THIRD INTERNATIONAL WORKSHOP ON THE DEVELOPMENT OF THE INTERNATIONAL CHEMISTRY OLYMPIADS (AMSTERDAM, OCTOBER 1990)

The best ICHO-tasks of the last years

According to the decision of the work shop of Amsterdam the delegation leaders of 8 countries made an attempt to rank the ICHO-tasks of the years 1980 ~ 1990 into the categories

excellent / good / not so good / not acceptable

The following pages indicate the ”top-twelve”, i.e. is the best tasks of the last years. This collection should be an aid for the ICHO-designers of the next years. Examples for tasks considered as ”not acceptable” are available for the next organisers too.

12. ICHO in LINZ (A) 1980:		exc.	good	n.s.g.	n. acc.
T-Problem 1	(chlorine detonating gas reaction)	3	3	1	0
T-Problem 2	(water gas equilibrium)	1	5	1	0
T-Problem 3	(redox reactions,$NaIO_4$)	3	4	0	0
T-Problem 4	(organic stereochemistry)	1	6	0	0
T-Problem 5	(inorganic chemistry, silane)	1	4	2	0
T-Problem 6	(organic synthesis)	2	3	2	0
P-Problem 7	(qualitative organic analysis)	1	3	2	1
P-Problem 8	(qualitative inorganic analysis)	0	5	2	0
P-Problem 9	(titration of $K_2S_2O_8$)	1	5	1	0

13. ICHO in BURGAS (BG) 1981:		exc.	good	n.s.g.	n. acc.
T-Problem 1	(inorganic chemistry, sulfur-scheme)	0	6	1	0
T-Problem 2	(protolysis of maleic acid)	1	4	2	0
T-Problem 3	(organic chemistry, glucose)	0	4	3	0
T-Problem 4	(thermal decomposition of water)	3	2	2	0
T-Problem 5	(organic chemistry, butadiene)	2	3	2	0
T-Problem 6	(first order kinetics)	2	4	1	0
P-Problem 7	(qualitative inorganic analysis)	0	7	0	0
P-Problem 8	(qualitative organic analysis)	0	7	0	0
P-Problem 9	(determination of Na_2CO_3/$NaHCO_3$)	0	6	0	1

14. ICHO in STOCKHOLM (S) 1982:		exc.	good	n.s.g.	n. acc.
T-Problem 1	IUPAC-names etc.)	1	4	2	0
T-Problem 2	(possible structures of $C_4H_8O_2$)	2	3	2	0
T-Problem 3	(titration of formaldehyde)	1	4	2	0
T-Problem 4	(chromium complexes)	2	4	1	0
T-Problem 5	(distribution of iodine)	2	4	1	0
T-Problem 6	(organic chemistry, barbituric acid)	0	5	2	0
T-Problem 7	(solubility of calcium oxalate)	2	5	0	0
P-Problem 8	(preparation of a buffer solution)	3	3	1	0
P-Problem 9	(qualitative inorganic analysis)	2	5	0	0
P-Problem 10	(determination of a solubility product)	1	6	0	0

15. ICHO in TIMISOARA (R) 1983:		exc.	good	n.s.g.	n. acc.
T-Problem 1	(inorganic chemistry)	2	2	3	0
T-Problem 2	(gas mixture of CO and $CO_{2)}$	1	2	4	0
T-Problem 3	(mixture of NaCl and KCl)	1	5	1	0
T-Problem 4	(kinetics, S_N reaction)	1	3	3	0
T-Problem 5	(equilibrium of ethanol dehydration)	0	4	3	0
T-Problem 6	(organic chemistry, aldol condensation	1	3	3	0
T-Problem 7	(benzoic acid scheme)	0	3	2	2
P-Problem 8	(qualitative organic analysis)	0	3	4	0
P-Problem 9	(determination of oxalic acid/oxalate)	1	5	1	0
P-Problem 10	(qualitative inorganic analysis)	0	7	0	0

16. ICHO in FRANKFURT (D) 1984:		exc.	good	n.s.g.	n. acc.
T-Problem 1	(radioactive decay)	3	3	2	0
T-Problem 2	(complex chemistry)	2	3	3	0
T-Problem 3	(organic chemistry 1)	1	3	4	0
T-Problem 4	(organic chemistry 2)	1	4	1	2
T-Problem 5	(physical chemistry, Lambert/Beer)	0	5	2	1
T-Problem 6	(physical chemistry, HC-combustion)	2	4	2	0
T-Problem 7	(biochemistry, DNA)	1	7	0	0
T-Problem 8	(biochemistry, peptide sequence)	1	4	3	0
P-Problem 1	(nitration of phenacetine)	2	4	2	0
P-Problem 2	(determ. of H_3PO_4 in Coca-Cola)	4	3	1	0

17. ICHO in BRATISLAVA (CS) 1985:		exc.	good	n.s.g.	n. acc.
T-Problem 1	(analysis of an aluminium-alloy)	1	5	2	0
T-Problem 2	(inorganic chemistry, O-bonding)	1	5	2	0
T-Problem 3	(inorganic chemistry, $CaSO_4$, EDTA)	2	3	3	0
T-Problem 4	(first order reaction of pinene)	1	5	2	0
T-Problem 5	(voltage of a galvanic cell)	0	7	1	0
T-Problem 6	(organic chemistry, acetophenone)	1	4	3	0
T-Problem 7	(organic chemistry, kinetics)	0	4	4	0
T-Problem 8	(biochemistry, glucose)	1	1	3	1
P-Problem 1	(molar mass of HA)	0	4	3	1

18. ICHO in LEIDEN (NL) 1986:		exc.	good	n.s.g.	n. acc.
T-Problem 1	(complex chemistry)	5	3	0	0
T-Problem 2	(inorganic chemistry, triphosphate)	2	3	3	0
T-Problem 3	(biochemistry, DNA)	2	5	1	0
T-Problem 4	(particle in the box theory)	3	3	2	0
T-Problem 5	(organic chemistry, rate determining)	1	2	4	1
T-Problem 6	(organic chemistry, lactic acid)	3	3	2	0
T-Problem 7	(chemical technology)	1	5	1	1
P-Problem 1	(synthesis/analysis of a nickel salt)	5	2	0	1

19. ICHO in VESZPREM (H) 1987:		exc.	good	n.s.g.	n. acc.
T-Problem 11	(waste water treatment)	1	4	2	0
T-Problem 12	(inorganic chemistry, $NaH_2PO_4 \cdot 2H_2O$)	0	4	3	0
T-Problem 13	(potentiometric titration)	0	6	1	0
T-Problem 14	(organic chemistry, indene)	1	4	3	0
T-Problem 15	(biochemistry)	0	2	4	1
P-Problem 21	(qualitative inorganic analysis)	1	6	1	0
P-Problem 22	(enthalpy change on mixing)	1	2	3	2
P-Problem 23	(iodometric determ. of HCl and KIO_3)	1	5	2	0

20. ICHO in HELSINKI (SF) 1988 :		exc.	good	n.s.g.	n. acc.
T-Problem 1	(quantum numbers, “Flatlandia”)	6	1	0	0
T-Problem 2	(inorganic chemistry, electron density)	2	4	1	0
T-Problem 3	(physical chemistry, C_8H_{18}-combustion)	4	3	0	0
T-Problem 4	(3 analytical tasks)	0	4	3	0
T-Problem 5	(organic chemistry, MS, cyclohexanol)	0	4	2	1
T-Problem 6	(organic chemistry, MS, chlorine comp.)	2	1	3	1
P-Problem 1	(organic synthesis)	1	6	0	0
P-Problem 2	(spectrophotometric determ. of pK_a)	1	4	2	0

21. ICHO in HALLE (DDR) 1989 :		exc.	good	n.s.g.	n. acc.
T-Problem 1	(solubility product of copper iodate)	1	6	1	0
T-Problem 2	(removal of SO_2 from waste gases)	3	2	3	0
T-Problem 3	(compression of a gas mixture)	1	4	3	0
T-Problem 4	(labelled P-compounds)	2	6	0	0
T-Problem 5	(cyclobutane dicarboxylic acid, R/S)	0	5		1
T-Problem 6	(biochemistry, phospholipid membrane)	0	4	4	0
P-Problem 1	(synthesis of aspirin)	2	4	2	0
P-Problem 2	(titration of aspirin)	1	3	3	1

22. ICHO in PARIS (F) 1990:		exc.	good	n.s.g.	n. acc.
T-Problem 1	(inorganic chemistry, apatite)	1	3	2	2
T-Problem 2	(physical chemistryt Cu^+/Cu^{2+})	1	7	0	0
T-Problem 3	(organic chemistry, haloperidol)	1	4	3	0
T-Problem 4/1	(physical chemistry, thermodynamics)	0	5	3	0
T-Problem 4/3	(physical chemistry, kinetics)	1	2	5	0
T-Problem 5	(biochemistry, fumarate/malate)	0	4	4	0
T-Problem 7	(chemical technology)	2	1	4	1
P-Problem 1	(synthesis of chalcon)	0	3	4	1
P-Problem 2	(qualitative inorganic analysis)	1	5	2	0
P-Problem 3	(oxygen determination in water)	0	5	3	0
P-Problem 4	(determination of a rate constant)	1	4	3	0

Problem No. 1: **Physical chemistry (periodic system, quantum numbers)**

The periodic system of the elements in our three-dimensional world is based on the four electron quantum numbers n = 1, 2, 3,...; l = 0, 1,..., n-1; m_l = 0, ±1, ±2,..., ±l; and m_s = ±1/2.

Let us move to Flatlandia. It is a two-dimensional world where the periodic system of the elements is based on three electron quantum numbers: n = 1, 2, 3,...; m = 0, ±1, ±2,..., ±(n-1); and m_s = ±1/2. m plays the combined role of l and m_l of the three dimensional worlds (For example s, p, d,... levels are related to m). The following tasks and the basic principles relate to this two-dimensional Flatlandia where the chemical and physical experience obtained from our common three-dimensional world is applicable.

a) Draw the first four periods of the Flatlandian periodic table of the elements. Number the elements according to their nuclear charge. Use the atomic numbers (Z) as the symbols of the elements. Write the electron configuration of each element. (3.0 points).

b) Draw the hybrid-orbitals of the elements with n = 2. Which element is the basis for the organic chemistry in Flatlandia (use the atomic number as a symbol)? Find the Flatlandian analogues for ethane, ethene and cyclohexane. What kind of aromatic ring compounds are possible in Flatlandia? (2.0 points)

c) Which rules in Flatlandia correspond to the octet and 18-electron rules in the three-dimensional world? (1.0 point)

d) Predict graphically the trends in the first ionisation energies of the Flatlandian elements with n = 2. Show graphically how the electronegativities of the elements increase in the Flatlandian periodic table. (1.0 point)

e) Draw the molecular orbital energy diagrams of the neutral homonuclear diatomic molecules of the elements with n = 2. Which of these molecules are stable in Flatlandia? (2.0 points)

f) Consider simple binary compounds of the elements (n = 2) with the lightest element (Z = 1). Draw their Lewis-structures, predict geometries and propose analogues for them in the three-dimensional world. (2.0 points)

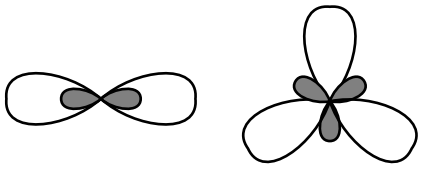
g) Consider elements with n ≤ 3. Propose an analog and write the chemical symbol from our three-dimensional world for each Flatlandian element. On the basis of this chemical and physical analogy predict which two-dimensional elements are solid, liquid or gas at the normal pressure and temperature. (1.0 point)

Solution of problem No. 1:

al The Flatlandian periodic table:

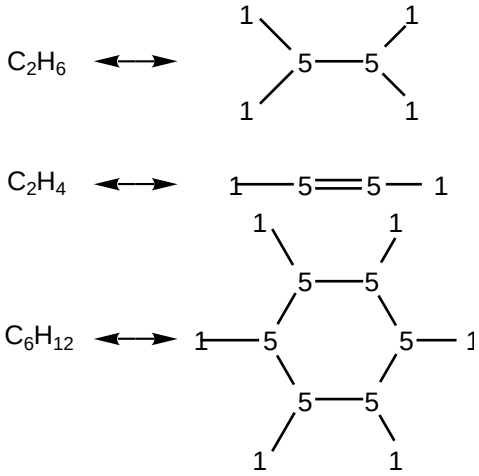
1 $1s^1$									2 $1s^2$
3 $[\,]2s^1$	4 $[\,]2s^2$					5 $[\,]2s^22p^1$	6 $[\,]2s^22p^2$	7 $[\,]2s^22p^3$	8 $[\,]2s^22p^4$
9 $[\,]3s^1$	10 $[\,]3s^2$					11 $[\,]3s^23p^1$	12 $[\,]3s^23p^2$	13 $[\,]3s^23p^3$	14 $[\,]3s^23p^4$
15 $[\,]4s^1$	16 $[\,]4s^2$	17 $[\,]4s^23d^1$	18 $[\,]4s^23d^2$	19 $[\,]4s^23d^3$	20 $[\,]4s^23d^4$	21 $[\,]4s^23d^4 4p^1$	22 $[\,]4s^23d^4 4p^2$	23 $[\,]4s^23d^4 4p^3$	24 $[\,]4s^23d^4 4p^4$

b)



sp^1 sp^2

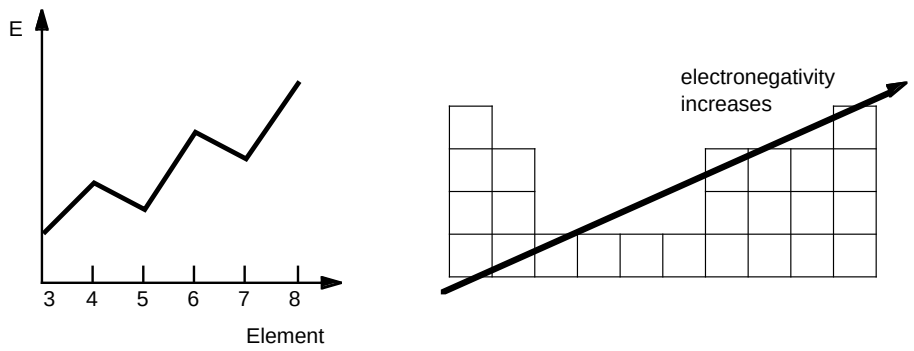
The element of Life: 5



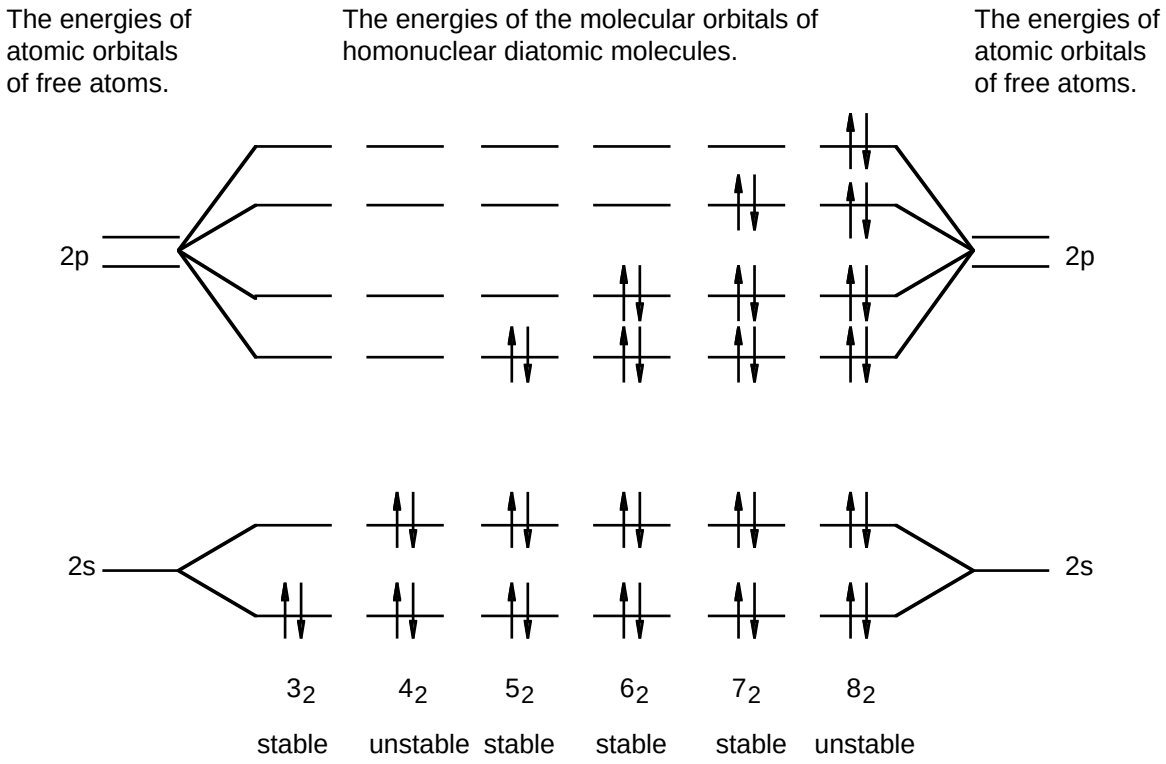
There are no aromatic ring compounds.

c)Sextet rule: 10 electron rule

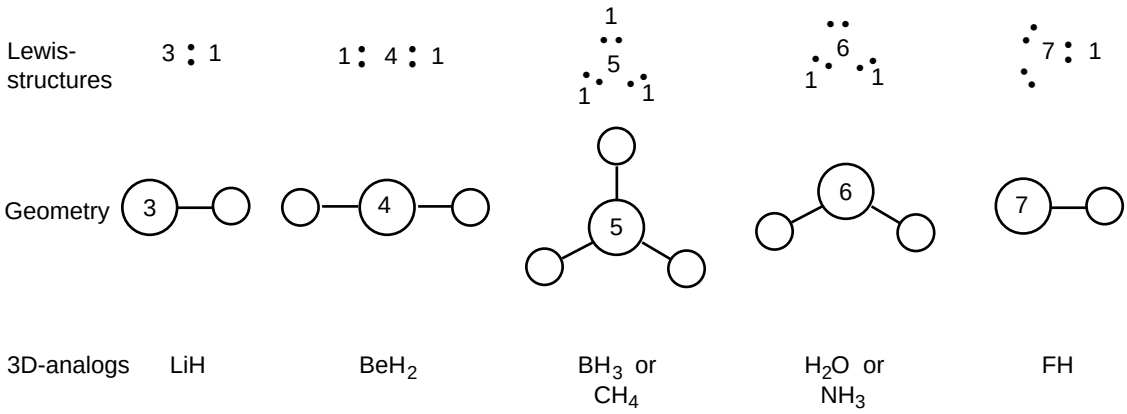
d) The ionisation energies and the trends in electronegativity:



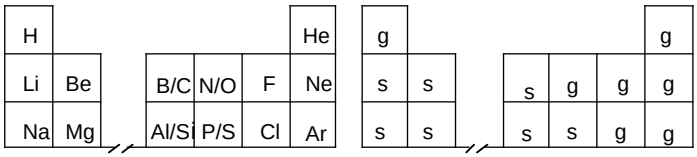
e) The molecular orbital diagram of the homonuclear X_2 molecules:



f) The Lewis structures and geometries:



g) The three-dimensional analogs and the states of Flatlandian e lemen ts:



Problem No. 2: **Inorganic chemistry (complex chemistry)**

Compounds containing divalent platinum with the general formula $[PtX_2(amine)_2]$ (where X = Cl or $X_2 = SO_4$, malonate, etc.) have over the last few years enjoyed an increasing scientific interest because of their biological activity, particularly in view of their properties in the treatment of tumours.

The best known compound, which is used on a large scale clinically, is $[PtCl_2(NH_3)_2]$. This compound, in which the platinum is coordinated in a square planar arrangement, has two geometrical isomers of which one shows the anti tumour activity.

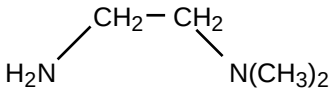
a) Sketch the spatial structures of the two possible isomers.

b) How many isomers has $[PtBrCl(NH_3)_2]$? Sketch these isomers.

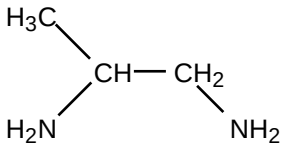
It is possible to replace the two ammine ligands by one ligand containing two donor atoms (N). Then one obtains a chelating ligand such as 1,2-diaminoethane (en for short).

c) Show by a drawing that [PtBrCl(en)] has only one stable structure.

The ligand (en) can be changed by substitution. For instance via methylation one can obtain:



dmen



pn(racemic)

d) Give spatial structures of all isomers of the following compounds:

$[PtCl_2$ (dmen)]
$[PtCl_2$ (pn)]
[PtBrCl (dmen)]
[PtBrCl (pn)]

Platinum compounds and in particular the analogous palladium compounds (which are also square planar coordinated when they contain bivalent metal ions) can isomerise in aqueous solutions, i.e. some isomers can transform into one another. Such an isomerisation usually proceeds through dissociation of a ligand, the weak ligand water transiently replaces one or more of the stronger ligands. Cl^- and Br^- are replaced relatively easily, but it is more difficult to replace the amine ligand, it usually requires heating the solution.

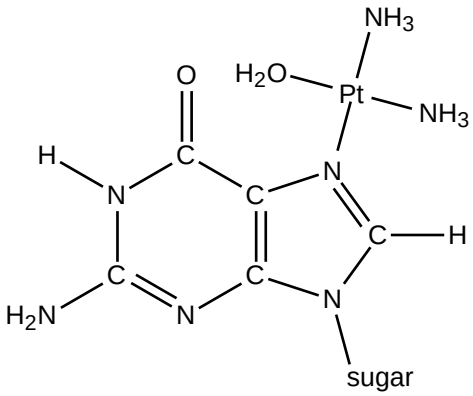
e) Considering each one of the isomers in answers 1a-1d, which can be converted to another isomer at room temperature?
N.B. In your answer give both the original molecule and the products.

f) Which compound would one expect and in what proportion, when one carries out the reaction of $[PtCl_2(en)]$ and Br^- in a molar proportion of 1:2 at room temperature. You can assume that the Pt—Br and Pt—Cl bonds are equally strong and that there is no perturbing influence from hydrolysis.

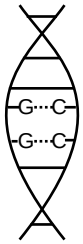
The compound $[PtCl_2(NH_3)_2]$ hydrolyses slowly in water to (amongst other compounds) $[Pt(H_2O)_2(NH_3)_2]^{2+}$ and $2Cl^-$. Patients are given the non-hydrolysed compound via injection into the bloodstream. The action in the tumour cell appears to derive from the special way in which bonding to the DNA occurs. In cells the Cl^- concentration is low, in blood it is fairly high (0.1 M)

g) Show with the aid of the equations for chemical equilibrium that hydrolysis hardly occurs in the blood, but that it does in the cells.

After hydrolysis in the tumour cell a reactive platinum ion is formed to which two NH_3 groups are still bound. It turns out that these NH_3 groups are still bound to platinum in the urine of patients treated with this compound. The reactive platinum ion appears to be bound to cellular DNA, where the bonding occurs via guanine to one of the N-atoms.



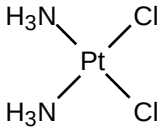
Because the platinum has two reactive sites and two unreactive NH_3 ligands, it can form a second bond to DNA in addition to the one shown above. Biochemical research has shown that this happens in particular with a second guanine base of the <u>same</u> strand of the DNA..



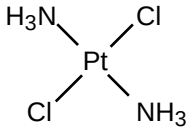
h) Show by means of a calculation which of the two isomers in question a) can form this bond.
(Note: Pt—N distance = 210 pm, DNA base distance = 320 pm).

Solution of problem No. 2:

a)

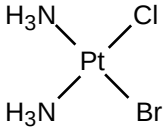


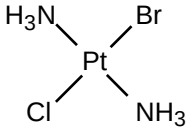
Isomer 1



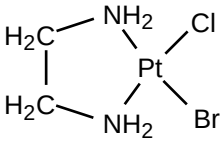
Isomer 2

b) The isomers are:



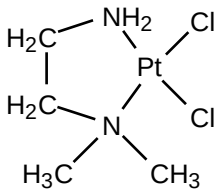


c) The structure is:



d) The isomers of $PtCl_2$(dmen) and $PtCl_2$(pn) are:

1.



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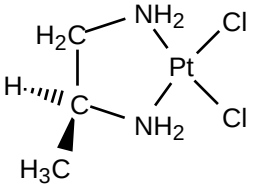

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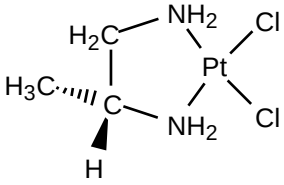
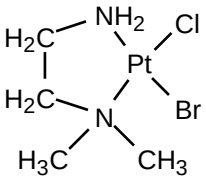


The isomers of [PtBrCl(dmen)] and [PtBrCl(pn)] are:

4.



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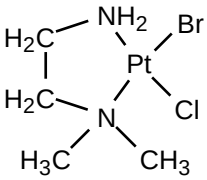

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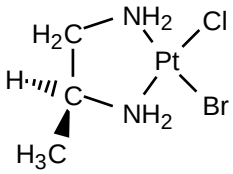

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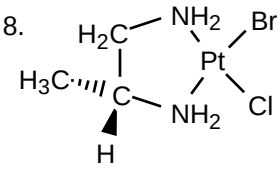

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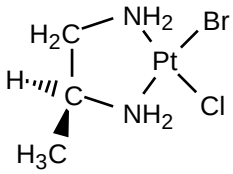

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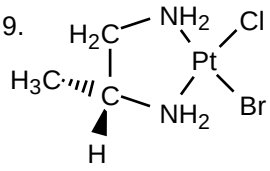


e) In a), b), c), no change. In d) 4 and 5 transform into one another, just like 6 and 7 and 8 and 9
BONUS: If one realises that $[PtCl_2(dmen)]$, $[PtBr_2(dmen)]$, $[PtCl_2(pn)]$ and $[PtBr_2(pn)]$ are also formed, even though they are not isomers.

f) One expects the products $[PtCl_2(en)]$, $[PtBr_2(en)]$ and [PtBrCl(en)] in the proportions 1:1:2.

g) We are concerned with the following equations for chemical equilibrium.

$$[PtCl_2(NH_3)_2] \xrightleftharpoons{H_2O} \;]^{2+}$$

$$Cl^- \; [(PtCl(H_2O)(NH_3)_2)]^+ \rightleftharpoons [Pt(H_2O)_2(NH_3)_2$$

In blood the hydrolysis does not occur to any great extent because the concentration of Cl^- is rather high and the equilibrium is on the left side.

h) The bond is due to the cis isomer because in that case the distance between the bases (320 pm) has to change only 210 x $\sqrt{2} \approx$ 300 pm, and with the trans compound 210 x 2 = 420 pm.

Problem No. 3: **Chemistry of ions (redox reactions)**

A white, crystalline solid exhibits the following reactions:

1. The flame of a Bunsen burner is intensely yellow coloured.

2. An aqueous solution is neutral; dropwise addition of sulfurous acid (an SO_2 solution) leads to a deep brown solution which is discoloured in the presence of excess sulfurous acid.

3. If an $AgNO_3$ solution is added to the discoloured solution obtained in 2. and acidified with HNO_3, a yellow precipitate that is insoluble on addition of NH_3, but that can be readily dissolved by adding CN^- or $S_2O_3^{2-}$, is obtained.

4. If an aqueous solution of the solid is treated with KI and dilute H_2SO_4, a deep brown solution is formed that can be discoloured by addition of sulfurous acid or a $Na_2S_2O_3$ solution.

5. An amount of 0.1000 g of the solid is dissolved in water, 0.5 g KI and a few mL of dilute H_2SO_4 are added. The deep brown solution formed is titrated with a 0.1000 M $Na_2S_2O_3$ solution until the solution is completely discoloured; the consumption, 37.40 mL.

a) What elements are contained in the solid?

b) What compounds can be considered as present on the basis of reactions 1-4.? Calculate their molecular weights.

c) Formulate the reactions corresponding to 2-4. for the compounds considered and write them as equations in the ionic form.

d) Decide on the basis of reaction 5 which compound is present.

Solution of problem No. 3:

a) The solid must contain Na and I: The yellow colouration of the flame of the Bunsen burner indicates the presence of Na; a yellow silver salt that is dissolved only by strong complexing agents, such as CN^- or $S_2O_3^{2-}$ must be AgI.

b) Reactions 1-4. indicate a Na salt of an oxygen-containing acid containing iodine.

Both SO_2 and I are oxidised, while in the first case I^- is formed with an intermediate of I_2 (or I_3^- brown solution) and in the second I_2 (or I_3^-) is formed.

As the solution is neutral, $NaIO_3$ and $NaIO_4$ come into consideration.

M ($NaIO_3$) = 22.99 + 126.905 + 3 x 16.000 = 197.895 = 197.90 g/mol
M ($NaIO_4$) = 22.99 + 126.905 + 4 x 16.000 = 213.895 = 213.90 g/mol

c) $2IO_4^- + 6H_2O + 7SO_2 \longrightarrow 7HSO_4^- + 5H^+ + I_2$

$2IO_3^- + 4H_2O + 5SO_2 \longrightarrow 5HSO_4^- + 3H^+ + I_2$

$I_2 + SO_2 + 2H_2O \longrightarrow HSO_4^- + 3H^+ + 2I^-$

$IO_4^- + 7I^- + 8H^+ \longrightarrow 4I_2 + 4H_2O$

$IO_3^- + 5I^- + 6H^+ \longrightarrow 3I_2 + 3H_2O$

$I_2 + 2S_2O_3^{2-} \longrightarrow 2I^- + S_4O_6^{2-}$

d) Experiment: 0 1000 g of the compound ……3.740 x 10^{-3} moles $S_2O_3^{2-}$

1. Hypothesis: The compound is $NaIO_3$

   1 mole $NaIO_3$ ≡ 197.90 g $NaIO_3$ ≡ 6 moles $S_2O_3^{2-}$

   0.1000 g $NaIO_3$ ≡ $\frac{0.1000 \times 6}{197.90}$ = 3.032 x 10^{-3} moles $S_2O_3^{2-}$

   The hypothesis is false.

2. Hypothesis: The compound is $NaIO_4$

   1 mole $NaIO_4$ ≡ 213.90 g $NaIO_4$ ≡ 8 moles $S_2O_3^{2-}$

   0.1000 g $NaIO_4$ ≡ $\frac{0.1000 \times 8}{213.90}$ = 3.740 x 10^{-3} moles $S_2O_3^{2-}$

   The compound is $NaIO_4$.

Problem No. 4: **Inorganic and physical chemistry (dissociation of chlorine)**

The dissociation of (molecular) chlorine is an endothermic process, $\Delta H = 24.36$ kJ mol^{-1}. The dissociation can also be attained by the effect of light.

1) At what wavelength can the dissociating effect of light be expected?

2) Can this effect also be obtained with light whose wavelength is smaller or larger than the calculated critical wavelength?

3) What is the energy of the photon with the critical wavelength?

When light that can effect the chlorine dissociation is incident on a mixture of gaseous chlorine and hydrogen, hydrogen chloride is formed. The mixture is irradiated with a mercury UV-lamp ($\lambda = 253.6$ nm. The lamp has a power input of 10 watt. An amount of 2% of the energy supplied is absorbed by the gas mixture (in a 10 litre vessel). Within 2.5 seconds of irradiation, 65 millimoles of HCl is formed.

4) How large is the quantum yield (= the number of the product molecules per absorbed photon)?

5) How can the value obtained be (qualitatively) explained? Describe the reaction mechanism.

Solution of problem No. 4:

1) $\lambda_1 = \frac{c}{\nu_1}$ from $\Delta H = N_A h \nu_1$ it follows that

$$\lambda_1 = \frac{c\, N_A\, h}{\Delta H} = \frac{3 \times 10^8 \times 6.02 \times 10^{23} \times 6.6 \times 10^{-34}}{2.436 \times 10^{-5}} = 4.91 \times 10^{-7} m = 491 \text{ nm}$$

2) Short-wave light ls effective, as its photons have a greater energy than required, whereas the photons of longer-wavelength light are too poor in energy to effect the dissociation.

3) $E_1 = h \nu_1 = \frac{h c}{\lambda_1} = \frac{6.6 \times 10^{-34} \times 3 \times 10^8}{4.91 \times 10^{-7}} J = 4.03 \times 10^{-19} J$

4) The quantum yield $(\phi) = \frac{\text{the number of HCl molecules formed}}{\text{the number of absorbed photons}}$

Now the number of HCl molecules formed = $n_{HCl} N_A$ and the number of photons absorbed = $\frac{E_{Total}}{E_{photon}}$

ie $\phi = \frac{n_{HCl} N_A}{E_{Total}} \times E_{photon}$

$= \frac{n_{HCl} N_A hc}{E_{Total} \lambda_2}$

$= \frac{6.5 \times 10^{-2} \times 6.02 \times 10^{23} \times 6.6 \times 10^{-34} \times 3 \times 10^8}{(0.2 \times 2.5) \times 2.536 \times 10^{-7}}$ ($E_{Total} = 0.02 \times 10 \times 2.5$ J)

$= 6.1 \times 10^4$

5) The observed quantum yield is based on a chain mechanism.

The start of the reaction chain $Cl_2 \xrightarrow{h\nu} 2Cl^{\bullet}$

The propagation of the chain $2Cl^{\bullet} + H_2 \longrightarrow HCl + H^{\bullet}$

$H^{\bullet} + Cl_2 \longrightarrow HCl + Cl^{\bullet}$

The chain termination, mainly by $2H^{\bullet} \longrightarrow H_2$

$2Cl^{\bullet} \longrightarrow Cl_2$

$H^{\bullet} + Cl^{\bullet} \longrightarrow HCl$

Problem No. 5: **Physical chemistry (thermodynamics)**

Carbon monoxide is one of the most serious environmental hazards caused by automobiles and extensive investigation is being carried out to develop efficient catalysts for the conversion of CO present in the exhaust gases to CO_2. Consider a typical family car. It has four cylinders with a total cylinder volume of 1600 cm^3 and a fuel consumption of 7.0 dm^3 /100 km when driving at a speed of 90 km/h. During one second each cylinder goes through 25 burn cycles and consumes 0.400 g of fuel. Assume that the fuel is composed of 2,2,4-trimethylpentane, C_8H_{18}. The compression ratio of the cylinder is 1:8 (the ratio between the smallest and the largest volume within the cylinder as the piston moves to and fro).

a) Calculate the air intake of the engine (m^3/s). The gasified fuel and air are introduced into the cylinder when its volume is largest until the pressure in the cylinder is 101.0 kPa. You may assume that the temperature of both the incoming fuel and air is 100.0 °C. (2.0 points)

Air contains 21.0% by volume of O_2 and 79.0% by volume of N_2. It is assumed that 10.0l% of carbon forms CO upon combustion and that nitrogen remains inert.

b) The gasified fuel and the air are then compressed until the volume in the cylinder is at its smallest. They are ignited. Calculate (1) the composition (% by volume) and (2) the temperature (K) of the exhaust gases immediately after the combustion (the exhaust gases have not yet started to expand). The following thermodynamic values are known. You can assume that both the enthalpies of formation and the molar heat capacities are independent of temperature and may be used in an approximate calculation of the temperature change. (5.0 points)

Compound	ΔH_f (kJ mol^{-1}	C_p (J $mol^{-1}K^{-1}$)
O_2 (g)	0.0	29.36
N_2 (g)	0.0	29.13
CO (g)	-110.53	29.14
CO_2 (g)	-395.51	37.11
H_2O (g)	-241.82	33.58
2,2,4-trimethylpentane,	-187.82	

c) Calculate the final temperature of the exhaust gases leaving the cylinder assuming that the piston has moved to expand the gases to the maximum volume in the cylinder, the gas mixture obeys the ideal gas equation and that the final pressure in the cylinder is 200.0 kPa. (2.0 points)

d) To convert the $CO_{(g)}$ to $CO_{2(g)}$ the exhaust gases are led through a bed of catalyst. The catalyst has the following work function:

$$\left(\frac{n(CO)}{n(CO_2)}\right) = \frac{1}{4} \times k \left(\frac{n(CO)}{n(CO_2)}\right)_i \times v \times e^{-\left(T/T_0\right)}$$

where $[n(CO)/n(CO_2)]$ is the molar ratio of CO and CO_2 leaving the catalyst, $[n(CO)/n(CO_2)]_i$ is the molar ratio before the catalyst, v is the flow rate of the exhaust gases (mol s^{-1}), T is the temperature of the exhaust gases entering the catalyst (assumed to be the same as the final temperature of the gases leaving the cylinder). T_0 is a reference temperature (373 K) and k is a constant (3.141 s mol^{-1}). Calculate the composition (% by volume) of the exhaust gases leaving the catalyst. (3.0 points)

Solution of problem No. 5:

a) M_f (C_8H_{18}) = 114.0

Consider one cylinder:

During each burn cycle: m_f = 0.400/25g = 0.0160 g
n_f = 1.4004 x 10^{-4} mol

Cylinder volume: V_0 = 4.00 x 10^{-4} m^3

Pressure: P_0 = 101.0 kPa = 101000 Nm^{-2}

Temperature: T_0 = 373 K

$$n_G = n_f + n_A = \frac{P_0 V_0}{R T_0} = \frac{101000\ Nm^{-2} \times 4\ 410^{-4}\ m^3}{8.314\ J\ mol^{-1}\ K^{-1} \times 373\ K} = 0.0130\ mol$$

n_A = air moles = $n_G - n_f$ = 0.0130 - 1.404 x 10^{-4} mol = 0.0129 mol

Air intake ($m^3\ s^{-1}$) (one cylinder; 25 burn cycles)

$$V_A^1 = \frac{25 \times n_A \times RT_0}{P_0} = \frac{25\ s^{-1} \times 0.0129\ mol \times 8.314\ JK^{-1}\ mol^{-1} \times 373\ K}{101000\ Nm^{-2}}$$

$$= 9.902 \times 10^{-3}\ m^3 s^{-1}$$

The air intake (engine; $m^3\ s^{-1}$):

V_A = 4 x 9.902 x 10^{-3} $m^3\ s^{-1}$ = 0.0396 $m^3\ s^{-1}$

b) 1) Composition of the exhaust gases (consider one cylinder and one burn cycle)

Before combustion: n_{oxygen} = 0.21 x n_A = 2.709 x 10^{-3} mol

$n_{nitrogen}$ = 0.79 x nA = 10.191 x 10^{-3} mol

0.1x $C_8H_{18} + 8.5\ O_2 \longrightarrow 8CO + 9H_2O$ (10% C)

0.9x $C_8H_{18} + 12.5\ O_2 \longrightarrow 8CO_2 + 9H_2O$ (90% C)

$C_8H_{18} + 12.1\ O_2 \longrightarrow 0.8CO + 7.2CO_2 + 9H_2O$

	No. of moles				
	C_8H_{18}	O_2	CO	CO_2	H_2O
before combustion	1.404 x 10^{-4}	2.709 x 10^{-3}	0	0	0
after combustion	0	10.10 x 10^{-4}	1.123 x 10^{-4}	10.11 x 10^{-4}	12.63 x 10^{-4}

After combustion $n_{nitrogen}$ = 10.191 x 10^{-3} mol

The composition of the gas after combustion:

Component	mol x 10^{-4}	%
N_2	101.91	75.0
O_2	10.10	7.4
CO	1.12	0.8
CO_2	10.11	7.5
H_2O	12.63	9.3
n_G	135.87	100.0

2) The temperature of gas immediately after combustion

$\Delta H = n_f[0.8 \times \Delta H_f(CO) + 7.2 \times \Delta H_f(CO_2) + 9 \times \Delta H_f(H_2O) - \Delta H_f(C_8H_{18})]$

$= 1.40 \times 10^{-4} [0.8 (-110.53) + 7.2 (-395.51) + 9 (-241.82) - (-187.82)] = -0.6914 \text{ kJ}$

$$-\Delta H = \int_{373}^{T_1} [n_{CO}\, C_p(CO) + n_{CO_2}\, C_p(CO_2) + n_{H_2O}\, C_p(H_2O) + n_{N_2}\, C_p(N_2) + n_{O_2}\, C_p(O_2)]$$

$= [1.12(29.14) + 10.11(37.11) + 12.63(33.58) +101.91(29.13) + 10.10(29.36)]\, 10^4(T_1 - 373) = 691.4 \text{ J}$

$\therefore \quad T_1 = 2060 \text{ K}$

c) Temperature of the exhaust gas leaving the cylinder

$P_2 = 200.0 \text{ kPa}$
$V = 4.00 \times 10^{-4} \text{ m}^3$
n_G = exhaust gas moles in one cylinder = 0.01359 mol

$$T_2 = \frac{P_2 V_0}{n_G R} = \frac{200000 \text{ N m}^{-2} \times 4.00 \times 10^{-4} \text{ m}^3}{0.01359 \text{ mol} \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1}} = 708 \text{ K}$$

d) Composition of the exhaust gas after the catalyst

Mass stream of the exhaust gas from all four cylinders:

$v = 4.0 \times 01359 \text{ mol} \times 25 \text{ s}^{-1} = 1.359 \text{ mol s}^{-1}$

$$\left(\frac{n(CO)}{n(CO_2)}\right) = \frac{1}{4} \times k \left(\frac{n(CO)}{n(CO_2)}\right)_i \times v \times e^{-\left(T/T_0\right)}$$

$$= 3.141 \frac{\text{s}}{\text{mol}} \times \frac{1.12 \times 10^{-4}}{10.11 \times 10^{-4}} \times 1.359 \frac{\text{mol}}{\text{s}} \times e^{-(708/373)} = 0.0177$$

The molar ratio $\left(\frac{n(CO)}{n(CO_2)}\right)$ can be calculated considering the amounts of exhaust gas components from one cycle.

Catalysed reaction: $CO + 0.5O_2 \longrightarrow CO_2$

moles x 10^4 (from 4 cylinders)			
Initial	4.48	40.40	40.44
Final	4.48 – x	40.40 – 0.5x	40.44 + x

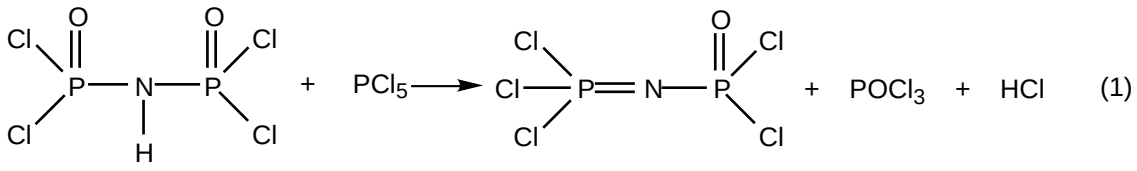
$$\left(\frac{n(CO)}{n(CO_2)}\right) = 0.0177 = \frac{4.48 - x}{40.44 + x} \qquad \therefore x = 3.70$$

Composition of the gas after the catalyst (one cycle):

	moles x 10^4			**%**
N_2	407.64	=	407.64	75.26
O_2	40.40 – 0.5x	=	8.55	7.12
CO	4.48 – x	=	0.78	0.15
CO_2	40.44 + x	=	44.14	8.14
H_2O	50.52	=	50.52	9.33
total			541 63	100.00

Problem No. 6: **Inorganic chemistry (labelled compounds)**

The course of chemical reactions can be followed by using labelled compounds. ^{32}P labelled phosphorus pentachloride (half life $t_{1/2}$ =14.3 days) is employed to establish reaction (1) as an electrophilic attack on a PCl_4^+ cation on nitrogen or on oxygen.



I II III IV

The reaction is carried out in tetrachloromethane and then the solvent and IV is distilled off.

Individually, samples of:
- III, remaining in the distillation flask.
- IV, in the distillate, and
- the radio-labelled starting material, II

are hydrolysed by heating with sodium hydroxide solution. The phosphate ions formed are precipitated as ammonium magnesium phosphate. The compounds are then recrystallised and dried. Exactly weighed samples of the three precipitates are dissolved in known volumes. The radioactivity is then determined and the specific radioactivities of the phosphates are calculated (per unit mass).

1) Write the reaction equation for labelled red phosphorus forming phosphorus pentachloride.

2) Write the reaction equations for the complete hydrolysis of the compounds II and III using sodium hydroxide solution.

3) After how many days (an integer) does the radioactivity decay to 10^{-3} of the initial value?

4) Write two alternative mechanisms for the reaction of labelled PCl_4^- with the anion of I.

5) After hydrolysis, the precipitated ammonium magnesium phosphates possess the following values of radioactivity:

   II. 2380 Bq for 128 mg of $Mg(NH_4)PO_4$.
   III. 28 Bq for 153 mg of $Mg(NH_4)PO_4$.
   IV. 2627 Bq for 142 mg of $Mg(NH_4)PO_4$.

   Using a calculation based on these data, what can you say about the nucleophilic centre attacked by PCl_4^+?

6) Given the following data,

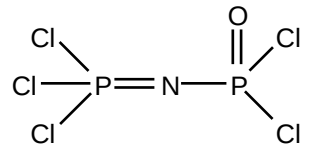
   H_3PO_4 pK_{a1} = 2.2
   pK_{a2} = 7.2
   pK_{a3} = 12.4
   pK_{sp} of $Mg(NH_4)PO_4$ = 12.6

   and the equilibrium concentration of NH_4^+ = 0.1 mol dm^{-3}. Calculate the solubility for $Mg(NH_4)PO_4$ in mol dm^{-3} under idealised conditions (activity coefficient equals one) at pH equals 10.

Solution of problem No. 6:

1) $2P + 5Cl_2 \longrightarrow 2\,PCl_5$ or $2\,^{32}P + 5Cl_2 \longrightarrow 2\,^{32}PCl_5$ (1)

2) $PCl_5 + 8OH^- \longrightarrow PO_4^{3-} + 5Cl^- + 4H_2O$ (2)



$+ 11OH^- \longrightarrow 2PO_4^{3-} + NH_3 + 5Cl^- + 4H_2O$ (3)

3) In the time dt dN nuclei are degradated. With λ as radio-active constant follows

$$\frac{dN}{dt} = -\lambda\, N(t) \qquad (4)$$

Solution of equation (4) gives

$$N(t) = N_0\, e^{-\lambda t} \qquad (\text{ie } \ln\frac{N(t)}{N_0} = -\lambda t) \qquad (5)$$

N_0 is the number of atoms present at time t = 0. With half-life value

$$\tau_{1/2} = \frac{\ln 2}{\lambda}$$

from equation (5) results

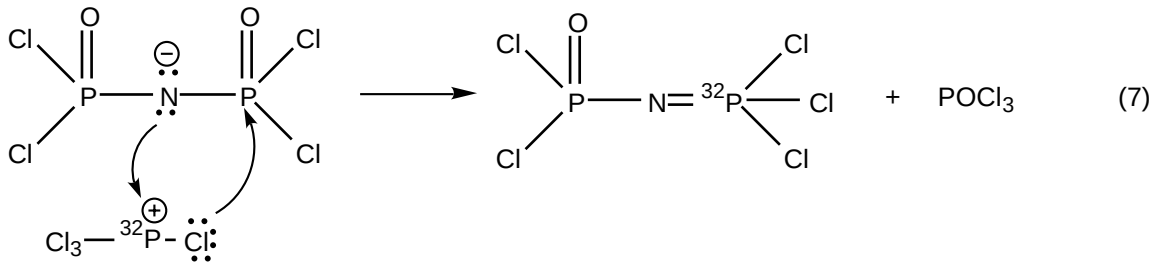
$$\ln\frac{N(t)}{N_0} = -\frac{t}{\tau_{1/2}}\ln 2$$

$$t = -\frac{\tau_{1/2}\ln\frac{N(t)}{N_0}}{\ln 2} \qquad (6)$$

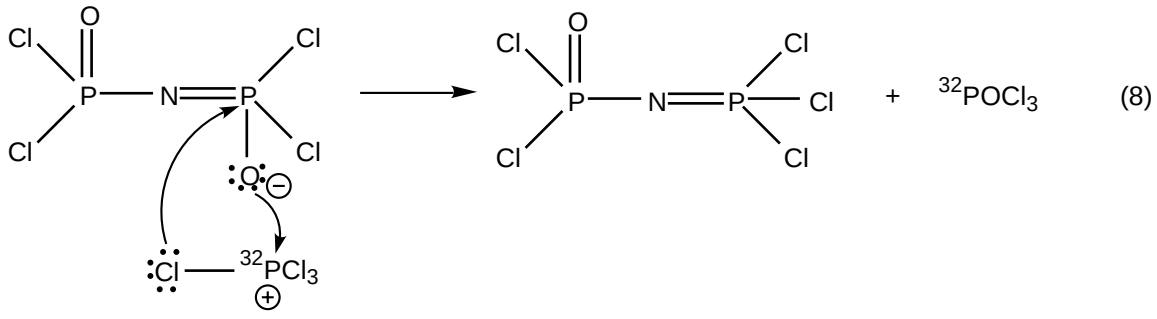
Set in the quantities

$$t = \frac{14.3\text{ d} \times \ln 10^{-3}}{\ln 2} = 143\text{ d}$$

4)



$+ \quad POCl_3$ (7)



$+ \quad ^{32}POCl_3$ (8)

5) Specific activities A_{sp} (II) = 18.6 Bq mg^{-1}

A_{sp} (III) = 0.18 Bq mg^{-1}

A_{sp} (IV) = 18.5 Bq mg^{-1}

Because A_{sp} (II) ≈ A_{sp} (IV) reaction (8) is right.

PCl_4^+ attacks the O-atom!

6) $K_L = c_{Mg^{2+}}\, c_{NH_4^+}\, c_{PO_4^{3-}}$ (9)

$H_3PO_4 + H_2O \rightleftharpoons H_2PO_4^- + H_3O^+$ (10) $PK_{a1} = 2.2$

$H_2PO_4^- + H_2O \rightleftharpoons HPO_4^{2-} + H_3O^+$ (11) $PK_{a2} = 7.2$

$HPO_4^{2-} + H_2O \rightleftharpoons PO_4^{3-} + H_3O^+$ (12) $PK_{a3} = 12.4$

At pH = 10 the main component is HPO_4^{2-}

It results

$L = c_{Mg^{2+}} = c_{HPO_4^{2-}}$ (13)

From (12) follows

$$c_{PO_4^{3-}} = K_{a3}\,\frac{c_{HPO_4^{2-}}}{c_{H_3O^+}} \qquad (14)$$

With (9), (13) and (14) results

$$K_L = c_{NH_4^+}\, L\, K_{a3}\,\frac{L}{c_{H_3O^+}}$$

$$L^2 = \frac{K_L\, c_{H_3O^+}}{K_{a3}\, c_{NH_4^+}}$$

$$pL = \frac{1}{2}(pK_L + pH - pK_{a3} + \log c_{NH_4^+})$$

$pL = \frac{1}{2}(12.6 + 10.0 - 12.4 - 1.0)$

$pL = 4.6$

$L = 2.5 \times 10^{-5}$ mol dm^{-3}

Problem No. 7: **Organic chemistry (stereochemistry)**

Lactic acid is produced industrially (by CCA-Biochem, the Netherlands) through the bacterial conversion of saccharose. In this process (S)-(+)-2-hydroxypropanoic acid (L-(+)-lactic acid) is formed, which is used in the food sector and also as a starting material for a number of chemical products.

a) Give the spatial formula and the Fischer projection of L-(+)-lactic acid.

A fine-chemical produced from L-(+)-lactic acid is the so-called dilactide, a cyclic ester in which 2 molecules have been esterified with one another. This dilactide is polymerized to a polylactide, which among other things is being used in surgery as a “biodegrading” thread in the suturing of surgical wounds.

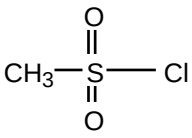
b) Draw the spatial structure of the dilactide prepared from (+)-lactic acid.

c) Sketch the spatial structure of the polylactide discussed above (at least three units). What is its tacticity? (isotactic, syndiotactic, atactic)

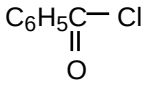
d) Draw the isomeric dilactides, which occur when one starts with racemic lactic acid and show the configuration of the chiral centres.

Note: In the questions b) and d), for convenience the ring may be considered planar.

L-(+)-lactic acid is also one of the starting materials for the preparation of the herbicide Barnon (manufactured by Shell Chemicals, used against wild oats). In this case (+)-lactic acid is esterified with 2-propanol and then the hydroxyl group is treated with methanesulfonyl chloride :



The product obtained is then submitted to a S_N2-reaction with 3-fluoro-4-chloroaniline*, in which reaction the methanesulfonate group leaves as $CH_3SO_3^-$. Finally a benzoyl group is introduced with the aid of benzoylchloride.



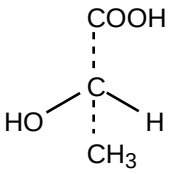
e) Draw the Fischer projection of the various consecutive reaction products.

*3-fluoro-4-chloroaniline is the same as 3-fluoro-4-chloro-phenylamine.

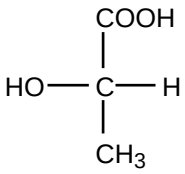
Solution of problem No. 7:

a) L-(+)-lactic acid

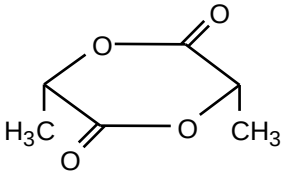
spatial formula:



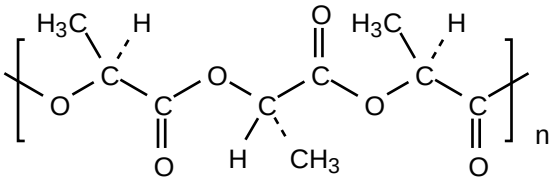
Fischer projection:



b) Dilactide of L-(+)-lactic acid, spatial formula:

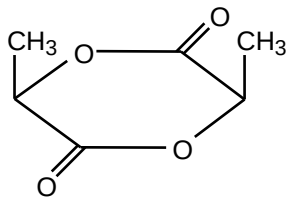


c) Polylactide of L-(+)-lactic acid; spatial formula:

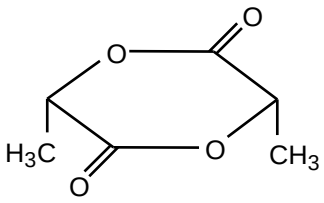


Tacticity: isotactic.

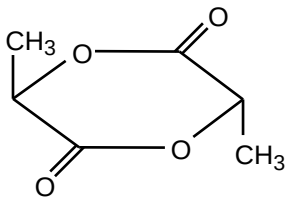
d) Dilactides of racemic lactic acid; spatial formulae with configurations:



(R, R)

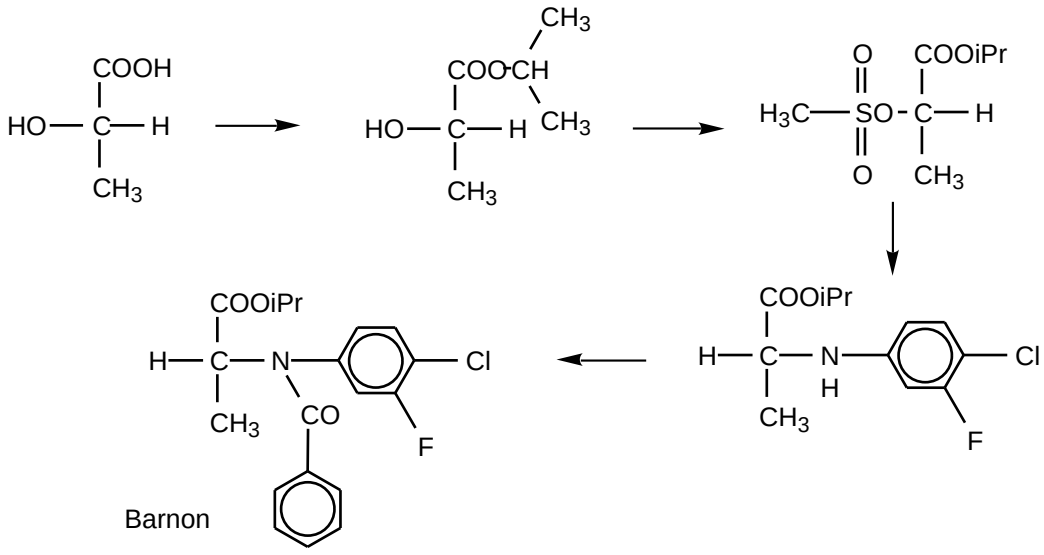


(S, S)



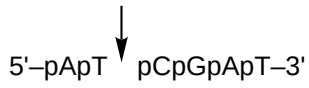
(R, S) meso compound

e) Consecutive products in Fischer projection:



Problem No. 8: **Biochemistry (DNA)**

In recombinant DNA technology one makes use of specific endonucleases. These are enzymes which recognise specific nucleotide sequences in double strand DNA and which catalyse the hydrolysis of a phosphoric ester bond in each of both strands. In this problem we consider two different endonucleases which carry the names Cla I and Taq I.
Cla I hydrolyses the bond between two nucleotides in the sequence:



a) Give the base sequence of the complementary strand in the 5'→3' direction and indicate with an arrow the location where the hydrolysis by Cla I occurs.

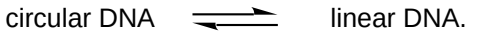
b) How often on average will this sequence occur in one strand of a DNA molecule of 10^5 base pairs? You can assume that the four bases occur equally often and that they are randomly distributed in the two chains.

Taq I hydrolyses a long double strand DNA molecule into fragments which are on average 256 base pairs long. The 3' end of these fragments created by cleavage turns out to be a thymine(T), and the 5' end is a cytosine(C).

c) How long is the sequence recognised by Taq I?

d) Give the two possible base sequences (in the direction 5'→3') which form the recognition pattern for Taq I.

It will be evident from the foregoing that the recognised part of DNA has a certain symmetry. The DNA of a phage which occurs as a close circle contains only one 5'–pApTpCpGpApT–3' sequence in each of the two strands. After treatment of this DNA with a Cla I an equilibrium is established:



e) Give a schematic drawing of the circular and linear molecules. Indicate the bases adjacent to the cleaving site in both strands. Indicate also the 3' and 5' ends.

In the figure on the next page the percentage of linear DNA molecules is given as a function of temperature, as measured in a solution of 0.15 M NaCl buffered with citrate at pH = 6.5.

f) Is the reaction as written endothermic or exothermic? Explain why.

This particular phage also has only one cleavage site for the endonuclease Taq I. The figure also shows the percentage of linear DNA versus temperature after cleavage by Taq I. As is evident, one obtains the same curve as after cleavage with Cla I.

g) Show, considering the information above, which of the two base sequences of the answer to d) is the correct one.

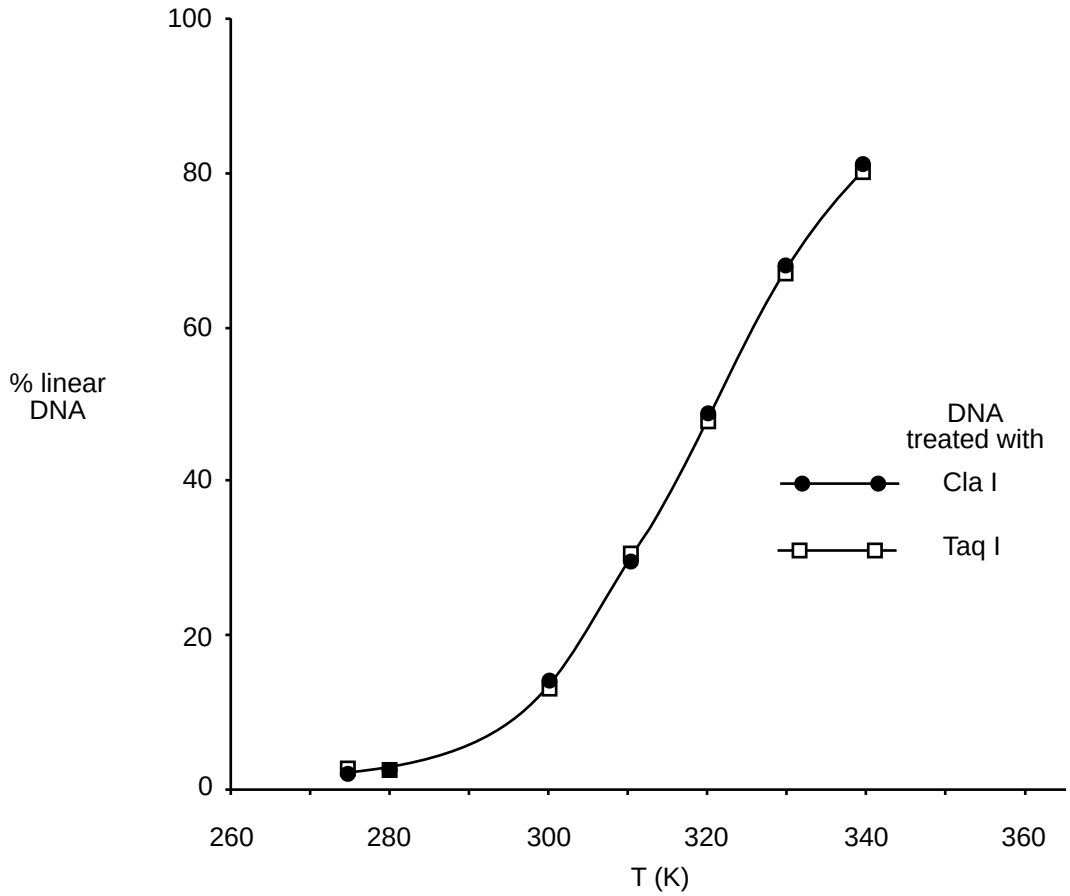
h) Copy the figure completely and show how the curve for Taq I would have been if the recognition pattern had been the other possibility of d).

A large DNA molecule is cut into fragments with the aid of Cla I. One fragment is isolated and purified. This fragment is then mixed one to one with phage DNA which was also cleaved with Cla I. So-called recombinant molecules can be formed through the reaction:

i) Would the ΔH^o of this reaction be positive, negative, or about zero?

k) Which combination of temperature, DNA concentration, and ionic strength (high or low in each case) will give the maximum percentage of recombinant molecules?

These recombinant molecules are used in genetic manipulation.


100
80
60
40
20
0
% linear DNA
260
280
300
320
340
360
T (K)
DNA treated with
Cla I
Taq I

Solution of problem No. 8:

a) 5'–pApT ↓ pCpGpApT–3'

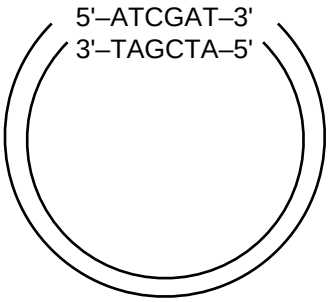
b) 1 in 4096, or about 25 times.

c) 4 bases.

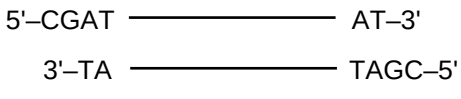
d) 5'–pTpCpGpA –3' or 5'–pGpApTpC–3'

(one sequence of four bases occurs in 256 times)

e)



and



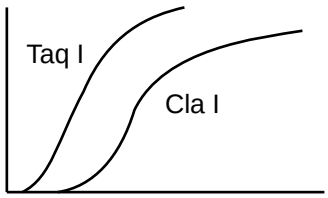
f) The reaction has a positivev ΔH^0, because the hydrogen bonds (between the G and the C bases) in the complementary strands are broken.

g) The two reactions show the same dependence on temperature. Therefore the ΔH^0 of the two reactions is the same. Then the interaction in the overlapping part of the double helix must be identical and therefore we must choose for the first recognition sequence of question d). The cleavage in the two cases occurs as follows:

Cla I: 5'–p A p T | p C p G p A p T–3'
3'–p T p A p G p C p T | p A–5'

Taq I: 5'–p T | p C p G p A–3'
3'–p A p G p C p | T–5'

h)



i) ΔH^0 is negative.

k) Temperature low, concentration DNA high, ionic strength high.

Practical problem No. 1: **Synthesis and analysis of a nickel complex**

Introduction

The experimental assignment consists of the synthesis and subsequently, the analysis of an amminenickel chloride: $NiCl_x(NH_3)_y$.

The synthesis proceeds in three steps:

a) preparation of a solution of nickel nitrate from nickel and concentrated nitric acid (green solution), time required about 20 min.;
b) preparation of amminenickel nitrate (blue crystals); and
c) preparation of amminenickel chloride (blue-violet crystals)

The analysis encompasses the determination of the percentages of the three components (ammonia, nickel and chlorine) of the salt, according to the instructions given in 2.

Report

Record in the indicated places on the report form the data asked in the experimental part 1, and all relevant experimental data, the calculation and the results from part 2.

Experimental

1. Synthesis of the Nickel Salt.

All work on the synthesis must be carried out in the fume hood. Use of (safety) glasses is obligatory. If necessary use other safety equipment such as rubber gloves and pipetting balloons.

a) Put a “dubbeltje” (Dutch coin of 10 c, containing 1.5 g of nickel), in a conical flask (Erlenmeyer flask) of 100 mL and add 10 mL of concentrated nitric acid (65%). Fit the flask with an “air cooled” condenser (no water) and heat the contents on a hot plate until a violent reaction occurs. Continue heating carefully until all metal has been dissolved.
   Cool the green solution in an ice-water mixture.
   Write in the report form the equation of the chemical reaction that has occurred.
b) Add, continuously cooling, in small portions 25 mL of ammonia solution (25%) to the ice cold solution. As soon as about 15 mL has been added, salt crystals start to precipitate.
   Having added all ammonia solution, filter the cold solution through a sintered glass filtering crucible by applying a vacuum with an aspirator. Wash the crystals three times with small portions of a cold ammonia solution(25%). Remove as much liquid as possible from the crystalline mass by maintaining the vacuum.
c) Dissolve the moist crystalline mass in 10 mL of hydrochloric acid (18%). Cool the blue solution in an ice water mixture and then add slowly 30 mL of a solution of 30 g ammonium chloride in 100 mL of ammonia solution (25%). This yields a blue-violet coloured crystalline mass. Cool the mixture and filter as in b).
   Wash with ammonia solution (25%), then with ethanol and finally with diethyl ether. Leave the crystals in air until all ether has evaporated. Determine the mass of the dry product and record this on the report form.

2. Analysis of the Nickel salt.

For the analysis of the salt, only one sample solution is prepared. The determination of the components is achieved by titrating each time 25 mL of the sample solution in duplicate.
For the determination of the ammonia and chlorine content a back titration is carried out. For that purpose a certain amount of reagent is added in excess. The total amount of reagent, available for the sample, is determined by following the same procedure for 25 mL of a blank solution.
This titration should not be carried out in duplicate.

Prepare the following solutions:

A) Sample solution:
   Pipette 25 mL 1.6 M nitric acid into a volumetric flask of 250 mL. Add a sample of about 1.2 g of the amminenickelchloride and dilute with water to a volume of 250 mL.

B) Blank solution:
   Pipette 25 mL of the same 1.6 M nitric acid and dilute this with water to a volume of 250 mL.

Note:

1) For the chlorine determination use conical (erlenmeyer) flasks with a ground glass stopper.

2) The nitric acid contains a small amount of hydrochloric acid. The total acid content is 1.6 M.

a) Determination of the ammonia content.

Titrate the solutions with a standard solution of NaOH (about 0.1 M).
Indicator: methyl red, 0.1% solution in ethanol.
Calculate the percentage of ammonia in the salt.

b) Determination of the nickel content.

Add about 100 mL of water, 2 mL of ammonia solution (25%) and 5 drops of murexide solution to the nickel solution, which now should have a yellow colour.
Titrate the solution with a standard solution of EDTA (about 0.025 M) until a sharp colour change from yellow to violet is observed. Calculate the percentage of nickel in the salt.

c) Determination of the chlorine content.

Execute the titrations as quickly as possible after the addition of the reagent!
Add to each solution 25 mL of 0.1 M silver nitrate solution. Add about 5 mL of toluene, shake vigorously, add indicator and titrate with the standard solution of ammonium thiocyanate (rhodanide, about 0.05 M) until a permanent colour change to red is observed.
At the end of the titration, shake vigorously again. The red coloration should persist.
Indicator: 1 mL of a saturated solution of iron(III)sulphate.
Calculate the percentage of chlorine in the salt.

Data: Atomic masses: H = 1; Cl = 35.5; N = 14; Ni = 58.7.

d) Calculate from the results obtained the molar ratio of the components, to two decimal points and enter this on the report form in the format: Ni : Cl: NH_3 = 1.00 : x : y.

Practical problem No. 2: **Potentiometric determination of phosphoric acid in Coca-Cola**

Apparatus:

Round bottom flask (500 mL), magnetic stirrer, reflux condenser, water bath, electric heater.

Reagents:

6.0 g charcoal,
standard solution of sodium hydroxide ($c = 0.05$ mol L^{-1}),
buffer solutions.

Preparation of the sample:

Pour the contents of a Cola can into a round-bottomed flask and add 6.0 g of powdered charcoal to the stirred solution. Cautiously raise the temperature of the solution and reflux for 10 minutes. Allow the solution to cool to room temperature and filter using a fluted filter paper. Repeat the filtration step.

Calibration of the potentiometer:

Calibrate the pH-meter by means of two buffer solutions.

Titration:

Titrate a 150 mL aliquot of your sample with sodium hydroxide solution ($c = 0.05$ mol L^{-1}) by measuring the pH using a pH-meter.
The first equivalence point occurs after the addition of about 6 mL NaOH solution. Continue the titration until at least 12 mL of sodium hydroxide solution has been added.

Evaluation:

a) Draw the titration curve. Determine the first equivalence point.
b) Give the pH-value of the boiled Cola-beverage and the pH-value of the first equivalence point.
c) Calculate the concentration of phosphoric acid in the Cola-beverage. Record the calculation and the result in the answer sheet.

Practical problem No. 3: **Preparation of a buffer solution**

A pH buffer solution has a well specified acidity, which changes only very slightly upon addition of moderate quantities of strong acid or base. The larger the quantity of acid or base that must be added to a certain volume of buffer solution in order to change its pH by a specified amount, the better its buffer action is said to be. A buffer solution is prepared by mixing a weak acid and its conjugate base in appropriate amounts in solution. An example of a useful buffer system in aqueous solution is the phosphate system.

Your task is to prepare a phosphate buffer solution with properties specified by the following two conditions:

1) pH = 7.20 in the buffer solution

2) pH = 6.80 in a mixture of 50.0 cm^3 of the buffer solution and 5.0 cm^3 hydrochloric acid with a concentration of 0.100 mol/dm^3.

Chemicals and equipment:

Aqueous solution of phosphoric acid, sodium hydroxide solution of known concentration, hydrochloric acid (0.100 mol/dm^3), solution of bromocresol green, distilled water.

Burettes, pipettes (25 cm^3 and 5 cm^3), Erlenmeyer flasks (100 cm^3 and 250 cm^3), volumetric flask (100 cm^3), beaker, and funnel.

Procedure:

Determine the concentration of the phosphoric acid solution by titration with the sodium hydroxide solution using bromocresol green as an indicator (pH range $3.8 < pH < 5.4$).

Make the buffer solution by mixing calculated volumes of phosphoric acid and sodium hydroxide solution in the volumetric flask and filling the flask to the mark with distilled water.

Mix 50.0 cm^3 buffer solution with 5.0 cm^3 hydrochloric acid in an Erlenmeyer flask.

Hand in your answer sheet to the referees who will also measure the pH of your two solutions and note your result.

The pK_a values of phosphoric acid are $pK_{a1} = 1.75$, $pK_{a2} = 6.73$ and $pK_{a3} = 11.50$.

Solution

The buffer solution must contain $H_2PO_4^-$ (concentration a mol/dm^3) and HPO_4^{2-} (concentration b mol/dm^3). The concentrations should satisfy the condition

$b/a = 10^{-6.73}/10^{-7.20}$

After addition of HCl, the condition will be

$(50.0 \times b - 0.50) / (50.0 \times a + 0.50) = 10^{-6.73}/10^{-6.80}$

From these equations, $a = 0.0122$ $b = 0.0361$

Total concentration of the phosphate system = 0.0483 mol/dm^3

Total concentration of $Na^+ = (a + 2b)$ $mol/dm^3 = 0.0844$ mol/dm^3

If the concentrations of both phosphoric acid and sodium hydroxide solutions are 0.500 mol/dm^3, then 100.0 cm^3 buffer solution will require

volume of H_3PO_4 solution = $0.0483 \times 0.1000/0.500$ $dm^3 = 9.7$ cm^3

volume of NaOH solution = $0.0844 \times 0.1000/0.500$ $dm^3 = 16.9$ cm^3

Practical problem No. 4: **Synthesis of aspirin**

Prepare 2-ethanoyloxybenzoic acid (acetylsalicylic acid, also known as aspirin) by ethanoylation (acetylation) of 2-hydroxybenzoic acid (salicylic acid) with ethanoic anhydride (acetic anhydride).

Relative atomic masses: C : 12.011; O : 15.999; H : 1.008

Reagents: 2-hydroxybenzoic acid (melting point 158°C)

Ethanoic anhydride (boiling point 140 °C)

Phosphoric acid (85 % H_3PO_4)

Ethanol
Deionised/distilled water

Question 1

Write the balanced chemical equation for the reaction using structural formulae.

Procedure

Take a 100 cm^3 Erlenmeyer/conical flask. In the flask, mix the 2.760 g of 2-hydroxybenzoic acid from weighing bottle A, the 5.100 g of ethanoic anhydride from flask B, and with cautious swirling, add 5 - 7 drops of 85 % phosphoric acid. Heat the flask to 70 - 80 °C in a beaker of near boiling water and maintain the mixture at this temperature for 15 minutes. Remove the flask from the water bath and, with gentle swirling, add dropwise 1 cm^3 of deionised water to the still hot flask; then immediately add 20 cm^3 of the cold deionised water all at once to the reaction flask. Place the flask in an ice bath. If no crystals are deposited or if an oil appears, gently scratch the inner surface of the flask with a glass rod whilst the flask remains in the ice bath.
Using the Buchner funnel, filter the product under suction. Rinse the flask twice with a small amount of cold deionised water. Recrystallise the crude product in a 100 cm^3 Erlenmeyer/conical flask using suitable amounts of water and ethanol. If no crystals form, or if an oil appears, gently scratch the inner surface of the flask with a glass rod. Filter the crystals under suction and wash with a small amount of cold deionised water.

Place the crystals on the porous plate to draw water from them. When the crystals have been air dried, transfer the product to the small glass dish labelled C. This dish has previously been weighed.

The dish containing the product should be given to a technician who will dry it in an oven for 30 minutes at 80 °C.

A technician should then weigh the cooled dish containing your product in your presence. Record that mass. The melting point will subsequently be taken by a technician to check the purity of your product.

Question 2

What is the percentage yield?

ANSWER SHEET

l. Write the balanced equation for the reaction.

2. Mass of vessel C and product = ……g

Mass of vessel C (tared weight) = ……g

Mass of product = ……g