ produced **M** and two equivalents of formaldehyde. Reduction of **M** produced **N**. The structure and stereochemistry of **N** was confirmed by the synthesis of **N** from D-(-)-tartaric acid through methylation followed by reduction (figure 4). A ^{1}H-NMR spectrum of **L** showed two distinct peaks for methyl groups. (There is no symmetry in L)

Figure 4.

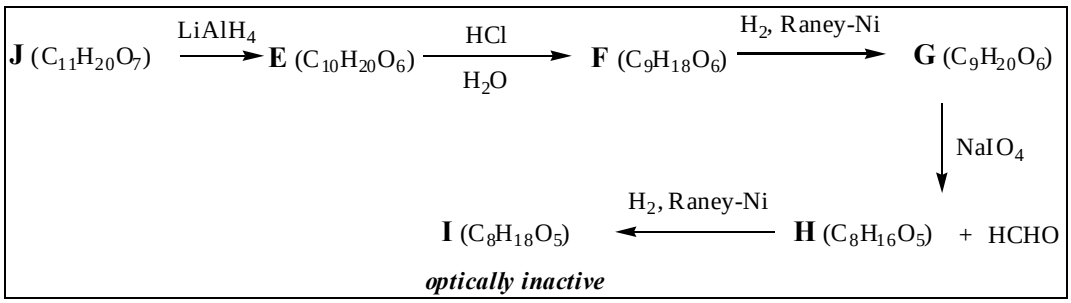


10-1. *<u>Complete</u> structures for **L , M, and N** in the answer sheet.*

10-2. *How many structures for **C** are possible? <u>Complete</u> possible structures for **C**.*

To determine the correct structure of **C**, following set of reactions were performed.
J was reduced to **E,** and acid hydrolysis of **E** produced **F**. Reduction of **F** generated **G,** and **G** was oxidized with $NaIO_4$ to **H** with formation of one equivalent of formaldehyde. **I** was obtained from **H** through reduction. Among all compounds from **A** to **I**, only **I** was optically inactive (figure 5).

Figure 5



10-3. *<u>Complete</u> structures for **G** and **I**.*

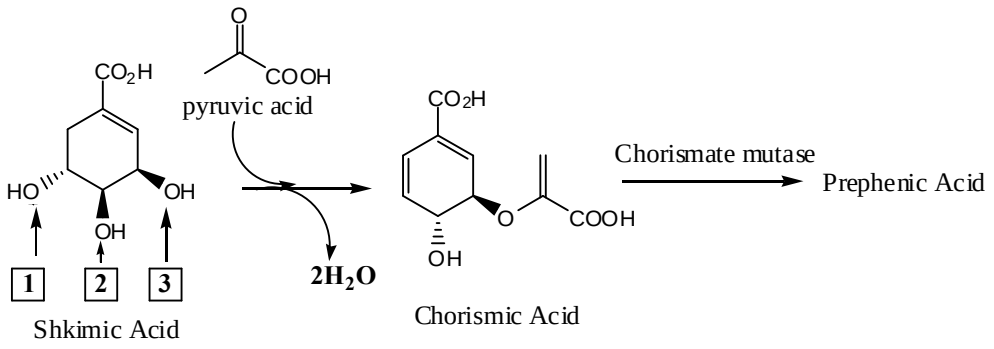
10-4. *Which one is the correct structure for **C** among ones you have drawn in **10-2**?*

10-5. *<u>Complete</u> structures for **B, D,** and **J**.*

10-6. *<u>Complete</u> the structure for Glycyrrhizin.*

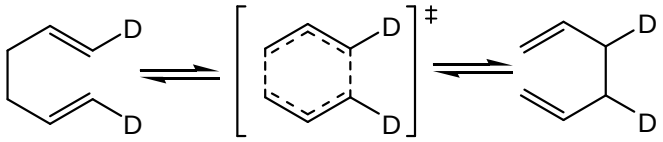
11. Enzyme Reaction

Shikimic acid biosynthesis is an important pathway for amino acids, alkaloids and heterocyclic natural product production. Nature converts shikimic acid to chorismic acid through a cascade of enzymatic reactions. Then chorismate mutase catalyzes the conversion of chorismic acid to prephenic acid at the branch point for the biosynthesis of aromatic amino acids such as tyrosine and phenylalanine.



11-1. *During the transformation of shikimic acid to chorismic acid, dehydration is occurring. Choose the hydroxyl group in shikimic acid that is lost through above dehydration among all possible reactions.*

11-2. *Chorismate mutase rearranges chorismic acid into prephenic acid without changing the molecular formula. Chorismic acid becomes prephenic acid through the Claisen rearrangement, a concerted pericyclic process like the Cope rearrangement as shown below:*

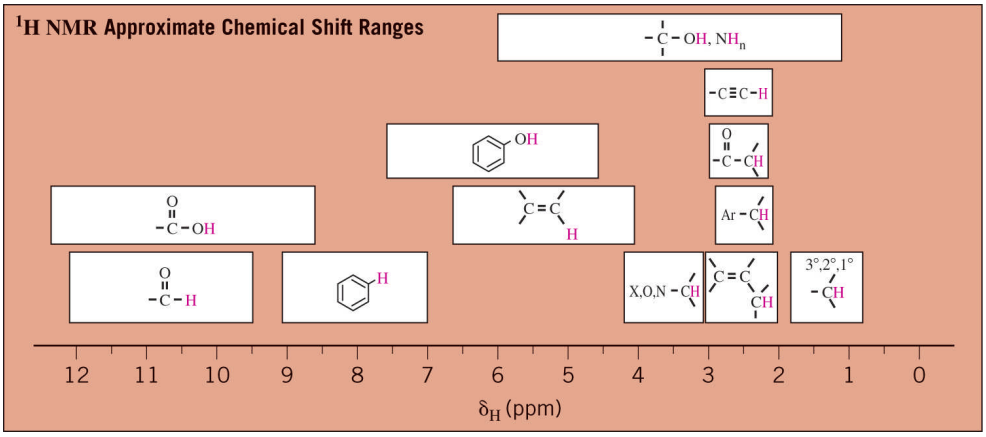


Based on the following spectral data, propose the structure of prephenic acid.

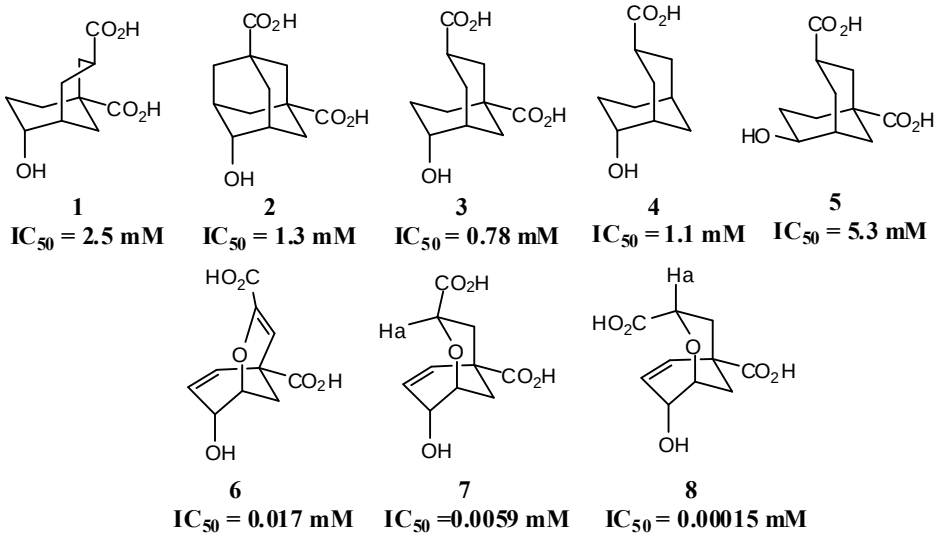
^{1}H-NMR (D_2O, 250 MHz): δ 6.01 (2H, d, J = 10.4 Hz), 5.92 (2H, dd J = 10.4, 3.1 Hz), 4.50 (1H, t, J = 3.1 Hz), 3.12 (2H, s). Note that there are three protons, which have been exchanged by D_2O very fast, and two protons at δ 3.12, which are exchanged slowly in prephenic acid.

^{13}C-NMR (D_2O, 75 MHz): 203, 178, 173, 132 (for two identical carbons), 127 (for two identical carbons), 65, 49, 48.

δ, chemical shift; H, integrals; d, doublet; dd, doublet of doublet; J, coupling constant; t, triplet; s, singlet



Chorismate mutase is believed to stabilize the transition state of Claisen rearrangement. Thus it is an interesting target for inhibitor design. Inhibitors, called transition state analog (TSA)s that resemble the transition state (TS, ***e.g.***, the species in brackets "[ ]" above) of the reaction are designed to occupy the active site. Several inhibitors were designed and synthesized, and among them eight turned out to be potent inhibitors of the enzyme. The lower the IC_{50} (inhibitor concentration of 50% of the enzymatic activity) value, the better the inhibitor.



1 IC_{50} = 2.5 mM

2 IC_{50} = 1.3 mM

3 IC_{50} = 0.78 mM

4 IC_{50} = 1.1 mM

5 IC_{50} = 5.3 mM

6 IC_{50} = 0.017 mM

7 IC_{50} =0.0059 mM

8 IC_{50} = 0.00015 mM

11-3. *<u>Choose</u> all correct statements based on the structures and IC_{50} values of above inhibitors. Increase of factor 5 is considered to be important.*

(a) Configuration of the hydroxyl group plays an important role in the TS and inhibitor design.

(b) The presence of both carboxylic groups is important in the TS and inhibitor design.

(c) Transition state of the reaction contains two six-membered rings with one chair and one twist-boat conformation.

(d) **7** and **8** can be distinguished on the basis of the ^{1}H-NMR of H_a.

11-4. *Draw the transition state of the transformation of chorismic acid to prephenic acid based on the TSA structures and their* IC_{50} *values.*

11-5. *Compared with the uncatalyzed thermal conversion, chorismate mutase accelerates conversion of chorismic acid to prephenic acid* 1.0×10^6 *fold at* 25^oC *by lowering the activation energy of the reaction. Calculate the decrease in activation energy of chorismate mutase at* 25^oC.

$\Delta H^{\neq}_{uncat}$ *is 86,900 J/mol for the thermal conversion of chorismic acid to prephenic acid. At what temperature will the rate of the uncatalyzed thermal conversion be the same as that of the enzyme-catalyzed conversion at* 25^oC, *assuming that* $E_a = \Delta H^{\neq}$.

Solutions to the Theoretical Problems of the IChO

1-1.

The mass of a water droplet:

$m = V\rho = [(4/3)\pi r^3]\rho = (4/3)\pi (0.5\times10^{-6}\ m)^3 (1.0\ g/cm^3) = 5.2\times10^{-16}$ kg

Average kinetic energy at 27°C:

KE = mv2/2 = (5.2x10-16 kg) (0.51x10-2 m/s)2/2 = 6.9x10-21 kg m2/s2 = 6.9 x10-21 J

1-2.

The average kinetic energy of an argon atom is the same as that of a water droplet.

KE becomes zero at –273 °C.

From the linear relationship in the figure, KE = aT (absolute temperature)

where a is the increase in kinetic energy of an argon atom per degree.

$a = KE/T = 6.9\times10^{-21}\ J/(27+273K) = 2.3\times10^{-23}$ J/K

S: specific heat of argon N: number of atoms in 1g of argon S = 0.31 J/g K = a x N

$N = S/a = (0.31\ J/g\ K) / (2.3\times10^{-23}\ J/K) = 1.4\times10^{22}$ Avogadro's number (N_A) : Number of argon atoms in 40 g of argon

$N_A = (40)(1.4\times10^{22}) = 5.6\times10^{23}$

2.1.

mass of a typical star = $(4/3)(3.1)(7\times10^8\ m)^3(1.4\ g/10^{-6}\ m^3) = 2\times10^{33}$ g

mass of protons of a typical star = $(2\times10^{33}\ g)(3/4 + 1/8) = 1.8\times10^{33}$ g

number of protons of a typical star = $(1.8\times10^{33}\ g)(6\times10^{23}/g) = 1\times10^{57}$

number of stellar protons in the universe = $(1\times10^{57})(10^{23}) = 1\times10^{80}$

2.2.

$\Delta E(2\rightarrow3) = C(1/4 - 1/9) = 0.1389\ C$ $\lambda(2\rightarrow3) = 656.3$ nm

$\Delta E(1\rightarrow2) = C(1/1 - 1/4) = 0.75\ C$ $\lambda(1\rightarrow2) = (656.3)(0.1389/0.75) = 121.5$ nm

2.3.

$T = (2.9\times10^{-3}\ m\ K)/1.215\times10^{-7}\ m = 2.4\times10^4$ K

2.4.

λ = 3 × 108 m/1.42 × 109 = 0.21 m T = (2.9 × 10-3 m K)/0.21 m = 0.014 K

2.5.

$^{14}N + {}^4He \rightarrow (\quad {}^{17}O \quad) + {}^1H$

3-1.

$k_{des} = A\ \exp(-E_{des}/RT) = (1\times10^{12}\ s^{-1})(5\times10^{-32}) = 5\times10^{-20}\ s^{-1}$ at T = 20 K

surface residence time, $\tau_{residence} = 1 / k_{des} = 2\times10^{19}\ s = 6\times10^{11}\ yr = 2\times10^{19}\ s$

(full credit for $\tau_{half\text{-}life} = \ln2 / k_{des} = 1\times10^{19}\ s = 4\times10^{11}\ yr$)

3-2.

The distance to be traveled by a molecule: $x = \pi r = 300$ nm.

$k_{mig} = A\ \exp(-E_{mig}/RT) = (1\times10^{12}\ s^{-1})(2\times10^{-16}) = 2\times10^{-4}\ s^{-1}$ at T = 20 K average time between migratory jumps, $\tau = 1 / k_{mig} = 5\times10^3$ s

the time needed to move 300 nm = (300 nm/0.3 nm) jumps x (5x103 s/jump) = 5x106 s = 50 days

(Full credit for the calculation using a random-walk model. In this case:
$t = \tau (x/d)^2 = 5 \times 10^9$ s = 160 yr. The answer is still (b).)

(a) **(b)** (c) (d) (e)

3-3.

k(20 K) / k(300 K) = exp[(E/R) ($1/T_1 - 1/T_2$)] = e^{-112} = ~ 10^{-49} for the given reaction

The rate of formaldehyde production at 20 K = ~ 10^{-49} molecule/site/s = ~ 10^{-42} molecule/site/ yr

(The reaction will not occur at all during the age of the universe (1×10^{10} yr))

rate = 10^{-42} molecules/site/yr

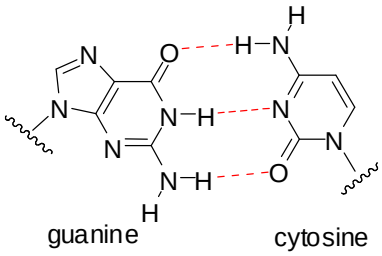
3-4. circle one

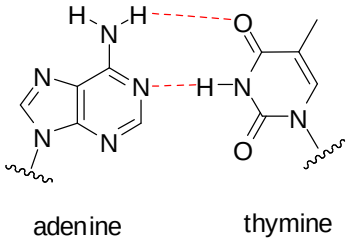
(a) (b) (c) (a, b) (a, c) **(b, c)** (a, b, c)

4.1

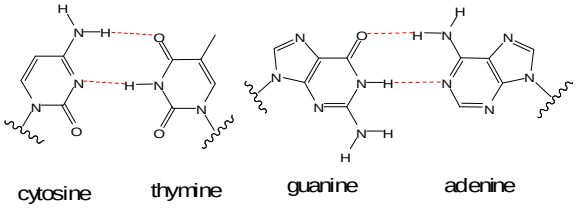
	H		P
Number of atoms	11.3	/	1
Theoretical wt %	3.43		

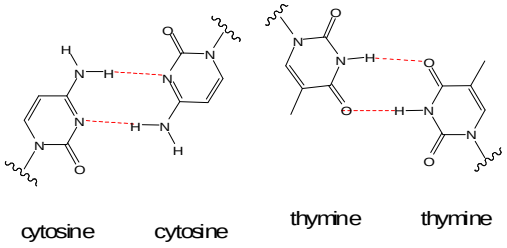
4-2.

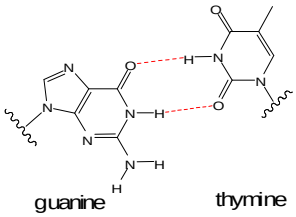


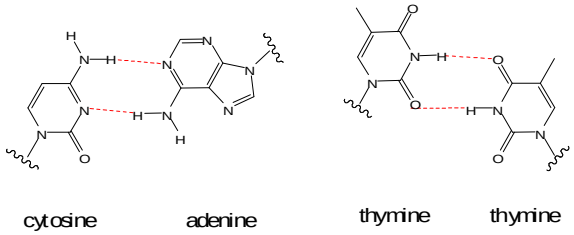


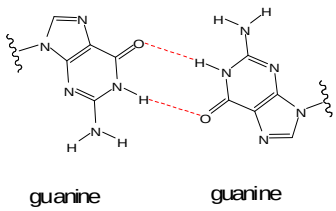
4.3 Full marks for three of the following structures

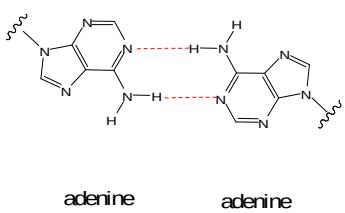




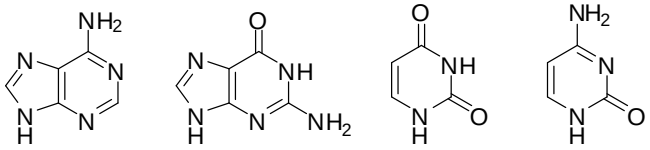








4-4.



adenine guanine Uracil cytosine

HCN	(**5**)	(**5**)	(**4**)	(**4**)
H_2O	(**0**)	(**1**)	(**2**)	(**1**)

5-1.

1st ionization is complete: $H_2SO_4 \rightarrow H^+ + HSO_4^-$ $[H_2SO_4] = 0$

2nd ionization: $[H^+][SO_4^{2-}]/[HSO_4^-] = K_2 = 1.2 \times 10^{-2}$ (1)

Mass balance: $[H_2SO_4] + [HSO_4^-] + [SO_4^{2-}] = 1.0 \times 10^{-7}$ (2)

Charge balance: $[H^+] = [HSO_4^-] + 2[SO_4^{2-}] + [OH^-]$ (3)

Degree of ionization is increased upon dilution. $[H_2SO_4] = 0$ Assume $[H^+]_{H2SO4} = 2 \times 10^{-7}$

From (1), $[SO_4^{2-}]/[HSO_4^-] = 6 \times 10^4$ (2nd ionization is almost complete) $[HSO_4^-] = 0$

From (2), $[SO_4^{2-}] = 1.0 \times 10^{-7}$

From (3), $[H^+] = (2 \times 10^{-7}) + 10^{-14}/[H^+]$ $[H^+] = 2.4 \times 10^{-7}$

$[OH^-] = 10^{-14}/(2.4 \times 10^{-7}) = 4.1 \times 10^{-8}$

From (1), $[HSO_4^-] = [H^+][SO_4^{2-}]/K_2 = (2.4 \times 10^{-7})(1.0 \times 10^{-7})/(1.2 \times 10^{-2}) = 2.0 \times 10^{-12}$

Check charge balance: $2.4 \times 10^{-7} \approx (2.0 \times 10^{-12}) + 2(1.0 \times 10^{-7}) + (4.1 \times 10^{-8})$

Check mass balance: $0 + 2.0 \times 10^{-12} + 1.0 \times 10^{-7} \approx 1.0 \times 10^{-7}$

Species	Concentration
HSO_4^-	2.0×10^{-12}
SO_4^{2-}	1.0×10^{-7}
H^+	2.4×10^{-7}
OH^-	4.1×10^{-8}

5-2.

mmol $H_3PO_4 = 0.85 \times 3.48$ mL $\times$ 1.69g/mL $\times$ 1 mol/98.00 g $\times$ 1000 = 51.0 [5 marks]

The desired pH is above pK_2.

A 1:1 mixture of $H_2PO_4^-$ and HPO_4^{2-} would have pH = pK_2 = 7.20.

If the pH is to be 7.40, there must be more HPO_4^{2-} than $H_2PO_4^-$.

We need to add NaOH to convert H_3PO_4 to $H_2PO_4^-$ and to convert to the right amount of $H_2PO_4^-$ to HPO_4^{2-}.

$H_3PO_4 + OH^- \rightarrow H_2PO_4^- + H_2O$

$H_2PO_4^- + OH^- \rightarrow HPO_4^{2-} + H_2O$

The volume of 0.80 NaOH needed to react with to to convert H_3PO_4 to $H_2PO_4^-$ is:

51.0 mmol / 0.80M = 63.75 mL

To get pH of 7.40 we need:

$H_2PO_4^- + OH^- \rightarrow HPO_4^{2-}$

Initial mmol	51.0	x	0
Final mmol	51.0-x	0	x

pH = pK_2 + log $[HPO_4^{2-}] / [H_2PO_4^-]$ 7.40 = 7.20 + log {x / (51.0-x)}; x = 31.27 mmol

The volume of NaOH needed to convert 31.27 mmol is : 31.27 mmol / 0.80 M = 39.09 mL

The total volume of NaOH = 63.75 + 39.09 = 102.84 mL , 103 mL

5-3.

pK = 3.52 pH = pK_a + log ($[A^-]/[HA]$) $[A^-]/[HA] = 10^{(pH-pKa)}$

In blood, pH =7.40, $[A^-]/[HA] = 10^{(7.40-3.52)} = 7586$ Total ASA = 7586 +1 = 7587

In stomach, pH = 2.00, $[A^-]/[HA] = 10^{(2.00-3.52)} = 3.02 \times 10^{-2}$ Total ASA = $1+ 3.02 \times 10^{-2} = 1.03$

Ratio of total aspirin in blood to that in stomach = 7587/1.03 = <u>7400</u>

6-1.

$4\ H_2O + 4\ e^- \rightarrow 2\ H_2(g) + 4\ OH^-$ (or $2\ H_2O + 2\ e^- \rightarrow H_2(g) + 2\ OH^-$)

6-2.

$2\ H_2O \rightarrow O_2 + 4\ H^+ + 4\ e^-$ (or $H_2O \rightarrow 1/2\ O_2 + 2\ H^+ + 2\ e^-$)

6-3.

$Cu \rightarrow Cu^{2+} + 2e^-$

6-4.

Reduction of sodium ion seldom takes place.

It has a highly negative reduction potential of –2.710 V.

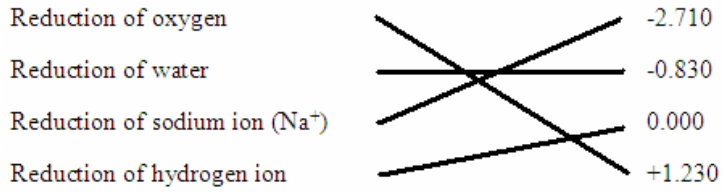
Reduction potential for water to hydrogen is negative (water is very stable).

But, it is not as negative as that for sodium ion. It is –0.830 V.

Reduction of both copper ion and oxygen takes place readily and the reduction potentials for both are positive.

In the present system, the reverse reaction (oxidation) takes place at the positive terminal. Copper is oxidized before water.

Reduction potential for hydrogen ion is defined as 0.000 V



6-5.

pOH = 14.00 – 4.84 = 9.16 $[OH^-] = 6.92 \times 10^{-10}$

$K_{sp} = [Cu^{2+}][OH^-]^2 = 0.100 \times (6.92 \times 10^{-10}) = 4.79 \times 10^{-20}$

6-6.

$E = E^o_{Cu2+/Cu} + (0.0592/2) \log [Cu^{2+}]$ $= +0.340 + (0.0592/2) \log [Cu^{2+}]$

$= +0.340 + (0.0592/2) \log (K_{sp} / [OH^-]^2)$ $= +0.340 + (0.0592/2) \log (K_{sp}) - (0.0592/2) \log [OH^-]^2$

$= +0.340 + (0.0592/2) \log (K_{sp}) - 0.0592 \log [OH^-]$,

By definition, the standard potential for $Cu(OH)_2(s) + 2e^- \rightarrow Cu(s) + 2OH^-$ is the potential where $[OH^-]$ = 1.00.

E = $E^o_{Cu(OH)2/Cu}$ = +0.340 + (0.0592/2) log (K_{sp}) = +0.340 + (0.0592/2) log (4.79×10^{-20})
= +0.340 - 0.572 = -0.232 V

One may solve this problem as following.

Eqn 1: $Cu(OH)_2(s) + 2e^- \rightarrow Cu + 2OH^-$ $E_+^o = E^o_{Cu(OH)2/Cu} = ?$

Eqn 2: $Cu(OH)_2(s) \rightarrow Cu^{2+} + 2OH^-$ $E^o = (0.05916/n) \log K_{sp}$
$= (0.05916/2) \log(4.79 \times 10^{-20}) = -0.5715$ V

Eqn 1 – Eqn 2 : $Cu^{2+} + 2e^- \rightarrow Cu$

$E_-^o = E_+^o - E^o = E^o_{Cu2+/Cu} = 0.34$ V Therefore, $E_+^o = E_-^o + E^o = +0.34 + (-0.5715) = -0.232$ V

6-7.

Below pH = 4.84, there is no effect of $Cu(OH)_2$ because of no precipitation.

Therefore, E = $E_{Cu2+/Cu}$ = +0.340 + (0.0592/2) log [Cu^{2+}] = +0.340 + (0.0592/2) log 0.100
= +0.340 – 0.0296 = +0.310 V

6-8.

1.00 g graphite = 0.0833 mol carbon

6 mol carbon to 1 mol lithium; 1 g graphite can hold 0.0139 mol lithium

To insert 1 mol lithium, 96487 coulombs are needed.

Therefore, 1 g graphite can charge 96487 × 0.0139 = 1340 coulombs

1340 coulombs / g = 1340 A sec / g = 1340 x 1000 mA × (1 / 3600) h = 372 mA h / g

7-1.

n/V = P/RT = (80×10^6 / 1.013×10^5 atm)/[(0.082 atm L/mol/K)(298K)] = 32 mol/L

density = mass/volume = d = 32 x 2 g/L = 64 kg/m^3

7-2.

$H_2(g) + 1/2\ O_2(g) \rightarrow H_2O(l)$; $\Delta H_{rexn-1} = \Delta H_f[H_2O(l)]$ = -286 kJ/mol = -143 kJ/g

$C(s) + O_2(g) \rightarrow CO_2(g)$; $\Delta H_{rexn-2} = \Delta H_f[CO_2(g)]$ = -394 kJ/mol = -33 kJ/g

$(-\Delta H_{rexn-1}) / (-\Delta H_{rexn-2})$ = 4.3 or $(-\Delta H_{rexn-2}) / (-\Delta H_{rexn-1})$ = 0.23

7-3.

$H_2(g) + 1/2\ O_2(g) \rightarrow H_2O(l)$

ΔH_c = -286 kJ/mol = -143 kJ/g = -143×10^3 kJ/kg

$\Delta G = \Delta H - T\Delta S$

ΔS_c = 70 – 131 – 205/2 = -163.5 J/K/mol

ΔG_c = -286 kJ/mol + 298K x 163.5 J/K/mol = -237 kJ/mol = -1.2×10^5 kJ/kg

(a) electric motor $W_{max} = \Delta G_c \times 1$ kg = -1.2×10^5 kJ

(b) heat engine W_{max} = efficiency x ΔH_c
= (1 – 298/573) x (-143×10^3 kJ) = -6.9×10^4 kJ

119×10^3 kJ = 1 W x t(sec)

t = 1.2×10^8 sec = 3.3×10^4 hr = 1.4×10^3 days = 46 month = 3.8 yr

$\Delta G = -nFE$ n = # of electrons involved in the reaction

F = 96.5 kC/mol $H_2(g) + 1/2\ O_2(g) \rightarrow H_2O(l)$ n = 2

E = $-\Delta G/nF$ = 237 kJ/mol / 2 / 96.5 kC/mol = 1.23 V I = W/E = 0.81 A

8-1-1. ① C ② C ③ CO

8-1-2.

③ $Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(s) + 3CO_2(g)$

① $C(s) + O_2(g) \rightarrow CO_2(g)$ $\Delta H_{①}^{\circ} = -393.51$ kJ $= \Delta H_f^{\circ}(CO_2(g))$

② $CO_2(g) + C(s) \rightarrow 2CO(g)$ $\Delta H_{②}^{\circ} = 172.46$ kJ

From ① and ②,

$\Delta H_f^{\circ}(CO(g)) = (1/2)\{172.46 + (-393.51)\} = -110.525$ kJ $\Delta H_f^{\circ}(Fe_2O_3) = -824.2$ kJ

$\Delta H_{③}^{\circ} = 3 \times \Delta H_f^{\circ}(CO_2(g)) - \Delta H_f^{\circ}(Fe_2O_3) - 3 \times \Delta H_f^{\circ}(CO(g))$

$= 3 \times (-393.51) - (-824.2) - 3 \times (-110.525) = -24.8$ kJ

$\Delta S_{③}^{\circ} = 2 \times 27.28 + 3 \times 213.74 - 87.4 - 3 \times 197.674 = 15.36$ J/K

$\Delta G_{③}^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} = -24.8\text{kJ} - 15.36\text{J/K} \times 1\text{kJ}/1000\text{J} \times 1473.15\text{K} = -47.43$ kJ

$K = e^{(-\Delta G^{\circ}/RT)} = e^{(47430\text{J}/(8.314\text{J/K} \times 1473.15\text{K}))} = 48$

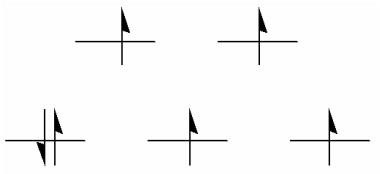
8-2-1.

One AB_2O_4 unit has available 4 (= 1 + (1/4) × 12) octahedral sites

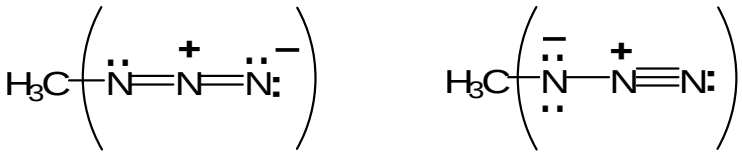
8-2-2.

Since one face-centered cube in AB_2O_4 represents one Fe_3O_4 unit in this case, it has 8 available tetrahedral sites. In one Fe_3O_4 unit, 1 tetrahedral site should be occupied by either one Fe^{2+} (normal-spinel) or one Fe^{3+} (inverse-spinel). Therefore, in both cases, the calculation gives (1/8) × 100% = 12.5% occupancy in available tetrahedral sites.

8-2-3.



9-1-1.



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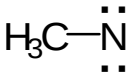
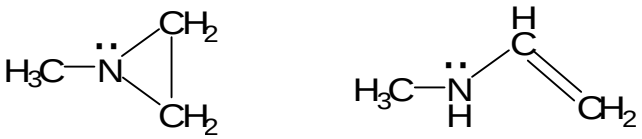
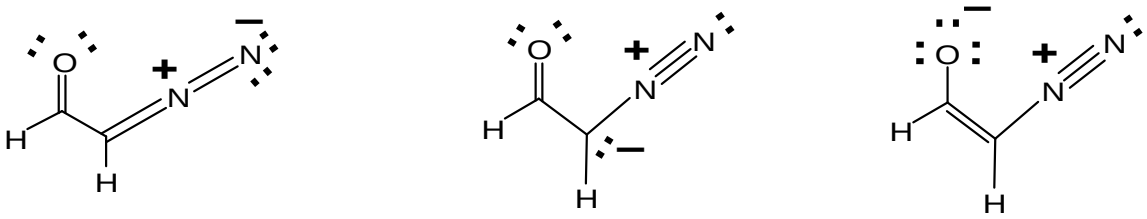


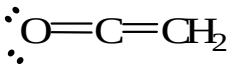
9-1-3.



9-2-1.



9-2-2.



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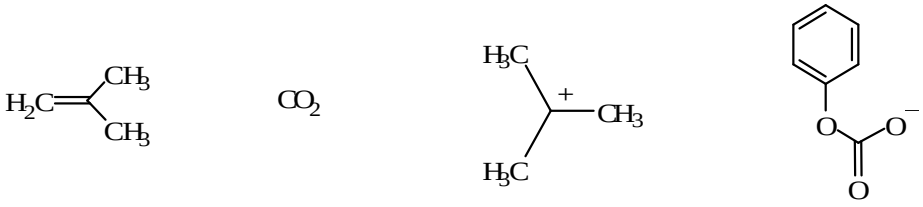
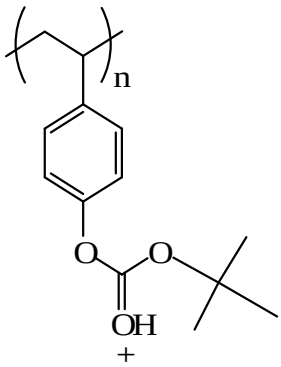


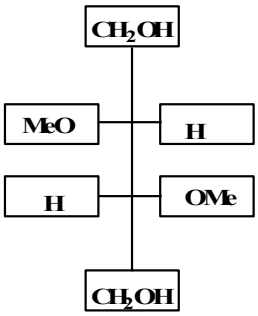
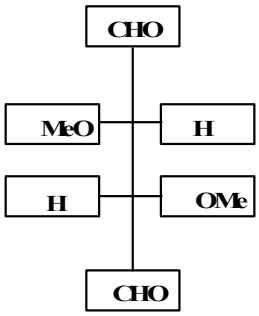
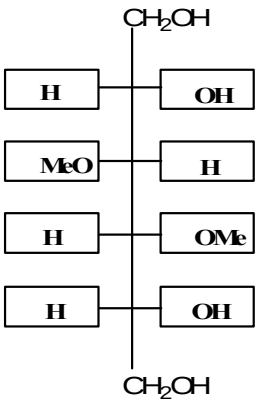
B **C** **D** **E**

9-3-2.



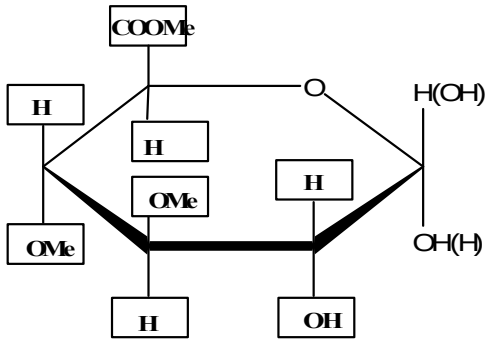
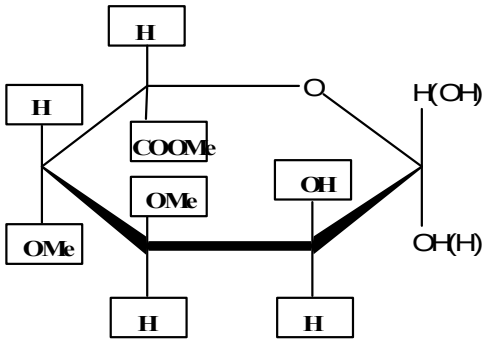
F

10-1.

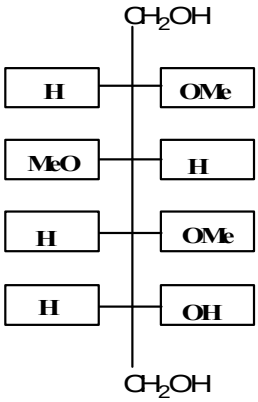
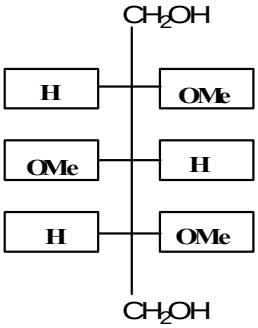
N	M	L
		

10-2

Number of possible structures	2

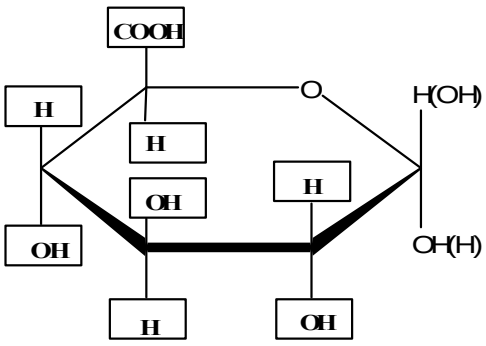
1	2
	
3	**4**

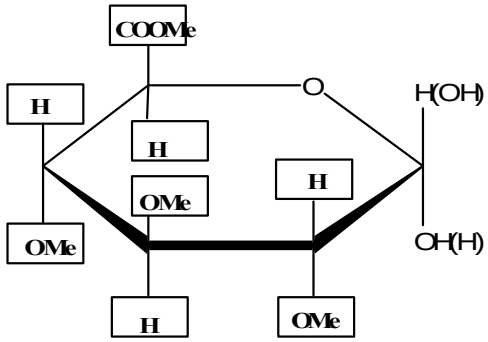
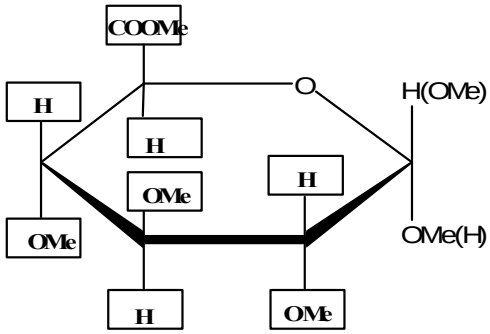
10-3.

G	I
	

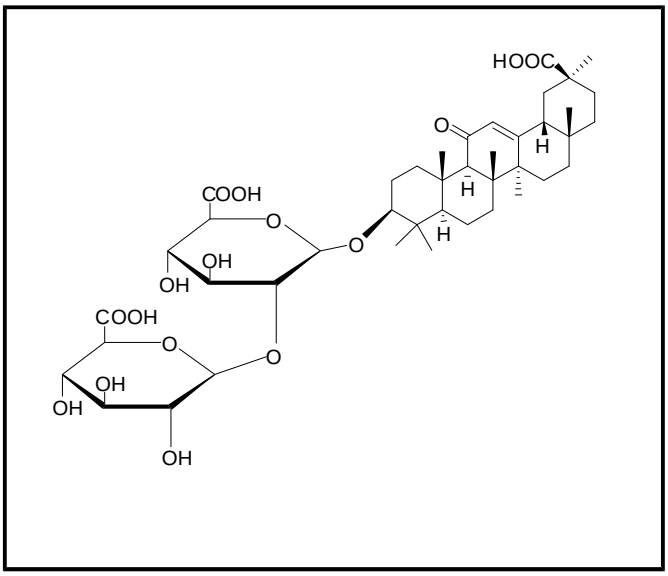
10-4. Number of the correct structure for **C** from 10-2: 1

10-5.

B	
	

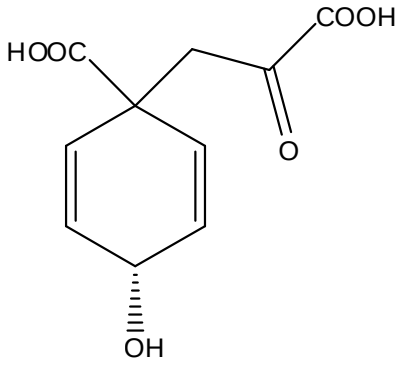
D	J
	

10-6.



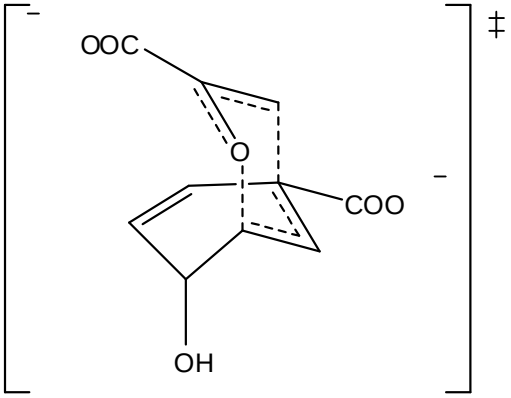
11-1. 3

11-2.



11-3. a, c, d

11-4.



Transition State

11-5.

For the enzyme-catalyzed reaction, Arrehnius equation could be applied.

k_{cat}/k_{uncat} = A exp ($-E_{a,\,cat}$ / RT) / A exp ($-E_{a,\,uncat}$ / RT)

= exp [$-\Delta E_{a,\,cat\text{-}uncat}$ / RT]

= exp [$-\Delta E_{a,\,cat\text{-}uncat}$ (J/mol) / (2,480 J/mol)] = 10^6

Therefore, $-\Delta E_{a,\,cat\text{-}uncat}$ = 34,300 J/mol

$k_{uncat,\,T}/k_{uncat,\,298}$ = exp ($-\Delta H^{\neq}_{uncat}$ / RT) / exp ($-\Delta H^{\neq}_{uncat}$ / 298R)

= exp [($-\Delta H^{\neq}_{uncat}$ /R)(1/T-1/298)]

ln($k_{uncat,\,T}/k_{uncat,\,298}$) = 13.8 = [(-86900/8.32)(1/T-1/298)]

Therefore, T = 491 K, or 218°C

Chemistry for Life,
Chemistry for better Life

Practical Test

2006. 7. 5
Gyeongsan, Korea

General Directions

- **You have 5 hours to finish the test. Manage your time wisely. You might spend about one hour for Test 1 (10 points), two hours for Test 2 (15 points), and two hours for Test 3 (15 points).**
- **Write your name and code number on each page of the Answer Sheet.**
- **There are 7 pages of Test and 7 pages of Answer Sheet.**
- **Write answers and calculations within the designated box.**
- **Use only the pen, ruler, and calculator provided**
- **An English-language version is available.**
- **Figures to supplement User's Instructions for the spectrophotometer, C-18 cartridge, and pipet filler are provided in a separate sheet.**
- **Additional samples or supplies will be provided with 1 pt penalty for each item. (except distilled water)**
- **You may go to the restroom with permission.**
- **After finishing the test, place all sheets (Test and Answer Sheets) in the envelope and seal.**
- **Remain seated until instructed to leave the room.**
- **You may take the pencil case, pen, ruler, calculator, and C-18 cartridges home.**

Safety and Disposal

- **Wear safety goggles and lab coat.**
- **No hazardous chemicals are used. All acid, alkali, and dye solutions are dilute. However, it is better to minimize contact with skin. Wipe off with wet Kimwipe in case of contact.**
- **Do not sniff reagents.**
- **Dispose used chemicals in the plastic bottle labeled "DISPOSABLE". Discard used test tubes and broken glasses in the "Waste Basket".**

Apparatus, Chemicals and Supplies

Test-1,2 (white basket)

spectrophotometer		1
cuvet (1 cm path-length)		1
C18 cartridge		4
10 mL syringe		1
1 mL syringe		1
pasteur pipet		3
1 mL pipet		1
5 mL pipet		1
pipet filler		1
10 mL volumetric flask		2
buret		1
test tube		20
test tube rack		1
50 mL Erlenmeyer flask		1
100 mL beaker		2
silicone bulb		2
three-color pen, ruler		1
sqeeze bottle		3
labeled as	Solution E	33% ethanol in water
	NaOH solution	less than 5 mM
	water	distilled water
100 mL bottle		6
labeled as	Solution R	red dye in Solution E
	Solution B	blue dye in Solution E
	Solution MD	mixed dye of B and R
	Solution MA	mixed acids; acetic acid & salcylic acid in water
	KHP	potassium hydrogen phthalate solution
	phenolphthalein	0.05% solution

Test-3 (black basket)

test tube		95
test tube rack		1
spatula		2
1.5 mL graduated pipet (polyethylene)		15
tweezers		1
pen (for writing on a test tube)		1
pH test paper		1
100 mL bottle		3
labeled as	95% EtOH	95% ethanol
	CH_3CN	acetonitrile
	water	distilled water
30 mL dropping bottle		6
labeled as	1M HCl	1M HCl solution
	1M NaOH	1M NaOH solution
	2,4-DNPH	3% 2,4-dinitrophenylhydrazine solution
	CAN	20% ceric ammonium nitrate solution
	0.5% $KMnO_4$	0.5% $KMnO_4$ solution
	2.5% $FeCl_3$	2.5% $FeCl_3$ solution
10 mL vial		7
labeled as	Set□ U-1	
	Set□ U-2	
	Set□ U-3	
	Set□ U-4	
	Set□ U-5	
	Set□ U-6	
	Set□ U-7	

How to Use the Spectrophotometer

The spectrophotometer has three compartments, the light source, the detector, and the cuvet holder. You will find the cover of the cuvet holder open. Leave it open. A cuvet is placed with the label facing the light source (Fig. A). Use this orientation throughout the experiment. The spectrophotometer has been stabilized and is ready for use. Follow the procedure below to take absorbance readings.

a) Fill the cuvet about 3/4-full with Solution E and insert into the cuvet holder. Do not close the cover of the cuvet holder.

b) Using the mouse of the computer, move the cursor to REFERENCE and click three times. Then click MEASURE three times and you will get absorbance readings close to zero at ten wavelengths between 470 and 650 nm at 20 nm intervals (Fig. B).

c) Fill the cuvet with sample solution and click MEASURE three times. You will get absorbance readings for your sample at the same wavelengths. Record absorbance values in the Table in the Answer Sheet.

How to Use the C18 Cartridge

a) The cartridge has an inlet and an outlet (Fig. C). The inlet has a larger diameter.

b) To wash or elute, first withdraw the liquid with a proper syringe and connect the syringe to the inlet of the cartridge. Then push the liquid slowly with a plunger into the cartridge. (Fig. C & E)

c) To load the sample, attach the 10 mL syringe to the inlet of the cartridge. Using a 1 mL pipet, transfer 1.00 mL aliquot of a sample solution to the syringe (Fig. D). Load the sample onto the cartridge using the plunger. Make sure that no amount of sample remains on the syringe. Try to avoid air entering into the cartridge after sample loading.

d) The cartridge can be reused after washing with Solution E.

e) Separate the syringe from the cartridge when removing the plunger from the syringe.

How to Use the Pipet Filler

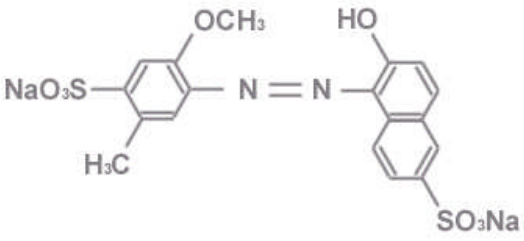
Move the dial downward to fill the pipet and upward to release the liquid (see Fig. F).

Practical Test 1

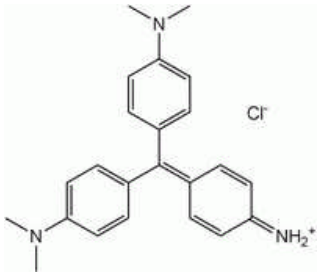
Reverse-phase Chromatography:

Spectrophotometric Analysis

Chromatographic separation followed by spectrophotometric analysis is one of the most widely practiced analytical techniques in chemical laboratories around the world. For example, organic compounds in a complex mixture are often analyzed by reverse-phase liquid chromatography with spectrophotometric detection. In reverse-phase chromatography, hydrophobic interactions between the stationary phase material (usually octadecyl group) and the nonpolar moiety of the analyte is utilized. The chromatogram can be simplified and the compound of interest selectively determined by proper choice of the detector wavelength. In this part of the Practical Test, spectrophotometric analysis of dyes, with and without separation, will be performed.



Food Red No. 40



Methyl Violet 2B

1-1. Spectrophotometric Analysis of R and B in a Mixed Solution

a) Measure absorbance of both Solutions R (3.02×10^{-5} M) and B (1.25×10^{-5} M) (Fig. A & B). Fill in the Table in the Answer Sheet with your measurements. Draw absorption spectra for the red dye in red ink and for the blue dye in blue ink (Fig. 1-1).

b) Repeat absorbance measurements for Solution MD. Solution MD is a mixture of Solution R and B in a certain ratio. Add the spectrum in black ink to Fig. 1-1.

c) Based on the Beer-Lambert law, determine the molar concentration of both dyes in Solution MD using the data in the Table. Do not determine the fraction of one dye by subtracting the fraction of another dye from 1.

1-2. Chromatographic Separation Followed by Spectrophotometric Analysis

a) Elute the cartridge with about 10 mL of Solution E using 10 mL syringe (Fig. C).

b) Load 1.00 mL of solution MD onto the cartridge (Fig. D).

c) Using 1 mL syringe, elute with Solution E (Fig. E). Collect the solution eluting through the outlet in a 10 mL volumetric flask. Repeat until the red compound is completely eluted and collected.

d) Fill the flask to the 10 mL mark with Solution E and mix. Call this Solution F.

e) Obtain the absorption spectrum of solution F as in Experiment 1-1. Dilution takes place during elution. Therefore, multiply the measured absorbance by 10 when drawing the spectrum for Solution F. Draw spectrum with broken line in Fig. 1-1 in red ink.

f) Dilute Solution R as necessary and construct a calibration curve, at a wavelength of your choice, for analysis of the red dye (R) in Solution F. Draw a calibration curve in the answer sheet (X-axis, concentration; Y-axis, absorbance, Fig. 1-2). Indicate the wavelength used. The calibration curve must have three points in addition to the origin. Mark the position of Solution F on the calibration curve.

g) Report the concentration of R in the original Solution MD.

h) Compare this concentration with the value you obtained in Experiment 1-1 and report the recovery (amount eluted/amount loaded) associated with chromatography.

Practical Test 2

Reverse-phase Chromatography:

Acid-Base Titration of Acetic Acid and Salicylic Acid

Acetic acid (AA) and salicylic acid (SA) are slightly different in polarity and thus can be separated on a reverse-phase cartridge using distilled water as eluent. AA is eluted first. The total amount of AA and SA in a mixed solution will be determined by titration. Then, AA and SA will be separately determined following chromatographic separation.

2-1. Determination of the Total Amount of AA and SA in a Mixed Acid (MA) Solution

a) Titrate 10 mL of distilled water with the NaOH (< 5 mM) solution provided. Report blank acidity in 1 mL of distilled water in terms of the volume of the NaOH solution. Take this blank acidity into account for all solutions in subsequent data analyses. Show corrections in the calculation part in the answer sheet.

b) Standardize NaOH solution with 2.00 mL of the standard KHP (potassium hydrogen phthalate) solution (1.00×10^{-2} M) provided. Repeat and report the concentration of the NaOH solution. Show how you accounted for the blank acidity.

c) Withdraw 1.00 mL of Solution MA and determine the total acidity. Repeat and report the total number of moles of AA and SA combined in 1.00 mL of Solution MA.

2-2. Reverse-phase Separation and Titration

a) Elute a new C-18 cartridge with about 10 mL of distilled water using 10 mL syringe.

b) Load 1.00 mL of Solution MA onto the cartridge. Collect the liquid eluting at the outlet in tube 1 (Fraction 1).

c) Elute with 1 mL of distilled water. Collect the eluent in a test tube (Fraction 2). Repeat until Fraction 20 is collected. You will have 20 test tubes with about 1 mL liquid in each tube.

d) Titrate acidity in each test tube. Report volume of the NaOH solution consumed and the amount of acid(s) in each test tube. Make a graph in the answer sheet (Fig. 2-2) showing the amount of acid(s) in each test tube.

e) Blank acidity and the background (due to leaching out of residual materials from the column) must be subtracted. In determining the amount of eluted AA, disregard tubes containing only trace amounts of acids. Tube 2 and 3 contain most AA. Calculate the total amount of AA eluted by adding the amount of AA in tubes. Similarly calculate the total amount of SA eluted. Indicate, in Fig. 2-2, which fractions you used to get the amount of each acid.

f) Calculate the mole percent of AA in solution MA.

Practical Test 3

Qualitative Analysis of Organic Compounds

In this experiment your task is to identify seven solid unknowns from the list of compounds on page 7 that are common drugs in everyday life and valuable agents in organic chemistry. To achieve this, perform chemical tests on unknowns according to the following procedures and analyze your results.

- Unknowns Labeled

Set□ U-1, Set□ U-2, Set□ U-3, Set□ U-4, Set□ U-5, Set□ U-6, Set□ U-7

Procedure

Helpful Comments

a) The weight of a spatula tip-full of a solid is about 15~20 mg.

b) Wipe spatula cleanly with Kimwipe between uses.

c) After adding any reagent described below to a solution of an unknown sample, mix the contents thoroughly and observe the resulting mixture carefully.

d) To get full marks, you should perform all the tests and fill out the table.

Test 1: Solubility test

To a test tube, add a spatula tip-full (15~20 mg) of an unknown sample and 1 mL of CH_3CN. Shake the test tube and report the solubility. Repeat the test with 1M HCl, water, and 1M NaOH.

Test 2: 2,4-DNPH test

Place about 15~20 mg of an unknown sample in a test tube and dissolve with 2 mL of 95% EtOH (For the water soluble unknowns, dissolve about 15~20 mg of an unknown in 1 mL of water). Add five drops of the 2,4-dinitrophenylhydrazine solution in concentrated sulfuric acid and 95% ethanol (labeled as 2,4-DNPH).

Test 3: CAN test

Mix 3 mL of the cerium(IV) ammonium nitrate solution in dilute HNO_3 (labeled as CAN) with 3 mL of CH_3CN in a test tube. In another test tube add about 15~20 mg of an unknown sample in 1 mL of the mixed solution. (For the water soluble unknown samples, dissolve about 15~20 mg of an unknown sample in 1 mL of water first, and then add 1 mL of CAN.) If there is a color change in the solution, the solution may contain alcohol, phenol or aldehyde.

Test 4: Baeyer test

In a test tube, dissolve about 15~20 mg of an unknown sample in 2 mL of CH_3CN (For the water soluble unknown samples, dissolve about 15~20 mg of an unknown in 1 mL of water). To the solution, slowly add five drops of the 0.5% $KMnO_4$ solution, drop by drop while shaking.

Test 5: pH test

In a test tube, dissolve about 15~20 mg of an unknown sample in 2 mL of 95% EtOH (For the water soluble unknown samples, dissolve about 15~20 mg of an unknown sample in 1 mL of water). Measure the pH of the solution with pH paper.

Test 6: Iron(III) chloride test

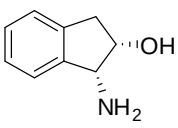
Take the solution from Test 5 and add five drops of a 2.5% $FeCl_3$ solution.

Results

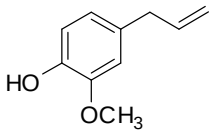
1. Record your test results in the answer sheet. Write *O* if soluble and *X* if insoluble for the solubility tests. Write (+) for the positive reactions and (–) for the negative reactions for tests 2 ~ 4 and 6. Write *a*, *b* and *n* for acidic, basic or neutral, respectively, for pH test 5.

2. Based on your test results, identify the most plausible structures for the unknown compounds from the provided list of compounds. Write the compound initial in appropriate box.

Possible Unknown Compounds



(A)



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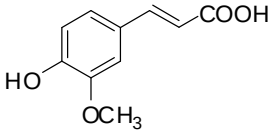
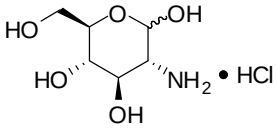
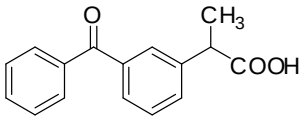


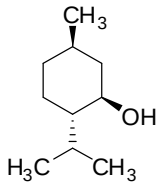
(F)



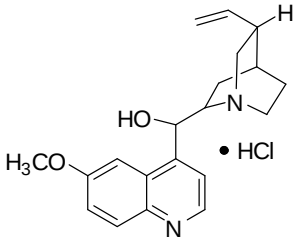
(G)



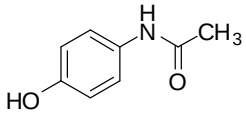
(K)



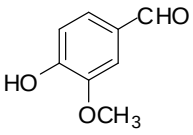
(M)



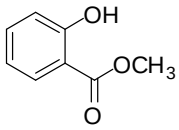
(Q)



(T)



(V)



(W)

About the history of the International Chemistry-Olympiads

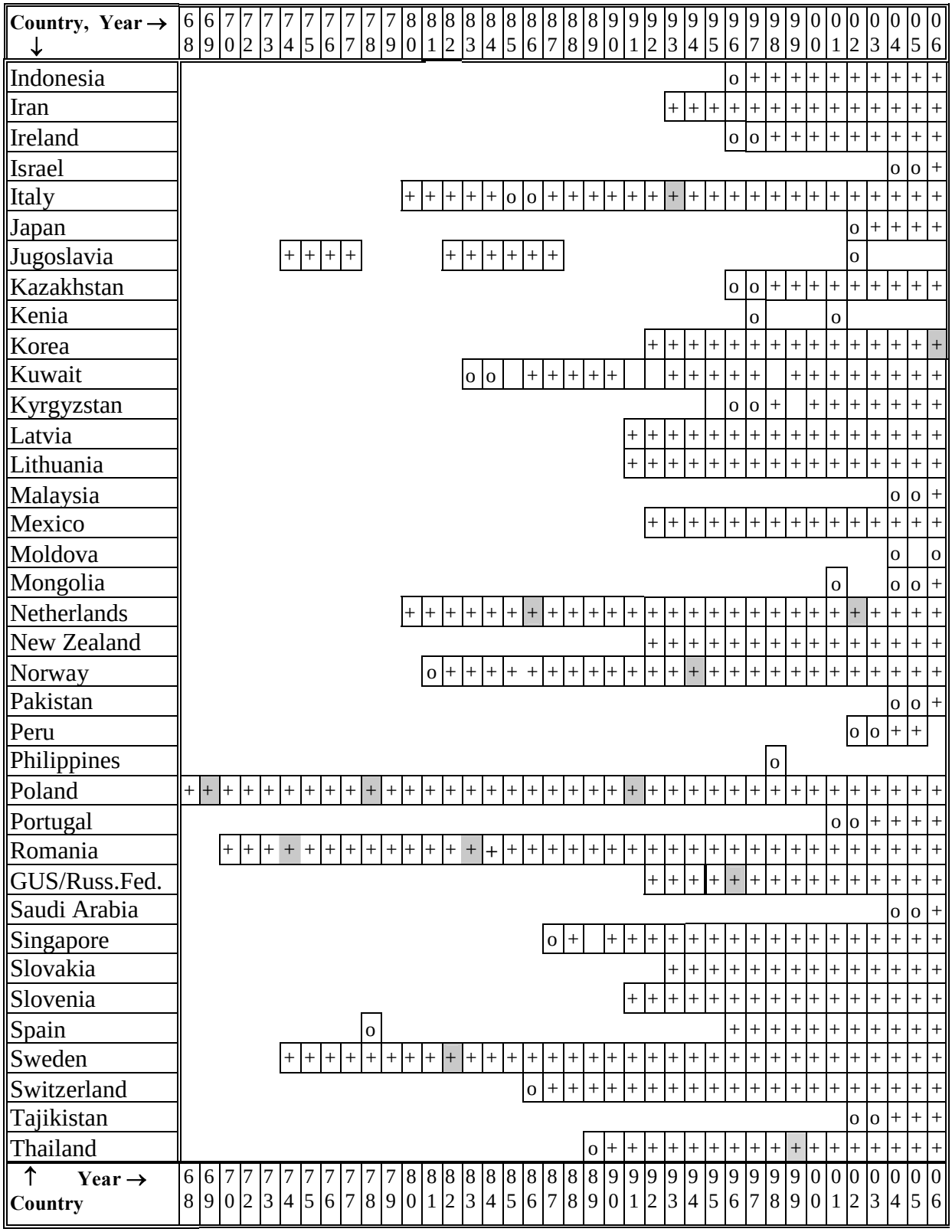
The idea of chemistry olympiads was born 1968 during an Czechoslovakian national olympiad that was attended by observers from Poland and Hungary. These three countries participated in the first IChO 1968 in Prague. The participating countries of the following years are shown in the table.

Participating Delegations

(in the alphabetical order of the German names)

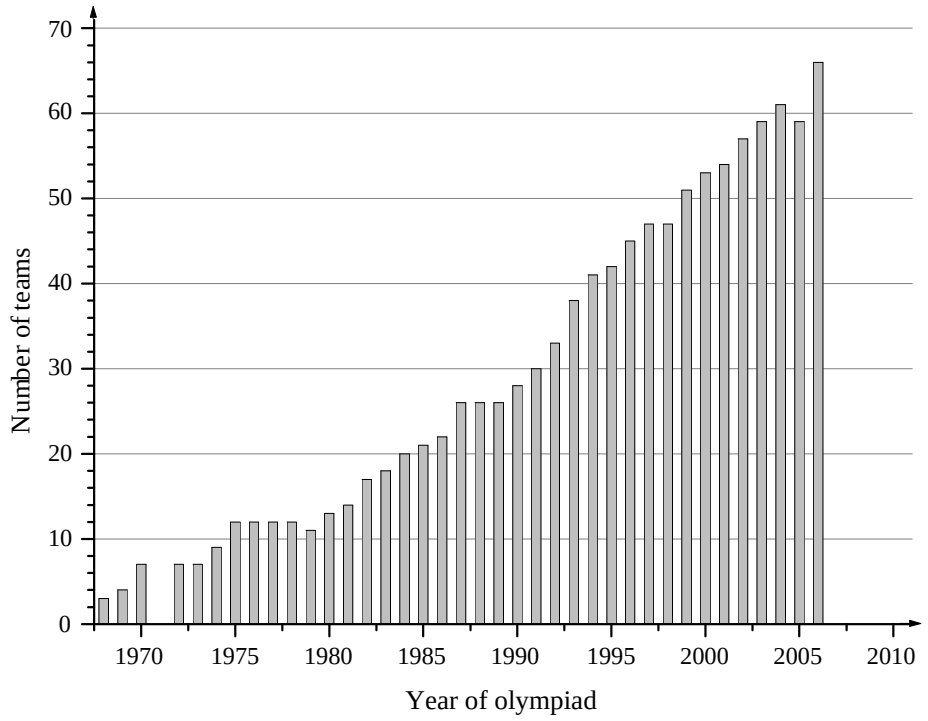
(+ = host, + = participant, o = observer)

Country, Year → ↓	68	69	70	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	00	01	02	03	04	05	06
Argentina																											+	+	+	+	+	+	+	+	+	+	+	+	+
Armenia																																				o	o	+
Australien																			o	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Austria							+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Azerbaijan																													o	o		+	+	+	+	+	+	+
Belarus																												+	+	+	+	+	+	+	+	+	+	+
Belgium							+	+	+			+				+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Brasil																													o	o	+	+	+	+	+	+	+	+
Bulgaria		+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Canada																o	o	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
China																			+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+		+
Chinese Taipei																								+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Croatia																														o	o	+	+	+	+	+	+	+
Cuba																	+	o	+	+	+	+		+	+	+	+	+		+		+	+	+	+	+	+
Cyprus																					o	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Czech Rep.																								+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Czechoslovakia	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+														
Denmark														+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
DDR		o	+	+	+	+	+	+	+	+	+	+	+	+	+		+	+	+	+	+	+																
Egypt																																o	o	+	+	+	+	+
Estonia																											+	+	+	+	+	+	+	+	+	+	+	+
Finland									o	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
France											o	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Germany							o	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Greece																+	+	+	+		+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Hungary	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Iceland																																o	o	+	+	+	+	+
India																													o	o	+	+	+	+	+	+	+	+
↑ Year → Country	68	69	70	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	00	01	02	03	04	05	06


Country, Year →
↓
68 69 70 72 73 74 75 76 77 78 79 80 81 82 83 84 85 86 87 88 89 90 91 92 93 94 95 96 97 98 99 00 01 02 03 04 05 06
Indonesia
Iran
Ireland
Israel
Italy
Japan
Jugoslavia
Kazakhstan
Kenia
Korea
Kuwait
Kyrgyzstan
Latvia
Lithuania
Malaysia
Mexico
Moldova
Mongolia
Netherlands
New Zealand
Norway
Pakistan
Peru
Philippines
Poland
Portugal
Romania
GUS/Russ.Fed.
Saudi Arabia
Singapore
Slovakia
Slovenia
Spain
Sweden
Switzerland
Tajikistan
Thailand
↑ Year →
Country

Country, Year → ↓	68	69	70	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	00	01	02	03	04	05	06
Turkey									o	+															o	+	+	+	+	+	+	+	+	+	+	+	+	+
Turkmenistan																															o	o	o	+	+	+		+
UdSSR			+	+	+	+	+	+	+	+	+		+	+	+	+	+	+	+	+	+		+															
Ukraine																										+	+	+	+	+	+	+	+	+	+	+	+	+
United Kingdom												o		o	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
United States													o		o	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Uruguay																													o	o	+	+	+	+	+	+	+	+
Venezuela														o		o									+	+	+	+	+	+	+	+	+	+	+	+	+	+
Vietnam																												+	+	+	+	+	+	+	+	+	+	+
↑ Year → Country	68	69	70	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	00	01	02	03	04	05	06
Number of teams	3	4	7	7	7	9	12	12	12	12	11	13	14	17	18	20	21	22	26	26	26	28	30	33	38	41	42	45	47	47	51	53	54	57	59	61	59	66

Number of teams attending the IChO



Inofficial ranking since 1974

(set up by adding the points of the teams, up to position 50)

	1974	1975	1976	1977	1978	1979	1980	1981	1982	1983	1984	1985	1986	1987	1988
IChO held in	**RO**	**H**	**DDR**	**CS**	**PL**	**SU**	**A**	**BG**	**S**	**RO**	**D**	**CS**	**NL**	**H**	**FIN**
1	SU	SU	DDR	CS	SU	PL	PL	H	CS	RO	D	SU	NL	SU	RC
.	RO	H	SU	SU	PL	SU	D	CS	D	SU	CS	CS	PL	RC	D
.	CS	PL	H	H	D	RO	DDR	PL	PL	D	SU	D	D	RO	USA
.	H	BG	PL	PL	DDR	CS	H	BG	NL	CS	H	A	SU	CS	PL
5	PL	RO	A	S	CS	A	A	A	A	H	A	NL	A	D	GB
.	DDR	DDR	RO	A	H	S	RO	D	SU	A	GB	H	USA	F	DDR
.	BG	S	BG	D	A	H	BG	DDR	H	F	PL	DDR	H	GB	N
.	YU	CS	CS	DDR	RO	D	CS	RO	BG	DDR	USA	PL	BG	PL	RO
.	S	A	S	RO	S	BG	S	SU	DDR	PL	RO	USA	F	H	H
10	D*	D	D	BG	BG	FIN	FIN	NL	S	NL	DK	F	RO	DDR	SU
.		YU	YU	YU	TR	DDR	NL	FIN	F	BG	S	GB	CS	NL	I
.		B	B	B	FIN		I	S	FIN	GB	NL	RO	GB	USA	NL
.							B	F	N	N	FIN	BG	S	BG	BG
.								I	RO	DK	F	N	DDR	A	CS
15			* hors concours						DK	FIN	BG	S	CDN	S	AUS
.									YU	S	N	FIN	N	FIN	SGP
.									I	I	I	YU	DK	N	F
.										YU	GR	B	B	DK	A
.											YU	GR	FIN	I	FIN
20											B	DK	GR	GR	CDN
.												C	KWT	C	DK
.													YU	B	C
.														YU	S
.														CDN	B
25														CH	CH
.														KWT	KWT

(List of abbreviations see page 141)

	1989	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000
IChO held in	**DDR**	**F**	**PL**	**USA**	**I**	**N**	**RC**	**RUS**	**CDN**	**AUS**	**T**	**DK**
1	DDR	RC	RC	RC	RC	RC	RC	IR	H	SGP	USA	RC
.	D	PL	RO	H	TPE	GB	IR	RC	D	USA	ROK	RUS
.	RC	D	H	PL	USA	USA	RO	RUS	TR	ROK	RC	USA
.	BG	USA	PL	USA	I	A	A	A	TPE	RC	IR	H
5	SU	CS	NL	A	GUS	SGP	D	D	IR	H	RO	TPE
.	H	RO	USA	GUS	H	ROK	GB	USA	RUS	RA	H	A
.	PL	F	I	D	D	TPE	SK	UA	ROK	RUS	TPE	SK
.	RO	A	D	RO	CDN	CZ	TPE	CZ	RC	AUS	UA	BY
.	CS	DDR	N	F	SGP	GUS	I	H	SGP	D	PL	VN
10	I	H	GB	I	CZ	IR	CZ	RO	PL	GB	AUS	TR
.	NL	GB	CS	SGP	A	D	RUS	GB	USA	PL	VN	SGP
.	GB	I	SU	CS	RO	H	H	TPE	UA	A	D	D
.	A	AUS	A	AUS	P	RO	AUS	BY	AUS	RO	RA	ROK
.	USA	SGP	AUS	NL	NZ	DK	SGP	SGP	CDN	TPE	BY	IR
15	S	NL	DK	DK	ROK	I	F	RA	RO	SK	T	CZ
.	F	N	SGP	ROK	LV	T	TR	TR	A	NL	F	FIN
.	N	DK	CDN	GB	IR	NZ	PL	F	T	IR	TR	T
.	AUS	T	BG	CH	DK	UA	USA	I	EST	UA	SGP	MEX
.	CDN	FIN	F	T	AUS	AUS	DK	AUS	CZ	VN	IND	GB
20	DK	CDN	S	LV	NL	F	RA	ROK	VN	LT	GB	AUS
.	FIN	BG	T	NZ	LT	PL	ROK	EST	F	TR	RUS	IND
.	B	C	CH	S	SK	NL	UA	CDN	S	BY	MEX	CDN
.	C	S	LV	LT	F	SK	LT	T	BY	F	A	RA
.	GR	CH	LT	N	C	CDN	T	VN	NZ	I	IRL	UA
25	CH	B	FIN	CDN	GB	LT	NL	SK	LV	T	NZ	PL
.	KWT	GR	C	SLO	T	S	CH	CH	RA	FIN	I	NZ
.		KWT	GR	BG	BG	N	BG	NL	SLO	CZ	CDN	BG
.		CY	B	TPE	B	BG	S	NZ	GB	CDN	LT	F
.			CY	B	S	FIN	NZ	DK	SK	S	NL	DK
30			SLO	FIN	FIN	EST	EST	PL	LT	BG	SK	NL
.				GR	SLO	LV	CDN	SLO	I	N	BG	B
.				CY	GR	CH	MEX	MEX	DK	MEX	KZ	RO
.				MEX	MEX	MEX	N	LV	NL	CH	DK	KZ
.					N	SLO	SLO	N	IRL	SLO	CH	LT
35					CH	B	LV	CY	N	EST	CZ	CH
.					YV	CY	CY	BG	MEX	CY	FIN	SLO
.					CY	GR	B	S	CH	LV	B	EST
.					KWT	TR	GR	LT	CY	DK	S	S
.						YV	FIN	E	E	NZ	CY	YV
40						C	YV	B	FIN	GR	EST	CY
.						KWT	KWT	GR	BG	KZ	LV	HR
.							C	FIN	YV	E	SLO	I
.								YV	GR	IRL	YV	RI
.								C	B	B	BR	N
45								KWT	RI	KS	E	AZ
.									KWT	YV	N	IRL
.									C	RI	RI	E
.											GR	LV
.											ROU	GR
50											C	BR

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	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012
IChO held in	**IND**	**NL**	**GR**	**D**	**TPE**	**ROK**	**RUS**	**H**	**GB**	**J**		
1	RC	RC	RC	RC	ROK	RC						
.	ROK	T	IR	ROK	VN	TPE						
.	USA	TPE	ROK	RUS	IR	ROK						
.	RUS	ROK	T	UA	RUS	RUS						
5	IR	A	BY	D	AZ	VN						
.	TR	UA	RUS	PL	TPE	T						
.	IND	USA	IND	TPE	T	J						
.	AUS	PL	SGP	H	RA	Pl						
.	TPE	IND	D	TR	D	IND						
10	T	D	TPE	VN	IND	D						
.	SGP	IR	UA	IND	A	SK						
.	PL	H	PL	IR	CZ	DK						
.	RO	RUS	CDN	RO	UA	SGP						
.	F	CDN	CZ	LT	PL	BR						
15	SK	TR	RO	CZ	AUS	CDN						
.	H	AUS	KZ	USA	TR	AZ						
.	VN	GB	VN	SGP	H	UA						
.	CZ	SGP	EST	CDN	SK	USA						
.	RA	E	GB	AZ	USA	H						
20	BY	SK	AUS	AUS	GB	CZ						
.	C	BY	H	KZ	RO	AUS						
.	D	VN	SK	GB	BY	IRL						
.	GB	FIN	USA	J	SGP	F						
.	UA	F	YV	A	J	IR						
25	A	LT	IND	BY	RI	A						
.	MEX	CZ	F	SK	LV	TR						
.	DK	KZ	A	T	BG	RI						
.	CDN	LV	I	RA	HR	GB						
.	EST	NL	TR	EST	MEX	RO						
30	RI	RO	AZ	F	KZ	NL						
.	HR	RA	MEX	NZ	LT	HR						
.	I	EST	LT	SLO	F	LT						
.	N	HR	NL	HR	EST	KZ						
.	BG	BG	FIN	LV	CDN	SLO						
35	CY	NZ	HR	NL	I	EST						
.	KZ	I	J	I	DK	RA						
.	B	DK	DK	CH	SLO	BR						
.	LT	SLO	RA	FIN	FIN	TJ						
.	NZ	N	GR	RI	NL	LV						
40	CH	YV	LT	S	IRL	MAL						
.	E	MEX	E	BG	GR	S						
.	FIN	BR	TM	KS	NZ	IRL						
.	SLO	S	BR	E	KS	IL						
.	NL	RI	BG	GR	S	FIN						
45	LV	TM	CH	BR	B	IS						
.	BR	B	NZ	TM	BR	I						
.	S	IRL	IS	CY	CH	CY						
.	YV	CH	IRL	YVA	P	N						
.	IRL	C	CY	IRL	IS	TM						
50	GR	CY	KS	IS	N	CH						

(List of abbreviations see page 141)

List of abbreviations

A	Austria
AUS	Australia
AZ	Azerbaijan
B	Belgium
BG	Bulgaria
BR	Brazil
BY	Belarus
C	Cuba
CDN	Canada
CH	Switzerland
CS	Czechoslovacia
CY	Cyprus Republic
CZ	Czech Republic
D	Germany
DDR	German Democratic Republic
DK	Denmark
E	Spain
EAK	Kenya
EST	Estonia
ET	Egypt
F	France
FIN	Finland
GB	United Kingdom
GR	Greece
GUS	Commonwealth of Independent States
H	Hungary
HR	Croatia
I	Italy
IL	Israel
IND	India
IR	Iran
IRL	Ireland
IS	Iceland
J	Japan
KS	Kyrgistan
KWT	Kuwait
KZ	Kasakhstan
LV	Latvia
LT	Lithuania
MAL	Malaysia
MEX	Mexico
MGL	Mongolei
N	Norway
NL	Netherlands
NZ	New Zealand
P	Portugal
PE	Peru
PL	Polen
RA	Argentina
RI	Indonesia
RC	China
RO	Romania
ROK	South Korea
ROU	Uruguay
RUS	Russian Federation
S	Sweden
SGP	Singapore
SK	Slovakia
SLO	Slowenia
SU	Sowjet Union
T	Thailand
TJ	Tadschikistan
TM	Turkmenistan
TPE	Chinese Taipei
TR	Turkey
UA	Ukraine
USA	United States of America
VN	Vietnam
WAN	Nigeria
YU	Yugoslavia
YV	Venezuela