National German competition and IChO

Volume 12
National German competition and IChO

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

Acknowledgements

It is a great pleasure to thank the many people whose help and suggestions were so valuable in preparing and reviewing all the problems and in helping us to perform the third and the fourth round.

Michael Hell, PD Dr. Sabine Nick, Alexander Rodenberg, Prof. Dr. Carsten Schmuck, Dr. Jörg Wagler, made essential contributions to develop the problems. Uwe Amthor, Henry Bittig, Nicole Fernandez-Biber, PD Dr. Sabine Nick, Alexander Rodenberg, were very important leading the chemistry camps.

I thank Dr. Angela Koch who reviewed my English translations.

Wolfgang Hampe
Contents

Part 1: The problems of the four rounds

Contact addresses ................................................................. 4
First round (problems solved at home) ................................. 6
Second round (problems solved at home) .............................. 9
Third round, test 1 (time 5 hours) ............................................ 17
Third round, test 2 (time 5 hours) .......................................... 24
Fourth round, theoretical test (time 5 hours) .......................... 32
Fourth round, practical test (time 5 hours) .............................. 42

Part 2: The solutions to the problems of the four rounds

First round ............................................................................. 46
Second round ........................................................................ 51
Third round, test 1 ............................................................... 64
Third round, test 2 ............................................................... 72
Fourth round, theoretical test ............................................... 81

Part 3: IChO

Problems .............................................................................. 98
Solutions to the theoretical problems ..................................... 115
Practical problems ............................................................... 125

Part 4: Appendix

Tables on the history of the IChO ......................................... 135
Contact addresses:

IPN, University of Kiel, z.H. Dr. Wolfgang Bünder  
Olshausenstraße 62  
D-24098 Kiel/Germany  
tel: +431-880-5013 (3168)  
fax: +431-880-5468  
email: buender@ipn.uni-kiel.de

Wolfgang Hampe  
Habichtweg 11  
D-24147 Klausdorf/Germany  
tel: +431-79433  
email: Hampe@t-online.de

Association to promote the IChO  
(Association of former participants and friends of the IChO)  
Christoph Jacob  
Erlenweg 4  
D-61138 Niederdorfelden/Germany  
tel. +6101-33100  
email: chjacob@web.de  
Internet address: www.fcho.de
Part 1

The problem set of the four rounds
Problems Round 1

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):

<table>
<thead>
<tr>
<th>sample</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>V(NaOH) in mL</td>
<td>20.15</td>
<td>19.65</td>
<td>21.30</td>
<td>20.40</td>
<td>20.35</td>
</tr>
</tbody>
</table>

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 Al₂O₃ 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 Al₂O₃) 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 approximately valid for 970 °C. They shall be used for the calculations in e).

<table>
<thead>
<tr>
<th></th>
<th>Al(l)</th>
<th>O_{2(g)}</th>
<th>Al_{2}O_{3(s)}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Δ_H in kJ/mol at 970 °C</td>
<td>48</td>
<td>38</td>
<td>-1610</td>
</tr>
<tr>
<td>S in J/(K·mol) at 970 °C</td>
<td>78</td>
<td>238</td>
<td>98</td>
</tr>
</tbody>
</table>

Using the free enthalpies of the process \(2 \text{Al}_{2}\text{O}_3 \rightarrow 4 \text{Al} + 3 \text{O}_2\) 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:

\[4 \text{Al} + 3 \text{O}_2 \rightleftharpoons 2 \text{Al}_2\text{O}_3 \quad \Delta G_1 = (-3351.4 + 0.6264 \cdot T/\text{K}) \text{kJmol}^{-1} \quad (T > 933 \text{ K})\]
\[2 \text{C} + \text{O}_2 \rightleftharpoons 2 \text{CO} \quad \Delta G_2 = (-221.06 - 0.17872 \cdot T/\text{K}) \text{kJmol}^{-1}\]
\[\text{C} + \text{O}_2 \rightleftharpoons \text{CO}_2 \quad \Delta G_3 = (-393.51 - 0.00286 \cdot T/\text{K}) \text{kJmol}^{-1}\]

g) **Calculate the minimum temperature above which the reduction of Al_{2}O_{3} by carbon is theoretically possible.** (Actually it is not possible because of the formation of Al_{4}C_{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 individual steps of the synthesis.

Problem 1-5 Aromatic Heterocyclic Compounds

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

\[ \text{Oxazole} \]

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.

\[ \text{Pyrrole} \]

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 ($E^\circ(\text{Cr}^{3+}|\text{Cr}_2\text{O}_7^{2-}) = +1.380$ 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 ($c(\text{Cr}^{3+}) = c(\text{Cr}_2\text{O}_7^{2-}) = 1$ mol/L) is able to release elemental iodine from a neutral solution which contains iodide ($E(\text{I}^-|\text{I}_2) = E^\circ(\text{I}^-|\text{I}_2) = +0.54$ 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 ($E^\circ(\text{Br}^-|\text{Br}_2) = +1.065$ V) the reaction of chromium(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 $E^\circ(\text{Br}^-|\text{Br}_2)$. Show your calculations.

   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.

   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 $\mu$ - especially for centres of metals of the first transition series - by $\mu = \sqrt{n(n+2)}$ ($n =$ 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 $\chi$ depending on temperature:

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

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

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

g) Determine the Curie constant $C$ of this complex.

The relative magnetic moment in terms of the Bohr magneton is

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

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

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

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

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 is 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)₂O₄ (M, M’ = metal cations), which owe their name to the so called "spinel" MgAl₂O₄.

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](image)

In spinels M²⁺ 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 CoAl₂O₄.**

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 CoAl₂O₄ 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 M²⁺ 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 SnCo₂O₄ exhibit?**

It is possible to determine the oxidation states of the metals in SnCo₂O₄ 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⁺⁺⁺⁻ but Co⁺⁺⁺⁻-ions occupy the tetrahedral holes.

A spinel X shows a composition 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 \( \text{MAI}_2\text{O}_4 \) shall be found by an experimental redox titration. The students found the results of the preparatory experiment:

<table>
<thead>
<tr>
<th>mL</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>10.5</th>
<th>11</th>
<th>11.5</th>
<th>12</th>
</tr>
</thead>
<tbody>
<tr>
<td>E</td>
<td>0.60</td>
<td>0.71</td>
<td>0.73</td>
<td>0.75</td>
<td>0.76</td>
<td>0.77</td>
<td>0.77</td>
<td>0.78</td>
<td>0.79</td>
<td>0.81</td>
<td>0.83</td>
<td>1.20</td>
<td>1.47</td>
<td>1.51</td>
<td></td>
</tr>
</tbody>
</table>

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 \( \text{mL} \) and \( E \) should be but the students know from former instructions that \( \text{mL} \) 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 \( \text{NO}_2 \) and \( \text{N}_2\text{O}_4 \) in a vessel (\( V = 15 \text{ L} \)). The temperature is constantly held at 300 K.

\( a) \) Calculate the pressure in the vessel when the equilibrium \( \text{NO}_2/\text{N}_2\text{O}_4 \) has established.

In another vessel there was at the beginning a mixture of \( \text{NO}_2 \) and \( \text{N}_2\text{O}_4 \) 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 \( \text{NO}_2 \) as a function of time and plot this function from \( t=0 \) h to \( t=1 \) h.

\( c) \) Determine the mole fraction of \( \text{NO}_2 \) 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 \( \Delta \text{H}_f^0 \) and \( S_f^0 \) under standard conditions (\( p = 1.0000 \cdot 10^5 \text{ Pa} (1) \), \( T = 298 \text{ K} \))

<table>
<thead>
<tr>
<th></th>
<th>( \Delta \text{H}_f^0 ) in kJ</th>
<th>( S_f^0 ) in JK(^{-1})mol(^{-1})</th>
<th>Cp in JK(^{-1})mol(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{NO}_2 )</td>
<td>33.20</td>
<td>240.1</td>
<td>37.2</td>
</tr>
<tr>
<td>( \text{N}_2\text{O}_4 )</td>
<td>9.16</td>
<td>304.3</td>
<td>77.8</td>
</tr>
</tbody>
</table>

Hints:
Take for granted that \( \text{NO}_2 \) and \( \text{N}_2\text{O}_4 \) are ideal gases.
In \( a) \) take the values of 298 K for \( \Delta \text{H}_f^0 \) und \( S_f^0 \) at \( T = 300 \text{ K} \).
In \( b) \) and \( c) \) the dependence of \( \Delta \text{H}_f^0 \) und \( S_f^0 \) 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 derivates 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 dioxide 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)

![NMR Spectrum](image)

**Ratio of intensities**

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 addition takes place at first followed by an elimination of dimethylamine to form compound C ($\text{C}_{12}\text{H}_{15}\text{N}$).

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 $^1\text{H}$-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 ($\text{C}_{20}\text{H}_{26}\text{Fe}$).

g) Draw the structures of all 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

5 hours,
write it on every answer sheet,
write them down in the appropriate boxes,
otherwise you will get no points
use only the periodic system given,
use only the values given in the table
only in the appropriate boxes of the
answer sheets.
nothing else will be marked
use the back of the pages of the problem booklet,
but everything written there will not be marked,
you may keep it.

Good Luck
Useful formulas and data

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

\[ S^0 (T) = S^0(298) + C_p \cdot \ln(T/298) \]

\[ \Delta U_{reaction} = \Delta H_{reaction} + W \quad \text{(p,V-work only at constant pressure: } W = - p \cdot \Delta V) \]
\[ K_{th} = K_p \cdot p_0^{-\Delta n} \quad ; \quad K_{th} = K_c \cdot (mol/l)^{-\Delta n} \]
\[ \ln (K_{p1}/K_{p2}) = -\Delta H/R \cdot (T_1^{-1} - T_2^{-1}) \]

\[ p \cdot V = n \cdot R \cdot T \]

Nernst equation :
\[ E = E_0 + \frac{R \cdot T}{z \cdot F} \cdot \ln \left( \frac{c_{Ox}}{c_{Red}} \right) \]

for metals \( c_{Red} = 1 \text{ mol/L} \)
for non-metals \( c_{Ox} = 1 \text{ mol/L} \)

rate laws

0. order \( c = c_o - k \cdot t \)
1. order \( c = c_o \cdot e^{-k \cdot t} \)
2. order \( c^{-1} = k_2 \cdot t + c^{-1}_o \)

Arrhenius equation:
\[ k = A \cdot e^{E_a/(R \cdot T)} \]

\( A \) pre-exponential factor,
\( E_a \) activation energy

Bragg’s equation:
\[ n \cdot \lambda = 2a \cdot \sin \theta \]

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

\( \varepsilon \) molar absorption coefficient
\( d \) length of the cuvette
\( c \) concentration

Henry’s law for dissolving gases in water (A(g) \( \rightarrow \) 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

\[ R = 8,314 \text{ JK}^{-1}\text{mol}^{-1} \quad F = 96485 \text{ Cmol}^{-1} \]
\[ N_A = 6,022 \cdot 10^{23} \text{mol}^{-1} \]
\[ p_o = 1,000 \cdot 10^5 \text{ Pa} \quad 1 \text{ atm} = 1,013 \cdot 10^5 \text{ Pa} \quad 1 \text{ bar} = 1 \cdot 10^5 \text{ Pa} \]

A periodic table was provided
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  \[ \text{A} + \text{B} \rightarrow 2 \text{C} \], \( K_p = 3.6 \) (5000 K). In a system it can be observed that \( p_A = 2.3 \text{ bar} \), \( p_B = 4.0 \text{ bar} \) and \( p_C = 3.6 \text{ bar} \). 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, \(^{79}\text{Br}\) and \(^{81}\text{Br}\), have a natural molar abundance of about 50% each. Which is the expected mass spectrum of the parent cation, \( \text{Br}_2^{2+} \)?

![Mass spectra](image)

A) 
B) 
C) 

D) 
E) 
F) 

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

\[ \text{E} \] \( \text{I}^- < \text{Te}^{2+} < \text{Ba}^{2+} < \text{Cs}^+ \)
\[ \text{B} \] \( \text{Ba}^{2+} < \text{Te}^{2+} < \text{Cs}^+ < \text{I}^- \)
\[ \text{C} \] \( \text{Cs}^+ < \text{Ba}^{2+} < \text{Te}^{2+} < \text{I}^- \)
\[ \text{D} \] \( \text{Te}^{2+} < \text{I}^- < \text{Cs}^+ < \text{Ba}^{2+} \)
\[ \text{E} \] \( \text{Ba}^{2+} < \text{Cs}^+ < \text{I}^- < \text{Te}^{2+} \)


e) A compound has the molecular formula \( \text{C}_4\text{H}_8 \). How many isomers may exist maximally?

A) 2  B) 3  C) 4  D) 5  E) 6
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 ($C_{21}H_{23}O_{6}N$) 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 $CaCl_2 \cdot 6H_2O$ 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 aqueous solution of acetic acid is 85%.

a) Determine the concentration of acetic acid ($K_a = 1.74 \cdot 10^{-5}$), 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.

![Graph showing pH vs. V(HCl)](image)

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

Problem 3-5  Equilibria

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

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

$$4 \text{ HCl} + \text{ O}_2 \rightleftharpoons 2 \text{ Cl}_2 + 2 \text{ H}_2\text{O}.$$ 

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

\[ \text{CCl}_4, \text{TeCl}_4 \text{ and } \text{XeF}_4 \]

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) Answer the questions in b) also for the following molecules

\[ \text{BeCl}_2, \text{SnCl}_2, \text{H}_2\text{S und XeF}_2 \]

(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:

\[
\begin{align*}
\text{NH}_3 & : 107^\circ \quad \rightarrow \quad \text{PH}_3 & : 93,6^\circ \\
\text{PH}_3 & : 93,6^\circ \quad \rightarrow \quad \text{PF}_3 & : 96,3^\circ 
\end{align*}
\]

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 crystallises 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 is 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:

\[ U_{lattice} = -f \cdot \frac{Z^+ \cdot Z^- \cdot M \cdot e^2}{r_+ + r_-} \left(1 - \frac{1}{n}\right) \]  
(U in kJ/mol)

The factor \( r \cdot e^2 \) 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) \textbf{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.

<table>
<thead>
<tr>
<th>temperature in °C</th>
<th>( c(\text{BBr}_3) ) in molL(^{-1} )</th>
<th>( c(\text{PBr}_3) ) in molL(^{-1} )</th>
<th>( c(\text{H}_2) ) in molL(^{-1} )</th>
<th>( r ) in mols(^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>800</td>
<td>2.25-10(^6)</td>
<td>9.00-10(^6)</td>
<td>0.070</td>
<td>4.60-10(^{-8})</td>
</tr>
<tr>
<td>800</td>
<td>4.50-10(^6)</td>
<td>9.00-10(^6)</td>
<td>0.070</td>
<td>9.20-10(^{-8})</td>
</tr>
<tr>
<td>800</td>
<td>9.00-10(^6)</td>
<td>9.00-10(^6)</td>
<td>0.070</td>
<td>18.4-10(^{-8})</td>
</tr>
<tr>
<td>800</td>
<td>2.25-10(^6)</td>
<td>2.25-10(^6)</td>
<td>0.070</td>
<td>1.15-10(^{-8})</td>
</tr>
<tr>
<td>800</td>
<td>2.25-10(^6)</td>
<td>4.50-10(^6)</td>
<td>0.070</td>
<td>2.30-10(^{-8})</td>
</tr>
<tr>
<td>800</td>
<td>2.25-10(^6)</td>
<td>9.00-10(^6)</td>
<td>0.035</td>
<td>4.60-10(^{-8})</td>
</tr>
<tr>
<td>880</td>
<td>2.25-10(^6)</td>
<td>9.00-10(^6)</td>
<td>0.070</td>
<td>19.6-10(^{-8})</td>
</tr>
</tbody>
</table>

g) \textbf{Determine the rate equation and the order of the reaction.}

Calculate the rate constants at 800°C and at 880°C.

h) \textbf{Calculate the activation energy of the formation of boron phosphide.}

* Extract from a formulary concerning a tetrahedron with the edge \( a \):

\[ V = a^3 \cdot \frac{\sqrt{2}}{12} \quad O = a^2 \cdot \frac{\sqrt{3}}{2} \quad h = a \cdot \frac{\sqrt{6}}{3} \quad r_{\text{circumcircle}} = a \cdot \frac{\sqrt{6}}{4} \quad r_{\text{incircle}} = a \cdot \frac{\sqrt{6}}{12} \]

**Problem 3-8 \textbf{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 \((c = 0.0100 \text{ mol/L})\) to reach the equivalent point.

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

a) \textbf{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 \( \text{DBE} = \frac{2a+2-b}{2} \) 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 forms 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.*
Problem 3-10  
Chirality of a Compound

The chirality of 1-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.
Problem 3-11

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

<p>| | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>B</td>
<td>C</td>
<td>D</td>
<td>E</td>
</tr>
<tr>
<td>NH&lt;sup&gt;4+&lt;/sup&gt;</td>
<td>BF&lt;sub&gt;4&lt;/sub&gt;&lt;sup&gt;-&lt;/sup&gt;</td>
<td>HF&lt;sub&gt;2&lt;/sub&gt;&lt;sup&gt;-&lt;/sup&gt;</td>
<td>SO&lt;sub&gt;4&lt;/sub&gt;&lt;sup&gt;2-&lt;/sup&gt;</td>
<td>S&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;&lt;sup&gt;2-&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

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

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>B</td>
<td>C</td>
<td>D</td>
</tr>
<tr>
<td>BF&lt;sub&gt;4&lt;/sub&gt;&lt;sup&gt;-&lt;/sup&gt;</td>
<td>CF&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>BF&lt;sub&gt;3&lt;/sub&gt;</td>
<td>BeF&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
</tbody>
</table>

c) Solutions containing H<sub>3</sub>PO<sub>4</sub> and/or NaH<sub>2</sub>PO<sub>4</sub> 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<sub>3</sub>PO<sub>4</sub>: pK<sub>1</sub> = 2.1, pK<sub>2</sub> = 7.2, pK<sub>3</sub> = 12.0).

(i) The solution contains H<sub>3</sub>PO<sub>4</sub> only
(ii) The solution contains H<sub>3</sub>PO<sub>4</sub> and NaH<sub>2</sub>PO<sub>4</sub> in the mole ratio 2:1
(iii) The solution contains H<sub>3</sub>PO<sub>4</sub> and NaH<sub>2</sub>PO<sub>4</sub> in the mole ratio 1:1.

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

![Parallelograms](image)

e) To 30 mL of a Ba(OH)<sub>2</sub> solution (0.10 mol/L) 30 mL of a H<sub>2</sub>SO<sub>4</sub> solution are added (0.10 mol/L). The increase of temperature is ΔT<sub>1</sub>. The experiment is repeated with 90 mL of each of the same solutions and the rise in temperature is ΔT<sub>2</sub>. Which of the following equation is correct?

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>B</td>
<td>C</td>
<td>D</td>
</tr>
<tr>
<td>ΔT&lt;sub&gt;2&lt;/sub&gt; = ΔT&lt;sub&gt;1&lt;/sub&gt;</td>
<td>ΔT&lt;sub&gt;2&lt;/sub&gt; = 3 ⋅ ΔT&lt;sub&gt;1&lt;/sub&gt;</td>
<td>ΔT&lt;sub&gt;2&lt;/sub&gt; = 6 ⋅ ΔT&lt;sub&gt;1&lt;/sub&gt;</td>
<td>ΔT&lt;sub&gt;2&lt;/sub&gt; = 9 ⋅ ΔT&lt;sub&gt;1&lt;/sub&gt;</td>
</tr>
</tbody>
</table>
Problem 3-12  Acids

Tea-flavours 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 gastric juice was 2.1 before drinking the tea due to the hydrochloric acid excreted by the stomach. \( K_{a1, \text{citric acid}} = 3.98 \times 10^{-6} \), \( K_{a2, \text{citric acid}} = 7.24 \times 10^{-11} \), \( K_{a3, \text{citric acid}} = 6.3 \times 10^{-20} \)

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

   \[
   \text{R} - \text{H} - \text{COOH}
   \]

   \[
   \text{H, CH}_3, \text{NO}_2, \text{OCH}_3, \text{Cl}
   \]

   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 \( (c = 0.0200 \text{ mol/L}) \), consumption 43.15 mL.

II \( \text{H}_2\text{O}_2 \) 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.

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

\[
\begin{align*}
\text{Sn}^{4+} & + 2 \, \text{e}^- \rightleftharpoons \text{Sn}^{2+} & \quad E^\circ = 0.154 \, \text{V} \\
\text{Fe}^{3+} & + \, \text{e}^- \rightleftharpoons \text{Fe}^{2+} & \quad E^\circ = 0.771 \, \text{V}
\end{align*}
\]

a) Write the overall reaction equation and calculate the standard free energy change ($\Delta G^\circ$) 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 ($E^\circ_{\text{calomel}} = 0.242 \, \text{V}$) 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 $E(\text{Sn}^{4+}/\text{Sn}^{2+}) = E(\text{Fe}^{3+}/\text{Fe}^{2+})$),

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 $p = 1.013 \cdot 10^5 \, \text{Pa}$:

<table>
<thead>
<tr>
<th>t in s</th>
<th>0</th>
<th>50</th>
<th>100</th>
<th>150</th>
<th>200</th>
<th>$\infty$</th>
</tr>
</thead>
<tbody>
<tr>
<td>V(Gas) in mL</td>
<td>0</td>
<td>11.6</td>
<td>20.2</td>
<td>26.1</td>
<td>30.4</td>
<td>41.5</td>
</tr>
</tbody>
</table>
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: \(2 \text{NOCl} \rightleftharpoons 2 \text{NO} + \text{Cl}_2\).

The following rate constants were found:

<table>
<thead>
<tr>
<th>Temperature in °C</th>
<th>150</th>
<th>170</th>
<th>190</th>
<th>210</th>
<th>230</th>
</tr>
</thead>
<tbody>
<tr>
<td>(k) (in (\text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1})) /10^3</td>
<td>3.65</td>
<td>12.9</td>
<td>43.0</td>
<td>123</td>
<td>370</td>
</tr>
</tbody>
</table>

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 \(\lambda = 512\ \text{nm}\) (\(\varepsilon = 10500 \ \text{Lmol}^{-1} \ \text{cm}^{-1}\)).

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 method). 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 m³/s and 150.0 m³/s respectively.

Stream ③ leaving the synthesis gas unit is a mixture of synthesis gas and an excess of one
reactant, which condenses at $\approx$ 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.

$\rho(\text{CH}_3\text{OH}) (\text{l}) = 0.791 \text{ g} \cdot \text{mL}^{-1}$.

Assumptions: All gases are perfect, total conversion in steps A and B, complete separation 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 m³/s (at 25°C and 101.3 kPa) of the following streams
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 $\textcircled{a}$ 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 $\textcircled{a}$ in mol/s.

In stream $\textcircled{a}$ 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 $\textcircled{a}$.

When the methanol reactor is large enough the reaction goes to equilibrium. The partial pressures in stream $\textcircled{a}$ obey the equation:

$$K_p = \frac{p(CH_3OH) \cdot p^2_0}{p(CO) \cdot p^2(H_2)}$$

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 Substitution**

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-bromosuccinimide 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 following reaction was performed:

![Chemical reaction diagram]

Four different products (I bis IV) of substitution were found.

![Structural formulas I to IV]
a) Give a mechanism for the formation of these four compounds.
   The explanation should 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 appropriate 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 (HIO₄) leads to two products C and D with the same molecular formula (C₅H₁₀O).

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(NH₃)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 targeting 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. They 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 $\frac{3}{4}$ of an hour have elapsed and
   (ii) the activity after $\frac{3}{4}$ of an hour and after dilution of 10mL of the pharmaceutical to 25 L

The modes of decay for these three isotopes are $\beta$-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 ($\text{GaC}_6\text{H}_5\text{O}_6\cdot 3\text{H}_2\text{O}$). 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:

<table>
<thead>
<tr>
<th>T in K</th>
<th>800</th>
<th>900</th>
<th>1000</th>
<th>1100</th>
<th>1200</th>
<th>1300</th>
</tr>
</thead>
<tbody>
<tr>
<td>$p$(CO$_2$) in hPa</td>
<td>0.50</td>
<td>10.0</td>
<td>112</td>
<td>800</td>
<td>4050</td>
<td>16100</td>
</tr>
</tbody>
</table>

a) Calculate $\Delta G$ of the decomposition of calcium carbonate at each of the temperatures given.

b) Calculate the change of enthalpy $\Delta H^\circ$ and the change of entropy $\Delta S^\circ$. Due to the reaction equation it is possible to predict the algebraic sign of $\Delta S^\circ$. State the reason.

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

Standard pressure $p_0 = 1.000 \cdot 10^5$ Pa
for simplification: $\Delta H$ and $\Delta S$ independent of temperature
Problem 4-3 Electrochemistry and Solubility Products

Given a solution A of silver nitrate and lead nitrate in water with $c(\text{AgNO}_3) = 0.050 \ \text{mol}\cdot\text{L}^{-1}$ and $c(\text{Pb(NO}_3)_2) = 0.100 \ \text{mol}\cdot\text{L}^{-1}$.

a) Calculate the pH of the solution.

10 mL of a solution of potassium iodid ($c = 0.250 \ \text{mol}\cdot\text{L}^{-1}$) and nitric acid ($c = 0.200 \ \text{mol}\cdot\text{L}^{-1}$) 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\text{L}^{-1} silver nitrate and 0.040 mol\cdot\text{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, $E_{\text{cell}}$ at 25°C (= 298 K).

c) Write the total cell reaction and calculate the equilibrium 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:

$\begin{align*}
\text{Ag}^+ + \text{H}_2\text{O} & \rightarrow \text{AgOH} + \text{H}^+ & K_1 = 10^{-11.70} \\
\text{Pb}^{2+} + \text{H}_2\text{O} & \rightarrow \text{PbOH}^+ + \text{H}^+ & K_2 = 10^{-7.80} \\
pK_{sp}(\text{AgI}) &= 16 & pK_{sp}(\text{PbI}_2) &= 7.86 & pK_{sp}(\text{AgSCN}) &= 12 & E^0(\text{Ag}^+/\text{Ag}) &= 0.799 \ \text{V}
\end{align*}$

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

$\begin{align*}
\text{V}^{3+} + \text{e}^- & \rightarrow \text{V}^{2+} & E^0 &= -0.255 \ \text{V} \\
\text{VO}^{2+} + 2 \text{H}^+ + \text{e}^- & \rightarrow \text{V}^{2+} + \text{H}_2\text{O} & E^0 &= 0.377 \ \text{V} \\
\text{VO}_2^+ + 2 \text{H}^+ + \text{e}^- & \rightarrow \text{VO}^{2+} + \text{H}_2\text{O} & E^0 &= 1.00 \ \text{V} \\
\text{V(OH)}_4^{2+} + 2 \text{H}^+ + \text{e}^- & \rightarrow \text{VO}^{2+} + 3 \text{H}_2\text{O} & E^0 &= 1.00 \ \text{V} \\
\text{V(OH)}_4^{2+} + 4 \text{H}^+ + 5 \text{e}^- & \rightarrow \text{V} + 4 \text{H}_2\text{O} & E^0 &= -0.25 \ \text{V}
\end{align*}$

f) Calculate $\Delta G^0$ for the reaction $\text{V}^{2+} + \text{H}_2 \rightarrow \text{V} + 2 \text{H}^+$
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

$$S + E \xrightleftharpoons[k_2]{k_1} ES \xrightarrow{k_3} P + E$$

$S$ = 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

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

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

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

c) Derive from a) and b) the Michaelis-Menten equation

$$v = \frac{v_{max} [S]}{K_M + [S]}.$$  

$$v_{max} = 3.0 \cdot 10^{-6} \text{ mol L}^{-1} \text{ s}^{-1}$$

$$v$$ in \ mol L$^{-1}$ s$^{-1}$

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

![Graph showing Michaelis-Menten equation with v max and K M values](image-url)
Often you find the Lineweaver-Burk plot \( \frac{1}{v} = f\left(\frac{1}{[S]}\right) \).

e) Show that

\[
\frac{1}{v} = \frac{K_M}{v_{\text{max}}} \frac{1}{[S]} + \frac{1}{v_{\text{max}}}
\]

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

<table>
<thead>
<tr>
<th>([S]_0 \cdot 10^6 \text{ in mol L}^{-1})</th>
<th>3.0</th>
<th>5.0</th>
<th>10</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td>(v_0 \cdot 10^5 \text{ in mol L}^{-1} \text{ min}^{-1})</td>
<td>1.06</td>
<td>1.55</td>
<td>2.37</td>
<td>3.21</td>
</tr>
</tbody>
</table>

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

In another enzymatic reaction the Michaelis constant is \( K_M = 1.5 \cdot 10^{-5} \text{ mol L}^{-1} \). The initial concentration of the substrate is \( 3 \cdot 10^{-5} \text{ mol L}^{-1} \).

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 \( k_{\text{cat}} \) (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 (\( M = 41977 \text{ g mol}^{-1} \)) cleaves the peptid bonding of proteins. In 10 mL of a solution \( 10^{-9} \text{ g pepsin} \) were dissolved. The maximum reaction rate was measured:

\( v_{\text{max}} = 7.15 \cdot 10^{-11} \text{ mol L}^{-1} \text{ min}^{-1} \).

h) Calculate the turnover 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 equivalence point.

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

A sample of 0.2250 g contains a mixture of iron and iron(III)-oxide. This sample is dissolved completely and then treated with a saturated solution of \( \text{SO}_2 \) in water. The excess of \( \text{SO}_2 \) 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 $K_{sp}(\text{Fe(OH)}_3) = 4 \cdot 10^{-38}$ \[ \text{and} \] $K_{sp}(\text{Ni(OH)}_2) = 6 \cdot 10^{-16}$

Problem 4-6

Measurements 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 exceeds 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 hydrogen 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.

\[ \text{Data: } \rho(\text{Hg}) = 13.55 \text{ g/cm}^3 \quad g = 9.81 \text{ m/s}^2 \]
Problems round 4 (theoretical)

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:

\[
\begin{align*}
\text{HUr (aq) + H}_2\text{O (l)} & \rightleftharpoons \text{Ur}^- \text{(aq) + H}_3\text{O}^+ \text{(aq)} \quad \text{pK} = 5.4 \text{ at } 37^\circ\text{C} \\
\text{Ur}^- \text{(aq) + Na}^+ \text{(aq)} & \rightleftharpoons \text{NaUr (s)}
\end{align*}
\]

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 \(c(\text{Na}^+) = 130 \text{ mmol/L.}\)

b) Calculate the maximum feasible 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. arthritis 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 RCH₂CHO 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 (pKₐ~17) and 2,4-pentadione (pKₐ~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 stereoisomers 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.

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. CH₃I) 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 (C₂H₄O)ₙ.

The structure of A is analysed 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 1730 cm⁻¹ and further bands between 2850 cm⁻¹ and 2930 cm⁻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.*

Thereeto:

- 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*
Problems round 4 (theoretical)

### Correlation of \(^1\text{H}\) Chemical Shift with Environment

<table>
<thead>
<tr>
<th>Type of proton</th>
<th>Formula</th>
<th>Chemical shift ((\delta))</th>
<th>Alkyl iodide</th>
<th>1–C–H</th>
<th>2.0–4.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference peak</td>
<td>(-\text{CH}_2\text{CH}_3)</td>
<td>0.7–1.3</td>
<td>Alkyl iodide</td>
<td>1–C–H</td>
<td>2.0–4.0</td>
</tr>
<tr>
<td>Saturated primary</td>
<td>(-\text{CH}_2)</td>
<td>1.2–1.4</td>
<td>Alcohol, other</td>
<td>O–C–H</td>
<td>3.3–4.0</td>
</tr>
<tr>
<td>Saturated secondary</td>
<td>(-\text{CH}_3)</td>
<td>1.4–1.7</td>
<td>Alkyl</td>
<td>C\equiv C–H</td>
<td>2.5–2.7</td>
</tr>
<tr>
<td>Saturated tertiary</td>
<td>(-\text{CH}_2)</td>
<td>2.1–2.4</td>
<td>Alkyl</td>
<td>C\equiv C–H</td>
<td>2.5–2.7</td>
</tr>
<tr>
<td>Allylic primary</td>
<td>(-\text{CH}_2\text{CH}_3)</td>
<td>1.6–1.9</td>
<td>Vinyl</td>
<td>C\equiv C–H</td>
<td>5.0–6.5</td>
</tr>
<tr>
<td>Methyl ketones</td>
<td>(-\text{CH}_2)</td>
<td>2.5–2.7</td>
<td>Aromatic</td>
<td>Ar–H</td>
<td>6.5–8.0</td>
</tr>
<tr>
<td>Aromatic methyl</td>
<td>(-\text{CH}_3)</td>
<td>3.0–4.0</td>
<td>Aldehyde</td>
<td>C–H</td>
<td>9.7–10.0</td>
</tr>
<tr>
<td>Alkyl chloride</td>
<td>(-\text{CH}_2)</td>
<td>2.5–4.9</td>
<td>Carboxylic acid</td>
<td>C–O–H</td>
<td>11.0–12.0</td>
</tr>
<tr>
<td>Alkyl bremside</td>
<td>(-\text{CH}_2)</td>
<td>2.5–4.9</td>
<td>Alcohol</td>
<td>C–O–H</td>
<td>Extremely variable (2.5–5.0)</td>
</tr>
</tbody>
</table>

### Regions of the \(^1\text{H}\) NMR Spectrum

<table>
<thead>
<tr>
<th>Region ((\delta))</th>
<th>Proton type</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>0–1.5</td>
<td>(-\text{CH}_2)</td>
<td>Protons on carbon next to saturated centers absorb in this region. Thus, the aliphatic portions of most organic molecules show complex absorption.</td>
</tr>
<tr>
<td>1.5–2.5</td>
<td>(-\text{CH}_2)</td>
<td>Protons on carbon next to unsaturated centers (allylic, benzyllic, next to carbonyl) show characteristic absorptions in this region, just downfield from other alkane resonance.</td>
</tr>
<tr>
<td>2.5–4.5</td>
<td>(-\text{CH}_2)</td>
<td>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.</td>
</tr>
<tr>
<td>4.5–6.5</td>
<td>(-\text{CH}_2)</td>
<td>Protons on double-bond carbons (vinyllic protons) are strongly deshielded by the neighboring pi bond and therefore absorb in this characteristic downfield region.</td>
</tr>
<tr>
<td>6.5–8.0</td>
<td>(-\text{CH}_2)</td>
<td>Protons on aromatic rings (aryl protons) are strongly deshielded by the pi orbitals of the ring and absorb in this characteristic low-field range.</td>
</tr>
</tbody>
</table>

![Wave number (cm\(^{-1}\))](image)

![Wavelength (μm)](image)
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 different possibilities at your disposal. You have to choose from

- Titration of the cations with a solution of EDTA \((c = 0.100\text{ mol/L})\) using Erio T as indicator.
- Separation of the cations by precipitation of calcium oxalate.
- Oxidimetric titration of an oxalate with a solution of potassium permanganate \((c = 0.020\text{ mol/L})\).
- 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 spatula-tipfull of indicator (as trituration NaCl: Erio T = 100 : 1).
Titrate with the solution of EDTA \((c = 0.100\text{ ml/L})\).

Separation 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 \(\text{NH}_3\) until the sample shows a slightly basic reaction heat it to boiling and add hot solution of \((\text{NH}_4)_2\text{-oxalate}\) 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 \((\text{NH}_4)_2\text{-oxalate}\) \((c=0.01\text{ mol/L})\) (small!) and then 1x carefully with a small amount of warm water.
The precipitate is dissolved in warm sulfuric acid \((3\text{ parts of H}_2\text{O with 1 part of conc. H}_2\text{SO}_4)\) and diluted with 50 mL of water.

Oxidimetric titration of oxalate with a solution of KMnO\(_4\) \((c = 0.020\text{ mol/L})\)
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\(_3\) \((c = 0.100\text{ mol/L})\) until a dark yellow 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 melting 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 filtered 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-dinitrophenylhydrazine with acetone as an example.

B) Identification of aldehyde and ketone

While the crystals are drying other reactions are used to identify 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

<table>
<thead>
<tr>
<th>Chosen Aldehydes / Ketones</th>
<th>Intervals of melting of the respective 2,4-dinitrophenyl hydrazones in °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crotonaldehyde</td>
<td>190 - 195</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>160 - 166</td>
</tr>
<tr>
<td>Propionaldehyde</td>
<td>150 - 155</td>
</tr>
<tr>
<td>Chloral</td>
<td>127 - 131</td>
</tr>
<tr>
<td>Heptanal</td>
<td>100 - 108</td>
</tr>
<tr>
<td>Ethyl methyl ketone</td>
<td>110 - 117</td>
</tr>
<tr>
<td>Isopropyl methyl ketone</td>
<td>120 - 123</td>
</tr>
<tr>
<td>Methyl propyl ketone</td>
<td>138 - 144</td>
</tr>
<tr>
<td>Diethyl ketone</td>
<td>150 - 156</td>
</tr>
<tr>
<td>Cyclohexanone</td>
<td>158 - 162</td>
</tr>
</tbody>
</table>
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) \[ 2 \text{H}_2\text{O}^+ + \text{SO}_4^{2-} + 2 \text{OH}^- \rightleftharpoons 4 \text{H}_2\text{O} + \text{SO}_4^{2-} \]

\[ c(\text{NaOH}) \cdot V(\text{NaOH}) = 2 \cdot c(\text{H}_2\text{SO}_4) \cdot V(\text{H}_2\text{SO}_4) \]

\[ 0.1760 \text{ mol/L} \cdot 20.37 \text{ mL} = 2 \cdot c(\text{H}_2\text{SO}_4) \cdot 10.00 \text{ mL} \]

\[ c(\text{H}_2\text{SO}_4) = 0.1793 \text{ mol/L} \]

b) \[ n = 0.5000 \text{ L} \cdot 0.1792 \text{ mol/L} = 0.0896 \text{ mol H}_2\text{SO}_4 \text{, 1 liter contains 17.93 mol H}_2\text{SO}_4. \]

\[ m(\text{H}_2\text{SO}_4) = 1759 \text{ g}, \quad 100\% \cdot \frac{1759}{1840} = 95.6\% \]

b) 1 L of sulphuric acid contains 1759 g of H$_2$SO$_4$ (17.93 mol) and 81 g of H$_2$O (4.50 mol)

\[ x = \frac{17.93}{17.93 + 4.00} = 0.799 \]

Solution to problem 1-2

a) Advantages:
   - Low density, alloys have nearly the same stability as steel, suitable for vehicle construction
   - corrosion resistant,
   - 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$_2$O$_3$ 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 separate 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:

\[
\begin{align*}
\text{Al}_2\text{O}_3 (s) + 3 \text{H}_2\text{O} (l) & \rightarrow 2 \text{Al(OH)}_3 (s) \\
\text{Al(OH)}_3 (s) + \text{OH}^- & \rightarrow [\text{Al(OH)}_4]^- \\
\text{Fe}_2\text{O}_3 (s) + 3 \text{H}_2\text{O} (l) & \rightarrow 2 \text{Fe(OH)}_3 (s)
\end{align*}
\]

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:

\[
(\text{CO}_2 + \text{OH}^- \leftrightarrow \text{HCO}_3^-)
\]

\[
\text{Al(OH)}_4^- \rightarrow \text{OH}^- + \text{Al(OH)}_3 (s)
\]

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

\[
2 \text{ Al(OH)}_3 (s) \rightarrow \text{Al}_2\text{O}_3 (s) + 3 \text{H}_2\text{O} (g)
\]

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

At the cathode

\[
\begin{align*}
\text{Al}_2\text{O}_3 & \rightarrow 2 \text{ Al}^{3+} + 3 \text{ O}^{2-} \\
\text{Al}^{3+} + 3 \text{e}^- & \rightarrow \text{Al}
\end{align*}
\]

At the anode

\[
\begin{align*}
2 \text{ O}^{2-} & \rightarrow \text{O}_2 + 4 \text{e}^- \\
\text{O}_2 + 2 \text{ C} & \rightarrow 2 \text{ CO}
\end{align*}
\]

Total reaction:

\[
2 \text{ Al}_2\text{O}_3 + 6 \text{ C} \rightarrow 4 \text{ Al} + 6 \text{ CO}
\]

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

Q = I \cdot t

Q = m \cdot M \cdot 3 \cdot 96485 \text{ As/mol} \quad M(\text{Al}) = 26.98 \text{ g/mol}

\[
\Rightarrow \quad m = \frac{130 \cdot 10^{-3} \cdot 366 \cdot 24 \cdot 3600 \cdot 0.95 - 26.98}{96485} \approx 364 \text{ t}
\]

d) W = P \cdot t \quad \text{and} \quad P = U \cdot I

\[
\begin{align*}
W & = U \cdot I \cdot t \\
W & = U \cdot Q \quad \text{and} \quad Q = n \cdot z \cdot F
\end{align*}
\]

with U = 5 V \quad n = (10^6/26.98) \text{ mol} \quad z = 3 \quad F = 96485 \text{ As/mol}

\[
\begin{align*}
W & = 5 \cdot 10^6 / 26.98 \cdot 3 \cdot 96485 \text{ As} \\
\text{efficiency} & = 95 \% \quad \Rightarrow \quad W_{(\text{for 1 t Al})} = 15700 \text{ kWh}
\end{align*}
\]

1 t bauxite contains 600 kg Al_2O_3 = 0.6 \cdot 10^5/101.96 \text{ mol Al}_2\text{O}_3
to form $1.2/101.96 \cdot 26.98 \text{ t Al} = 0.318 \text{ t Al}$. \(\Rightarrow m_{\text{for 1 t Al}} = 0.318^{-1} \text{ t}
\)
\(m_{\text{for 1 t Al}} \approx 3 \text{ t bauxite.}
\)

(In literature you often find 4 t.)

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

e) \(2 \text{ Al}_2\text{O}_3 \rightarrow 4 \text{ Al} + 3 \text{ O}_2\)

\(\Delta R_H = [4 \cdot 48 + 3 \cdot 38 - 2 \cdot (-1610)] \text{ kJ/mol} = 3526 \text{ kJ/mol}
\)
\(\Delta R_S = [4 \cdot 78 + 3 \cdot 238 - 2 \cdot 98] \text{ kJ/(K mol)} = 830 \text{ kJ/(K mol)}
\)
\(\Delta R_G = \Delta R_H - T \Delta R_S
\)
\(\Delta E = \Delta R_G / (z \cdot F)
\)

\(\Delta E = 2.15 \text{ V}
\)

f) According to the negative standard potential of aluminium \(E^0(\text{Al}^{3+}/\text{Al}) = - 1.66 \text{ V}\) hydrogen is formed at the cathode.

g) Possible reactions

I \(2 \text{ Al}_2\text{O}_3 + 6 \text{ C} \rightarrow 4 \text{ Al} + 6 \text{ CO}\) with \(\Delta G_I = 3 \cdot \Delta G_2 - \Delta G_1
\)

II \(2 \text{ Al}_2\text{O}_3 + 3 \text{ C} \rightarrow 4 \text{ Al} + 3 \text{ CO}_2\) with \(\Delta G_{II} = 3 \cdot \Delta G_3 - \Delta G_1
\)

\(\Delta G < 0: 3 \cdot (-221.06 - 0.17872 \cdot T) \text{ kJ/mol} - (-3351.4 + 0.6264 \cdot T) \text{ kJ/mol} < 0
\)
\(\Rightarrow 2688.22 < 1.16256 \cdot T \Rightarrow T > 2313 \text{ K}
\)

\(\Delta G_{II} < 0: 3 \cdot (393.51 - 0.00286 \cdot T) \text{ kJ mol}^{-1} - (- 3351.4 + 0.6264 \cdot T) \text{ kJ mol} < 0
\)
\(\Rightarrow 2170.87 < 0.63498 \cdot T \Rightarrow T > 3419 \text{ K}, \text{ at this temperature CO}_2 \text{ does not form.}
\)

\(T > 2313 \text{ K} = 2040^\circ \text{C}\) (Actually it is not possible because of the formation of \(\text{Al}_2\text{C}_3\).)

Solution to problem 1-3

a) Observation 1:

\[
\text{Fe}^{3+}_{(aq)} + 3 \text{ SCN}^-_{(aq)} \leftrightsquigarrow \text{Fe(SCN)_3}^{(aq)}
\]

(yellow) (coulourless) (red)

or \(\text{[Fe(H}_2\text{O)}_6]^{3+} + 3 \text{ SCN}^- \leftrightsquigarrow \text{Fe[SCN}_3\text{(H}_2\text{O)}_3] + 3 \text{ H}_2\text{O}}
\]

Not only \(\text{Fe(SCN)_3}^{(aq)}\) is reason for the red colour but also complexes like \(\text{Fe[SCN}_x\text{(H}_2\text{O)}_{6-x}]^{3-x}\) with \(x\) ranging from 1 to 6.

Observation 2:

\[
K = \frac{c_{eq}(\text{Fe(SCN)}_3)}{c_{eq}(\text{Fe}^{3+}) \cdot c_{eq}(\text{SCN}^-)}.
\]

Dilution decreases the concentrations from \(c_{eq}\) to \(c_{eq}/10.\)
$$Q = \frac{c_{eq}(\text{Fe(SCN)}_3)/10}{[c_{eq}(\text{Fe}^{3+})/10][c_{eq}^{3-}(\text{SCN}^-)]/10^3} = K \cdot 1000.$$ 

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 additional 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 \( \pi \)-elektron system,
- fulfills Hückel’s rule to contain \( 4n + 2 \) (with \( n = 1 \)) electrons.

b) \( \pi \)-elektron system of pyrrole:

In pyrrole the free electron pair of the N Atom is part of the \( \pi \)-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 \( \pi \)-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) \( \text{Cr}_2\text{O}_7^{2-} + 14 \text{H}^+ + 6 \text{e}^- \rightleftharpoons 7 \text{H}_2\text{O} + 2 \text{Cr}^{3+} \)

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

\[
E = 1,38 \text{ V} + \frac{R \cdot T}{6 \text{ F}} \ln \frac{c(\text{Cr}_2\text{O}_7^{2-}) \cdot c(\text{H}^+)^{14}}{c(\text{Cr}^{3+})^2} \quad E = 1,38 \text{ V} + \frac{8,314.298}{6.96485} \text{ V} \cdot \ln (10^{-7})^{14}
\]

\[E = 0,414 \text{ V}\]

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

b) **Reaction with potassium nitrate/soda:**

\( \text{Cr}_2\text{O}_3 + 3 \text{KNO}_3 + 2 \text{Na}_2\text{CO}_3 \rightarrow 2 \text{Na}_2\text{CrO}_4 + 2 \text{CO}_2 + 3 \text{KNO}_2 \)

**Reaction with hydogenperoxide:**

\[2 \text{Cr}^{3+} + 3 \text{H}_2\text{O}_2 + 10 \text{OH}^- \rightarrow 2 \text{CrO}_4^{2-} + 8 \text{H}_2\text{O} \quad \text{or}\]

\[2 \text{Cr}^{3+} + 3 \text{H}_2\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{Cr}_2\text{O}_7^{2-} + 8 \text{H}^+ \]

**Reaction with sodium peroxodisulfate:**

\[2 \text{Cr}^{3+} + 3 \text{Na}_2\text{S}_2\text{O}_8 + 16 \text{OH}^- \rightarrow 2 \text{CrO}_4^{2-} + 6 \text{SO}_4^{2-} + 6 \text{Na}^+ + 8 \text{H}_2\text{O} \quad \text{or}\]

\[2 \text{Cr}^{3+} + 3 \text{Na}_2\text{S}_2\text{O}_8 + 7 \text{H}_2\text{O} \rightarrow \text{Cr}_2\text{O}_7^{2-} + 6 \text{SO}_4^{2-} + 6 \text{Na}^+ + 14 \text{H}^+ \]

**Reaction with bromine:**

\[2 \text{Cr}^{3+} + 3 \text{Br}_2 + 16 \text{OH}^- \rightarrow 2 \text{CrO}_4^{2-} + 6 \text{Br}^- + 8 \text{H}_2\text{O} \quad \text{or}\]

\[2 \text{Cr}^{3+} + 3 \text{Br}_2 + 7 \text{H}_2\text{O} \rightarrow \text{Cr}_2\text{O}_7^{2-} + 6 \text{Br}^- + 14 \text{H}^+ \]

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 \((\text{Cr}^{3+}|\text{Cr}_2\text{O}_7^{2-})\) being smaller than the standard potential of the system \((\text{Br}^-|\text{Br}_2)\).

\[
1.065 > 1.38 + \frac{8,314.298}{6.96485} \cdot \ln c(\text{H}^+)^{14} \quad \Leftrightarrow \quad - 73.60 > \ln c(\text{H}^+)^{14} \\
\sqrt{e^{-73.60}} = 5.21 \cdot 10^{-3} > c(\text{H}^+) \quad 2.28 < \text{pH}
\]

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 permanganate 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.

\[
\begin{align*}
\text{Cr}^{+II} & \quad \text{O} \quad \text{O} \\
\text{O} & \quad \text{Cr}^{+VI} \quad \text{O} \quad \text{O} \\
\text{O} & \quad \text{O} \\
\end{align*}
\]

\[
\text{Cr}_{2}O_{7}^{2-} + 4 \text{H}_{2}O_{2} + 2 \text{H}^{+} \rightarrow 2 \text{CrO}_{5} + 5 \text{H}_{2}O
\]

f)

![Graph showing the relationship between temperature in K and suszeptibility in cm³/g](image)

\[
\mu = 2.83 \text{ BM.}
\]

i) Comparing \( \mu = 2.83 \) 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) (d⁵-system) or for Cr(II) (d⁴-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 aqueous 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 \( \mu = \sqrt{4 \times (4 + 2)} \), \( \mu = 4.90 \).

**Solution to problem 2-2**

a) \( x = \) centres of octahedral holes

![Diagram of octahedral holes](image)

b) \( 8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4 \) oxide ions per cube \( \Rightarrow \) 1 formula unit \( \text{CoAl}_2\text{O}_4 \) per cube

12 \( \times \frac{1}{4} + 1 = 4 \) octahedral holes for 2 \( \text{Al}^{3+} \) ions \( 50\% \)

8 tetrahedral holes for 1 \( \text{Co}^{2+} \) ion \( 12.5\% \)

c) Length of the edge of the unit cell = 912 pm \( \Rightarrow \) length of the cube = 456 pm

\[ V_{\text{cube}} = (4.56 \times 10^{-10} \text{m})^3 \]

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

\[ m = \frac{[(58.93 + 2 \times 26.98 + 4 \times 16.00)/N_A]}{g} \]

\[ \rho = \frac{m}{V} = \frac{176.89 \text{ g/mol}^{-1}}{6.022 \times 10^{23} \text{ mol}^{-1} \times (4.56 \times 10^{-10} \text{m})^3} = 3097904 \text{ g/m}^3 \]

\[ \rho = 3.1 \text{ g/cm}^3 \]

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

\[ 4 \times r(O^{2-}) = \text{length of a diagonal of the plane} = 456 \times \sqrt{2} \text{ pm} \]
\[ r(O^{2-}) = 114 \cdot \sqrt{2} \text{ pm} = 161.22 \text{ pm} \]

length of the edge of the tetrahedron
\[ a = 2 \cdot r(O^{2-}) = 322.44 \text{ pm} \]
radius of the circumcircle of the tetrahedron
\[ r = a \cdot \frac{\sqrt{6}}{4} = 197.45 \text{ pm} \]

\[ r(M^{2+}) = r - r(O^{2-}) \]
\[ r(M^{2+}) = 36.23 \text{ pm} \]

\[ r(M'^{3+}) = \frac{\text{[edge length of the cube} - 2 \cdot r(O^{2-})]}{2} \]
\[ r(M'^{3+}) = \frac{[456 \text{ pm} - 322.44 \text{ pm}]}{2} \]
\[ r(M'^{3+}) = 66.78 \text{ pm} \]

e) \quad \text{Sn(II)Co(III)}_2\text{O}_4 \quad \text{and} \quad \text{Sn(IV)Co(II)}_2\text{O}_4

\( \text{Sn(0)Co(IV)}_2\text{O}_4 \) shows a very unfavourable oxidation state of Co, so this is an unlikely possibility.

f) \quad \text{Sn(II)Co(III)}_2\text{O}_4:
\[ \text{Sn:0 unpaired electrons} \]
\[ \text{Co:} \]
\[ 0 \text{ unpaired electrons in case of low-spin octahedron}, \]
\[ 4 \text{ unpaired electrons in case of high-spin octahedron}, \]
\[ 2 \text{ unpaired electrons in case of low-spin tetrahedron}, \]
\[ 4 \text{ unpaired electrons in case of high-spin tetrahedron}, \]
\[ \text{thus: 0, (6,) 8 possible} \]
\[ (6 \text{ drops out as for the same ligand the octahedron splitting is far larger than the tetrahedron splitting and thus the coexistence of high-spin octahedron and low-spin tetrahedron is impossible}) \]

\text{Sn(IV)Co(II)}_2\text{O}_4:
\[ \text{Sn:0 unpaired electrons} \]
\[ \text{Co:} \]
\[ 1 \text{ unpaired electron in case of low-spin octahedron}, \]
\[ 3 \text{ unpaired electrons in case of high-spin octahedron}, \]
\[ 3 \text{ unpaired electrons in case of tetrahedron (you cannot distinguish between high- and low-spin because the number of unpaired electrons is equal)}, \]
\[ \text{thus: 2, 4, 6 possible} \]

g) \quad 43.9 \% \text{ O:} \quad 43.9 / 16 = 2.74375 \\
\quad 18.5 \% \text{ Al:} \quad 18.5 / 26.98 = 0.68569 \quad \text{37.6 \% remainder} \\
\Rightarrow \quad n(\text{Al}) : n(\text{O}) = 1 : 4 \quad \text{compound MM'}\text{AlO}_{4} \\
\quad 37.6 \% \text{ (M + M')} \\
\quad \text{for the sum x of the atom masses of M and M' you find} \\
\quad 18.5 / 26.98 = 37.6 \text{ g} \cdot \text{mol}^{-1} / x \quad x = 54.84 \text{ g} \cdot \text{mol}^{-1} \]
### Answers Round 2

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

\[ X = \text{LiTiAlO}_4 \]

h) \[ E = E^° + \frac{R \cdot T}{n \cdot F} \ln \frac{C_{\text{Ox}}}{C_{\text{Red}}} \]

From the image: equivalence point at 11
at \( V = 5.5 \) is \( c_{\text{Ox}} = c_{\text{Red}} \) and thus \( E = E^° \Rightarrow E^° = 0.77 \ V = E^°(Fe^{2+}/Fe^{3+}) \)
As the function is rising, \( c_{\text{Ox}} \) is rising during the titration, so in the original solution you find \( Fe^{2+} \).

If \( \ln(c_{\text{Ox}}/c_{\text{Red}}) = 1 \) then \( c_{\text{Ox}}/c_{\text{Red}} = e \) and you can calculate \( n \):
\[ \frac{c_{\text{Ox}}}{c_{\text{Red}}} = \frac{V}{(11 \ \text{mL} - V)} \quad V = e \cdot (11 \ \text{mL} - V) \quad \text{V} = 8.04 \ \text{mL} \approx 8 \ \text{mL} \]
\[ E(V=8 \ \text{mL}) = 0.79 \ \text{V} \]
\[ 0.79 \ V = 0.77V + \frac{(8.314 \cdot 298 \ \text{Jmol}^{-1})}{(96485 \ \text{C} \cdot \text{mol}^{-1})} \Rightarrow \text{V} = 1.28 \]
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.

\[ 2 \text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_4 \]

\[ \Delta H = (9160 - 2 \times 33200) \text{Jmol}^{-1} = -57240 \text{Jmol}^{-1} \]

\[ \Delta S = (304.3 - 2 \times 240.1) \text{JK}^{-1}\text{mol}^{-1} = -175.9 \text{JK}^{-1}\text{mol}^{-1} \]

\[ \Delta G = (-57240 + 300 \times 175.9) \text{Jmol}^{-1} = -4470 \text{kJmol}^{-1} \]

\[ \ln K = -\Delta G/RT \]

\[ \ln K = 4470/8.314 \times 300 \quad K = 6.00 \]

This K is dimensionless and stands for the term

\[ K = \frac{p(\text{N}_2\text{O}_4)/p_{\text{standard}}}{p^2(\text{NO}_2)/p_{\text{standard}}^2} \]

\[ Kp = K/p_{\text{standard}} \quad Kp = 6.00 \times 10^{-5} \text{Pa}^{-1} \]

(Standard pressure \( p_0 = 1.0000 \times 10^5 \text{ Pa set by IUPAC} \)

You may start your calculation of the equilibrium with any composition of the mixture of NO\(_2\) and N\(_2\)O\(_4\), e.g. you can assume that only NO\(_2\) exists in the beginning: \( n(\text{NO}_2) = 64 \times 46 \times 10^{-3} \text{ gmol}^{-1} = 1.40 \text{ mol} \)

\[ 2 \text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_4 \]

Amount of substance in equilibrium: \((1.40 - 2x)\text{mol} \quad x \text{ mol} \)

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

partial pressures in equilibrium:

\[ p(\text{NO}_2) = (n(\text{NO}_2)/n_{\text{total}}) \cdot p_{\text{total}} \]

\[ p(\text{N}_2\text{O}_4) = (n(\text{N}_2\text{O}_4)/n_{\text{total}}) \cdot p_{\text{total}} \]

\[ Kp = \frac{p(\text{N}_2\text{O}_4)}{p^2(\text{NO}_2)} \]

\[ 6.00 \times 10^{-5} \text{Pa}^{-1} = \frac{n(\text{N}_2\text{O}_4) \cdot n_{\text{total}}}{n^2(\text{NO}_2) \cdot p_{\text{total}}} \quad \text{and} \quad p_{\text{total}} = n_{\text{total}} \times R \times T/V \]

\[ 6.00 \times 10^{-5} = \frac{x(1.40-x)}{15 \times 10^{-3}} \frac{15 \times 10^{-3}}{(1.40-2x)^2} \]

\[ x^2 + x \cdot \frac{1}{2} (-5.6 - 15/18.8 \times 314)) + \frac{1}{4} \cdot 1.4^2 = 0 \]

\[ x_1 = 0.846 \quad (\text{not relevant because of } 1.40 - 2x < 0) \]

\[ x_2 = 0.579 \]

\[ n(\text{N}_2\text{O}_4) = 0.579 \text{ mol} \quad n(\text{NO}_2) = 0.241 \text{ mol} \quad n_{\text{total}} = 0.821 \text{ mol} \]

\[ p_{\text{total}} = (0.821 \times 8.314 \times 300 / 15 \times 10^{-3}) \text{ Pa} = 136.516 \text{ Pa} \quad p_{\text{total}} \approx 1.37 \text{ bar} \]

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:
\[ p_{\text{gesamt}} = p_0 \cdot \text{total} \cdot e^{kt} \text{ with } k = 0.001 \text{ s}^{-1} \]

**Determination of the equilibrium constant:**

\[ \Delta H = \Delta H_{\text{products}} - \Delta H_{\text{reactants}} + (C_{p\text{products}} - C_{p\text{reactants}}) \cdot \Delta T \]

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

\[ \Delta S = \Delta S_{\text{products}} - \Delta S_{\text{reactants}} + (C_{p\text{products}} - C_{p\text{reactants}}) \cdot \ln(T_2/T_1) \]

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

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

\[ \ln K = -\frac{4310}{(8.314 \cdot 350)} \quad K = 0.227 \quad K_p = 2.27 \cdot 10^{-6} \text{ Pa}^{-1} \]

\[ K_p = \frac{p(N_2O_4)}{p^2(NO_2)} \text{ and } p(N_2O_4) + p(NO_2) = p_{\text{total}} \text{ with } p_{\text{total}} = p_0 \cdot \text{total} \cdot e^{-0.001/s \cdot t} \]

\[ p(N_2O_4) + p(NO_2) = p_{\text{gesamt}} \cdot e^{-0.001/s \cdot t} \]

\[ K_p = \frac{3.00 \cdot 10^5 \text{Pa} \cdot e^{-0.001 s^{-1} \cdot t} - p(NO_2)}{p^2(NO_2)} \]

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

\[ p(NO_2) = \frac{-1}{2 \cdot K_p} + \sqrt{\frac{1}{4 \cdot K_p^2} + \frac{3.00 \cdot 10^5 \text{Pa} \cdot e^{-0.001 s^{-1} t}}{K_p}} \]

or

\[ p(NO_2) = [-220 \cdot 10^3 \pm \sqrt{4.85 \cdot 10^{10} + 1.32 \cdot 10^{11} \cdot e^{-0.001 s^{-1} t}}] \text{ Pa} \]
c) Molar fraction \( x = \frac{p(\text{NO}_2)}{p_{\text{total}}} \)

\[
(1) \quad x = \left( -\frac{1}{2K_p} + \frac{1}{4K_p^2} \frac{3.00 \times 10^5 \text{Pa} \cdot e^{-0.001 \text{ s}^{-1} \cdot t}}{K_p} \right) / (3.00 \times 10^5 \text{ Pa} \cdot e^{0.001 \text{ s}^{-1} \cdot t})
\]

or \( K_p = 2.27 \times 10^{-6} \text{ Pa}^{-1} \) inserted and rounded with three significant figures:

\[
(2) \quad x = \frac{-0.734 + \sqrt{0.539 + 1.47 \cdot e^{-0.001 \text{ s}^{-1} \cdot t}}}{e^{-0.001 \text{ s}^{-1} \cdot t}}
\]

(Function (1) reacts very sensitive on rounding. The graphs of (1) and (2) hardly differ in the time interval asked for but already at \( t > 4000 \text{ s} \) 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):

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

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.

\[ n(\text{C}) : n(\text{H}) = 5:4 \]

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:

\[
\begin{align*}
\text{N} & \text{NO}_2 \text{NO}_2 \\
\text{Cl} & \text{Cl}^{-} + 2(\text{CH}_3)_2\text{NH} \\
\text{N} & \text{Cl}^{-} (\text{CH}_3)_2\text{NH}
\end{align*}
\]

A

\[
\begin{align*}
+ \text{\text{C}} & \text{Cl} \text{NO}_2 \\
\text{S}_2\text{Ar} & \text{Cl}^{-} + 2(\text{CH}_3)_2\text{NH}
\end{align*}
\]

B

\[
\begin{align*}
\text{C} & \text{Azulene} \\
\text{D} & \text{Pyridine is used as C5 module which can be condensed with cyclopentadiene to form azulene. In a first step pyridine is transferred into a reactive pyridinium salt by reaction with 2,4-dinitrochlorobenzene (nucleophilic substitution).}
\end{align*}
\]
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)

\[
\text{Thermodynamisch stabileres Produkt, für Weiterreaktion aber unerheblich}
\]

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 dimethylamine (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 \( \text{C} \) as shown above.

d)  

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

Triplet is due to the coupling of an \(^1\text{H}\) 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 \( \text{D} \) 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 electrophilic 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 \( \text{I} \)

![Pair of Enantiomers](image1)

![Meso Compound](image2)

**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 \( \text{I} \).

There exist three stereoisomers of \( \text{I} \) according to the position of the remaining two double bonds: a pair of enantiomers and a meso compound.

**Structure of \( \text{J} \)**

![Structure of J](image3)
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) $\text{Ca} + 2 \text{H}_2\text{O} \rightarrow \text{Ca}^{2+} + 2 \text{OH}^- + \text{H}_2$
$2 \text{K} + 2 \text{H}_2\text{O} \rightarrow 2 \text{K}^+ + 2 \text{OH}^- + \text{H}_2$
b) $2 \text{Al} + 6 \text{H}_3\text{O}^+ \rightarrow 2 \text{Al}^{3+} + 6 \text{H}_2\text{O} + 3 \text{H}_2$
$\text{Zn} + 2 \text{H}_2\text{O}^+ \rightarrow \text{Zn}^{2+} + 2 \text{H}_2\text{O} + \text{H}_2$
$\text{Fe} + 2 \text{H}_3\text{O}^+ \rightarrow \text{Fe}^{2+} + 2 \text{H}_2\text{O} + \text{H}_2$
c) $2 \text{Al} + 6 \text{H}_2\text{O} + 2 \text{OH}^- \rightarrow 2 [\text{Al(OH)}_4]^- + 3 \text{H}_2$
$\text{Zn} + 2 \text{H}_2\text{O} + 2 \text{OH}^- \rightarrow [\text{Zn(OH)}_4]^{2-} + \text{H}_2$
d) $3 \text{Ag} + \text{HNO}_3 + 3 \text{H}_3\text{O}^+ \rightarrow 3 \text{Ag}^+ + \text{NO} + 5 \text{H}_2\text{O}$
$3 \text{Cu} + 2 \text{HNO}_3 + 6 \text{H}_2\text{O}^+ \rightarrow 3 \text{Cu}^{2+} + 2 \text{NO} + 10 \text{H}_2\text{O}$
e) $n(\text{Me}) = n(\text{Cu}) = n(\text{Pb})$
$\text{Me} + \text{Pb}^{2+} \rightarrow \text{Me}^{2+} + \text{Pb}$
$\text{Me} + \text{Cu}^{2+} \rightarrow \text{Me}^{2+} + \text{Cu}$
$100 \text{g} - n \cdot x + n \cdot 207.2 \text{g/mol} = 119 \text{g}$
$100 \text{g} - n \cdot x + n \cdot 63.55 \text{g/mol} = 90.2 \text{g}$
$9.8 \text{g} + n \cdot 63.55 \text{g/mol} = -19 \text{g} + n \cdot 207.2 \text{g/mol}$
$n = 0.2 \text{mol}$
$x = M(\text{Me}) = 112.4 \text{g/mol}$
$\text{Me} = \text{Cadmium}$

Solution to problem 3-3
a) $n_{\text{total}} = \rho \cdot \text{V} \cdot \text{R} \cdot \text{T}$
$n_{\text{total}} = 71800 \cdot 100 \cdot 10^{-6}/(8.314 \cdot 298)$
$n_{\text{total}} = 2.90 \cdot 10^{-3} \text{mol}$
$M_1 = \text{M(C}_{21}\text{H}_{33}\text{O}_{5}\text{N}) = 369.45 \text{g/mol}$
$M_2 = \text{M(C}_{12}\text{H}_{22}\text{O}_{11}) = 342.34 \text{g/mol}$
$n = m/M$
$n_1 + n_2 = n_{\text{total}}$
$m_1 + m_2 = 1 \text{g}$
$(1 - m_2)/M_1 + m_2/M_2 = 2.90 \cdot 10^{-3} \text{mol}$
$m_2 = 0.902 \text{g (90.2 %)}$
$m_1 = 0.098 \text{g (9.8 %)}$
b) Together with the sample water is brought into the solution. Cristallisation takes water out of the solution.
$M(\text{CaCl}_2) = 110.98 \text{g/mol}$
$M(\text{CaCl}_2 \cdot 6 \text{H}_2\text{O}) = 219.1 \text{g/mol}$
In 74.9 g CaCl$_2$ 6 H$_2$O (residue) are
$74.9 \text{g} \cdot 110.98/219.1 = 37.94 \text{g CaCl}_2$
total mass - mass of residue = mass of the saturated solution
230.00 g - 74.90 g = 155.10 g

x = mass of CaCl₂  
y = mass of H₂O 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 CaCl₂ (0.939 mol) and
150 g - 104.16 g = 45.84 g H₂O (2.54 mol)  \Rightarrow \approx 2.7 \text{ mol } H₂O \text{ per } 1 \text{ mol } CaCl₂

Solution to problem 3-4

a)  
c(Ac⁻) = c₀(HAc)·α.  
c(Ac⁻) = c(H₃O⁺)  
\[K_a = \frac{(c_0 \cdot \alpha)^2}{c_0(1 - \alpha) \cdot \text{mol/L}}\]

\[1.74 \cdot 10^{-5} = \frac{c_0 \cdot 0.1^2}{0.9 \cdot \text{mol/L}}\]

\[c_0 = 1.566 \cdot 10^{-3} \text{ mol/L}\]

c(Ac⁻) = c(H₃O⁺) = 1.566 · 10⁻⁴ 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(\text{NaOH})) = -14 + pH = -1.82

c(\text{NaOH}) = 0.015 \text{ mol/L}.

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

\[c(\text{HCl}) = \frac{20 \cdot 0.015 \text{ mol/L}}{15} = 0.02 \text{ mol/L}\]

consumption for the titration of Pr⁻ = 15 mL HCl

\Rightarrow c(\text{NaPr in the parent solution}) = 0.015 \text{ mol/L}

M(\text{NaC₂H₅COO}) = 96.09 g/mol  
m(\text{NaPr}) = 0.25 \cdot 96.09 \cdot 0.015 g = 0.360 g

Solution to problem 3-5

a)  
\[K'_p = \frac{p^2(\text{H}_2) \cdot p(\text{O}_2)}{p^2(\text{H}_2\text{O})} = \frac{(p \cdot \alpha_1)^2}{p^2 \cdot (1 - \alpha_1)^2}\]

\[K'_p = 7.63 \cdot 10^{-21} \cdot p\]

2 HCl \rightarrow H₂ + Cl₂

\[K''_p = \frac{(0.5 \cdot \alpha_2)^2}{(1 - \alpha_2)^2} = 3.03 \cdot 10^{11}\]

4 HCl + O₂ \rightarrow 2 Cl₂ + 2 H₂O

\[K_p = \frac{p^2(\text{H}_2\text{O}) \cdot p^2(\text{Cl}_2)}{p(\text{O}_2) \cdot p^4(\text{HCl})}\]

\[K_p = \frac{K'_p \cdot K''_p}{K'_p \cdot K''_p} = K'_p \cdot K''_p = 0.12 \cdot p^{-1}\]

\[K = K'_p \cdot p_0\]

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

\[
\begin{align*}
\text{CCl}_4 & & \text{TeCl}_4 \\
\text{(more stable)} & & \text{(more stable)} \\
\text{XeF}_4 & & \\
\end{align*}
\]

c)  

\[
\begin{align*}
\text{BeCl}_2 & & \text{SnCl}_2 & & \text{H}_2\text{S} \\
\text{Cl} \quad \text{Be} \quad \text{Cl} & & \text{Sn} & & \text{S} \quad \text{H} \\
\text{angle} = 180^\circ & & \text{angle} \leq 120^\circ & & \text{angle} \leq 109.5^\circ \\
\end{align*}
\]
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 down-
wards 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) NH₃/PH₃ (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.
PH₃/PF₃ (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 PH₃), the binding electrons at P can not be pushed away as easily.

Solution to problem 3-7
a) BBr₃ + PBr₃ + 3 H₂ ➔ 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
\[
\rho = \frac{m}{V} \quad \text{where} \quad m = 4 \cdot M(BP)/N_A \quad V = (4.78 \text{ Å})^3
\]
\[
\rho = \frac{4.4178 \cdot 10^{-3} \text{ kg/mol}}{6.022 \cdot 10^{23} \text{ mol}^{-1} \cdot (4.78 \cdot 10^{-10} \text{ m})^3} \quad \rho = 2541 \text{ kg/m}^3
\]

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 \( r_{\text{circumcircle}} \) of the tetrahedron, the basic edge of the tetrahedron is equal to half of the plane diagonal of the elementary unit.
\[
a/2 = 4.78 \text{ Å} \cdot \sqrt{2}/2 \quad \text{distance B-P} = 4.78 \text{ Å} \cdot \sqrt{3}/4 \quad \text{distance B-P} = 2.070 \text{ Å}
\]

f) \( U_{\text{lattice}} = - \frac{3.3 \cdot 1.638 \cdot 1390}{2.070} \left( \frac{1}{7} - \frac{1}{7} \right) \text{ J/mol} \)

\( U_{\text{lattice}} = - 8485 \text{ kJ/mol} \)

g) \( r = k \cdot c(BBr_3)^n \cdot c(PBr_3)^m \cdot c(H_2)^p \)
From the data given: \( n = 1, \quad m = 1, \quad p = 0 \)
\( k_{880} = 4.60 \cdot 10^8/(2.25 \cdot 10^{-6} \cdot 9 \cdot 10^{-6}) \)

\( r = k \cdot c(BBr_3) \cdot c(PBr_3) \)
overall order = 2
\( k_{880} = 2272 \text{ (mol/L)}^{-1} \text{s}^{-1} \)
\( k_{880} = 9679 \text{ (mol/L)}^{-1} \text{s}^{-1} \)

h) \( k = A \cdot e^{E_a/(R \cdot T)} \ln(k_{880}/k_{880}) = - E_a/(R \cdot 1073 \text{ K}) + E_a/(R \cdot 1153 \text{ K}) \)
\( E_\Delta = R \cdot \ln(k_{880}/k_{880})/(1/1153 - 1/1073) \)

\( E_\Delta = 186 \text{ kJ/mol} \)
Solution to problem 3-8

a) \[ n \text{ (C)} : n \text{ (H)} : n \text{ (O)} = \frac{65.2}{12.01} : \frac{8.75}{1.007} : \frac{26.05}{16} \]
\[ n \text{ (C)} : n \text{ (H)} : n \text{ (O)} = 5.43 : 8.69 : 1.63 = 3.33 : 5.33 : 1 = 10 : 16 : 3 \]
\[ M \text{ (C}_{10}\text{H}_{16}\text{O}_{3}) = 184.13 \text{ g/mol} \]
\[ \Rightarrow X = \text{C}_{10}\text{H}_{16}\text{O}_{3}. \]

Assumption: one COOH-group is responsible for the acidity.

Titration shows: amount of acid groups \( n = 0.237 \text{ mmol} \)
\[ \Rightarrow M = 184 \text{ g/mol}. \]
Just 1 COOH-group in \( X \).
\[ \text{DBE} = \frac{2a+2-b}{2} = 3 \]
\( X \) 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 (\(-\text{C}=\text{O}\)).

c) 
\[ \text{C } \xrightarrow{\text{ ozonolysis }} \xrightarrow{\text{ oxidation }} \text{CH}_{3}\text{--COOH + } \]
\[ \text{HO} \text{(CH}_{2}\text{)}_{6} \text{--COOH} \]

Compound C: \( \text{CH}_{3} \text{ - CH = CH - (CH}_{2}\text{)}_{6} \text{ - COOH} \)

If you get oxalic acid from the ozonolysis of \( X \) then \( X \) must have the structure
\[ R_{1} \text{ - HC = CH - COOH} \]
\[ \Rightarrow \]
\[ \text{H}_{3}\text{C--(CH}_{2}\text{)}_{5}\text{--C=C--CH--OH} \xrightarrow{\text{H}_{2}\text{(Pt)}} \text{H}_{3}\text{C--(CH}_{2}\text{)}_{7}\text{--C=C--OH} \]

69
d) **Z,E- isomerism**

\[ \text{Z-compound (cis)} \]

\[ \text{E-compound (trans)} \]

**Solution to problem 3-9**

\[ \text{Reduction i.e., Zn/HCl} \]

\[ \text{NaNO}_2 / \text{HCl} \quad T < 5^\circ C \]

\[ \text{Cu(CN)}^- \text{-N}_2 \]

\[ \text{H}^+ / \text{H}_2\text{O} \]

Another possibility:

\[ \text{RN}^+ \xrightarrow{\text{CuBr}} \text{RBr} \xrightarrow{\text{Mg}} \text{RMgBr} \xrightarrow{\text{CO}_2} \text{RCOOMgBr} \xrightarrow{\text{H}^+} \text{RCOOH} \]
Solution to problem 3-10

a) \(2^3 = 8\)

b) Stereoisomers

\[
\begin{align*}
\text{Br} & \quad \text{Cl} \quad \text{Cl} \\
\text{Cl} & \quad \text{Cl} \quad \text{Cl} \\
\text{Br} & \quad \text{Cl} \quad \text{Cl} \quad \text{Cl}
\end{align*}
\]

meso-compound (optically inactive)

\[
\begin{align*}
\text{Br} & \quad \text{Cl} \quad \text{Cl} \\
\text{Cl} & \quad \text{Cl} \quad \text{Cl} \\
\text{Br} & \quad \text{Cl} \quad \text{Cl} \quad \text{Cl}
\end{align*}
\]

meso-compound (optically inactive)

\[
\begin{align*}
\text{Br} & \quad \text{Cl} \quad \text{a} \\
\text{Cl} & \quad \text{a} \quad \text{Cl} \\
\text{Br} & \quad \text{Cl} \quad \text{a} \quad \text{Cl}
\end{align*}
\]

enantiomers (optically active)

\[
\begin{align*}
\text{Br} & \quad \text{Cl} \quad \text{a} \\
\text{Cl} & \quad \text{a} \quad \text{Cl} \\
\text{Br} & \quad \text{Cl} \quad \text{a} \quad \text{Cl}
\end{align*}
\]

enantiomers (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) \[ m = m(\text{H}_3\text{Cit in 6 tablets})/6 = n_0 (\text{H}_3\text{Cit in 6 tablets}) \cdot M(\text{H}_3\text{Cit})/6 \]
   \[ c_0(\text{H}_3\text{Cit}) = n_0 (\text{H}_3\text{Cit in 6 tablets})/L \]  \[ M(\text{H}_3\text{Cit}) = 192.14 \text{ g/mol} \]
   \[ K_{a1. \text{citric acid}} = \frac{c(\text{H}_2\text{Cit}^-) \cdot c(\text{H}_3\text{O}^+)}{c(\text{H}_3\text{Cit})} \]
   \[ \text{with} \quad c(\text{H}_2\text{Cit}^-) = c(\text{H}_3\text{O}^+) \]
   \[ \text{and} \quad c(\text{H}_3\text{Cit}) = c_d(\text{H}_3\text{Cit}) - c(\text{H}_2\text{Cit}^-) \]
   \[ \Rightarrow \quad 7.1 \cdot 10^{-4} = \frac{10^{-8.4} \text{ mol/L}}{c_0(\text{H}_3\text{Cit}) - 10^{-4.2} \text{ mol/L}} \Rightarrow c_0(\text{H}_3\text{Cit}) = 6.87 \cdot 10^{-5} \text{ mol/L} \]
   \[ m = 6.87 \cdot 10^{-5} \cdot 192.12 \text{ g / 6 tablets} \]
   \[ m = 2.2 \cdot 10^{-3} \text{ g citric acid/tablet} \]

b) \[ m = c_d(\text{H}_3\text{Cit}) \cdot M(\text{H}_3\text{Cit})/6 \]
   \[ c_0(\text{H}_3\text{Cit}) = c_d(\text{H}_3\text{Cit}) + c(\text{H}_2\text{Cit}^-) + c(\text{H}^2\text{Cit}) \]
   \[ K_{a1. \text{citric acid}} = \frac{c(\text{H}_2\text{Cit}^-) \cdot c(\text{H}_3\text{O}^+)}{c(\text{H}_3\text{Cit})} = 7.1 \cdot 10^{-4} = \frac{c(\text{H}_2\text{Cit}^-) \cdot 10^{-4.2}}{c(\text{H}_3\text{Cit})} \]
   \[ K_{a2. \text{citric acid}} = \frac{c(\text{H}^2\text{Cit}) \cdot c(\text{H}_3\text{O}^+)}{c(\text{H}_3\text{Cit})} = 1.68 \cdot 10^{-5} = \frac{c(\text{H}^2\text{Cit}) \cdot 10^{-4.2}}{c(\text{H}_3\text{Cit})} \]
   \[ c(\text{H}_3\text{O}^+) = c(\text{H}_2\text{Cit}^-) + 2 \cdot c(\text{H}^2\text{Cit}) \]
   \[ 10^{-4.2} \text{ mol/L} = c(\text{H}_2\text{Cit}^-) + 2 \cdot c(\text{H}^2\text{Cit}) \]

   \[ c(\text{H}_3\text{O}^+) = c_0(\text{H}_3\text{Cit}) - n(\text{H}_2\text{Cit}^-) \]

   \[ c_0(\text{H}_3\text{Cit in tea}) = 3 \cdot 10^{-3} \text{ g citric acid/tablet} \]
   \[ 3 \cdot 10^{-3} \text{ g} = c_0(\text{H}_3\text{Cit in tea}) \cdot 1 \text{ L} \cdot (192.14 \text{ g/mol})/6 \]  \[ c_0(\text{H}_3\text{Cit in tea}) = 9.37 \cdot 10^{-5} \text{ mol/L} \]

degree of protolysis in tea \[ \alpha_1 = c(\text{H}_2\text{Cit})/ c_0(\text{H}_3\text{Cit}) = 10^{-4.1}/9.37 \cdot 10^{-5} = 0.85 \]

degree of protolysis in the stomach
\[ V_1. \text{ before drinking} = 2.30 \text{ L} \]
\[ n_1(\text{H}_3\text{O}^+) = 2.3 \text{ L} \cdot 10^{-2.1} \text{ mol/L} \]
\[ V_2. \text{ after drinking} = 2.62 \text{ L} \]
\[ n_2(\text{H}_3\text{O}^+) = n_1(\text{H}_3\text{O}^+) \]
\[ c_2(\text{H}_3\text{O}^+) = \frac{2.3 \cdot 10^{-2.1} \text{ mol}}{2.62 \text{ L}} = 6.97 \cdot 10^{-3} \text{ mol/L} \]

This is the concentration of H$_3$O$^+$-ions, the degree of protolysis of citric acid has to be determined:
\[ c_0(\text{H}_3\text{Cit in the stomach}) = \frac{9.37 \cdot 10^{-5} \text{ mol/L} \cdot 0.32 \text{ L}}{2.62 \text{ L}} = 1.14 \cdot 10^{-5} \text{ mol/L} \]
K_{a1, citric acid} = \frac{c(H_2Cit^-) \cdot c(H_3O^+)}{c(H_2Cit)}

7.1 \cdot 10^{-4} = \frac{c(H_2Cit^-) \cdot 6.97 \cdot 10^{-3}}{1.14 \cdot 10^{-5} \text{ mol/L} - c(H_2Cit^-)} \quad \Rightarrow c(H_2Cit) = 1.05 \cdot 10^{-6} \text{ mol/L}

\alpha_2 = \frac{1.05 \cdot 10^{-6}}{1.14 \cdot 10^{-5}} \quad \alpha_2 = 9.21 \cdot 10^{-2}

\frac{\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 \quad \Rightarrow pK_a = 3.41
- following Cl with a -I and a smaller +M effect \quad \Rightarrow pK_a = 4.01
- most powerfull donator is OCH\_3 with a -I and a strong +M effect \quad \Rightarrow pK_a = 4.46
- following CH\_3 with a +I effect \quad \Rightarrow pK_a = 4.35
- without effects is H \quad \Rightarrow pK_a = 4.21

Solution to problem 3-13

a) \quad p \cdot V = n \cdot R \cdot T \quad n(B) = \frac{101300 \text{ Pa} \cdot 0.211 \cdot 10^{-3} \text{ m}^3}{8.314 \text{ JK}^{-1} \text{ mol}^{-1} \cdot 298 \text{ K}} = 8.63 \cdot 10^{-3} \text{ mol}

\quad M = m/n \quad M(B) = 0.38 \text{ g} / 8.63 \cdot 10^{-3} \text{ mol} \quad M(B) \approx 44 \text{ g/mol}

\Rightarrow B = CO\_2

A = FeCO\_3 \quad B = CO\_2 \quad C = FeSO\_4 \quad D = Fe(OH)\_3 \quad E = FeCl\_3

Reactions:
\begin{align*}
2 \text{ H}_3\text{O}^+ + \text{ SO}_4^{2-} + \text{ FeCO}_3 & \rightarrow \text{ Fe}^{2+} + \text{ SO}_4^{2-} + 3 \text{ H}_2\text{O} + \text{ CO}_2 \\
5 \text{ Fe}^{2+} + \text{ MnO}_4^- + 8 \text{ H}_3\text{O}^+ & \rightarrow 5 \text{ Fe}^{3+} + \text{ Mn}^{2+} + 12 \text{ H}_2\text{O} \\
2 \text{ Fe}^{2+} + 3 \text{ H}_2\text{O}_2 + 2 \text{ H}_3\text{O}^+ & \rightarrow 2 \text{ Fe}^{3+} + 4 \text{ H}_2\text{O} \\
\text{ Fe}^{3+} + 3 \text{ OH}^- & \rightarrow \text{ Fe(OH)}_3 \\
\text{ Fe(OH)}_3 + 3 \text{ H}_3\text{O}^+ + 4 \text{ Cl}^- & \rightarrow \text{ FeCl}_4^- + 6 \text{ H}_2\text{O} \\
\text{ FeCl}_4^- + 3 \text{ SCN}^- & \rightarrow \text{ Fe(SCN)}_3 + 4 \text{ Cl}^- \\
\end{align*}

(instead of FeCl\_4^- and Fe(SCN)\_3 there are other possibilities)

b) weighed portion: \quad n(FeCO\_3) = 1g / 115.86 \text{ g mol}^{-1} = 8.631 \cdot 10^{-3} \text{ mol}

\quad titration: \quad \frac{1}{2} \cdot n(\text{Fe}^{2+}) = 5 \cdot n(\text{MnO}_4^-)

\quad n(\text{Fe}^{2+}) = 2 \cdot 5 \cdot 0.02 \text{ mol/L} \cdot 43.15 \cdot 10^{-3} \text{ L} = 8.631 \cdot 10^{-3} \text{ mol}

the total amount reacted
Solution to problem 3-14

a) \[ \text{Sn}^{2+} + 2 \text{Fe}^{3+} \rightarrow \text{Sn}^{4+} + 2 \text{Fe}^{2+} \quad \text{mit} \quad \Delta G^° \]
\[ \Delta G^° = -E° \cdot zF \quad \Delta G_1 = -2 \cdot F \cdot 0.154 \text{ V} \]
\[ \Delta G^° = 2 \Delta G_2 - \Delta G_1 \quad \Delta G^° = -1.234 \cdot 96485 \text{ J/mol} \quad \Delta G^° \approx -119 \text{ kJ/mol} \]

b) \[ \Delta G = - R \cdot T \cdot \ln K \quad \ln K = -\frac{(-119 \text{ kJ/mol})}{(8.314 \text{ JK}^{-1}\text{mol}^{-1} \cdot 298 \text{ K})} \]
\[ K = 7.23 \cdot 10^{20} \]

c) The cell consists of the calomel electrode (positive potential) and the half cell with the solution to be titrated. \( \Rightarrow \) voltage of the cell = \( E^{°}_\text{Kalomel} - E^{°}_\text{Lösung} \)
In the solution \( c(Sn^{4+})/c(Sn^{2+}) = 1/3 \)
\[ E^{°}_\text{solution} = 0.154 \text{ V} + \frac{8.314 \cdot 298}{2 \cdot 96485} \text{ V} \cdot \ln(1/3) \quad E^{°}_\text{solution} = 0.140 \text{ V} \]

\[ \text{voltage of the cell} = 0.242 \text{ V} - 0.140 \text{ V} = 0.102 \text{ V} \]

d) \[ \text{Voltage of the cell} = E^{°}_\text{calomel} - E(\text{Fe}^{3+}/\text{Fe}^{2+}) \]
\[ = 0.242 \text{ V} - (0.771 \text{ V} + \frac{R \cdot T}{F} \cdot \ln \frac{c(F^{3+})}{c(F^{2+})}) \quad (1) \]
\[ K = \frac{c(Sn^{4+}) \cdot c^2(Fe^{2+})}{c(Sn^{2+}) \cdot c^2(F^{3+})} \]
K at the equivalence point \( c(Sn^{4+}) = 0.5 \cdot c(F^{3+}) \) therefore \( 0.5 \cdot c(F^{3+}) = c(Sn^{2+}) \)
\[ \Rightarrow K = \frac{c^3(F^{2+})}{c^3(F^{3+})} \Rightarrow \frac{c(F^{3+})}{c(F^{2+})} = \frac{1}{K} \quad \text{inserted in (1)} \]
\[ \text{voltage of the cell} = 0.242 \text{ V} - (0.771 \text{ V} + \frac{R \cdot T}{F} \cdot \ln \frac{1}{\sqrt[3]{7.23 \cdot 10^{20}}}) = -0.118 \text{ V} \]

e) Beyond the equivalence point you use \( c(Fe^{3+})/c(Fe^{2+}) \) to calculate \( E^{°}_\text{solution} \)
\[ c(Fe^{3+})/c(Fe^{2+}) = \frac{1}{2} \quad E^{°}_\text{solution} = 0.771 \text{ V} + \frac{8.314 \cdot 298}{96485} \text{ V} \cdot \ln 0.5 = 0.753 \text{ V} \]

\[ \text{voltage of the cell} = 0.242 \text{ V} - 0.753 \text{ V} = -0.511 \text{ V} \]

Solution to problem 3-15

a) 43.5 mL OH\(^-\) solution \( \Rightarrow \) 2.175 mmol OH\(^-\) for 0.1 g X \( \Rightarrow \) \( M(X) = 46 \text{ g/mol} \)
\( \Rightarrow X = \text{HCOOH}, \text{ formic acid} \)

b) \( \text{HCOOH} \rightarrow \text{H}_2\text{O} + \text{CO} \quad \text{S = sulfuric acid, H}_2\text{SO}_4 \)
c) \( n_\text{r}(\text{CO}) = n_\text{i}(\text{HCOOH}) = \frac{p \cdot V}{R \cdot T} = \frac{101300 \cdot 41.5 \cdot 10^{-6}}{8314 \cdot 298} \) 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:

\[ k = \frac{1}{t} \ln \frac{c_0}{c} \]

with \( \frac{c_0}{c} = \frac{n_\text{i}(\text{HCOOH})}{n_\text{r}(\text{HCOOH})} = \frac{1.70 \cdot 10^{-3}}{170 \cdot 10^{-3} - n(\text{CO})} \)

<table>
<thead>
<tr>
<th>t (in s)</th>
<th>0</th>
<th>50</th>
<th>100</th>
<th>150</th>
<th>200</th>
<th>( \infty )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( n_\text{i} ) (in mol) \cdot 10^3</td>
<td>1.70</td>
<td>1.23</td>
<td>0.874</td>
<td>0.633</td>
<td>0.457</td>
<td>0</td>
</tr>
<tr>
<td>\ln(c_0/c)</td>
<td>0</td>
<td>0.324</td>
<td>0.665</td>
<td>0.988</td>
<td>1.31</td>
<td>-</td>
</tr>
<tr>
<td>k (in s^{-1}) \cdot 10^{-3}</td>
<td>-</td>
<td>6.48</td>
<td>6.65</td>
<td>6.59</td>
<td>6.55</td>
<td>-</td>
</tr>
</tbody>
</table>

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

e) Arrhenius equation

\[ k = A \cdot e^{\frac{E_a}{R \cdot T}} \Rightarrow \ln k = \ln A - \frac{E_a}{R \cdot T} \]

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

<table>
<thead>
<tr>
<th>( 1/T ) (in K^{-1}) \cdot 10^3</th>
<th>2.36</th>
<th>2.26</th>
<th>2.16</th>
<th>2.07</th>
<th>1.99</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \ln k )</td>
<td>8.20</td>
<td>9.46</td>
<td>10.7</td>
<td>11.7</td>
<td>12.8</td>
</tr>
</tbody>
</table>

reading off two points

(1.97/13) und (2.3/9)

\[ m = - \frac{E_a}{R} \]

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

\( E_a = 101 \) kJ/mol

Solution problem 3-16

a) \( I/I_0 = 98/100 \)

\[ A = 10^\log (100/98) = 0.00877 \quad A = \varepsilon \cdot c \cdot d \]

0.00877 = 10500 Lmol^{-1}cm^{-1} \cdot c_{\text{min}} \cdot 1 \text{ cm} \]

\( c_{\text{min}} = 8.352 \cdot 10^{-7} \) mol/L

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

1.6990 = 10500 Lmol^{-1}cm^{-1} \cdot c_{\text{max}} \cdot 1 \text{ cm} \]

\( c_{\text{max}} = 1.618 \cdot 10^{-4} \) mol/L
c) $A(x_M = 0.33) = 0$ (the complex does not absorb) $\Rightarrow 0.33 = c_M/c_M + c_L$

$d) x_M = 0 \Rightarrow c_M/(c_M + c_L) = 0 \quad \Rightarrow c_M = 0$

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 $A = 1$

$\Rightarrow \varepsilon_L/\varepsilon_M = A_L/A_M = 0.5/1$

$\varepsilon_M = 2\varepsilon_L$

Solution to problem 3-17

a) $\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3 \text{H}_2$

$\text{CO} + 2 \text{H}_2 \rightarrow \text{CH}_3\text{OH}$

b) $55.0 \text{ m}^3/\text{s}$ methane: $p = 250 \cdot 10^3 \text{ Pa}, \text{T} = 298 \text{ K}$

$n = \frac{250 \cdot 10^3 \text{ Pa} \cdot 55 \text{ m}^3}{8.314 \text{ JK}^{-1} \text{ mol}^{-1} \cdot 298 \text{ K}}$

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

$150.0 \text{ m}^3/\text{s}$ water vapor: $p = 200 \cdot 10^3 \text{ Pa}, \text{T} = 423 \text{ K}$

$n = \frac{200 \cdot 10^3 \text{ Pa} \cdot 150 \text{ m}^3}{8.314 \text{ JK}^{-1} \text{ mol}^{-1} \cdot 423 \text{ K}}$

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

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

in step A $5.55 \cdot 10^3 \text{ mol/s CO and 3} \cdot 5.55 \cdot 10^3 \text{ mol/s H}_2$ form

in step B $5.55 \cdot 10^3 \text{ mol/s CO and 2} \cdot 5.55 \cdot 10^3 \text{ mol/s H}_2$ are consumed

$\Rightarrow$ excess in step $\ominus$: $5.55 \cdot 10^3 \text{ mol/s hydrogen (H}_2\text{)}$

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

ii) stream $\ominus$ methanol: $5.55 \cdot 10^3 \text{ mol/s CH}_4 \Rightarrow 5.55 \cdot 10^3 \text{ mol/s CH}_3\text{OH}$

$\Rightarrow 177.9 \text{ kg/s CH}_3\text{OH} \Rightarrow 225 \text{ L/s}$

iii) stream $\odot$ hydrogen: $5.55 \cdot 10^3 \text{ mol/s H}_2$ at $25^\circ\text{C}$ and $101.3 \text{ kPa}$

$\Rightarrow 135.7 \text{ m}^3/\text{s H}_2 \Rightarrow 135.7 \cdot 10^3 \text{ L/s}$

d) $1500 \text{ mol/s CH}_4$ and $4500 \text{ mol/s H}_2$ flow in

$\Rightarrow$ after step 2 in stream $\ominus$: $1000 \text{ mol/s CH}_3\text{OH}, 500 \text{ mol/s CO and 2500 mol/s H}_2$

e) $p = p_{\text{total}}\cdot n_i/n_{\text{total}}$

$p_{\text{total}} = 10 \text{ MPa}$

$n_{\text{total}} = 4000 \text{ mol}$

$p(\text{CH}_3\text{OH}) = 10 \text{ MPa} \cdot (1000/4000) = 2.50 \text{ MPa}$

$p(\text{CO}) = 10 \text{ MPa} \cdot (500/4000) = 1.25 \text{ MPa}$

$p(\text{H}_2) = 10 \text{ MPa} \cdot (2500/4000) = 6.25 \text{ MPa}$
f) \[ K = 2.50 \cdot (0.1)^2 / (1.25 \cdot 6.25^2) \quad K = 5.12 \cdot 10^{-4} \]
read from the diagram \( T \approx 630 \text{ K} \) (\( \approx 360^\circ \text{C} \))

Solution to problem 3-18

a) Main products:

\[
\begin{align*}
\text{ortho:} & \quad \text{para:} \\
\begin{array}{c}
\text{CH}_3 \\
\text{NO}_2 \\
\text{CH}_3 \\
\text{NO}_2
\end{array} & \begin{array}{c}
\text{CH}_3 \\
\text{NO}_2
\end{array}
\end{align*}
\]

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 bond 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)
Answers round 3 test 2

reaction with Tollens reagent (detection of aldehydes)

\[
\text{(compound C)} + 2\left[\text{Ag} (\text{NH}_3)_2\right]^+ + 3 \text{OH}^- \rightarrow 2 \text{Ag}^+ + \text{R}^+ - \text{H}_2\text{O} + 2\text{NH}_3 + 2\text{H}_2\text{O}
\]

reaction mit 2,4 Dinitrophenylhydrazine (detection of ketons)

b) optical active compounds

compound A

compound B

compound C
c) [Chemical Reaction]

\[ \text{O}_3 \quad T < 0^\circ \text{C} \]

[Primary ozonide]

[Secondary ozonide]

compound C + compound D
Answers round 4

Solution to problem 4-1

a) \( I_t = I_0 \cdot e^{-\ln 2/t_{1/2}} \).

<table>
<thead>
<tr>
<th>nuclide</th>
<th>( I_t ) in Bq mL(^{-1} )</th>
<th>( I_t ) after dilution in Bq mL(^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( ^{71}\text{Zn} )</td>
<td>1.59 ( \cdot 10^2 )</td>
<td>0.064</td>
</tr>
<tr>
<td>( ^{67}\text{Ga} )</td>
<td>6.95 ( \cdot 10^7 )</td>
<td>2.78 ( \cdot 10^4 )</td>
</tr>
<tr>
<td>( ^{68}\text{Ge} )</td>
<td>7.00 ( \cdot 10^7 )</td>
<td>2.80 ( \cdot 10^4 )</td>
</tr>
</tbody>
</table>

b) \( ^{71}\text{Zn} \) \( \xrightarrow{\text{30}} \) \( ^{71}\text{Ga} + ^{0}\text{e} (+\gamma) \)
\( ^{67}\text{Ga} \) + \( ^{0}\text{e} \) \( \xrightarrow{\text{31}} ^{67}\text{Zn} (+\gamma) \)
\( ^{68}\text{Ge} \) + \( ^{0}\text{e} \) \( \xrightarrow{\text{32}} ^{68}\text{Ga} (+\gamma) \)

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

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

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

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

\( I_t = k \cdot z_t(\text{^{67}Ga}) \).

\( I_t \) = activity in Bq at time \( t \).

\( z_t = \) amount of atoms at time \( t \).

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

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

\( t = 9 \text{ h:} \quad I_9 = I_0 \cdot e^{-9 \cdot \ln 2/78.25} \quad I_9 = 1.006 \cdot 10^{6} \text{ Bq/mL} \)

\( I_{\text{blood}} = 165.6 \text{ Bq/mL} \)

factor of dilution \( I_9 / I_{\text{blood}} = 1.006 \cdot 10^{6} / 165.6 = 6075. \quad \Rightarrow \quad V_{\text{blood}} = 6.1 \text{ L} \)

Solution to problem 4-2

a) \( \text{CaCO}_3 \rightleftharpoons \text{CaO} + \text{CO}_2 \)

\( K_p = p(\text{CO}_2) \)

\( \Delta G = - R \cdot T \cdot \ln K \) \quad \text{mit} \quad K = K_p/p_0 \)

<table>
<thead>
<tr>
<th>( T ) in K</th>
<th>800</th>
<th>900</th>
<th>1000</th>
<th>1100</th>
<th>1200</th>
<th>1300</th>
</tr>
</thead>
<tbody>
<tr>
<td>( K_p ) in Pa</td>
<td>50</td>
<td>1000</td>
<td>11,200</td>
<td>80,000</td>
<td>405,000</td>
<td>1,610,000</td>
</tr>
<tr>
<td>( K )</td>
<td>( 5 \cdot 10^{-4} )</td>
<td>0.01</td>
<td>0.112</td>
<td>0.8</td>
<td>4.050</td>
<td>16.1</td>
</tr>
<tr>
<td>( \Delta G ) in kJ\text{ mol}^{-1}</td>
<td>50.6</td>
<td>34.5</td>
<td>18.2</td>
<td>2.04</td>
<td>-14.0</td>
<td>-30.0</td>
</tr>
</tbody>
</table>
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 ΔG = ΔH° - T·ΔS°.

Whether a straight line is formed you can prove by a plot or by calculation of the slopes:

<table>
<thead>
<tr>
<th>T in K</th>
<th>800</th>
<th>900</th>
<th>1000</th>
<th>1100</th>
<th>1200</th>
<th>1300</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔG in J mol⁻¹</td>
<td>50,600</td>
<td>34,500</td>
<td>18,200</td>
<td>2,040</td>
<td>-14,000</td>
<td>-30,000</td>
</tr>
<tr>
<td>m with (800/50,600)</td>
<td>-</td>
<td>-</td>
<td>-161.0</td>
<td>-162.0</td>
<td>-161.9</td>
<td>-161.5</td>
</tr>
</tbody>
</table>

\[
ΔG = (-0.162 \text{ K}^{-1} \cdot T + 180) \text{kJ mol}^{-1}
\]

\[
ΔS° = 162 \text{J K}^{-1} \cdot \text{mol}^{-1}
\]

\[
ΔH° = 180 \text{kJ mol}^{-1}
\]

prediction: ΔS° is positive because a gas forms and the number of particles increases, saying the disorder, i.e. entropy, increases.

c) reaction spontaneous \(\iff\) \(ΔG < 0 \text{kJ mol}^{-1}\)

\(-0.162 \text{ K}^{-1} \cdot T + 180 < 0\)

\(T > 180 \text{ K} / 0.162 = 1111 \text{ K}\) or 1110 K to be read from the plot

as of \(\sim 840°C\) the reaction is spontaneous.

Solution to problem 4-3

a) \(\text{Ag}^+ + \text{H}_2\text{O} \rightarrow \text{AgOH} + \text{H}^+\)

\(K_1 = 10^{-11.70}\)

\(\text{Pb}^{2+} + \text{H}_2\text{O} \rightarrow \text{PbOH}^+ + \text{H}^+\)

\(K_2 = 10^{-7.80}\)

Only the second equilibrium determines the value of pH as \(K_2 \gg K_1\) ist.

\[
\text{equilibrium conc. in mol L}^{-1}: \quad 0.10 - x \quad x \quad x
\]

\[
\frac{x^2}{0.10-x} = 10^{-7.80} \quad \Rightarrow \quad x = 3.98 \cdot 10^{-5} \quad \Rightarrow \quad \text{pH} = 4.40
\]

b) The concentration of Ag⁺ has to be determined in both half cells.

Half cell 1: After unifying both solutions it would be

\(c(\text{Ag}^+) = 0.025 \text{ mol L}^{-1}\), \(c(\text{Pb}^{2+}) = 0.050 \text{ mol L}^{-1}\), \(c(I^-) = 0.125 \text{ mol L}^{-1}\), \(c(\text{H}^+) = 0.10 \text{ mol L}^{-1}\)
The amount of I\(^-\) is equivalent to the amount of Ag\(^+\) and Pb\(^{2+}\), thus AgI and PbI\(_2\) will precipitate completely.

\[
\begin{align*}
\text{AgI} & \quad \text{Ag}^+ + \text{I}^- & K_{sp}(\text{AgI}) &= 1 \cdot 10^{-16} \\
\text{PbI}_2 & \quad \text{Pb}^{2+} + 2 \text{I}^- & K_{sp}(\text{PbI}_2) &= 1 \cdot 10^{-7.86}
\end{align*}
\]

[The formation of PbOH\(^+\) can be neglected because of c(H\(^+\)) = 0.10 mol\(\cdot\)L\(^{-1}\):

\[
\frac{c(\text{PbOH}^+)}{c(\text{Pb}^{2+})} = \frac{10^{-7.8}}{0.1} = 10^{-6.8} \Rightarrow c(\text{PbOH}^+) \ll c(\text{Pb}^{2+})
\]

As \(K_{sp}(\text{AgI}) \ll K_{sp}(\text{PbI}_2)\), only \(K_{sp}(\text{PbI}_2)\) determines the iodine concentration and thus the concentration of the silver ions.

\[
x \cdot (2x)^2 = 1 \cdot 10^{-7.86} \Rightarrow x = 1.51 \cdot 10^{-3} \quad c(\text{I}^-) = 3.02 \cdot 10^{-3} \text{ mol}\(\cdot\)L\(^{-1}\)
\]

\[
c(\text{Ag}^+) \cdot 3.02 \cdot 10^{-3} \text{ mol}\(\cdot\)L\(^{-1}\)^2 = 10^{-16} \quad c(\text{Ag}^+) = 3.31 \cdot 10^{-14} \text{ mol}\(\cdot\)L\(^{-1}\)
\]

**Potential of half cell 1 for Ag\(^+\) + e\(^-\) \rightarrow Ag:**

\[
E_1 = E^\circ(\text{Ag}^+/\text{Ag}) + \frac{R \cdot T}{F} \cdot \ln c(\text{Ag}^+) = 2 \cdot 10^{-3} \text{ V}
\]

**Half cell 2:** AgSCN precipitates:

\[
\begin{align*}
\text{Ag}^+ + \text{SCN}^- & \rightarrow \text{AgSCN} & K_{sp}(\text{AgSCN}) &= 10^{-12} \\
x \cdot (0.03 + x) &= 10^{-12} & x &= 3.33 \cdot 10^{-11} \quad c(\text{Ag}^+) = 3.33 \cdot 10^{-11} \text{ mol}\(\cdot\)L\(^{-1}\)
\end{align*}
\]

\[
E_2 = 0.179 \text{ V}
\]

\[
\Rightarrow \Delta E = E_{cell} = E_2 - E_1 \quad E_{cell} = 0.177 \text{ V}
\]

\[
c) \quad \text{Total cell reaction:} \quad \text{Ag} + \text{I}^- \rightarrow \text{AgI} + \text{e}^- \\
\text{AgSCN} + \text{e}^- \rightarrow \text{Ag} + \text{SCN}^- \\
\text{AgSCN} + \text{I}^- \rightarrow \text{AgI} + \text{SCN}^-
\]

\[
K = \frac{c(\text{SCN}^-) \cdot c(\text{Ag}^+)}{c(\text{I}^-) \cdot c(\text{Ag}^+)} = \frac{K_{sp}(\text{AgSCN})}{K_{sp}(\text{AgI})} = \frac{10^{-12}}{10^{-16}} = K = 10^4
\]

\[
d) \quad \text{Case 1: The amount of NaOH is so small that the acid is not neutralised. Then the formation of Pb(OH)^+ doesn't play a role further on, the concentrations of lead, iodine and silver stay constant, the voltage does not change.}
\]

\[
\text{Case 2: The amount of NaOH added is sufficient to neutralise the acid. Then Pb(OH)^+ is formed in a remarkable amount, c(Pb}^{2+}\text{) decreases , c(I}^-\text{) increases and c(Ag}^+\text{) decreases. Thus } E_1 \text{ decreases and the voltage increases}
\]

83
Answers round 4

e) Fe³⁺ + SCN⁻ → FeSCN²⁺ → Fe(SCN)²⁺

(c(SCN⁻) decreases, c(Ag⁺) increase and for this reason E₂ also. The voltage increases.

f) You have to calculate the standard potential E° of V²⁺ + 2 e⁻ → V

because standard potentials refer to a standard hydrogen cell with E° = 0 V.

ΔG° = - n·F·E°
n = 2

E° = ?

\[
\begin{align*}
V(OH)_4^+ & \xrightarrow{1.00} VO^{2+} \xrightarrow{0.337} V^{3+} \xrightarrow{-0.255} V^{2+} \xrightarrow{x} V \\
1.00 + 0.337 - 0.255 + 2 x &= 5(-0.25) \\
x &= -1.17 \\
E°(V^{2+}/V) &= -1.17 \text{ V}
\end{align*}
\]

ΔG° = - 2·96485·(-1.17) J

ΔG° = 226 kJ

Solution to 4-4

a) Steady state: \[ \frac{d([ES])}{dt} = 0 \]

\[ k_1·[E]·[S] - k_2·[ES] - k_3·[ES] = 0 \]

\[ [E] = [E]_{total} - [ES] \]

\[ k_1·([E]_{total} - [ES])·[S] = (k_2 + k_3)·[ES] \]

\[ k_1·[E]_{total}·[S] = (k_2 + k_3 + k_1·[S])·[ES] \]

\[ [ES] = \frac{k_1·[E]_{total}·[S]}{k_2 + k_3 + k_1·[S]} \]

\[ [ES]_{max} = [E]_{total} \quad \Rightarrow \quad v_{max} = k_3·[E]_{total} \]

b) \[ \frac{d([P])}{dt} = k_3·[ES] \]

\[ [ES]_{max} = [E]_{total} \quad \Rightarrow \quad v_{max} = k_3·[E]_{total} \]

c) \[ \frac{d([P])}{dt} = k_3·[ES] \]

with a): \[ [ES] = \frac{[E]_{total}·[S]}{K_M + [S]} \]

\[ v = k_3·\frac{[E]_{total}·[S]}{K_M + [S]} \]

with b): \[ k_3·[E]_{total} = v_{max} \]

\[ v = \frac{v_{max}·[S]}{K_M + [S]} \]

d) With c) \[ v = \frac{1}{2}·v_{max} \]

\[ K_M = [S] \]

read the value of [S] at \[ v = 1.5·10^{-6} \text{ mol L}^{-1} \text{ s}^{-1} \]
Answers round 4

\[ v_{\text{max}} = 3.0 \cdot 10^{-6} \text{ mol L}^{-1} \text{ s}^{-1} \]

\[ K_M = 0.5 \cdot 10^{-4} \text{ mol L}^{-1} \]

e) with c):

\[ v = \frac{v_{\text{max}} [S]}{K_M + [S]} \Rightarrow \frac{1}{v} = \frac{K_M + [S]}{v_{\text{max}} [S]} \Rightarrow \frac{1}{v} = \frac{K_M}{v_{\text{max}}} \cdot \frac{1}{[S]} + \frac{1}{v_{\text{max}}} \]

f)

<table>
<thead>
<tr>
<th>[S]_0 \cdot 10^6 \text{ in mol L}^{-1}</th>
<th>[S]^0 \cdot 10^5 \text{ in mol}^{-1} \text{ L}</th>
<th>v_0 \cdot 10^5 \text{ in mol L}^{-1} \text{ min}^{-1}</th>
<th>v_0^{-1} \text{ in mol}^{-1} \text{ L min}^{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>3.33 \cdot 10^5</td>
<td>1.06</td>
<td>9.43 \cdot 10^4</td>
</tr>
<tr>
<td>5</td>
<td>2.00 \cdot 10^5</td>
<td>1.55</td>
<td>6.45 \cdot 10^4</td>
</tr>
<tr>
<td>10</td>
<td>1.00 \cdot 10^5</td>
<td>2.37</td>
<td>4.22 \cdot 10^4</td>
</tr>
<tr>
<td>20</td>
<td>0.50 \cdot 10^5</td>
<td>3.21</td>
<td>3.12 \cdot 10^4</td>
</tr>
</tbody>
</table>

\[ \frac{1}{v} = \frac{K_M}{v_{\text{max}}} \cdot \frac{1}{[S]} + \frac{1}{v_{\text{max}}} \] (1)
**Answers round 4**

intersection \( 1/[S] = 0 \) \( \Rightarrow \) \( \frac{1}{v_{\text{max}}} = 2 \cdot 10^4 \text{ mol}^{-1} \text{ L min} \)

mit \( [E]_{\text{total}} = 1,0 \cdot 10^{-9} \text{ mol L}^{-1} \) \( \Rightarrow \) [with b)] \( k_3 = 5 \cdot 10^4 \text{ min}^{-1} \)

with equation (1) for the straight line \( K_M = 1.1 \cdot 10^{-5} \text{ mol/L} \)

g) \( f_{\text{ES}} = \frac{v_0}{v_{\text{max}}} = \frac{[S]_0}{K_M + [S]_0} \)

\[ f_{\text{ES}} = \frac{3 \cdot 10^{-5} \text{ mol L}^{-1}}{1.5 \cdot 10^{-5} \text{ mol L}^{-1} + 3 \cdot 10^{-5} \text{ mol L}^{-1}} \]

\[ f_{\text{ES}} = 0.67 \]

h) \( k_{\text{kat}} = k_3 \) from the equation given in b) \( v_{\text{max}} = k_3 [E]_{\text{total}} \)

\[ [E]_{\text{total}} = \frac{10^{-9} \text{ g}}{0.01 \text{ L}^{-1} \cdot 41977 \text{ g mol}^{-1}} = 2.38 \cdot 10^{-12} \text{ mol L}^{-1} \]

\[ k_{\text{kat}} = \frac{7.15 \cdot 10^{-11} \text{ mol L}^{-1} \cdot \text{min}^{-1}}{2.38 \cdot 10^{-12} \text{ mol L}^{-1}} = 30 \text{ min}^{-1} \]

\[ k_{\text{kat}} = 0.5 \text{ s}^{-1} \]

**Solution to problem 4-5**

a) \( 2 \text{ MnO}_4^- + 5 \text{ C}_2\text{O}_4^{2-} + 16 \text{ H}_3\text{O}^+ \longrightarrow 2 \text{ Mn}^{2+} + 10 \text{ CO}_2 + 24 \text{ H}_2\text{O} \)

\[ n(\text{C}_2\text{O}_4^{2-}) = \frac{0.1702 \text{ g}}{134.02 \text{ g mol}^{-1}} = 0.01702 \text{ g} \]

\[ n(\text{C}_2\text{O}_4^{2-}) = 1.27 \cdot 10^{-3} \text{ mol} \]

\[ 0.4 \cdot n(\text{C}_2\text{O}_4^{2-}) = n(\text{MnO}_4^-) \]

\[ c(\text{MnO}_4^-) = 0.4 \cdot 1.27 \cdot 10^{-3} \text{ mol } / 26.70 \cdot 10^{-3} \text{ L} \]

\[ c(\text{MnO}_4^-) = 0.019 \text{ mol L}^{-1} \]

b) \( \text{Fe} + 2 \text{ H}_3\text{O}^+ \longrightarrow \text{Fe}^{2+} + \text{ H}_2 + 2 \text{ H}_2\text{O} \)

\( \text{Fe}_2\text{O}_3 + 6 \text{ H}_2\text{O}^+ \longrightarrow 2 \text{ Fe}^{3+} + 9 \text{ H}_2\text{O} \)

\( 2 \text{ Fe}^{3+} + \text{ SO}_3^{2-} + 3 \text{ H}_2\text{O} \longrightarrow 2 \text{ Fe}^{2+} + \text{ SO}_4^{2-} + 2 \text{ H}_3\text{O}^+ \)

\( \text{SO}_3^{2-} + 2 \text{ H}_2\text{O}^+ \longrightarrow \text{SO}_2 + 3 \text{ H}_2\text{O} \)

\( \text{MnO}_4^- + 5 \text{ Fe}^{2+} + 8 \text{ H}_3\text{O}^+ \longrightarrow \text{Mn}^{2+} + 5 \text{ Fe}^{3+} + 12 \text{ H}_2\text{O} \)

\( n(\text{Fe}_{\text{total}}) = 5 \cdot n(\text{MnO}_4^-) = 5 \cdot 0.019 \text{ mol L}^{-1} \cdot 37.5 \cdot 10^{-3} \text{ L} = 3.56 \cdot 10^{-3} \text{ mol} \)

\( n(\text{Fe}_{\text{total}}) = n(\text{Fe}) + 2 \cdot n(\text{Fe}_2\text{O}_3) \)

\[ n(\text{Fe}) = 3.56 \cdot 10^{-3} \text{ mol } - 2 \cdot n(\text{Fe}_2\text{O}_3) \]

\( m_{\text{total}} = n(\text{Fe}) \cdot M(\text{Fe}) + n(\text{Fe}_2\text{O}_3) \cdot M(\text{Fe}_2\text{O}_3) \)

\[ 0.225 \text{ g} = [3.56 \cdot 10^{-3} \text{ mol } - 2 \cdot n(\text{Fe}_2\text{O}_3)] \cdot 55.85 \text{ g/mol} + n(\text{Fe}_2\text{O}_3) \cdot 159.7 \text{ g/mol} \]

\[ n(\text{Fe}_2\text{O}_3) = 5.45 \cdot 10^{-4} \text{ mol} \]

\[ m(\text{Fe}_2\text{O}_3) = 0.087 \text{ g} \]

\[ 38.7 \% \text{ Fe}_2\text{O}_3 \]

\[ 61.3 \% \text{ Fe} \]
c) \( c(\text{Ni}) = 1.70 \times 10^{-3} \) mol/L

no precipitate of \( \text{Ni(OH)}_2 \):
\[
c(\text{OH}) \leq \sqrt[2]{\frac{6 \times 10^{-16}}{1.7 \times 10^{-3}}} \text{ mol/L} = 5.94 \times 10^{-7} \text{ mol/L}
\]
\[\text{pH} \leq 7.7 \quad \text{(at 7.8} \, \text{Ni(OH)}_2 \text{precipitates)}\]
\[c(\text{Fe})_{\text{before precipitation}} = 1.25 \times 10^{-2} \text{ mol/L} \]
\[c(\text{Fe})_{\text{after precipitation}} \leq 1.25 \times 10^{-5} \text{ mol/L} \]

maximum concentration of the solution \( 1.25 \times 10^{-5} \) mol/L:
\[
c(\text{OH}) \geq \sqrt[2]{\frac{4 \times 10^{-38}}{1.25 \times 10^{-5}}} \text{ mol/L} = 1.47 \times 10^{-11} \text{ mol/L}
\]
\[\text{pH} \geq 3.2 \quad \text{(at 3.1 error > 0.1%)} \]

precipitation in the range \( 3.2 \leq \text{pH} \leq 7.7 \)

Solution to problem 4-6

a) \( 1.0 \times 10^6 \) molecules/cm\(^3\) = \( 1.0 \times 10^{12} \) molecules/m\(^3\)
\[
p \cdot V = n \cdot R \cdot T \quad \Rightarrow \quad p = \frac{10 \times 10^{12} \cdot 8.314 \cdot 1200}{6,022 \cdot 10^{23}} \text{ Pa} \quad p = 1.66 \times 10^8 \text{ Pa}
\]

b) \( p = \frac{F}{A} \quad F = m \cdot g \quad m = V \cdot \rho(\text{Hg}) \quad \Rightarrow \quad p = A \cdot h \cdot \rho(\text{Hg}) \cdot g \)
\[\text{e.g.} \quad A = 1 \text{ m}^2 \quad \Rightarrow \quad p = (1 \text{ m}^2 \cdot 10^{-12} \text{ m} \cdot 13.55 \cdot 10^3 \text{ kg/m}^3 \cdot 9.81 \text{ m/s}^2) / 1 \text{ m}^2
\]
\[p = 1.33 \times 10^{-7} \text{ N/m}^2 \quad \text{p = 1.33} \times 10^{-7} \text{ Pa}
\]
(or 1 mm Hg equals 1 Torr equals \( 1.013 \times 10^5 / 760 \) Pa ect.)

c) Analogous to a) \( 1.33 \times 10^{-7} \cdot 0.254 \times 10^{23} \) molecules/m\(^3\) = \( 3.23 \times 10^{13} \) molecules/m\(^3\)
\[= 3.23 \times 10^7 \text{ molecules/cm}^3, \text{ 32 times more than in the oxosphere.}
\]

d) \( \vec{v} = \sqrt{\frac{8 \cdot R \cdot T}{\pi \cdot M}} \quad \vec{v}_{1200} = \sqrt{\frac{8 \cdot 8.314 \text{JK}^{-1}\text{mol}^{-1} \cdot 1200 \text{K}}{\pi \cdot 1.008 \times 10^{-3} \text{kgmol}^{-1}}} \quad \vec{v}_{1200} \approx 5000 \text{ m/s}
\]
\[\vec{v}_{298} \approx 2500 \text{ m/s} \quad \vec{v}_{1200} : \vec{v}_{298} = 2 : 1
\]

e) \[
\begin{array}{c|c}
\text{Mean speed} \, \vec{v} & \text{Mean speed} \, \vec{v} \\
\hline
\vec{v}_1 = 2400 \text{ m/s} & \vec{v}_2 = \sqrt{\frac{8 \cdot 8.314 \text{JK}^{-1}\text{mol}^{-1} \cdot 2.7 \text{K}}{\pi \cdot 1.008 \times 10^{-3} \text{kgmol}^{-1}}} = 238 \text{ m/s}
\end{array}
\]
Answers round 4

<table>
<thead>
<tr>
<th>Volume of collision cylinder = ( \pi \cdot (1 \cdot 10^{-10} \text{m})^2 \cdot \sqrt{2} \cdot \bar{v} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( V_1 = \pi \cdot (1 \cdot 10^{-10} \text{m})^2 \cdot \sqrt{2} \cdot 2400 \text{ m/s} )</td>
</tr>
<tr>
<td>( V_1 = 1.066 \cdot 10^{-16} \text{ m}^3/\text{s} )</td>
</tr>
<tr>
<td>( V_2 = 1.057 \cdot 10^{-17} \text{ m}^3/\text{s} )</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Density of particles</th>
</tr>
</thead>
<tbody>
<tr>
<td>40 ( \cdot ) ( 10^{15} )/m³</td>
</tr>
<tr>
<td>1/m³</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Number of collisions/s = (volume of collision cylinder) • (density of particles)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( z_1 = 1.066 \cdot 10^{-16} \text{ m}^3/\text{s} \cdot 40 \cdot 10^{15}/\text{m}^3 )</td>
</tr>
<tr>
<td>( z_1 = 4.264 \text{ /s} )</td>
</tr>
<tr>
<td>( z_2 = 1.057 \cdot 10^{-17}/\text{s} )</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>mean time until first collision = ( 1/z )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \bar{t}_1 = 0.235 \text{ s} )</td>
</tr>
<tr>
<td>( \bar{t}_2 = 9.46 \cdot 10^{-16} \text{ s} \approx 3 \cdot 10^9 \text{ years} )</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>free path (_1 = 564 \text{ m} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>free path (_2 = 2.25 \cdot 10^{19} \text{ m} \approx 2400 \text{ light years} )</td>
</tr>
</tbody>
</table>

Solution to 4-7

a) \( K_{sp} = (8 \cdot 10^{-3} \text{ mol/L})^2 = 6.4 \cdot 10^{-5} \text{ (mol/L)}^2 \)

b) \( c(\text{Na}^+) = 0.130 \text{ mol/L} \implies c(\text{Ur}^-) = 6.4 \cdot 10^{-5} / 0.130 \text{ mol/L} = 4.9 \cdot 10^{-4} \text{ mol/L} \)

c) The lower the temperature the smaller \( K_{sp} \).


d) \( pH = pK + \log \frac{c(\text{Ur}^-)}{c(\text{HU}r)} \)
\( pH = 7.4 \implies 7.4 = 5.4 + \log \frac{c(\text{Ur}^-)}{c(\text{HU}r)} \) (1)

If NaUr does not precipitate then \( c(\text{Ur}^-) \leq 4.9 \cdot 10^{-4} \text{ mol/L} \) (see b) and with (1)

\( c(\text{HU}r) \leq 4.9 \cdot 10^{-6} \text{ mol/L} < \text{solubility of HUr in water.} \)

e) \( pH = 5.4 + \log \frac{c(\text{Ur}^-)}{c(\text{HU}r)} \)
\( c(\text{HU}r) + c(\text{Ur}^-) = 2 \cdot 10^{-3} \text{ mol/L} \)
\( c(\text{HU}r) \geq 0.5 \cdot 10^{-3} \text{ mol/L} \)

\( \implies pH \leq 5.4 + \log \frac{1.5 \cdot 10^{-3}}{0.5 \cdot 10^{-3}} \)

\( pH \leq 5.9 \)

f) \( t = 0 \text{ h} \) 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 \( t_{1/2} = 40 \text{ hours} \)
\( k = \ln 2 / t_{1/2} \)
\( k = 1.73 \cdot 10^{-2} \text{ h}^{-1} \)

\( P: \) half life \( t_{1/2} = 40 \text{ hours} \)
\( k = \ln 2 / t_{1/2} \)
\( k = 1.73 \cdot 10^{-2} \text{ h}^{-1} \)
Solution to Problem 4-8

a)

\[
\text{CH}_3\text{CH}_2\text{C} = \text{O} \rightleftharpoons \text{OH}^- \rightleftharpoons \text{CH}_3\text{CH}\text{C} = \text{O} + \text{H}_2\text{O} \rightleftharpoons \text{C}_2\text{H}_5\text{C} = \text{H}
\]

b) The base abstracts the hydroxyl proton to yield a \(\beta\)-keto alkoxide ion which fragments to give one molecule of enolate ion

\[
\text{RCH}_2\text{CHO} \rightleftharpoons \text{OH}^- \rightleftharpoons \text{RCHCHO} + \text{H}_2\text{O} \rightleftharpoons \text{RCH} = \text{CH} - \text{O}^-
\]

electrophilic reactant: \(\text{RCH}_2\text{CHO}\)

nucleophilic reactant: \(\text{RCH} = \text{CH} - \text{O}^-\)

The enolate ion (nucleophil) reacts with the C-atom of the carbonyl group (electrophil)

\[
\text{RCH}_2\text{CHO} + \text{RCH} = \text{CH} - \text{O}^- \rightarrow \text{RCH} = \text{CH} - \text{O}^- \text{RCH}_2\text{CHO}
\]

Precondition ketones or aldehydes with an \(\alpha\)-hydrogen atom

c) 1. \(\text{HCHO} + \text{CH}_3\text{CHO} \rightleftharpoons \text{OH}^- \rightleftharpoons \text{HCHO} + \text{CH}_2\text{CHO} \rightleftharpoons \text{H}^+ \rightleftharpoons \text{CH}_2\text{CH}_2\text{C} = \text{O} \rightleftharpoons \text{CH}_2\text{CH}_2\text{C} = \text{O}
\]
2. CH₃CHO $\xrightarrow{\text{OH}^-}$ CH₂CHO  $\xleftarrow{\text{H}^+}$ CH₃C=O

Formaldehyde contains no $\alpha$-H atom and thus cannot form an enolate ion to condense with itself.

d) Aldol reaction of acetaldehyde and 2,4-pentadione, favoured reaction:

\[
\text{CH}_3\text{CHO} + \text{H}_3\text{C-} \xrightarrow{\text{base}} \xrightarrow{\text{H}^+} \text{CH}_3\text{C}=\text{O}
\]

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

\[
\begin{align*}
\text{CH}_3\text{C}-\text{C} & \quad \text{H}_2 \quad \text{C} - \text{C} - \text{C} - \text{C} - \text{O} \\
\text{CH}_3\text{C} & \quad \text{CCH}_2 \quad \text{CH}_2\text{CH}_2\text{C} & \quad \text{CH}_3
\end{align*}
\]

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)

\[
\begin{align*}
\text{D-Glucose} & \quad \text{mirror} \quad \text{L-Glucose}
\end{align*}
\]

b) There are 4 stereogenic centres in L-glucose. D- and L-glucose are enantiomers.
Answers round 4

c) \(\alpha\)-D-Glucopyranose

\[\text{HO} \quad \text{HOH}_2\text{C} \quad \text{e} \quad \text{O} \]

\[\text{HO} \quad \text{e} \quad \text{e} \quad \text{OH} \quad \text{a} \quad \text{OH} \]

\(\beta\)-L-Glucopyranose

\[\text{OH} \quad \text{CH}_2\text{OH} \quad \text{OH} \quad \text{OH} \quad \text{OH} \]

\[\beta\)-D-glucopyranose

\[\text{HO} \quad \text{HOH}_2\text{C} \quad \text{e} \quad \text{O} \]

\[\text{HO} \quad \text{e} \quad \text{e} \quad \text{OH} \quad \text{a} \quad \text{OH} \]

\(\beta\)-L-Glucopyranose

\[\text{OH} \quad \text{CH}_2\text{OH} \quad \text{OH} \quad \text{OH} \quad \text{OH} \]

\[\text{Turning the chair}\]

\[\text{HO} \quad \text{HOH}_2\text{C} \quad \text{e} \quad \text{O} \]

\[\text{HO} \quad \text{e} \quad \text{e} \quad \text{OH} \quad \text{a} \quad \text{OH} \]

\(\beta\)-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) C₄H₈O₂.

b) Band at 1730 cm⁻¹ according to carbonyl compound or ester
   Band at ~2850 cm⁻¹ – 2930 cm⁻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 specific molecular motion, we can see what kind of molecular motions a sample has by measuring its infrared spectrum.

d) Proposal for a structure:
   \[
   \begin{align*}
   &\text{O} \\
   &\text{CH₃COCH₂}
   \end{align*}
   \]

**Asingments:**

There are three different peaks and peak groups respectively. That is there are three protons or proton groups with different surroundings:

- The singulet at \( \delta = 2.1 \text{ ppm} \) leads to an acetyl group (2.1 ppm – 2.4 ppm).
- The triplet at \( \delta = 1.3 \text{ ppm} \) indicates a CH₃ group adjacent to a CH₂ group.
- The quartet bei \( \delta = 4.1 \text{ ppm} \) is difficult to interprete.

( \( X \) \[ \phi \] \( \text{C} \) \[ \phi \] \( \text{H} \) \( ? \) \( X = \text{O} \) etc.)

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 CH₃ group, the triplet another CH₃ group and the quartet a CH₂ group.
Answers round 4

Couplings:

- The CH\textsubscript{3} group at the carbonyl hydrogen has no further hydrogen to couple with. That results to a singulet.
- The triplet at $\delta = 1.3$ ppm is caused by a terminal CH\textsubscript{3} group which couple with an adjacent CH\textsubscript{2} group.
- The quartet at $\delta = 4.1$ ppm arises from the coupling with the three H atoms of the CH\textsubscript{3} Gr..

The structure of A is $\text{CH}_3\text{COCH}_2$ (ethylacetate)
Answers round 4
Problems of the IChO

Chemistry for Life,
Chemistry for better Life

Theoretical Test

2006. 7. 7
Gyeongsan, Korea
Constants and useful formulas

Gas constant \( R = 8.314 \text{ J} \text{ K}^{-1} \text{ mol}^{-1} \)
Faraday constant \( F = 96485 \text{ C} \text{ mol}^{-1} \)
Use as standard pressure: \( p = 1.013 \cdot 10^5 \text{ Pa} \)
Use as standard temperature: \( T = 25^\circ \text{C} = 298.15 \text{ K} \)
Avogadro’s number \( N_A = 6.022 \cdot 10^{23} \text{ mol}^{-1} \)
Planck constant \( h = 6.626 \cdot 10^{-34} \text{ J} \text{ s} \)
Speed of light \( c = 3.00 \cdot 10^8 \text{ m s}^{-1} \)

\[ \Delta G = \Delta H - T\Delta S \]
\[ \Delta G^0 = -RT\ln K \]
\[ \Delta G = \Delta G^0 + RT\ln Q \quad \text{with} \quad Q = \frac{\text{product of } c(\text{products})}{\text{product of } c(\text{reactands})} \]

\[ \Delta H(T_1) = \Delta H^0 + (T_1 - 298.15 \text{ K}) \cdot C_p \quad (C_p = \text{constant}) \]

Arrhenius equation \( k = A \cdot e^{-\frac{E_a}{RT}} \)

Ideal gas law \( pV = nRT \)

Nernst equation \( E = E^0 + \frac{RT}{nF} \cdot \ln \frac{c_{\text{ox}}}{c_{\text{red}}} \)

Beer- Lambert Law \( A = \log \frac{P_0}{P} = \varepsilon \cdot c \cdot d \)

\[ V(\text{cylinder}) = \pi r^2 h \]
\[ A(\text{sphere}) = 4\pi r^2 \]
\[ V(\text{sphere}) = \frac{4}{3} \pi r^3 \]

1 J = 1 N m \quad 1 \text{ N} = 1 \text{ kg m s}^{-2} \quad 1 \text{ Pa} = 1 \text{ N m}^{-2} \]
1 W = 1 A V = 1 J s\(^{-1}\) \quad 1 C = 1 A s
1. Avogadro's number

Spherical water droplets are dispersed in argon gas. At 27°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°C. The density of a water droplet is 1.0 g/cm³.

1-1. Calculate the average kinetic energy \( (mv^2/2) \) of this droplet at 27°C. The volume of a sphere is given by \( (4/3) \pi r^3 \) 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°C and 100°C as a function of temperature is found to be linear. Assume that it remains linear below 0°C.

At thermal equilibrium, 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. **Calculate 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/cm³; 3/4 hydrogen and 1/4 helium by mass). Estimate 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 \( \Delta E(n \rightarrow n_i) = -C\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) \), 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 (\( \lambda \)) corresponding to the maximum light intensity emitted from a blackbody at temperature \( T \) is given by \( \lambda T = 2.9 \times 10^{-3} \text{ m K} \). **Calculate the surface temperature of a star whose blackbody radiation has a peak intensity corresponding to the \( n = 1 \rightarrow n = 2 \) 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 CH₂, CH₃, 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 \( A = 1 \times 10^{12} \text{ s}^{-1} \) and \( E_{\text{des}} = 12 \text{ kJ mol}^{-1} \).

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 (\( E_{\text{mig}} \)) is 6 kJ mol⁻¹, and the IIG is a sphere with a 0.1 \( \mu \text{m} \) radius. Each migratory jump laterally advances the molecule by 0.3 nm. Show work and choose your answer from (a)-(e) below.

(a) \( t \leq 1 \text{ day} \)  
(b) \( 10 \text{ day} \leq t \leq 10^2 \text{ yr} \)  
(c) \( 10^3 \text{ yr} \leq t \leq 10^6 \text{ yr} \)  
(d) \( 10^7 \text{ yr} \leq t \leq 10^{10} \text{ yr} \)  
(e) \( t \geq 10^{11} \text{ yr} \)

3-3. Consider the reaction of CO with \( \text{H}_2 \) to form \( \text{H}_2\text{CO} \). 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. Estimate 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 (\( 1 \times 10^{10} \text{ yr} \)), the reaction energy barrier must be absent or negligible.

(a) \( \text{ (a, b) } \) \( \text{ (a, c) } \) \( \text{ (b, c) } \) \( \text{ (a, b, c) } \)

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, NH₃, and H₂O has been demonstrated in the laboratory. **Write** the minimum number of HCN and H₂O molecules required for formation of the following compounds.

![Adenine, Guanine, Uracil, Cytosine](image)

5. **Acid-Base Chemistry**

5-1. **Calculate** [H⁺], [OH⁻], [HSO₄⁻], and [SO₄²⁻] in a 1.0 x 10⁻⁷ M solution of sulfuric acid (Kₗ = 1.0 x 10⁻¹⁴, K₂ = 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. (H₃PO₄ (aq), purity = 85 % wt/wt, density = 1.69 g/mL, FW = 98.00) (pK₁ = 2.15, pK₂ = 7.20, pK₃ = 12.44).

5-3. The efficacy of a drug is greatly dependent on its ability to be absorbed into the bloodstream. Acid-base chemistry plays an important role in drug absorption.

![Membrane Diagram](image)
Assume that the ionic form (A\textsuperscript{-}) 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\textsuperscript{-}]) 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).

\[
\begin{align*}
\text{Reduction of copper ion (Cu}^{2+}) & \quad \cdot \quad \cdot \quad \cdot \quad +0.340 \\
\text{Reduction of oxygen} & \quad \cdot \quad \cdot \quad \cdot \quad -2.710 \\
\text{Reduction of water} & \quad \cdot \quad \cdot \quad \cdot \quad -0.830 \\
\text{Reduction of sodium ion (Na}^+) & \quad \cdot \quad \cdot \quad \cdot \quad 0.000 \\
\text{Reduction of hydrogen ion} & \quad \cdot \quad \cdot \quad \cdot \quad +1.230
\end{align*}
\]
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.

\[
\text{LiCoO}_2 \rightleftharpoons \text{Li}_{1-x} \text{CoO}_2 + x \text{Li}^+ + x \text{e}^- \\
\text{C} + x \text{Li}^+ + x \text{e}^- \rightleftharpoons \text{CLi}_x
\]

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 \(\rightarrow\) oil \(\rightarrow\) natural gas \(\rightarrow\) 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. \(\Delta H^0_{f}[\text{H}_2\text{O}(l)] = -286 \text{ kJ/mol, } \Delta H^0_{f}[\text{CO}_2(g)] = -394 \text{ kJ/mol.}\)

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 $T_{\text{cold}}$ and $T_{\text{hot}}$ is given by $[1 - T_{\text{cold}}/T_{\text{hot}}]$.

$S^\circ_{298}[\text{H}_2(\text{g})] = 131 \text{ J/(K mol)}$

$S^\circ_{298}[\text{O}_2(\text{g})] = 205 \text{ J/(K mol)}$

$S^\circ_{298}[\text{H}_2\text{O}(\text{l})] = 70 \text{ J/(K mol)}$.

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.

$$\text{C(s) + O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) \quad \Delta H^\circ = -393.51 \text{ kJ/(mol)} \quad \overset{\text{1}}{\text{----}}$$

$$\text{CO}_2(\text{g}) + \text{C(s)} \rightarrow 2\text{CO(}g\text{)} \quad \Delta H^\circ = 172.46 \text{ kJ/(mol)} \quad \overset{\text{2}}{\text{----}}$$

$$\text{Fe}_2\text{O}_3(\text{s}) + \text{CO(}g\text{)} \rightarrow \text{Fe(}s\text{)} + \text{CO}_2(\text{g}) \quad \Delta H^\circ = \text{?} \quad \overset{\text{3}}{\text{------------}}$$

8-1-1. **Indicate the reducing agent in each reaction.**

8-1-2. **Balance reaction 2 and calculate the equilibrium constant of reaction 3 at 1200 °C.** ($\Delta H^\circ(\text{Fe}_2\text{O}_3(\text{s})) = -824.2 \text{ kJ/mol}$, $S^\circ(\text{J/mol/K})$: Fe(s) = 27.28, $\text{Fe}_2\text{O}_3(\text{s})$ = 87.40, C(s) = 5.74, CO(g) = 197.674, CO$_2$(g) = 213.74)

8-2. In the manufacture of celadon pottery, $\text{Fe}_2\text{O}_3$ is partially reduced in a charcoal kiln to mixed oxides of $\text{Fe}_3\text{O}_4$ and FeO. The amount of the different oxides seems to be related to the “mystic” color of celadon ceramics.

$\text{Fe}_3\text{O}_4$ (magnetite) itself is a mixed oxide containing $\text{Fe}^{2+}$ and $\text{Fe}^{3+}$ ions and belongs to a group of compounds with a general formula of $\text{AB}_2\text{O}_4$. 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 \( \text{AB}_2\text{O}_4 \) unit? Certain sites are shared by neighboring units.

\( \text{AB}_2\text{O}_4 \) 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 \( \text{Fe}^{2+} \) or \( \text{Fe}^{3+} \) ion in \( \text{Fe}_3\text{O}_4 \)?

8-2-3 \( \text{Fe}_3\text{O}_4 \) has an inverse-spinel structure. Draw the crystal field splitting pattern of \( \text{Fe}^{2+} \) 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.
9-1-1. **Draw 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. **Draw the Lewis structure of nitrene expected from CH$_3$-N$_3$.**

9-1-3. **Draw the structures for two possible products, when this nitrene from CH$_3$-N$_3$ reacts with ethylene gas (CH$_2$CH$_2$).**

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.

When irradiated, diazonaphthaquinone undergoes photochemical decomposition followed by rearrangement eventually producing a carboxylic acid.

9-2-1. **Draw three Lewis structures of diazoacetaldehyde (see below), the simplest compound having the same active functional group of diazonaphthaquinone. Indicate formal charges.**

9-2-2. **Draw 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$_3$CO$_2$H.**
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 (Glycyrrhiza. 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 \((C_{6}H_{10}O_{7})\) were obtained in a 1:2 molar ratio (figure 1).
```

**Figure 1.**

When glycyrrhizin was methylated with methyl iodide (Mel) 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 Mel produced the same isomeric mixture of compounds, J (figure 3.)

**Figure 3.**
Theoretical Problems of the IChO

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.**

![Chemical structure diagram](image)

10-1. Complete structures for L, M, and N in the answer sheet.

10-2. How many structures for C are possible? Complete 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**

![Chemical structure diagram](image)

10-3. Complete 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. Complete structures for B, D, and J.

10-6. Complete 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.

\[
\text{Shikimic Acid} \xrightarrow{\text{dehydration}} \text{Chorismic Acid} \xrightarrow{\text{Chorismate mutase}} \text{Prephenic Acid}
\]

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.

\[\text{H-NMR (D}_2\text{O, 250 MHz): } \delta \ 6.01 (2H, d, J = 10.4 \text{ Hz}), 5.92 (2H, dd J = 10.4, 3.1 \text{ Hz}), 4.50 (1H, t, J = 3.1 \text{ Hz}), 3.12 (2H, s). \text{ Note that there are three protons, which have been exchanged by D}_2\text{O very fast, and two protons at } \delta 3.12, \text{ which are exchanged slowly in prephenic acid.}\]

\[\text{C-NMR (D}_2\text{O, 75 MHz): } \delta 203, 178, 173, 132 (\text{for two identical carbons}), 127 (\text{for two identical carbons}), 65, 49, 48.\]

\(\delta\), 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.

11-3. Choose 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$_a$. 

(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$_a$. 

(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$_a$. 

(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\textsubscript{50} values.

11-5. Compared with the uncatalyzed thermal conversion, chorismate mutase accelerates conversion of chorismic acid to prephenic acid \(1.0 \times 10^{6}\) fold at 25°C by lowering the activation energy of the reaction. Calculate the decrease in activation energy of chorismate mutase at 25°C. 

\(\Delta H^\ddagger_{\text{uncat}}\) 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°C, assuming that \(E_a = \Delta H^\ddagger\)?
Solutions to the Theoretical Problems of the IChO

1-1.
The mass of a water droplet:
\[ m = V \rho = \left( \frac{4}{3} \pi r^3 \right) \rho = \left( \frac{4}{3} \pi \right) \left( 0.5 \times 10^{-6} \text{ m} \right)^3 \left( 1.0 \text{ g/cm}^3 \right) = 5.2 \times 10^{-16} \text{ kg} \]

Average kinetic energy at 27°C:
\[ \text{KE} = \frac{mv^2}{2} = \frac{(5.2 \times 10^{-16} \text{ kg}) \left( 0.51 \times 10^{-2} \text{ m/s} \right)^2}{2} = 6.9 \times 10^{-21} \text{ kg m}^2/\text{s}^2 = 6.9 \times 10^{-21} \text{ J} \]

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.
\[ a = \frac{\text{KE}}{T} = \frac{6.9 \times 10^{-21} \text{ J}}{27+273 \text{ K}} = 2.3 \times 10^{-23} \text{ J/K} \]

S: specific heat of argon
N: number of atoms in 1g of argon
\[ S = 0.31 \text{ J/g K} = \frac{a \times N}{27+273} \]

Avogadro’s number (\( N_A \)): Number of argon atoms in 40 g of argon
\[ N_A = (40)(1.4 \times 10^{22} \text{ J/K}) = 5.6 \times 10^{23} \]

2.1.
Mass of a typical star = \( \frac{4}{3} \pi \left( 3.1 \times 10^8 \text{ m} \right)^3 \left( 1.4 \text{ g/10}^{-6} \text{ m}^3 \right) = 2 \times 10^{33} \text{ g} \)

Mass of protons of a typical star = \( 2 \times 10^{33} \text{ g} \left( \frac{3}{4} + \frac{1}{8} \right) = 1.8 \times 10^{33} \text{ g} \)

Number of protons of a typical star = \( 1.8 \times 10^{33} \text{ g} \left( 6 \times 10^{23} / \text{g} \right) = 1 \times 10^{57} \)

Number of stellar protons in the universe = \( 1 \times 10^{57} \left( 10^{23} \right) = 1 \times 10^{80} \)

2.2.
\[ \Delta E(2\rightarrow3) = C \left( \frac{1}{4} - \frac{1}{9} \right) = 0.1389 \text{ C} \]
\[ \lambda(2\rightarrow3) = 656.3 \text{ nm} \]

\[ \Delta E(1\rightarrow2) = C \left( \frac{1}{1} - \frac{1}{4} \right) = 0.75 \text{ C} \]
\[ \lambda(1\rightarrow2) = \frac{656.3 \text{ nm}}{0.1389/0.75} = 121.5 \text{ nm} \]

2.3.
\[ T = \frac{(2.9 \times 10^{-3} \text{ m K})}{1.215 \times 10^7 \text{ m}} = 2.4 \times 10^4 \text{ K} \]

2.4.
\[ \lambda = 3 \times 108 \text{ m/1.42 \times 109 = 0.21 m} \]
\[ T = (2.9 \times 10^{-3} \text{ m K})/0.21 \text{ m} = 0.014 \text{ K} \]

2.5.
\[ ^{14}\text{N} + ^{4}\text{He} \rightarrow ( ^{17}\text{O} + ^{1}\text{H} ) \]

3-1.
\[ k_{\text{des}} = A \exp(-E_{\text{des}}/RT) = (1 \times 10^{12} \text{ s}^{-1})(5 \times 10^{-33}) = 5 \times 10^{-20} \text{ s}^{-1} \text{ at } T = 20 \text{ K} \]

Surface residence time, \( \tau_{\text{residence}} = 1 / k_{\text{des}} = 2 \times 10^{19} \text{ s} = 6 \times 10^{11} \text{ yr} = 2 \times 10^{19} \text{ s} \)

(full credit for \( \tau_{\text{half-life}} = \ln2 / k_{\text{des}} = 1 \times 10^{19} \text{ s} = 4 \times 10^{11} \text{ yr} \) )

3-2.
The distance to be traveled by a molecule: \( x = 3 \pi r = 300 \text{ nm} \).
\[ k_{\text{mig}} = A \exp(-E_{\text{mig}}/RT) = (1 \times 10^{12} \text{ s}^{-1})(2 \times 10^{-16}) = 2 \times 10^4 \text{ s}^{-1} \text{ at } T = 20 \text{ K} \]

Average time between migratory jumps, \( \tau = 1 / k_{\text{mig}} = 5 \times 10^3 \text{ s} \)

The time needed to move 300 nm = \( 300 \text{ nm/0.3 nm} \) jumps \( \times (5 \times 103 \text{ s/jump}) = 5 \times 106 \text{ s} = 50 \text{ days} \)
Solutions to the Theoretical Problems of the IChO

(Full credit for the calculation using a random-walk model. In this case:
\[ t = \tau \left( \frac{x}{d} \right)^2 = 5 \times 10^9 \text{ s} = 160 \text{ yr}. \] The answer is still (b).

(a) (b) (c) (d) (e)

3-3.
\[ k(20 \text{ K}) / k(300 \text{ K}) = \exp\left[\frac{E}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)\right] = e^{112} = \sim 10^{-49} \text{ for the given reaction} \]
The rate of formaldehyde production at 20 K = \sim 10^{-49} \text{ molecule/site/s} = \sim 10^{-42} \text{ molecule/site/yr} (The reaction will not occur at all during the age of the universe (1x10^{10} \text{ yr}))

rate = 10^{-42} \text{ molecules/site/yr}

3-4. circle one
(a) (b) (c) (a, b) (a, c) (b, c) (a, b, c)

4.1

\[
\begin{array}{c|cc}
 & H & P \\
Number of atoms & 11.3 & 1 \\
Theoretical wt % & 3.43 & \\
\end{array}
\]

4-2.

4.3 Full marks for three of the following structures
4-4.

![Chemical structures]

- Adenine
- Guanine
- Uracil
- Cytosine

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 \( [H^+]_{H_2SO_4} = 2 \times 10^{-7} \)

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), \( [H^+] = (2.4 \times 10^{-7}) + 10^{-14} / [H^+] \) \( [H^+] = 2.4 \times 10^{-7} \)
\( [OH^-] = 10^{-14} / (2.4 \times 10^{-7}) = 4.1 \times 10^{-8} \)

From (1), \( [HSO_4^-] = [H^+] [SO_4^{2-}] / K_2 = (2.4 \times 10^{-7}) \times (1.0 \times 10^{-7}) / (1.2 \times 10^{-5}) = 2.0 \times 10^{-12} \)

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: \( 0 + 2.0 \times 10^{-12} + 1.0 \times 10^{-7} = 1.0 \times 10^{-7} \)

<table>
<thead>
<tr>
<th>Species</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>HSO_4^-</td>
<td>2.0 \times 10^{-12}</td>
</tr>
<tr>
<td>SO_4^{2-}</td>
<td>1.0 \times 10^{-7}</td>
</tr>
<tr>
<td>H^+</td>
<td>2.4 \times 10^{-7}</td>
</tr>
<tr>
<td>OH^-</td>
<td>4.1 \times 10^{-8}</td>
</tr>
</tbody>
</table>

5-2.

\( \text{mmol} \ H_3PO_4 = 0.85 \times 3.48 \text{ mL} \times 1.69 \text{g/mL} \times 1 \text{ mol} / 98.00 \text{ g} \times 1000 = 51.0 \) [5 marks]
The desired pH is above \( pK_a \).
A 1:1 mixture of \( H_3PO_4^- \) 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 \( H_3PO_4^- \).
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 convert \( H_3PO_4 \) to \( H_2PO_4^- \) is:
\[
51.0 \text{ mmol} / 0.80 \text{M} = 63.75 \text{ mL}
\]
To get pH of 7.40 we need:
H_2PO_4^- + OH^- → HPO_4^{2-}

Initial mmol 51.0  x  0
Final mmol 51.0-x  0  x

pH = pK_a + 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)} = 3.02x10^{-2}  Total ASA = 1+ 3.02x10^{-2} = 1.03

Ratio of total aspirin in blood to that in stomach = 7587/1.03 = 7400

6-1.
4 H_2O + 4 e^- → 2 H_2(g) + 4 OH^- (or 2 H_2O + 2 e^- → H_2(g) + 2 OH^-)

6-2.
2 H_2O → O_2 + 4 H^+ + 4 e^- (or H_2O → 1/2 O_2 + 2 H^+ + 2 e^-)

6-3.
Cu → 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
Reduction of oxygen -2.710
Reduction of water -0.830
Reduction of sodium ion (Na^+) 0.000
Reduction of hydrogen ion +1.230

6-5.
pOH = 14.00 - 4.84 = 9.16  [OH^-] = 6.92 x 10^{-10}
K_sp = [Cu^{2+}][OH^-]^2 = 0.100 x (6.92 x 10^{-10}) = 4.79 x 10^{-20}

6-6.

E = E^o_{Cu^{2+}/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^- → Cu(s) + 2OH^- is the potential where [OH^-]
= 1.00.
One may solve this problem as following.

Eqn 1: \[ \text{Cu(OH)}_2(s) + 2e^- \rightarrow \text{Cu} + 2\text{OH}^- \]  
\[ E^\circ = E^\circ_{\text{Cu(OH)}_2/\text{Cu}} = ? \]

Eqn 2: \[ \text{Cu(OH)}_2(s) \rightarrow \text{Cu}^{2+} + 2\text{OH}^- \]  
\[ E^\circ = (0.05916/n) \log K_{sp} = (0.05916/2) \log (4.79 \times 10^{-20}) = -0.5715 \text{ V} \]

Eqn 1 – Eqn 2: \[ \text{Cu}^{2+} + 2e^- \rightarrow \text{Cu} \]  
\[ E^- = E^\circ_{\text{Cu}^{2+}/\text{Cu}} + E^\circ_{\text{Cu(OH)}_2/\text{Cu}} = 0.340 + (-0.5715) = -0.232 \text{ V} \]

6-7.

Below pH = 4.84, there is no effect of \( \text{Cu(OH)}_2 \) because of no precipitation.

Therefore, \( E = E^\circ_{\text{Cu}^{2+}/\text{Cu}} + 0.340 + (0.0592/2) \log [\text{Cu}^{2+}] = +0.340 + (0.0592/2) \log 0.100 = +0.340 – 0.0296 = +0.310 \text{ V} \)

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 \times 0.0139 = 1340 coulombs
1340 coulombs / g = 1340 A sec / g = 1340 \times 1000 \text{ mA} \times (1 / 3600) \text{ h} = 372 \text{ mA h / g}

7-1.

\[ n/V = P/RT = (80 \times 10^6 / 1.013 \times 10^5 \text{ atm})/[(0.082 \text{ atm L/mol/K})(298K)] = 32 \text{ mol/L} \]

\[ \text{density} = \text{mass} / \text{volume} = d = 32 \times 2 \text{ g/L} = 64 \text{ kg/m}^3 \]

7-2.

\[ \text{H}_2(g) + 1/2 \text{O}_2(g) \rightarrow \text{H}_2\text{O}(l); \Delta H_{\text{react-1}} = \Delta H[\text{H}_2\text{O}(l)] = -286 \text{ kJ/mol} = -143 \text{ kJ/g} \]

\[ \text{C(s)} + \text{O}_2(g) \rightarrow \text{CO}_2(g); \Delta H_{\text{react-2}} = \Delta H[\text{CO}_2(g)] = -394 \text{ kJ/mol} = -33 \text{ kJ/g} \]

\[ (-\Delta H_{\text{react-1}}) / (-\Delta H_{\text{react-2}}) = 4.3 \text{ or } (-\Delta H_{\text{react-2}}) / (-\Delta H_{\text{react-1}}) = 0.23 \]

7-3.

\[ \text{H}_2(g) + 1/2 \text{O}_2(g) \rightarrow \text{H}_2\text{O}(l) \]

\[ \Delta H_c = -286 \text{ kJ/mol} = -143 \text{ kJ/g} = -143 \times 10^3 \text{ kJ/kg} \]

\[ \Delta G = \Delta H - T\Delta S \]

\[ \Delta S_c = 70 - 131 - 205/2 = -163.5 \text{ J/K/mol} \]

\[ \Delta G_c = -286 \text{ kJ/mol} + 298K \times 163.5 \text{ J/K/mol} = -237 \text{ kJ/mol} = -1.2 \times 10^5 \text{ kJ/kg} \]

(a) electric motor \( W_{\text{max}} = \Delta G_c \times 1 \text{ kg} = -1.2 \times 10^5 \text{ kJ} \)

(b) heat engine \( W_{\text{max}} = \text{efficiency} \times \Delta H_c \)

\[ = (1 - 298/573) \times (-143 \times 10^3 \text{ kJ}) = -6.9 \times 10^4 \text{ kJ} \]

119 \times 10^3 \text{ kJ} = 1 \text{ W x t(sec)}

\[ t = 1.2 \times 10^6 \text{ sec} = 3.3 \times 10^4 \text{ hr} = 1.4 \times 10^3 \text{ days} = 46 \text{ month} = 3.8 \text{ yr} \]

\[ \Delta G = -nFE \quad n = \# \text{ of electrons involved in the reaction} \]

\[ F = 96.5 \text{ kC/mol} \quad \text{H}_2(g) + 1/2 \text{O}_2(g) \rightarrow \text{H}_2\text{O}(l) \quad n = 2 \]

\[ E = -\Delta G/nF = 237 \text{ kJ/mol} / 2 / 96.5 \text{ kC/mol} = 1.23 \text{ V} \]

I = \text{W/E} = 0.81 \text{ A}
8-1-1. ① C  ② C  ③ CO

8-1-2.
③ Fe₂O₃(s) + 3CO(g) → 2Fe(s) + 3CO₂(g)
① C(s) + O₂(g) → CO₂(g)  ΔH° = -393.51 kJ = ΔH°(CO₂(g))
② CO₂(g) + C(s) → 2CO(g)  ΔH° = 172.46 kJ
From ① and ②,
ΔH°(CO(g)) = (1/2)(172.46 + (-393.51)) = -110.525 kJ  ΔH°(Fe₂O₃) = -824.2 kJ
ΔH°₃ = 3 x ΔH°(CO₂(g)) - ΔH°(Fe₂O₃) - 3 x ΔH°(CO(g))
= 3 x (-393.51) - (-824.2) - 3 x (-110.525) = -24.8 kJ
ΔS°₃ = 2 x 27.28 + 3 x 213.74 = 15.36 J/K
ΔG°₃ = ΔH°₃ - TΔS°₃ = -24.8kJ - 15.36J/K x 1kJ/1000J x 1473.15K = -47.43 kJ
K = e^(-ΔG°₃/RT) = e^((47430J)/(8.314J/K x 1473.15K)) = 48

8-2-1.
One AB₂O₄ unit has available 4 (= 1 + (1/4) x 12) octahedral sites

8-2-2.
Since one face-centered cube in AB₂O₄ represents one Fe₂O₄ unit in this case, it has 8 available tetrahedral sites. In one Fe₂O₄ unit, 1 tetrahedral site should be occupied by either one Fe²⁺ (normal-spinel) or one Fe³⁺ (inverse-spinel). Therefore, in both cases, the calculation gives (1/8) x 100% = 12.5% occupancy in available tetrahedral sites.

8-2-3.

9-1-1.
H₃C\(\begin{array}{c}
\uparrow
\end{array}\)
\(\begin{array}{c}
\uparrow
\end{array}\)
\(\begin{array}{c}
\uparrow
\end{array}\)
H₃C\(\begin{array}{c}
\uparrow
\end{array}\)
\(\begin{array}{c}
\uparrow
\end{array}\)
\(\begin{array}{c}
\uparrow
\end{array}\)

9-1-2.
H₃C⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋护肤品

9-1-3.
H₃C⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~-~

120
9-2-1.

\[ \begin{align*}
  &\text{H} \quad \text{O} \\
  &\text{N} \\
  &\text{N} \\
  &\text{H} \\
  &\text{N} \\
  &\text{N} \\
  &\text{H} \\
  &\text{H} \\
  &\text{O} \\
\end{align*} \]

9-2-2.

\[ \begin{align*}
  &\text{O} \\
  &\text{C} \\
  &\text{H} \\
\end{align*} \]

9-3-1.

\[ \begin{align*}
  &\text{H}_2\text{C} \\
  &\text{CH}_3 \\
  &\text{CO}_2 \\
  &\text{H}_3\text{C} \\
  &\text{OH} \\
  &\text{H}_3\text{C} \\
  &\text{CH} \\
  &\text{CHO} \\
\end{align*} \]

9-3-2.

\[ \begin{align*}
  &\text{O} \\
  &\text{C} \\
  &\text{H} \\
\end{align*} \]

10-1.

<table>
<thead>
<tr>
<th>N</th>
<th>M</th>
<th>L</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CH}_3\text{OH} )</td>
<td>( \text{CHO} )</td>
<td>( \text{CH}_2\text{CH} )</td>
</tr>
<tr>
<td>( \text{MeO} )</td>
<td>( \text{H} )</td>
<td>( \text{H} )</td>
</tr>
<tr>
<td>( \text{H} )</td>
<td>( \text{OMe} )</td>
<td>( \text{OH} )</td>
</tr>
<tr>
<td>( \text{CH}_3\text{OH} )</td>
<td>( \text{CHO} )</td>
<td>( \text{CH}_2\text{OH} )</td>
</tr>
<tr>
<td>( \text{MeO} )</td>
<td>( \text{H} )</td>
<td>( \text{H} )</td>
</tr>
<tr>
<td>( \text{H} )</td>
<td>( \text{OMe} )</td>
<td>( \text{OH} )</td>
</tr>
</tbody>
</table>
10-2

Number of possible structures

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><img src="image1.png" alt="Structure 1" /></td>
<td><img src="image2.png" alt="Structure 2" /></td>
</tr>
<tr>
<td>2</td>
<td><img src="image3.png" alt="Structure 3" /></td>
<td><img src="image4.png" alt="Structure 4" /></td>
</tr>
</tbody>
</table>

10-3.

<table>
<thead>
<tr>
<th>G</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image5.png" alt="Structure 5" /></td>
<td><img src="image6.png" alt="Structure 6" /></td>
</tr>
</tbody>
</table>

10-4. Number of the correct structure for C from 10-2: 1

10-5.
Solutions to the Theoretical Problems of the IChO

10-6.

11-1. 3

11-2.

11-3. a, c, d
11-4.

Transition State

11-5.

For the enzyme-catalyzed reaction, Arrhenius equation could be applied.

\[
k_{\text{cat}}/k_{\text{uncat}} = A \exp (-E_{a,\text{cat}} / RT) / A \exp (-E_{a,\text{uncat}} / RT)
\]

\[
= \exp [-E_{a,\text{cat-uncat}} / RT]
\]

Therefore, \(-E_{a,\text{cat-uncat}} = 34,300 \text{ J/mol}\)

\[
k_{\text{uncat, T}}/k_{\text{uncat, 298}} = \exp (-\Delta H^\circ_{\text{uncat}} / RT) / \exp (-\Delta H^\circ_{\text{uncat}} / 298R)
\]

\[
= \exp [(-\Delta H^\circ_{\text{uncat}} / R)(1/T-1/298)]
\]

\[
\ln(k_{\text{uncat, T}}/k_{\text{uncat, 298}}) = 13.8 = [(-86900/8.32)(1/T-1/298)]
\]

Therefore, \(T = 491 \text{ K, or } 218^\circ\text{C}\)
Practical Problems of the IChO

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)

<table>
<thead>
<tr>
<th>Item</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>spectrophotometer</td>
<td>1</td>
</tr>
<tr>
<td>cuvet (1 cm path-length)</td>
<td>1</td>
</tr>
<tr>
<td>C18 cartridge</td>
<td>4</td>
</tr>
<tr>
<td>10 mL syringe</td>
<td>1</td>
</tr>
<tr>
<td>1 mL syringe</td>
<td>1</td>
</tr>
<tr>
<td>pasteur pipet</td>
<td>3</td>
</tr>
<tr>
<td>1 mL pipet</td>
<td>1</td>
</tr>
<tr>
<td>5 mL pipet</td>
<td>1</td>
</tr>
<tr>
<td>pipet filler</td>
<td>1</td>
</tr>
<tr>
<td>10 mL volumetric flask</td>
<td>2</td>
</tr>
<tr>
<td>buret</td>
<td>1</td>
</tr>
<tr>
<td>test tube</td>
<td></td>
</tr>
<tr>
<td>test tube rack</td>
<td></td>
</tr>
<tr>
<td>50 mL Erlenmeyer flask</td>
<td>1</td>
</tr>
<tr>
<td>100 mL beaker</td>
<td>2</td>
</tr>
<tr>
<td>silicone bulb</td>
<td>2</td>
</tr>
<tr>
<td>three-color pen, ruler</td>
<td>1</td>
</tr>
<tr>
<td>squeeze bottle</td>
<td>3</td>
</tr>
</tbody>
</table>

| Solution E                          | 33% ethanol in water |
| NaOH solution                       | less than 5 mM       |
| water                               | distilled water      |

## Test-3 (black basket)

<table>
<thead>
<tr>
<th>Item</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>test tube</td>
<td>95</td>
</tr>
<tr>
<td>test tube rack</td>
<td>1</td>
</tr>
<tr>
<td>spatula</td>
<td>2</td>
</tr>
<tr>
<td>1.5 mL graduated pipet</td>
<td>15</td>
</tr>
<tr>
<td>(polyethylene)</td>
<td></td>
</tr>
<tr>
<td>tweezers</td>
<td>1</td>
</tr>
<tr>
<td>pen (for writing on a test tube)</td>
<td>1</td>
</tr>
<tr>
<td>pH test paper</td>
<td>1</td>
</tr>
<tr>
<td>100 mL bottle</td>
<td>3</td>
</tr>
<tr>
<td>95% EtOH</td>
<td>95% ethanol</td>
</tr>
<tr>
<td>CH₃CN</td>
<td>acetonitrile</td>
</tr>
<tr>
<td>water</td>
<td>distilled water</td>
</tr>
<tr>
<td>30 mL dropping bottle</td>
<td>6</td>
</tr>
<tr>
<td>1M HCl</td>
<td>1M HCl solution</td>
</tr>
<tr>
<td>1M NaOH</td>
<td>1M NaOH solution</td>
</tr>
<tr>
<td>2,4-DNPH</td>
<td>3% 2,4-dinitrophenylhydrazine solution</td>
</tr>
<tr>
<td>CAN</td>
<td>20% ceric ammonium nitrate solution</td>
</tr>
<tr>
<td>0.5% KMnO₄</td>
<td>0.5% KMnO₄ solution</td>
</tr>
<tr>
<td>2.5% FeCl₃</td>
<td>2.5% FeCl₃ solution</td>
</tr>
</tbody>
</table>

| 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 & salicylic acid in water |
| KHP                                 | potassium hydrogen phthalate solution |
| phenolphthale in                    | 0.05% solution |

| 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 x 10^{-5} M) and B (1.25 x 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 x 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.
Practical Problems of the IChO

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$_3$CN. 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$_3$CN 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$_3$CN (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

![Possible Unknown Compounds]
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 | 6 | 7 | 8 | 9 | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 0 | 1 | 2 | 3 | 4 | 5 | 6 |
| Argentina    | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + |
| Armenia      | o | o | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + |
| Australien   | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o |
| Austria      | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + |
| Azerbaijan   | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o |
| Belarus      | o | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + |
| Belgium      | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + |
| Brasil       | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o |
| Bulgaria     | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + |
| Canada       | o | o | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + |
| China        | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + |
| Chinese Taipei | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + |
| Croatia      | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o |
| Cuba         | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + |
| Cyprus       | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o |
| Czech Rep.   | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + |
| Czechoslovakia | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + |
| Denmark      | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + |
| DDR          | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o |
| Egypt        | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + |
| Estonia      | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + |
| Finland      | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o |
| France       | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o |
| Germany      | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o |
| Greece       | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + |
| Hungary      | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + |
| Iceland      | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o |
| India        | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o |

135
## About the History of the IChO

<table>
<thead>
<tr>
<th>Country</th>
<th>Year</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
<th>12</th>
</tr>
</thead>
<tbody>
<tr>
<td>Indonesia</td>
<td></td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
</tr>
<tr>
<td>Iran</td>
<td></td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Ireland</td>
<td></td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
</tr>
<tr>
<td>Israel</td>
<td></td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
</tr>
<tr>
<td>Italy</td>
<td></td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Japan</td>
<td></td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
</tr>
<tr>
<td>Jugoslavia</td>
<td></td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Kazakhstan</td>
<td></td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
</tr>
<tr>
<td>Kenya</td>
<td></td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
</tr>
<tr>
<td>Korea</td>
<td></td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Kuwait</td>
<td></td>
<td>o</td>
<td>o</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Kyrgyzstan</td>
<td></td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
</tr>
<tr>
<td>Latvia</td>
<td></td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Lithuania</td>
<td></td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Malaysia</td>
<td></td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
</tr>
<tr>
<td>Mexico</td>
<td></td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Moldova</td>
<td></td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
</tr>
<tr>
<td>Mongolia</td>
<td></td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
</tr>
<tr>
<td>Netherlands</td>
<td></td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>New Zealand</td>
<td></td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Norway</td>
<td></td>
<td>o</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Pakistan</td>
<td></td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
</tr>
<tr>
<td>Peru</td>
<td></td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
</tr>
<tr>
<td>Philippines</td>
<td></td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
</tr>
<tr>
<td>Poland</td>
<td></td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Portugal</td>
<td></td>
<td>o</td>
<td>o</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Romania</td>
<td></td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>GUS/Russ.Fed.</td>
<td></td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Saudi Arabia</td>
<td></td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
</tr>
<tr>
<td>Singapore</td>
<td></td>
<td>o</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Slovakia</td>
<td></td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Slovenia</td>
<td></td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Spain</td>
<td></td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
</tr>
<tr>
<td>Sweden</td>
<td></td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Switzerland</td>
<td></td>
<td>o</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Tajikistan</td>
<td></td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
</tr>
<tr>
<td>Thailand</td>
<td></td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
</tr>
</tbody>
</table>

### Year → Country

<table>
<thead>
<tr>
<th>Year</th>
<th>Country</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>7</td>
<td>7</td>
</tr>
<tr>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>9</td>
<td>9</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>7</td>
<td>7</td>
</tr>
<tr>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>9</td>
<td>9</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>6</td>
<td>6</td>
</tr>
</tbody>
</table>

136
About the history of the IChO

Country, Year →

| Year | 6 | 6 | 7 | 7 | 7 | 7 | 7 | 7 | 8 | 8 | 8 | 8 | 8 | 8 | 8 | 9 | 9 | 9 | 9 | 9 |
| Turkey | o | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + |
| Turkmenistan | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o |
| UdSSR | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + |
| Ukraine | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o |
| United Kingdom | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o |
| United States | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o |
| Uruguay | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o |
| Venezuela | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o |
| Vietnam | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o | o |

Number of teams attending the IChO

Number of teams

Year of olympiad
### Inofficial ranking since 1974

(set up by adding the points of the teams, up to position 50)

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>IChO held in</td>
<td>RO</td>
<td>H</td>
<td>DDR</td>
<td>CS</td>
<td>PL</td>
<td>SU</td>
<td>A</td>
<td>BG</td>
<td>S</td>
<td>RO</td>
<td>D</td>
<td>CS</td>
<td>NL</td>
<td>H</td>
<td>FIN</td>
</tr>
<tr>
<td>1</td>
<td>SU</td>
<td>SU</td>
<td>DDR</td>
<td>CS</td>
<td>SU</td>
<td>PL</td>
<td>PL</td>
<td>H</td>
<td>CS</td>
<td>RO</td>
<td>D</td>
<td>SU</td>
<td>NL</td>
<td>SU</td>
<td>RC</td>
</tr>
<tr>
<td>2</td>
<td>RO</td>
<td>H</td>
<td>DDR</td>
<td>CS</td>
<td>SU</td>
<td>PL</td>
<td>PL</td>
<td>D</td>
<td>CS</td>
<td>D</td>
<td>SU</td>
<td>CS</td>
<td>CS</td>
<td>PL</td>
<td>RC</td>
</tr>
<tr>
<td>3</td>
<td>CS</td>
<td>PL</td>
<td>H</td>
<td>H</td>
<td>D</td>
<td>DDR</td>
<td>PL</td>
<td>PL</td>
<td>D</td>
<td>SU</td>
<td>D</td>
<td>D</td>
<td>RO</td>
<td>USA</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>H</td>
<td>CG</td>
<td>PL</td>
<td>PL</td>
<td>DDR</td>
<td>CS</td>
<td>H</td>
<td>BG</td>
<td>NL</td>
<td>CS</td>
<td>H</td>
<td>A</td>
<td>SU</td>
<td>CS</td>
<td>PL</td>
</tr>
<tr>
<td>5</td>
<td>PL</td>
<td>RO</td>
<td>A</td>
<td>S</td>
<td>CS</td>
<td>A</td>
<td>A</td>
<td>A</td>
<td>H</td>
<td>A</td>
<td>NL</td>
<td>A</td>
<td>D</td>
<td>GB</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>DDR</td>
<td>DDR</td>
<td>RO</td>
<td>A</td>
<td>H</td>
<td>S</td>
<td>RO</td>
<td>D</td>
<td>SU</td>
<td>A</td>
<td>GB</td>
<td>H</td>
<td>USA</td>
<td>F</td>
<td>DDR</td>
</tr>
<tr>
<td>7</td>
<td>BG</td>
<td>S</td>
<td>BG</td>
<td>D</td>
<td>A</td>
<td>H</td>
<td>BG</td>
<td>DDR</td>
<td>H</td>
<td>F</td>
<td>PL</td>
<td>DDR</td>
<td>H</td>
<td>GB</td>
<td>N</td>
</tr>
<tr>
<td>8</td>
<td>YU</td>
<td>CS</td>
<td>CS</td>
<td>DDR</td>
<td>RO</td>
<td>D</td>
<td>CS</td>
<td>RO</td>
<td>BG</td>
<td>DDR</td>
<td>USA</td>
<td>PL</td>
<td>BG</td>
<td>PL</td>
<td>RO</td>
</tr>
<tr>
<td>9</td>
<td>S</td>
<td>A</td>
<td>S</td>
<td>RO</td>
<td>S</td>
<td>BG</td>
<td>S</td>
<td>SU</td>
<td>DDR</td>
<td>PL</td>
<td>RO</td>
<td>USA</td>
<td>F</td>
<td>H</td>
<td>H</td>
</tr>
<tr>
<td>10</td>
<td>D*</td>
<td>D</td>
<td>D</td>
<td>BG</td>
<td>BG</td>
<td>FIN</td>
<td>FIN</td>
<td>NL</td>
<td>S</td>
<td>NL</td>
<td>DK</td>
<td>F</td>
<td>RO</td>
<td>DDR</td>
<td>SU</td>
</tr>
<tr>
<td>11</td>
<td>YU</td>
<td>YU</td>
<td>YU</td>
<td>TR</td>
<td>DDR</td>
<td>NL</td>
<td>FIN</td>
<td>F</td>
<td>BG</td>
<td>S</td>
<td>GB</td>
<td>CS</td>
<td>NL</td>
<td>I</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>B</td>
<td>B</td>
<td>B</td>
<td>FIN</td>
<td>I</td>
<td>S</td>
<td>FIN</td>
<td>GB</td>
<td>NL</td>
<td>RO</td>
<td>GB</td>
<td>USA</td>
<td>NL</td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>B</td>
<td>F</td>
<td>N</td>
<td>N</td>
<td>FIN</td>
<td>BG</td>
<td>S</td>
<td>BG</td>
<td>BG</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>I</td>
<td>RO</td>
<td>DK</td>
<td>F</td>
<td>N</td>
<td>DDR</td>
<td>A</td>
<td>CS</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>* hors concours</td>
<td>DK</td>
<td>FIN</td>
<td>BG</td>
<td>S</td>
<td>CDN</td>
<td>S</td>
<td>AUS</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>YU</td>
<td>S</td>
<td>N</td>
<td>FIN</td>
<td>N</td>
<td>FIN</td>
<td>SGP</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>I</td>
<td>I</td>
<td>I</td>
<td>YU</td>
<td>DK</td>
<td>N</td>
<td>F</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>YU</td>
<td>GR</td>
<td>B</td>
<td>B</td>
<td>DK</td>
<td>A</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>YU</td>
<td>GR</td>
<td>FIN</td>
<td>I</td>
<td>FIN</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>B</td>
<td>DK</td>
<td>GR</td>
<td>GR</td>
<td>CDN</td>
<td>C</td>
<td>KWT</td>
<td>C</td>
<td>DK</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>YU</td>
<td>B</td>
<td>C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>YU</td>
<td>S</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>23</td>
<td>CDN</td>
<td>B</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>24</td>
<td>CH</td>
<td>CH</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>KWT</td>
<td>KWT</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(List of abbreviations see page 141)
### About the history of the IChO

<table>
<thead>
<tr>
<th>Year</th>
<th>DDR</th>
<th>F</th>
<th>PL</th>
<th>USA</th>
<th>I</th>
<th>N</th>
<th>RC</th>
<th>RUS</th>
<th>CDN</th>
<th>AUS</th>
<th>T</th>
<th>DK</th>
</tr>
</thead>
<tbody>
<tr>
<td>1989</td>
<td>DDR</td>
<td>RC</td>
<td>RC</td>
<td>RC</td>
<td>RC</td>
<td>RC</td>
<td>IR</td>
<td>H</td>
<td>SGP</td>
<td>USA</td>
<td>RC</td>
<td></td>
</tr>
<tr>
<td>1990</td>
<td>D</td>
<td>PL</td>
<td>RO</td>
<td>H</td>
<td>TPE</td>
<td>GB</td>
<td>IR</td>
<td>RC</td>
<td>D</td>
<td>USA</td>
<td>ROK</td>
<td>RUS</td>
</tr>
<tr>
<td>1991</td>
<td>RC</td>
<td>D</td>
<td>H</td>
<td>PL</td>
<td>USA</td>
<td>USA</td>
<td>RO</td>
<td>RUS</td>
<td>TR</td>
<td>ROK</td>
<td>RC</td>
<td>USA</td>
</tr>
<tr>
<td>1992</td>
<td>BG</td>
<td>USA</td>
<td>PL</td>
<td>USA</td>
<td>I</td>
<td>A A</td>
<td>A</td>
<td>TPE</td>
<td>RC</td>
<td>IR</td>
<td>H</td>
<td>USA</td>
</tr>
<tr>
<td>1993</td>
<td>SU</td>
<td>CS</td>
<td>NL</td>
<td>A</td>
<td>GUS</td>
<td>SGP</td>
<td>D</td>
<td>D</td>
<td>IR</td>
<td>H</td>
<td>RO</td>
<td>TPE</td>
</tr>
<tr>
<td>1994</td>
<td>H</td>
<td>RO</td>
<td>USA</td>
<td>GUS</td>
<td>H</td>
<td>RO</td>
<td>GB</td>
<td>USA</td>
<td>RUS</td>
<td>RA</td>
<td>H</td>
<td>A</td>
</tr>
<tr>
<td>1995</td>
<td>PL</td>
<td>F</td>
<td>I</td>
<td>D</td>
<td>D</td>
<td>TPE</td>
<td>SK</td>
<td>UA</td>
<td>ROK</td>
<td>RUS</td>
<td>TPE</td>
<td>SK</td>
</tr>
<tr>
<td>1996</td>
<td>RO</td>
<td>A D</td>
<td>RO</td>
<td>CDN</td>
<td>CZ</td>
<td>TPE</td>
<td>CZ</td>
<td>RC</td>
<td>AUS</td>
<td>USA</td>
<td>BY</td>
<td>USA</td>
</tr>
<tr>
<td>1997</td>
<td>CS</td>
<td>DDR</td>
<td>N</td>
<td>F</td>
<td>SGP</td>
<td>GUS</td>
<td>I</td>
<td>H</td>
<td>SGP</td>
<td>D</td>
<td>PL</td>
<td>VN</td>
</tr>
<tr>
<td>1998</td>
<td>I</td>
<td>H</td>
<td>GB</td>
<td>I</td>
<td>CZ</td>
<td>IR</td>
<td>CZ</td>
<td>RL</td>
<td>PL</td>
<td>GB</td>
<td>AUS</td>
<td>TR</td>
</tr>
<tr>
<td>1999</td>
<td>NL</td>
<td>GB</td>
<td>CS</td>
<td>SGP</td>
<td>A</td>
<td>D</td>
<td>RUS</td>
<td>GB</td>
<td>USA</td>
<td>PL</td>
<td>VN</td>
<td>SGP</td>
</tr>
<tr>
<td>2000</td>
<td>GB</td>
<td>I</td>
<td>SU</td>
<td>CS</td>
<td>RO</td>
<td>H</td>
<td>H</td>
<td>TPE</td>
<td>UA</td>
<td>A</td>
<td>D D</td>
<td></td>
</tr>
<tr>
<td></td>
<td>A</td>
<td>AUS</td>
<td>A</td>
<td>AUS</td>
<td>P</td>
<td>RO</td>
<td>AUS</td>
<td>BY</td>
<td>AUS</td>
<td>USA</td>
<td>RA</td>
<td>ROK</td>
</tr>
<tr>
<td></td>
<td>USA</td>
<td>SGP</td>
<td>AUS</td>
<td>NL</td>
<td>NZ</td>
<td>DK</td>
<td>SGP</td>
<td>CDN</td>
<td>TPE</td>
<td>BY</td>
<td>IR</td>
<td>USA</td>
</tr>
</tbody>
</table>

(List of abbreviations see page 141)
About the history of the IChO

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>2001</td>
<td>RC</td>
<td>RC</td>
<td>RC</td>
<td>ROK</td>
<td>RC</td>
<td>ROK</td>
<td>RC</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2002</td>
<td>ROK</td>
<td>T</td>
<td>IR</td>
<td>ROK</td>
<td>VN</td>
<td>TPE</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2003</td>
<td>USA</td>
<td>TPE</td>
<td>ROK</td>
<td>RUS</td>
<td>IR</td>
<td>ROK</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2004</td>
<td>RUS</td>
<td>ROK</td>
<td>T</td>
<td>UA</td>
<td>RUS</td>
<td>RUS</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2005</td>
<td>IR</td>
<td>A</td>
<td>BY</td>
<td>D</td>
<td>AZ</td>
<td>VN</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2006</td>
<td>TR</td>
<td>UA</td>
<td>RUS</td>
<td>PL</td>
<td>TPE</td>
<td>T</td>
<td>J</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2007</td>
<td>AUS</td>
<td>PL</td>
<td>SGP</td>
<td>H</td>
<td>RA</td>
<td>PI</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2008</td>
<td>TPE</td>
<td>IND</td>
<td>D</td>
<td>TR</td>
<td>D</td>
<td>IND</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2009</td>
<td>T</td>
<td>D</td>
<td>TPE</td>
<td>VN</td>
<td>IND</td>
<td>D</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2010</td>
<td>SGP</td>
<td>IR</td>
<td>UA</td>
<td>IND</td>
<td>A</td>
<td>SK</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2011</td>
<td>PL</td>
<td>H</td>
<td>PL</td>
<td>IR</td>
<td>CZ</td>
<td>DK</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2012</td>
<td>RO</td>
<td>RUS</td>
<td>CDN</td>
<td>RO</td>
<td>UA</td>
<td>SGP</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(List of abbreviations see page 141)
### List of abbreviations

<table>
<thead>
<tr>
<th>A</th>
<th>Austria</th>
<th>KZ</th>
<th>Kasakhstan</th>
</tr>
</thead>
<tbody>
<tr>
<td>AUS</td>
<td>Australia</td>
<td>LV</td>
<td>Latvia</td>
</tr>
<tr>
<td>AZ</td>
<td>Azerbaijan</td>
<td>LT</td>
<td>Lithuania</td>
</tr>
<tr>
<td>B</td>
<td>Belgium</td>
<td>MAL</td>
<td>Malaysia</td>
</tr>
<tr>
<td>BG</td>
<td>Bulgaria</td>
<td>MEX</td>
<td>Mexico</td>
</tr>
<tr>
<td>BR</td>
<td>Brazil</td>
<td>MGL</td>
<td>Mongolei</td>
</tr>
<tr>
<td>BY</td>
<td>Belarus</td>
<td>N</td>
<td>Norway</td>
</tr>
<tr>
<td>C</td>
<td>Cuba</td>
<td>NL</td>
<td>Netherlands</td>
</tr>
<tr>
<td>CDN</td>
<td>Canada</td>
<td>NZ</td>
<td>New Zealand</td>
</tr>
<tr>
<td>CH</td>
<td>Switzerland</td>
<td>P</td>
<td>Portugal</td>
</tr>
<tr>
<td>CS</td>
<td>Czechoslovakia</td>
<td>PE</td>
<td>Peru</td>
</tr>
<tr>
<td>CY</td>
<td>Cyprus Republic</td>
<td>PL</td>
<td>Polen</td>
</tr>
<tr>
<td>CZ</td>
<td>Czech Republic</td>
<td>RA</td>
<td>Argentina</td>
</tr>
<tr>
<td>D</td>
<td>Germany</td>
<td>RI</td>
<td>Indonesia</td>
</tr>
<tr>
<td>DDR</td>
<td>German Democratic Republic</td>
<td>RC</td>
<td>China</td>
</tr>
<tr>
<td>DK</td>
<td>Denmark</td>
<td>RO</td>
<td>Romania</td>
</tr>
<tr>
<td>E</td>
<td>Spain</td>
<td>ROK</td>
<td>South Korea</td>
</tr>
<tr>
<td>EAK</td>
<td>Kenya</td>
<td>ROU</td>
<td>Uruguay</td>
</tr>
<tr>
<td>EST</td>
<td>Estonia</td>
<td>RUS</td>
<td>Russian Federation</td>
</tr>
<tr>
<td>ET</td>
<td>Egypt</td>
<td>S</td>
<td>Sweden</td>
</tr>
<tr>
<td>F</td>
<td>France</td>
<td>SGP</td>
<td>Singapore</td>
</tr>
<tr>
<td>FIN</td>
<td>Finland</td>
<td>SK</td>
<td>Slovakia</td>
</tr>
<tr>
<td>GB</td>
<td>United Kingdom</td>
<td>SLO</td>
<td>Slovenia</td>
</tr>
<tr>
<td>GR</td>
<td>Greece</td>
<td>SU</td>
<td>Sowjet Union</td>
</tr>
<tr>
<td>GUS</td>
<td>Commonwealth of Independent States</td>
<td>T</td>
<td>Thailand</td>
</tr>
<tr>
<td>H</td>
<td>Hungary</td>
<td>TJ</td>
<td>Tadschikistan</td>
</tr>
<tr>
<td>HR</td>
<td>Croatia</td>
<td>TM</td>
<td>Turkmenistan</td>
</tr>
<tr>
<td>I</td>
<td>Italy</td>
<td>TPE</td>
<td>Chinese Taipei</td>
</tr>
<tr>
<td>IL</td>
<td>Israel</td>
<td>TR</td>
<td>Turkey</td>
</tr>
<tr>
<td>IND</td>
<td>India</td>
<td>UA</td>
<td>Ukraine</td>
</tr>
<tr>
<td>IR</td>
<td>Iran</td>
<td>USA</td>
<td>United States of America</td>
</tr>
<tr>
<td>IRL</td>
<td>Ireland</td>
<td>VN</td>
<td>Vietnam</td>
</tr>
<tr>
<td>IS</td>
<td>Iceland</td>
<td>WAN</td>
<td>Nigeria</td>
</tr>
<tr>
<td>J</td>
<td>Japan</td>
<td>YU</td>
<td>Yugoslavia</td>
</tr>
<tr>
<td>KS</td>
<td>Kyrgyzstan</td>
<td>YV</td>
<td>Venezuela</td>
</tr>
<tr>
<td>KWT</td>
<td>Kuwait</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>