

INTERNATIONAL CHEMISTRY
OLYMPIADS

1986 - 1994

Problems and Solutions

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Problems

1. Analytical chemistry

IChO Veszprém - Budapest 1987

25.00 ml of a neutral solution containing potassium chloride and potassium cyanide are potentiometrically titrated with a standard 0.1000 molar silver nitrate solution at 25°C using a silver electrode and a normal calomel half-cell with KNO₃ - salt bridge. The protonation of cyanid ions is negligible. The potentiometric curve obtained (emf (V)) vs. burette readings (in ml) is shown in Fig. 1.

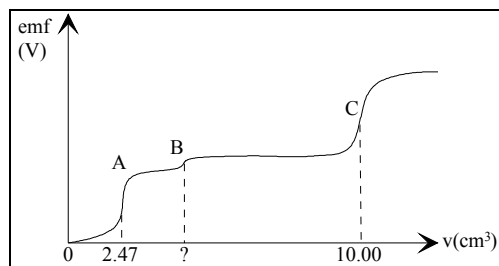


Fig. 1 Potentiometric titration curve

- The end point of the reaction taking place during the titration are marked with A, B and C. Write the balanced ionic equation for each reaction.
- What volume of the titrant is required to reach point B ?
- Calculate the concentrations of KCl and KCN in the sample solution.
- Calculate the emf readings at the points A and C in volts.
- What is the molar ratio Cl⁻/CN⁻ in the solution and in the precipitate at point C ?

Data:

$$E^{\circ}(\text{Ag}^+/\text{Ag}): \quad 0.800 \text{ V}$$

$$E^{\circ}(\text{Calomel}): \quad 0.285 \text{ V}$$

$$K_{\text{sp}}(\text{AgCN}): \quad 10^{-15.8} \text{ mol}^2/\text{l}^2$$

$$K_{\text{sp}}(\text{AgCl}): \quad 10^{-9.75} \text{ mol}^2/\text{l}^2$$

$$\beta_2 = \frac{[\text{Ag}(\text{CN})_2^-]}{[\text{Ag}^+][\text{CN}^-]^2} = 10^{21.1} \text{ mol}^{-2} \text{ l}^2$$

IChO Helsinki 1988

Chloride ions are analytically determined by precipitating them with silver nitrate. The precipitate is undergoing decomposition in presence of light and forms elemental silver and chlorine. In aqueous solution the latter disproportionates to chlorate (V) and chloride. With excess of silver ions, the chloride ions formed are precipitated whereas chlorate (V) ions aren't.

- Write the balanced equations of the reactions mentioned above.
- The gravimetric determination yielded a precipitate of which 12% by mass was decomposed by light. Determine the size and direction of the error caused by this decomposition.

- c) Consider a solution containing two weak acids HA and HL, 0.020 molar and 0.010 molar solutions respectively. The acid constants are $1 \cdot 10^{-4}$ for HA and $1 \cdot 10^{-7}$ mol/l for HL. Determine graphically the pH of the solution using a logarithmic diagram, $\log C = f(-\log[H^+])$. Calculate the pH of the solution.
- d) M forms a complex ML with the acid H_2L with the formation constant K_1 . The solution contains an other metal ion N that forms a complex NHL with the acid H_2L . Determine the conditional equilibrium constant, K'_1 for the complex ML in terms of $[H^+]$ and K values.

$[M']$ = total concentration of M not bound in ML

$[L']$ = the sum of the concentrations of all species containing L except ML

$$K_1 = \frac{[ML]}{[M][L]}$$

$$K'_1 = \frac{[ML]}{[M'][L']}$$

$$K_{NHL} = \frac{[NHL]}{[N][L][H^+]}$$

In addition to K_1 , the acid constants K_{a1} and K_{a2} of H_2L as well as the formation constant K_{NHL} of NHL are known. You may assume that the equilibrium concentration $[H^+]$ and $[N]$ are known, too.

ICHO Pittsburgh 1992

The minimum concentration of chloride ions needed in oyster beds for normal growth is 8 ppm (8 mg/l). To 50.00 ml a sample of bay water a few drops of a K_2CrO_4 -solution are added. The sample is then titrated with 16.16 ml of a 0.00164 M $AgNO_3$ -solution when a bright red-orange precipitate starts to form.

- What is the molar concentration of chloride in the sample ? Does the water contain sufficient chloride for the normal growth of oysters ?
- Write a balanced equation for the reaction of the analyte with the titrant.
- Write a balanced net-ionic equation that describes the reaction responsible for the colour change at the endpoint of the titration. Which compound produces the brick-red colour ?
- The concentration of chromate at the endpoint is 0.020 M. Calculate the concentration of chloride in the solution when the red precipitate is formed.
- For this titration to work most efficiently, the solution being titrated must be neutral or slightly basic. Write a balanced equation for the competing reaction that would occur in acidic medium influencing the observed endpoint of this titration.

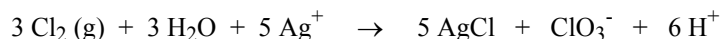
Typically, a buffer is added to the solution being titrated to control the pH. Suppose the pH of the sample of bay water was 5.10, thus too acidic to perform the analysis accurately.

- Select a buffer from the list that would enable you to establish and maintain a pH of 7.20 in aqueous medium. Show the calculations which leads your choice.

Buffer systems	K_a of weak acid
1. 0.1 M lactic acid / 0.1 M sodium lactate	$1.4 \cdot 10^{-4}$
2. 0.1 M acetic acid / 0.1 M sodium acetate	$1.8 \cdot 10^{-5}$
3. 0.1 M sodium dihydrogen phosphate / 0.1 M sodium hydrogen phosphate	$6.2 \cdot 10^{-8}$
4. 0.1 M ammonium chloride / 0.1 M ammonia	$5.6 \cdot 10^{-10}$

- g) Using the selected buffer system, calculate the number of grams of weak acid and of conjugated base you would need to dissolve in distilled water to prepare 500 ml of a stock solution buffered at a pH of 7.2.
- h) The chloride concentration in another 50.00 ml sample was determined by the Vollhard method. In this method an excess of AgNO_3 is added to the sample. The excess Ag^+ is titrated with standardized KSCN , forming a precipitate of AgSCN . The endpoint is signalled by the formation of the reddish-brown FeSCN^{2+} complex that forms when Ag^+ is depleted. If the excess Ag^+ from the addition of 50.00 ml of 0.00129 M AgNO_3 to the water sample required 27.46 ml of $1.41 \cdot 10^{-3}$ M KSCN for titration, calculate the concentration of chloride in the bay water sample.

In natural waters with much higher concentration of Cl^- , it can be determined gravimetrically by precipitating them as AgCl . A complicating feature of this method is the fact that AgCl is susceptible to photodecomposition as shown by the reaction: $\text{AgCl}(\text{s}) \rightarrow \text{Ag}(\text{s}) + \frac{1}{2} \text{Cl}_2(\text{g})$. Furthermore, if this photodecomposition occurs in the presence of excess Ag^+ , the following additional reaction occurs:



- i) Will the apparent weight of AgCl be too high or too low? Explain your answer showing by how many grams the two values will differ.

data: K_{sp} for $\text{AgCl} = 1.78 \cdot 10^{-10}$ K_{sp} for $\text{Ag}_2\text{CrO}_4 = 1.00 \cdot 10^{-12}$

IChO Perugia 1993

The reflux of bile and duodenal matter is suspected to be the major cause of gastritis and medical therapy is based on treatment with antiacids that, by binding bile acids and lysolecithin, buffer the pH of gastric juices. The separation of two bile acids, i.e. cholic acid (CA) and glycocholic acid (GCA) was achieved with high performance liquid chromatography (HPLC). Two chromatographic columns (A and B, respectively) were selected on the basis of published literature data. The retention times (t) of the two acids, of a substance not retained and of a compound used as internal standard (i.s.) are shown on the Table 1. Both columns are 25 cm long and show an efficiency of $2.56 \cdot 10^4$ theoretical plates per meter (N/m). In actual analysis, an artificial gastric juice was extracted with appropriate solvents and the final solution (1mL) contained 100% of the two acids present in the original mixture. 100 μL of the extract added with 2.7 μL of internal standard were analyzed by HPLC using the selected column. The response factors (F) of CA and GCA with respect to the i.s. and chromatographic peak areas of the two compounds are reported in the Table given below.

	Column A t (sec)	Column B t (sec)	F	Area
Unretained compound	120	130		
Cholic Acid (CA)	380	350	0.5	2200
Glycocholic Acid (GCA)	399	395	0.2	3520
Internal standard (i.s.)	442	430		2304

Note that:

$$R = (\sqrt{N} / 4) \cdot [(\alpha - 1) / \alpha] \cdot [K' / (K' + 1)]$$

$$\alpha = t'_2 / t'_1 = (t_2 - t_0) / (t_1 - t_0)$$

$$K' = t_2' / t_0 = (t_2 - t_0) / t_0$$

- a) Using R , α and K' values, demonstrate which of the two chromatographic columns would be best to use, considering that an accurate determination requires the best possible (baseline) separation of all compounds (do not take into account the unretained compound) ?
- b) Calculate the amounts of each acid in the extract solution.

IChO Oslo 94

Lactic acid is formed in the muscles during intense activity (anaerobic metabolism). In the blood, lactic acid is neutralized by reaction with hydrogen carbonate ions. This will be illustrated by the following calculations:

Lactic acid, written HL, is monoprotic, and the acid dissociation constant is $K_{HL} = 1.4 \times 10^{-4}$. The acid dissociation constants for carbonic acid are: $K_{a1} = 4.5 \times 10^{-7}$ and $K_{a2} = 4.7 \times 10^{-11}$. All carbon dioxide remains dissolved during the reactions.

- a) Calculate the pH of a 3.00×10^{-3} M solution of HL.
- b) Calculate the value of the equilibrium constant for the reaction between lactic acid and hydrogen carbonate ions.
- c) 3.00×10^{-3} mol of lactic acid (HL) is added to 1.00 L of 0.024 M solution of NaHCO_3 (no change in volume, HL completely neutralized). Calculate the pH of the solution of NaHCO_3 before HL is added. Calculate the pH of the solution after the addition of HL.
- d) The pH of the blood in a person changed from 7.40 to 7.00 due to the lactic acid which formed during physical activity. Let an aqueous solution having pH = 7.40 and $[\text{HCO}_3^-] = 0.022$ M represent blood in the following calculation and in f). Calculate the number of moles of lactic acid which must be added to 1.00 L of this solution so that the pH becomes 7.00.
- e) In a saturated aqueous solution of $\text{CaCO}_3(\text{s})$ the pH is measured as 9.95. Calculate the solubility of calcium carbonate in water and show that the calculated value for the solubility product constant K_{sp} is 5×10^{-9} .
- f) Blood contains calcium ions. Calculate the maximum concentration of "free" calcium ions in the solution given in d). (pH = 7.40, $[\text{HCO}_3^-] = 0.022$ M)

2. Inorganic chemistry

IChO Leiden 1986

Compounds containing divalent platinum with the general formula $\text{PtX}_2(\text{amine})_2$ ($\text{X} = \text{Cl}_2, \text{SO}_4^{2-}$, malonate, etc.) have met a lot of scientific interest because of their biological activity, particularly in view of their properties in the treatment of tumours. The best known compound used clinically is $\text{PtCl}_2(\text{NH}_3)_2$. This compound, in which platinum is coordinated in a planar square, has two geometrical isomers of which only one shows the antitumour activity.

- a) Sketch the spatial structures of the two possible isomers.
- b) How many isomers has $\text{PtBrCl}(\text{NH}_3)_2$? Sketch all of them.

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

c) Show graphically that PtBrCl(en) has only one stable structure.

The ligand en can be substituted via methylation to form dmen or pn (racedmic).

d) Give spatial structures of all isomers of the following compounds: PtCl₂(dmen), PtCl₂(pn), PtBrCl(dmen) and PtBrCl(pn).

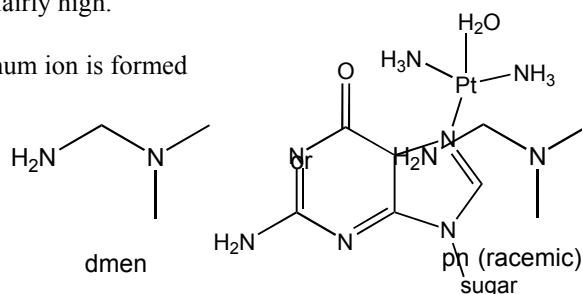
These compounds can isomerize in aqueous solution through dissociation of a ligand and transient replacement of the stronger ligands by the weak ligand water. Cl⁻ and Br⁻ are replaced relatively easily, but it is more difficult to replace the amine ligands, which usually requires heating.

e) Considering each of the isomers in the previous questions a-d, indicate which isomers can be converted to another at room temperature. Give both the original molecule and the products.

f) PtCl₂(en) reacts with Br⁻ in a molar proportion of 1:2 at room temperature. Which compound would you expect to form in what proportion? You can assume that the Pt-Br and Pt-Cl bonds are equally strong and that there is no perturbing influence from hydrolysis.

g) Using the equation to express chemical equilibrium, show that hydrolysis hardly ever occurs in blood but that it does occur in the cells. Note: PtCl₂(NH₃)₂ hydrolyses to Pt(NH₃)₂(H₂O)₂²⁺ and 2 Cl⁻. In cells the Cl⁻ concentration is low, in blood it is fairly high.

After hydrolysis in the tumour cell a reactive platinum ion is formed to which two NH₃ groups are still bound, which were found 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.



As a result of the two reactive sites of platinum and the two unreactive NH₃ ligands, it can form a second bond to DNA in addition. Research has shown that this happens in particular with a second guanine base from the same strand of DNA.

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

ICHO Leiden 1986

The compound Na₅P₃O₁₀ is used as an additive for detergents to bind the Ca²⁺ and Mg²⁺ ions present in water in order to prevent the precipitation of their fatty acid salts on the laundry.

a) Draw the structure of the ions (P₃O₁₀)⁵⁻ and (P₃O₉)³⁻ assuming that P-P bonds do not occur.

b) Assuming an octahedral coordination of the Mg²⁺ ion give a drawing of the Mg(P₃O₁₀)(H₂O)_n³⁻ ion also indicating the value for n.

The complex ions of Mg²⁺ and Ca²⁺ and triphosphate are well soluble in water. They are, among other things, responsible for the wild growth of algae in surface waters. They could be removed by precipitation as an insoluble compound.

- c) Give some possibilities (ions) to precipitate the triphosphates bound to Ca^{2+} or Mg^{2+} .
 d) Calculate the number of grams of $\text{Na}_5\text{P}_3\text{O}_{10}$ necessary in a washing machine of 20 liters to reduce the amount of Ca^{2+} in city water (0.225 g/l) to an acceptable maximum of 0.02 g/l. Effects of the pH, the precipitation of $\text{Ca}(\text{OH})_2$ and possible effects by other positive ions can be neglected. The following data is given:

$$K_1 = \frac{[\text{Ca}^{2+}][\text{P}_3\text{O}_{10}^{5-}]}{[\text{CaP}_3\text{O}_{10}^{3-}]} = 1.0 \cdot 10^{-6}$$

Molar mass of $\text{Na}_5\text{P}_3\text{O}_{10}$ is 366 g, the atomic mass of Ca is 40 g/mol.

IChO Veszprém - Budapest 1987

500 mg of a hydrated sodium salt of phosphoric acid are dissolved in 50.0 ml of 0.1 molar sulphuric acid. This solution is diluted with distilled water to 100.0 ml and 20.0 ml thereof are titrated with 0.100 molar NaOH solution using thymolphthalein as indicator. The average of the burette reading is 26.53 ml. The pH at the end-point is 10.00. The cumulative protonation constants are given by

$$K_n = \frac{[\text{H}_n\text{PO}_4^{n-3}]}{[\text{PO}_4^{3-}][\text{H}^+]^n}$$

where $\text{p}K_1 = -11.70$; $\text{p}K_2 = -18.6$; $\text{p}K_3 = -20.6$. Relative atomic masses are: Na = 23.0 and P = 31.0

- a) Calculate the percentage distribution, by moles, of all protonated $\text{H}_n\text{PO}_4^{n-3}$ species at the end point.
 b) What is the stoichiometric formula of the salt ?

IChO Helsinki 1988

Upon heating of a mixture of A and fluorine (molar ratio 1:9, high pressure) to 900 °C three compounds (B, C and D) are formed. All three products are crystalline solids with melting points below 150 °C. The fluorine content of C is found to be 36.7% and that of D 46.5% (by weight). When B is treated with anhydrous HOSO_2F at -75°C a compound E is formed: $\text{B} + \text{HOSO}_2\text{F} \rightarrow \text{E} + \text{HF}$

E is a solid which is stable for weeks at 0°C, but decomposes in days at room temperature. The electron density distribution of E obtained through X-ray diffraction studies is shown on two intersecting, mutually perpendicular planes (see Fig. 2). The numbers indicated on the maps relate to the electron density in the neighbourhood of the atoms of E as a function of the spatial coordinates. The maxima found in these maps coincide with the locations of the atoms and the values are approximately proportional to the number of electrons in the atom in question.

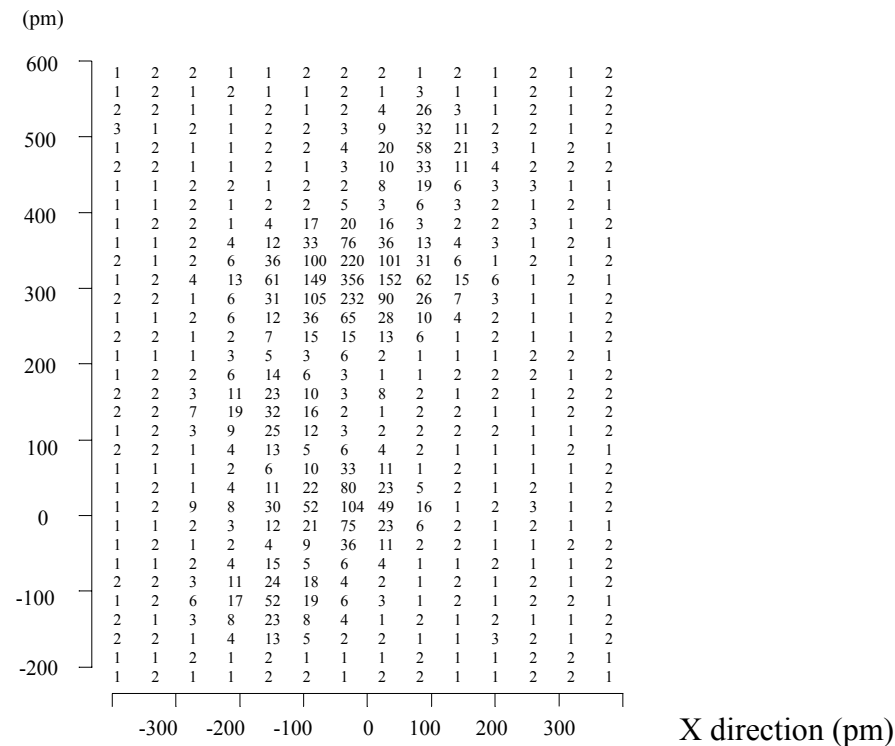
- a) Show where the maxima lie by drawing the contour curves around the maxima, connecting points of equal electron densities. Label each maximum to show the identities of the atoms in E.
 b) When 450.0 mg of C was treated with an excess of mercury, 53.25 ml of A was liberated at a pressure of 101.0 kPa at a temperature of 25°C. Calculate the relative atomic mass of A.
 c) Identify A, B, C, D and E.
 d) Use the valence-shell electron-pair repulsion theory (VSEPR) to propose electron-pair geometries for B and C. Using the two electron density maps, sketch the molecular geometry of E.

The original mixture was hydrolysed in water. B reacts to A while liberating oxygen and producing aqueous hydrogen fluoride. Hydrolysis of C leads to A and oxygen (in molar ratio of 4:3) and yields an

aqueous solution of AO_3 and hydrogen fluoride. D hydrolyses to an aqueous solution of AO_3 and hydrogen fluoride.

- e) Write the equations for the three hydrolysis reactions.
- f) Quantitative hydrolysis of a mixture of B,C and D gives 60.2 ml of gas (measured at 290 K and 100 kPa). The oxygen content of this gas is 40.0% (by volume). The amount of AO_3 dissolved in water is titrated with an aqueous 0.1 molar $FeSO_4$ solution and 36.0 ml used thereby. During the titration Fe^{2+} is oxidized to Fe^{3+} and AO_3 is reduced to A. Calculate the composition (% by moles) of the original mixture of A, B, C and D.

Y-direction



Z-direction

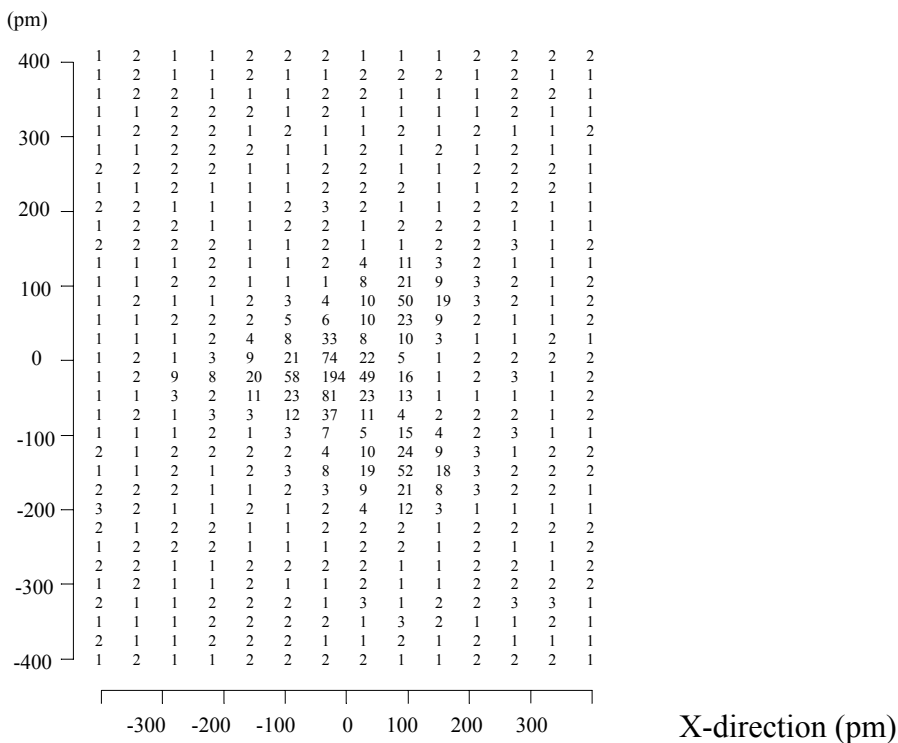


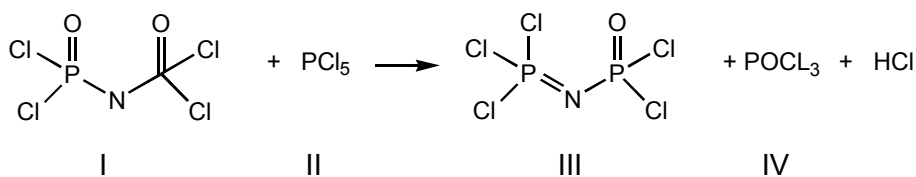
Fig. 2 Electron density distribution of compound E

ICHO Halle 1989

To determine the solubility product of copper(II) iodate ($\text{Cu}(\text{IO}_3)_2$) by iodometric titration in an acidic solution ($T=25^\circ\text{C}$) 20.00 ml of a saturated aqueous solution 30.00 ml of a 0.10 molar sodium thiosulphate solution are needed.

- a) Write the sequence of balanced equations for the above described reactions.
- b) Calculate the initial concentration of Cu^{2+} and the solubility product of copper(II) iodate. Activity coefficients can be neglected.

ICHO Halle 1989



^{32}P labelled phosphorus pentachloride (half-life $t_{1/2} = 14.3$ days) is used to study the electrophilic attack of a PCl_4^+ cation on nitrogen or on oxygen. The reaction is carried out in CCl_4 and the solvent and product IV distilled off.

Samples of III (remaining in the distillation flask), of IV (in the distillate) and samples of the starting material II are hydrolyzed by heating with a strong sodium hydroxide solution. The phosphate ions formed are precipitated as ammonium magnesium phosphate. Purified samples of the three precipitates are then dissolved by known volumes of water and the radioactivity measured.

- Write the balanced equations for the reaction of red phosphorus forming PCl_5
- Write the reaction equations for complete hydrolysis of the compounds II and III using sodium hydroxide.
- How long does it take in order to lower the initial radioactivity to 10^{-3} of the initial value?
- Write two alternative mechanisms for the reaction of labelled PCl_4^+ with the anion of I.
- After hydrolysis the precipitated ammonium magnesium phosphates show the following values for radioactivity:
 - 2380 Bq for 128 mg of $\text{Mg}(\text{NH}_4)\text{PO}_4$
 - 28 Bq for 153 mg of $\text{Mg}(\text{NH}_4)\text{PO}_4$
 - 2627 Bq for 142 mg of $\text{Mg}(\text{NH}_4)\text{PO}_4$

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

Data:

H_3PO_4 : $\text{pK}_1 = 2.2$, $\text{pK}_2 = 7.2$, $\text{pK}_3 = 12.4$

solubility product of $\text{Mg}(\text{NH}_4)\text{PO}_4$: $\text{pK}_{\text{sp}} = 12.6$

equilibrium concentration of $\text{NH}_4^+ = 0.1 \text{ mol/l}$

- Calculate the solubility for $\text{Mg}(\text{NH}_4)\text{PO}_4$ at pH equal to 10 under idealized conditions (activity coefficients can be neglected).

ICHO Paris 1990

The mineral apatite is a mixture of tricalcium diphosphate $\text{Ca}_3(\text{PO}_4)_2$, calcium sulphate, calcium fluoride, calcium carbonate and silica. An elemental analysis gave the following result:

	CaO	P_2O_5	SiO_2	F	SO_3	CO_2
% by mass	47.3	28.4	3.4	3.4	3.5	6.1

A sample of m_0 g of this mineral is treated with 50.0 ml of a solution containing 0.500 mol/L phosphoric acid and 0.100 mol/l sulphuric acid. The mixture is completely dehydrated by heating up to 70 °C. Toxic gases are emitted thereby. m_1 g of dry residue is obtained. In these conditions, only phosphate $\text{Ca}(\text{H}_2\text{PO}_4)_2$ is formed, silica and silicate do not react.

1.00 g of this residue is treated with 50.0 ml of water at 40 °C, filtered, dried and m_2 g obtained. This new residue is mainly containing gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) whose solubility between 20 °C and 50 °C is equal to 2.3 g/l.

- Write the balanced equations for all reactions. From what mass of apatite should one start if the reactions are stoichiometric?
- Starting with m_0 g of apatite, $m_1 = 5.49$ g of residue are obtained. What mass should theoretically have been obtained? This result is due to the presence of two products that are not expected to be in the residue. Which product are these?

Traditionally, the yield is expressed as percentage of oxide. The phosphorous content is expressed as if it were P_2O_5 . If n_2 is the amount of soluble product obtained, n_1 the amount of substances added as acid, n_0 the amount of apatite added, the yield is:

$$r_{\text{exp}} = 100 \cdot \frac{n_2}{n_1 + n_0}$$

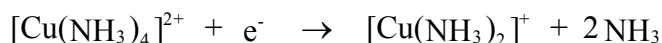
- c) $m_2 = 0.144$ g of residue is obtained on the filter. Calculate r_{exp} .
d) The experimental yield is over 100 %. Calculate a value of r nearer to the real yield.

ICHO Paris 1990

- a) Consider a $1.00 \cdot 10^{-2}$ solution of copper(II) nitrate. The pH of this solution is 4.65. Give the equation for the formation of the conjugate base of the hydrated Cu^{2+} ion and calculate the pK_a of the corresponding acid-base pair. The solubility product of copper(II) hydroxide is $K_{\text{sp}} = 10^{-20}$. At what pH would $\text{Cu}(\text{OH})_2$ precipitate from the solution under consideration? Justify your calculation, showing that the conjugate base of this hydrated Cu^{2+} ion is present in negligible quantity.
- b) Write down the equation for the disproportionation of copper(I) ions and calculate the corresponding equilibrium constant. $E_1^0(\text{Cu}^+/\text{Cu}) = 0.52$ V, $E_2^0(\text{Cu}^{2+}/\text{Cu}^+) = 0.16$ V. Calculate the composition in mol/l of the solution obtained on dissolving $1.0 \cdot 10^{-2}$ mol of copper(I) in 1.0 l of water. Name two chemical species which also disproportionate in aqueous solution; write down the equations and describe the experimental conditions under which disproportionation is observed.
- c) Consider the stability of copper(I) oxide (Cu_2O) in contact with a $1.00 \cdot 10^{-2}$ mol/l solution of Cu^{2+} ions. The stability product of copper(I) oxide is $K_{\text{sp}} = [\text{Cu}^+][\text{OH}^-] = 10^{-15}$. Quote a simple experiment allowing the observation of the precipitation of Cu_2O .
- d) The dissociation constant of the complex ion $[\text{Cu}(\text{NH}_3)_2]^+$ is $K_D = 10^{-11}$. Calculate the standard electrode potential of the couple:



- e) The emf of the couple $[\text{Cu}(\text{NH}_3)_4]^{2+} + 2e^- \rightleftharpoons \text{Cu} + 4\text{NH}_3$ is $E_3^0 = -0.02$ V. Calculate the dissociation constant of the complex ion $[\text{Cu}(\text{NH}_3)_4]^{2+}$. Deduce from it the emf of the couple:



Does the disproportionation of the cation $[\text{Cu}(\text{NH}_3)_2]^+$ take place?

ICHO Lodz 1991

- a) Show that 0.1 mol of Ti_2S dissolves in a 1M solution of any strong monoprotic non-coordinating acid.
b) Show that 0.1 CuS dissolves in a 1M HNO_3 but not in a 1M HCl solution.

Information:

Assume that Cu^{2+} ions don't form stable complexes with chloride ions in aqueous solutions.

$$E^0(\text{S}/\text{S}^{2-}) = -0.48 \text{ V} \quad E^0(\text{NO}_3^-/\text{NO}_{(\text{aq})}) = 0.96 \text{ V}$$

$$\text{p}K_a(\text{H}_2\text{S}) = 7 \quad \text{p}K_a(\text{HS}^-) = 13$$

$$K_{\text{sp}}(\text{Tl}_2\text{S}) = 10^{-20} \quad K_{\text{sp}}(\text{CuS}) = 10^{-35}$$

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \quad F = 96487 \text{ C mol}^{-1}$$

IChO Lodz 1991

Type II electrodes are made of a metal covered with a sparingly soluble salt of the metal that are dipped into a soluble salt solution containing an anion of the sparingly soluble salt. The silver/silverchloride ($\text{Ag}, \text{AgCl}/\text{Cl}^-$) and the calomel electrode ($\text{Hg}, \text{Hg}_2\text{Cl}_2/\text{Cl}^-$) are examples of such electrodes. The standard emf of a cell built of those electrodes (-) $\text{Ag}, \text{AgCl}/\text{Cl}^-/\text{Hg}_2\text{Cl}_2/\text{Hg}$ (+) is $E^0 = 0.0455 \text{ V}$. at $T = 298 \text{ K}$. The temperature coefficient for this cell is $dE^0/dT = 3.38 \cdot 10^{-4} \text{ V/K}$.

- Give the equations of the reactions taking place at both the cell electrodes and the overall cell reaction.
- Calculate the Gibbs free energy change (ΔG^0) for the process taking place in the cell. What does its sign imply ?
- Calculate the enthalpy change for the process taking place at 298 K, given $\Delta S = n F dE/dT$.
- Knowing the standard potential of Ag/Ag^+ electrode is $E^0 = 0.799 \text{ V}$ and the solubility product of AgCl $K_{\text{sp}} = 1.73 \cdot 10^{-10}$, calculate the standard electrode potential value of the silver/silver chloride electrode. Derive an expression showing the dependence between $E^0(\text{Ag}/\text{Ag}^+)$ and $E^0(\text{Ag}, \text{AgCl}/\text{Cl}^-)$.
- Calculate the solubility product of Hg_2Cl_2 knowing that the standard potential of the calomel electrode is $E^0 = 0.798 \text{ V}$.

IChO Pittsburgh 1992

Many streams drain in areas where coal or metallic ores are mined. These streams have become acidic and contain high concentrations of dissolved iron and sulfate, due to sulfur-containing ores being exposed to the atmosphere or to oxygenated waters. The most common sulfur-containing mineral is pyrite, FeS_2 , in which the oxidation state of iron is +2. As the iron-rich streams mix with other waters, the dissolved iron precipitates as goethite, $\text{FeO}(\text{OH})$, which coats the stream bottom while the water remains acidic.

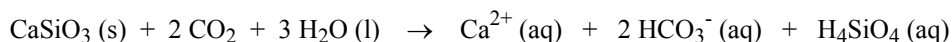
- Draw the electron dot structure that illustrates the bonding in the S_2^{2-} -ion, showing all valence electrons.
- Write a balanced chemical equation to show how hydrogen ions (H^+) are generated during the oxidation of pyrite to form iron(II) ions and sulphate.
- Write a balanced equation to show how many additional moles of hydrogen are generated when iron(II) ions are oxidized to form the mineral goethite, $\text{FeO}(\text{OH})$.
- Calculate how many moles of pyrite would be required to bring 1.0 litre of pure water to a pH of 3.0 if the pyrite was completely converted into $\text{FeO}(\text{OH})$ and H^+ . Neglect the formation of HSO_4^- .
- The concentration of iron as $\text{Fe}(\text{II})$ in a stream is 0.00835 M. At a very narrow point in the stream it empties into a large pond, with a flow rate of 20.0 l/min. The water in this stream is sufficiently aerated that 75% of the iron(II) is oxidized to $\text{Fe}(\text{III})$ which immediately precipitates as $\text{Fe}(\text{OH})_3$ later aging to become Fe_2O_3 . What mass of Fe_2O_3 will be deposited on the bottom of the pond in two years ?

IChO Pittsburgh 1992

Diatoms, microscopic organisms, produce carbohydrates from carbon dioxide and water by normal photosynthesis: $6 \text{CO}_2 + 6 \text{H}_2\text{O} + \text{solar energy} \rightarrow \text{C}_6\text{H}_{12}\text{O}_6 + 6 \text{O}_2$

During the first five years of life whales gain 75 kg of mass per day by feeding on krill. The whale must consume ten times this mass of krill each day. The krill must consume 10.0 kg of diatoms to produce 1.0 kg of krill.

- Assuming that the mass gain in the first years of a whale's life is due to the consumption of carbohydrates, calculate the volume of CO_2 at 0°C and 101kPa that must be used by the diatoms to produce the carbohydrates consumed by a blue whale in its first five years of life.
- There is 0.23 mL of dissolved CO_2 per l sea water (at 24°C and 101kPa). If diatoms can completely remove carbon dioxide from the water they process, what volume of water would they process to produce the carbohydrates required by a blue whale during the first five years of life ?
- 3% of the mass of a $9.1 \cdot 10^4$ kg adult whale is nitrogen. What is the maximum mass of NH_4^+ that can become available for other marine organisms if one adult whale dies ?
- 18% of a adult whale's mass is carbon which can be returned to the atmosphere as CO_2 being removed from there by weathering of rocks containing calcium silicate.



What are the maximum number of grams of CaSiO_3 that can be weathered by the carbon dioxide produced from the decomposition of 1000 blue whales, the number estimated to die annually ?

IChO Pittsburgh 1992

The Pourbaix diagrams of water, nitrogen and manganese are depicted in Fig. 3.

- Which species of nitrogen is predominant in a₁) O_2 -rich lakes of $\text{pH} \sim 6$, a₂) O_2 -depleted lakes of $\text{pH} \sim 3$ b) Which species of manganese is predominant in b₁) O_2 -rich lakes of $\text{pH} \sim 6$, b₂) highly O_2 -depleted lakes of $\text{pH} \sim 12$?
- People often find that clear, slightly acidic ($\text{pH} \sim 5$) water drawn from wells deposits a black manganese-containing solid on standing in toilet bowls. What is the chemical formula of the black solid ? What is the corresponding species of manganese found in well water while it is still underground ?
- Which of the two species of nitrogen oxidize $\text{Mn} (\text{s})$ to $\text{Mn}^{2+} (\text{aq})$ according to the Pourbaix diagrams ? Which one of this actually (in practice) does not oxidize $\text{Mn} (\text{s})$ at room temperature ?
- Which of the following compounds oxidize $\text{NH}_3 (\text{aq})$ or $\text{NH}_4^+ (\text{aq})$ to $\text{N}_2 (\text{g})$?
 $\text{Mn}, \text{Mn}(\text{OH})_2, \text{Mn}^{2+}, \text{Mn}_3\text{O}_4, \text{Mn}_2\text{O}_3, \text{MnO}_2, \text{MnO}_4^{2-}, \text{MnO}_4^-$

We shall discuss the properties of the two salts ammonium permanganate, NH_4MnO_4 , and ammonium manganate, $(\text{NH}_4)_2\text{MnO}_4$, which is a rarely known salt.

- Are the salts NH_4MnO_4 and $(\text{NH}_4)_2\text{MnO}_4$ thermodynamically stable ?
- Write the balanced equation of the decomposition of both salts to give MnO_2 , Mn and N_2 .
- Is it dangerous to grind together h₁) potassium nitrate and manganese metal, h₂) KNO_3 and MnO_2 ?
- The standard reduction potential for the reduction of MnO_4^- to MnO_2 is 1.692 V. Applying the Nernst equation, calculate the reduction potential for the reduction of 0.00100 M MnO_4^- at a $\text{pH} = 4.0$.

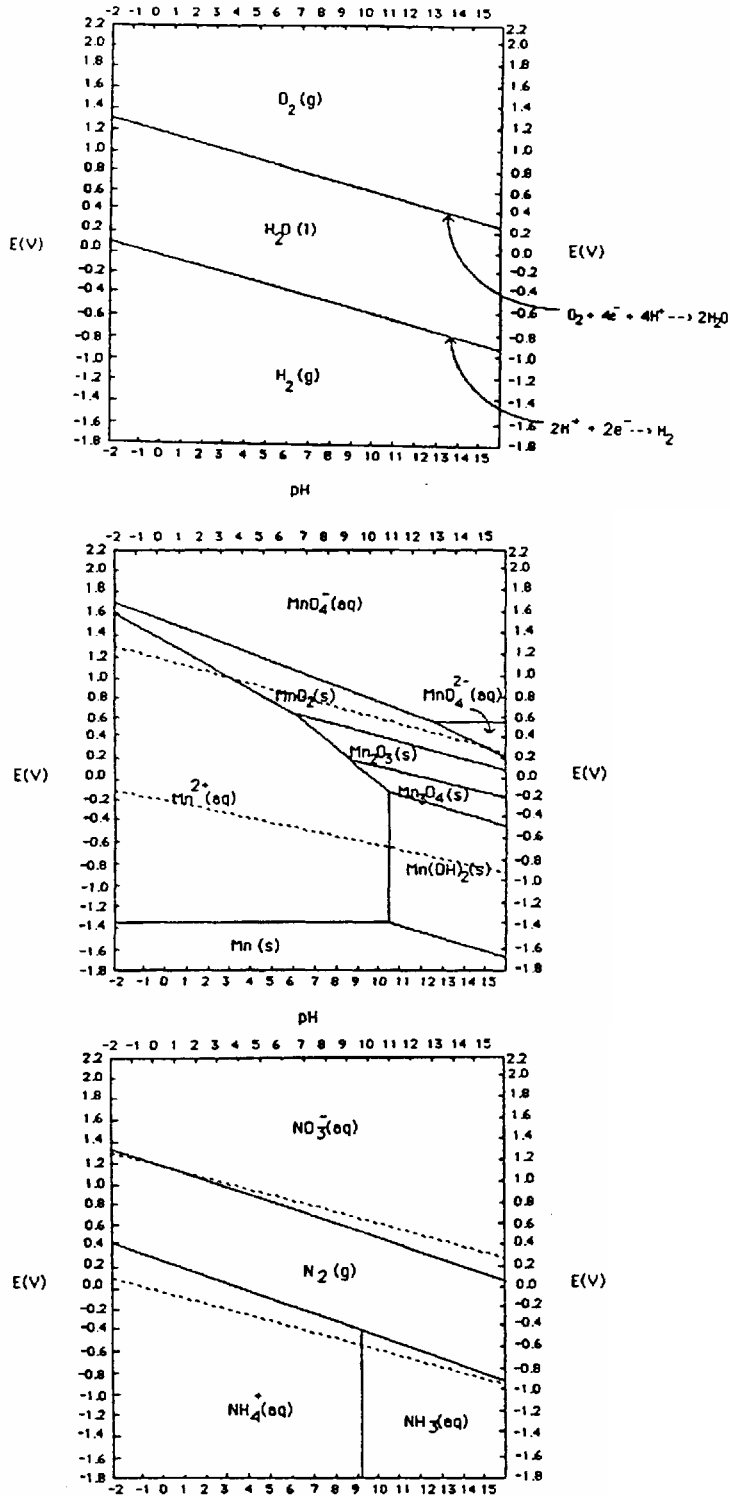


Fig. 3 Pourbaix diagrams of H₂O, N and Mn

IChO Perugia 93

^{131}I is a radioactive isotope of iodine (e^- emitter) used in nuclear medicine for analytical procedures to determine thyroid endocrine disorders by scintigraphy. The decay rate constant, k , is $9.93 \cdot 10^{-7} \text{ s}^{-1}$.

- Write the decay reaction of ^{131}I
- Calculate the half-life of ^{131}I expressed in days
- Calculate the time necessary (expressed in days) for a sample of ^{131}I to reduce its activity to 30% of the original value.
- Knowing that a Geiger counter detects activities of the order of $10^{-4} \mu\text{c}$, calculate the the minimum amount of ^{131}I which could be detected by this counter. Note that 1 Curie (c) is the amount of radioisotopes that produces $3.7 \cdot 10^{10}$ disintegrations per second.

IChO Oslo 1994

Sulfur forms many different compounds with oxygen and halogens (sulfur as the central atom). These compounds are mainly molecular, and many are easily hydrolysed in water.

- Write Lewis structures for the molecules SCl_2 , SO_3 , SO_2ClF , SF_4 , and SBrF_5 . Show all non-bonding electrons.
- Carefully draw the geometries of the same 5 molecules. (Disregard small deviations from "ideal" angles.)
- A compound, consisting of sulfur (one atom per molecule), oxygen, and one or more of the elements F, Cl, Br, and I, was examined. A small amount of the substance was reacted with water. It was completely hydrolyzed without any oxidation or reduction, and all reaction products dissolved. 0.1M solutions of a series of test reagents were added to separate, small portions of a diluted solution of the substance.

State which ions were being tested for in the following tests:

- Addition of HNO_3 and AgNO_3 .
- Addition of $\text{Ba}(\text{NO}_3)_2$.
- Adjustment to $\text{pH} = 7$ with NH_3 and addition of $\text{Ca}(\text{NO}_3)_2$

Write the equations for the possible reactions in the following tests:

- Addition of KMnO_4 to an acidified solution of the substance followed by addition of $\text{Ba}(\text{NO}_3)_2$
 - Addition of $\text{Cu}(\text{NO}_3)_2$.
- d) In practice, the tests in c) gave the following results:
- A yellowish precipitate
 - No precipitate
 - No visible reaction
 - The main features were that the characteristic colour of KMnO_4 disappeared, and a white precipitate was formed upon subsequent addition of $\text{Ba}(\text{NO}_3)_2$
 - No precipitate

Write the formulae of the possible compounds, taking the results of these tests into account.

- e) Finally, a simple quantitative analysis was undertaken: 7.190 g of the substance was weighed out and dissolved in water to give 250.0 mL solution. To 25.00 mL of this solution, nitric acid, and enough AgNO_3 to secure complete precipitation, was added. The precipitate weighed 1.452 g after washing and drying. Determine the formula of the compound.
- f) Write the equation describing the reaction of the compound with water.
If you have not arrived at a formula for the compound, use SOCIF for this equation.

ICHO Oslo 1994

- a) Nitrogen in agricultural materials is often determined by the Kjeldahl method. The method involves a treatment of the sample with hot concentrated sulphuric acid, to convert organically bound nitrogen to ammonium ion. Concentrated sodium hydroxide is then added, and the ammonia formed is distilled into hydrochloric acid of known volume and concentration. The excess hydrochloric acid is then back-titrated with a standard solution of sodium hydroxide, to determine nitrogen in the sample.

Calculate the percentage by mass of nitrogen in the sample.

- b) Calculate the pH of the solution during the titration in a), after 0 mL, 9.65 mL, 19.30 mL and 28.95 mL of sodium hydroxide have been added. Disregard any volume change during the reaction of ammonia gas with hydrochloric acid.

K_a for ammonium ion is 5.7×10^{-10}

- c) Draw the titration curve based on the calculations in b).
- d) State the pH range of the indicator which could be used for the back titration.
- e) The Kjeldahl method can also be used to determine the molecular weight of amino acids. In a given experiment, the molecular weight of a naturally occurring amino acid was determined by digesting 0.2345 g of the pure acid, and distilling the ammonia into 50.00 mL of 0.1010 M hydrochloric acid. A titration volume of 17.50 mL was obtained for the back titration with 0.1050 M sodium hydroxide. Calculate the molecular weight of the amino acid based on one and two nitrogen groups in the molecule, respectively.

3. Physical chemistry

ICHO Leiden 1986

In order to explain why dyes are coloured, they can be considered as rod-like, one-dimensional molecules over which the electrons are distributed. The wave lengths of the electrons should fit to the available space, which is the length l . When absorbing light, an electron makes a transition from a lower to a higher energy state. The energy difference is given by:

$$\Delta E = \frac{h \cdot c}{\lambda} \quad \text{where } \lambda = \frac{h}{p}$$

- a) Give a general expression for possible wavelengths of the electron as a function of the length l .

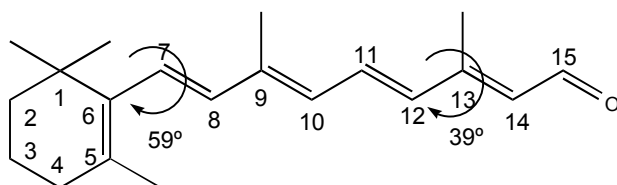
In the 'particle in the box' model, only the variations in the kinetic energy of the electrons are considered.

- b) Give an expression for the possible energies that electrons in the molecule can have (as a function of l).
 c) Show that for a chain of length l with k electrons, the longest wavelength absorption occurs at:

$$\gamma = \frac{8mcl^2}{h(k+1)} \quad \text{for even values of } k$$

- d) Derive an expression for the wavelength of the first electronic transition as a function of the number of C-atoms for even values of n .
 e) Calculate the minimum number of C-atoms (conjugated systems) to obtain a visible colour. C-C bond length is 142 pm.

The retina in the human eye contains rhodopsin, a light absorbent.



The C-atoms 7 through 12 are planar. The angle between the bonds C5-C6, C7-C8, C11-C12 and C13-C14 is about 39° . According to the 'particle in the box' theory fragment C7 through C12 should absorb at about 213 nm. In reality the absorption of retinal occurs at 308 nm.

- f) Give a reason for the longer wavelength that is observed in praxis using the above mentioned theories.
 g) When retinal is bound to opsin to form rhodopsin, the absorption occurs around 600 nm. Which atoms must be forced into one plane by the protein? Show by calculation that it's true.

IChO Helsinki 1988

A typical family car has four cylinders with a total cylinder volume of 1600 cm^3 and a fuel consumption of 7.0 l per 100 km when driving at a speed of 90 km / h. During one second each cylinder goes through 25 burn cycles and consumes 0.4 g of fuel. Assume that fuel consists of 2,2,4 - trimethyl - pentane, C_8H_{18} . The compression ratio of the cylinder is 1:8.

- 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 is 101.0 kPa. Temperature of both incoming air and fuel are 100°C . Air contains 21.0 % (by volume) of O_2 and 79.0 % of N_2 . It is assumed that 10.0 % of the carbon forms CO upon combustion and that nitrogen remains inert.
 b) The gasified fuel and the air are compressed until the volume in the cylinder is at its smallest and then ignited. Calculate the composition (% by volume) and the temperature of the exhaust gases immediately after the combustion (exhaust gases have not yet started to expand). The following data is given:

Compound	H_f (kJ / mol)	C_p (J / mol K)
$\text{O}_2(\text{g})$	0.0	29.36
$\text{N}_2(\text{g})$	0.0	29.13
$\text{CO}(\text{g})$	-110.53	29.14
$\text{CO}_2(\text{g})$	-395.51	37.11
$\text{H}_2\text{O}(\text{g})$	-241.82	33.58
2,2,4 - trimethylpentane	-187.82	

- c) Calculate the final temperature of the leaving gases assuming that the piston has moved to expand the gases to the maximum volume of the cylinder and that the final gas pressure in the cylinder is 200 kPa.
- d) To convert CO(g) into CO₂(g) the exhaust gases are led through a bed of catalysts with the following work function:

$$\frac{n(\text{CO})}{n(\text{CO}_2)} = \frac{1}{4} k \frac{n(\text{CO})}{n(\text{CO}_2)_1} v e^{-\frac{T}{T_0}}$$

where $[n(\text{CO}) / n(\text{CO}_2)]_1$ is the molar ratio before the catalyst, v is the flow rate in mol / s and T the temperature of the gases entering the catalyst (the same as the temperature of the leaving exhaust gases). T_0 is a reference temperature (373 K) and k is equal to 3.141 s / mol. Calculate the composition (% by volume) of the exhaust gases leaving the catalyst.

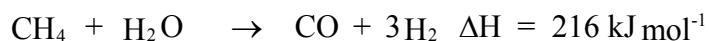
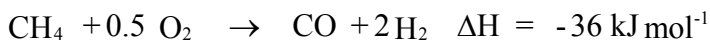
IChO Helsinki 1988

The periodic system of the elements in our three-dimensional world is based on the four electron quantum numbers $n = 1, 2, 3, \dots$; $l = 0, 1, \dots, n-1$, $m = 0, \pm 1, \pm 2, \dots, \pm l$; and $s = \pm 1/2$. In Flatlandia, a two-dimensional world, the periodic system is thus based on three electron quantum numbers: $n = 1, 2, 3, \dots$; $m_1 = 0, \pm 1, \pm 2, \dots, \pm (n-1)$; and $s = \pm 1/2$ where m_1 plays the combined role of l and m of the three dimensional world. The following tasks relate to this two-dimensional world, where the chemical and physical experience obtained from our world is supposed to be still applicable.

- Draw the first four periods of the Flatlandian periodic table of the elements. Number them according to their nuclear charge. Use the atomic numbers (Z) as symbols of the specific element. Write the electron configuration for each point.
- Draw the hybrid orbitals of the elements with $n = 2$. Which element is the basis for the organic chemistry in Flatlandia? Find the Flatlandian analogous for ethane, ethene and cyclohexane. What kind of aromatic ring compounds are possible ?
- Which rules in Flatlandia correspond to the octet and the 18-electron rules in the three dimensional world?
- Predict graphically the trends in the first ionization energies of the Flatlandian elements with $n = 2$. Show graphically how the electronegativities of the elements increase in the Flatlandian periodic table.
- 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?
- Consider simple binary compounds of the elements ($n=2$) with $Z=1$. Draw their Lewis structure, predict their geometries and propose analogs for them in the three dimensional world.
- Consider elements with $n \leq 3$. Propose an analog and write the chemical symbol from our world for each of these Flatlandian elements. On the basis of this chemical and physical analog predict which two-dimensional elements are solid, liquid or gaseous at normal pressure and temperature.

IChO Halle 1989

A mixture of gases containing mainly carbon monoxide and hydrogen is produced by the reaction of alkanes with steam:



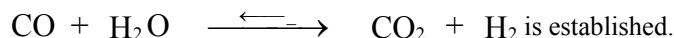
- a) Using equations (1) and (2) write down an overall reaction (3) so that the net enthalpy change is zero.

- b) The synthesis of methanol from carbon monoxide and hydrogen is carried out either
1. in two steps, where the starting mixture corresponding to equation (3) is compressed from $0.1 \cdot 10^6$ Pa to $3 \cdot 10^6$ Pa, and the mixture of products thereof compressed again from $3 \cdot 10^6$ Pa to $6 \cdot 10^6$ Pa
or
 2. in one step, where the mixture of products corresponding to equation (3) is compressed from $0.1 \cdot 10^6$ Pa to $6 \cdot 10^6$ Pa.

Calculate the work of compression, W_a , according to the two step reaction for 100 ml of starting mixture and calculate the difference in the work of compression between the reactions 1. and 2.

Assume for calculations a complete reaction at constant pressure. Temperature remains constant at 500 K, ideal gas behaviour is assumed.

To produce hydrogen for the synthesis of ammonia, a mixture of 40.0 mol CO and 40.0 mol of hydrogen, 18.0 mol of carbon dioxide and 2.0 mol of nitrogen are in contact with 200.0 mol of steam in a reactor where the conversion equilibrium



- c) Calculate the number of moles of each gas leaving the reactor.

ICHO Paris 1990

- a) Show that burning zinc sulphide in air according to



is self-sustaining at 1350 K, i.e that the heat produced is sufficient to bring the reactants from ambient temperature to the heat temperature.

- b) Starting with a stoichiometric mixture of one mole zinc blende only containing ZnS and a necessary quantity of air at 298 K, calculate the temperature to which the mixture would raise at 1350 K under standard pressure. Is the reaction self-sustaining? Air is considered to be a mixture of oxygen and nitrogen in a volume ration equal to 1:4.
- c) In fact, zinc blende is never pure and always mixed with a gangue consisting of silica SiO_2 . Assuming that the gangue does not react, calculate the minimum ZnS content of the mineral so that the reaction would be self-sustaining. Give the answer in grams of ZnS per hundred grams of zinc blende.

Data:

Standard molar heat capacities (in $\text{J K}^{-1} \text{ mol}^{-1}$):

ZnS(solid):	58.05	ZnO(solid):	51.64
SO ₂ (gas):	51.10	O ₂ (gas):	34.24
N ₂ (gas):	30.65	SiO ₂ (solid):	72.50

Molar masses (in g mol^{-1}):	ZnS:	97.5
	SiO ₂ :	60.1

IChO Paris 1990

Nitramid NO_2NH_2 decomposes slowly in aqueous solution according to



with the experimental kinetic law

$$\frac{d[\text{N}_2\text{O}]}{dt} = k \frac{[\text{NO}_2\text{NH}_2]}{[\text{H}_3\text{O}^+]}$$

- a) What is the apparent order of reaction in a buffered solution ?
 b) Which of the following mechanisms is the most appropriate for the interpretation of this kinetic law. Ju-

mechanism 1:

$$\text{NO}_2\text{NH}_2 \xrightarrow{k_1} \text{N}_2\text{O} + \text{H}_2\text{O} \text{ (rate limiting step)}$$

mechanism 2:

$$\begin{aligned} \text{NO}_2\text{NH}_2 + \text{H}_3\text{O}^+ &\xrightleftharpoons[k_2']{k_2} \text{NO}_2\text{NH}_3^+ + \text{H}_2\text{O} \text{ (rapid equilibrium)} \\ \text{NO}_2\text{NH}_3^+ &\xrightarrow{k_3} \text{N}_2\text{O} + \text{H}_3\text{O}^+ \text{ (rate limiting step)} \end{aligned}$$

mechanism 3:

$$\begin{aligned} \text{NO}_2\text{NH}_2 + \text{H}_2\text{O} &\xrightleftharpoons[k_4']{k_4} \text{NO}_2\text{NH}^- + \text{H}_3\text{O}^+ \text{ (rapid equilibrium)} \\ \text{NO}_2\text{NH}^- &\xrightarrow{k_5} \text{N}_2\text{O} + \text{OH}^- \text{ (rate limiting step)} \\ \text{H}_3\text{O}^+ + \text{OH}^- &\xrightarrow{k_6} 2 \text{H}_2\text{O} \text{ (very fast reaction)} \end{aligned}$$

stify your answer.

- c) Show the relationship between the experimentally observed rate constant and the rate constants in the selected mechanism.
 d) Show that hydroxyl ions catalyze the decomposition of nitramid.
 e) The decomposition is studied in a buffered solution of constant volume V at a constant temperature by measuring the partial pressure of the gas N_2O , insoluble in water, in a constant volume of the same value V above the solution. The following results are obtained:

t(min)	0	5	10	15	20	25
p(Pa)	0	6800	12400	17200	20800	24000

After a sufficiently long time, the pressure stabilises at 40000 Pa. Express the pressure P as a function of time and the constant k' such that $k' = k / [\text{H}_3\text{O}^+]$. Verify graphically that the kinetic law is confirmed by these experimental results. Calculate k' , giving its units.

IChO Lodz 1991

The energy of stable states of the hydrogen atom is given by: $E_n = -2.18 \cdot 10^{-18} n^{-2} \text{ J}^{-1}$ where n denotes the principal quantum number.

- Calculate the energy differences between $n = 2$ (first excited state) and $n = 1$ (ground state) and between $n = 7$ and $n = 1$.
- In what spectral range are the Lyman series lying ?
- Can a single photon emitted in the first and/or sixth line of the Lyman series ionize
 - another hydrogen atom in its ground state ?
 - a copper atom in the Cu crystal ?

The electron work function of Cu is $\phi_{\text{Cu}} = 7.44 \cdot 10^{-19}$.

- Calculate the de Broglie wavelength of the electrons emitted from a copper crystal when irradiated by photons from the first line and the sixth line of the Lyman series.

IChO Pittsburgh 1992

The paramagnetic gas NO_2 can dimerize to give the diamagnetic gas N_2O_4 : $2 \text{NO}_2 (\text{g}) \rightarrow \text{N}_2\text{O}_4 (\text{g})$

- With a diagram, show the bonding present in $\text{NO}_2 (\text{g})$ using the concept of resonance if necessary. Use dots to represent electrons.
- Show, with bonding diagrams, how two molecules of $\text{NO}_2 (\text{g})$ combine to give a molecule of $\text{N}_2\text{O}_4 (\text{g})$.
- At 298 K, the ΔG° of formation for $\text{N}_2\text{O}_4 (\text{g})$ is 98.28 kJ, whereas for $\text{NO}_2 (\text{g})$ it is 51.84 kJ. Starting with one mole of $\text{N}_2\text{O}_4 (\text{g})$ at 1.0 atm and 298 K, calculate what fraction will be decomposed if the total pressure is kept constant at 1.0 atm and the temperature is maintained at 298 K.
- If ΔH° for the reaction $\text{N}_2\text{O}_4 (\text{g}) \rightarrow 2 \text{NO}_2 (\text{g})$ is 53.03 kJ, at what temperature would the fraction of N_2O_4 decomposed be double the one calculated in part c) ?
- The dissociation of $\text{N}_2\text{O}_4 (\text{g})$ to give $\text{NO}_2 (\text{g})$ is a first order process with a specific rate constant of $5.3 \cdot 10^4 \text{ s}^{-1}$ at 298 K. Starting with an initial concentration of 0.10 M, how many seconds would it take for 20 % of the original N_2O_4 to decompose ?
- The association of $\text{NO}_2 (\text{g})$ to give $\text{N}_2\text{O}_4 (\text{g})$ is a second-order process with a specific rate constant of $9.8 \cdot 10^6 \text{ L mol}^{-1} \text{ s}^{-1}$ at 298 K. Calculate the concentration equilibrium constant, K_c , at 298 K for the reaction $2 \text{NO}_2 (\text{g}) \rightarrow \text{N}_2\text{O}_4 (\text{g})$

IChO Pittsburgh 1992

The concentration of carbon dioxide in the atmosphere has increased substantially during this century. The $[\text{CO}_2]$ is expected to be about 440 ppm ($440 \cdot 10^{-6} \text{ atm}$) in the year 2020.

- Calculate the concentration, in mol/l, of CO_2 dissolved in distilled water equilibrated with the atmosphere in the year 2020. What is its pH-value ?
- Calculate the enthalpy of reaction between $\text{CO}_2 (\text{aq})$ and H_2O .
- Will the pH increase or decrease if the temperature of an equilibrated solution of CO_2 in water is increased and the concentration of dissolved CO_2 maintained constant ?

Data:

Henry's Law constant for CO₂ at 298 K: 0.0343 l mol⁻¹ atm⁻¹

Thermodynamic values, in kJ/mol at 298 K are:

	ΔG_0^f	ΔH_0^f
CO ₂ (aq)	-386.2	-412.9
H ₂ O (l)	-237.2	-285.8
HCO ₃ ⁻ (aq)	-587.1	-691.2
H ⁺ (aq)	0.00	0.00

ICHO Peruggia 93

Poisoning by carbon monoxide produced by ill-adjusted heating systems is a serious problem. In a methane burner the following reactions occur:

	CH ₄	O ₂	CO ₂	CO	H ₂ O
ΔH_0^f (kJmol ⁻¹)	-74.9	0	-393.5	-110.5	-241.8
S^0 (JK ⁻¹ mol ⁻¹)	186.2	205.0	213.6	197.6	188.7

- Calculate the equilibrium constants of both reactions at T = 1500 K, assuming that the values of ΔH^0 and ΔS^0 are independent of temperature.
- Find the relationship between the mole numbers of oxygen and carbon monoxide at equilibrium (T = 1500 K, P = 1 atm) when air is admitted into the burner in such amount that the mole ration CH₄/O₂ is 2:1. Assume the following volume composition for air: 80% N₂ and 20% O₂. Make the approximation that n_{CH₄} = 0 at equilibrium and justify it on the basis of the answers to question a).
- Calculate the equilibrium mole fraction (x) of CO in the conditions given in b). Assume that the mole fraction of CO is very small in comparison with that of CO₂ and consequently the total number of moles does not appreciably vary during the combustion. Justify this assumption.
- Repeat the calculations of items b) and c) assuming that twice the amount of air (compared to the conditions of questions b) is admitted into the burner (4 mol O₂ / 1 mol CH₄).
- Calculate the concentrations of CO (expressed as ppm by volume) in the fumes after condensation of water vapour under the conditions of questions b) and d), assuming that the composition does not change during the cooling from 1500 K to room temperature and neglecting the contributions of water vapour in the composition of the gas phase.

ICHO Oslo 1994

Platinum(IV) oxide is not found in the nature, but can be prepared in a laboratory. Solid platinum(IV) oxide is in equilibrium with platinum metal and oxygen gas at 1 atm (101.3 kPa) at 650 °C.

- This suggests that the conditions on the Earth, when platinum minerals were formed, were:
 - pO₂ = 1 atm, t = 650 °C;
 - pO₂ < 1 atm, t < 650 °C;
 - pO₂ > 1 atm, t < 650 °C;
 - pO₂ < 1 atm, t > 650 °C;
 - pO₂ > 1 atm, t > 650 °C

Mark the most probable alternative [1] - [5] on the answer sheet.

b) What are ΔG and K_p for the formation of platinum(IV) oxide at 1 atm oxygen pressure and 650 °C?

The preparation of platinum(IV) oxide involves boiling a solution which contains hexachloroplatinate(IV) ions with sodium carbonate. In this process $\text{PtO}_2 \cdot n\text{H}_2\text{O}$ is formed and is subsequently converted by filtration and heat treatment to platinum(IV) oxide. In the following we assume $n=4$. $\text{PtO}_2 \cdot 4\text{H}_2\text{O}$ (or $\text{Pt}(\text{OH})_4 \cdot 2\text{H}_2\text{O}$) can be dissolved in acids and strong bases.

c) Write the balanced equations for the preparation of platinum(IV) oxide according to the procedure given above.

d) Write the balanced equations for the dissolution of $\text{PtO}_2 \cdot 4\text{H}_2\text{O}$ in both hydrochloric acid and sodium hydroxide.

Platinum is mainly found in nature as the metal (in a mixture or alloyed with other precious metals). Hexachloroplatinate(IV) ions are formed by dissolving platinum in aqua regia. Aqua regia is a mixture of concentrated hydrochloric and nitric acids in proportion 3:1. Upon mixing, this forms nitrosyl chloride (NOCl) and atomic chlorine. The latter is believed to be the active dissolving component.

The hexachloroplatinate(IV) ions can be precipitated as diammonium hexachloroplatinate(IV). By thermal decomposition of this compound, finely powdered platinum and gaseous products are formed.

e) Write the balanced equations for the formation of aqua regia and its reaction with platinum.

f) Write the balanced equation for the thermal decomposition of diammonium hexachloroplatinate(IV) at elevated temperature.

From diammonium hexachloroplatinate(IV) we can prepare $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$ which occurs in the cis ($\Delta H_{\text{fo}} = -467.4$ kJ/mol, $\Delta G_{\text{fo}} = -228.7$ kJ/mol) and trans ($\Delta H_{\text{fo}} = -480.3$ kJ/mol, $\Delta G_{\text{fo}} = -222.8$ kJ/mol) forms.

g) The occurrence of the isomers shows that the geometry of $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$ is

1. linear ?
2. planar ?
3. tetrahedral ?
4. octahedral ?

h) Indicate whether the cis or trans isomer is thermodynamically more stable. If you choose cis, mark [1] on the answer sheet. If you choose trans, mark [2].

Platinum is used as a catalyst in modern automobiles. In the presence of the catalyst, carbon monoxide ($\Delta H_{\text{fo}} = -110.5$ kJ/mol, $\Delta G_{\text{fo}} = -137.3$ kJ/mol) reacts with oxygen to form carbon dioxide ($\Delta H_{\text{fo}} = -393.5$ kJ/mol, $\Delta G_{\text{fo}} = -394.4$ kJ/mol).

I) Is the reaction spontaneous at 25 °C? [1] yes or [2] no. Is the reaction endothermic or exothermic? If you choose endothermic, mark [1] on the answer sheet. If you choose exothermic, mark [2]. Calculate ΔS_0 for the reaction. Determine whether the entropy of the reaction system [1] increases or [2] decreases.

j) Derive an expression for the temperature dependence of the equilibrium constant in this case.

The overall catalytic reaction is simple, whereas the reaction mechanism in the gas phase is very complicated, with a large number of reaction steps. With platinum as the catalyst the significant reaction steps are:

1. (i) adsorption of CO and adsorption/dissociation of O_2 ($\Delta H = -259$ kJ per mol CO + O),
2. (ii) their activation (105 kJ per mol CO + O) and
3. (iii) the reaction to and the desorption of CO_2 ($\Delta H = 21$ kJ per mol CO_2).

A one-dimensional energy-diagram for the platinum catalyzed oxidation of carbon monoxide to dioxide can be represented as:

[Image]

k) Mark the correct alternative of [1] - [4] on the answer sheet.

ICHO Oslo 1994

a) When an ideal, monatomic gas expands reversibly from volume V_1 to volume V_2 , work

$$w = -\int_{V_1}^{V_2} P dV$$

is performed on the system by the surroundings. In this equation, w is the work and P is the pressure of the gas. Determine the work performed when one mole ideal gas expands isothermally from $V_1 = 1.00 \text{ dm}^3$ to $V_2 = 20.0 \text{ dm}^3$ at temperature $T = 300.0 \text{ K}$. Given: The gas constant $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$

b) Determine how much heat must be added to the gas during the process given under a).

c) The gas will perform less work in an adiabatic expansion than in an isothermal expansion. Is this because the adiabatic expansion is characterized by (check the square you think is most important).

1. The volume of the gas is constant
2. The expansion is always irreversible
3. No heat is supplied to the gas

d) The cyclic process shown schematically in Figure 1 shows the four steps in a refrigeration system with an ideal gas as working medium. Identify the isothermal and adiabatic steps in the process. Here, T_H and T_C represent high and low temperature, respectively. Specify for each step whether it is adiabatic or isothermal.

4. Technical chemistry

ICHO Leiden 1986

The equilibrium constant of the reaction $A_{(g)} + 2 B_{(g)} \rightarrow 2 C_{(g)}$ is $K_p = 10.0 \text{ MPa}^{-1}$. The starting materials are supplied at $25 \text{ }^\circ\text{C}$ and heated to $100 \text{ }^\circ\text{C}$ where complete equilibration takes place. Below $100 \text{ }^\circ\text{C}$ the reaction rate is negligibly small. The whole process is executed continuously in a stationary state. The boiling points at 0.1 MPa of A, B and C are $40 \text{ }^\circ\text{C}$, $80 \text{ }^\circ\text{C}$ and $60 \text{ }^\circ\text{C}$, respectively. The three compounds have the same heat of evaporation: $q \text{ J/mol}$. The heat capacities of A,B and C may be neglected. A schematic diagram of a distillation is shown below (Fig. 4).

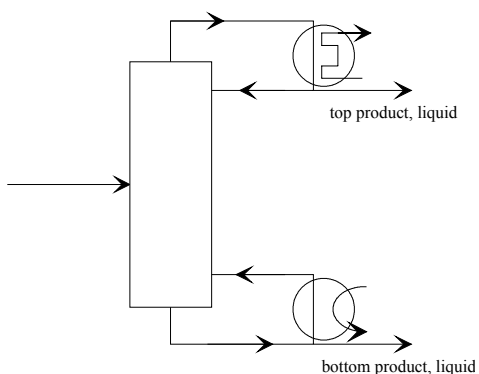


Fig. 4 Schematic diagram of a distillation

The total heat used at each of the two distillations is $3q$ J/mol (of the top product). Apart from distillation columns (each with its own evaporator and condenser) the pieces of apparatus shown of Fig. 5 are available.

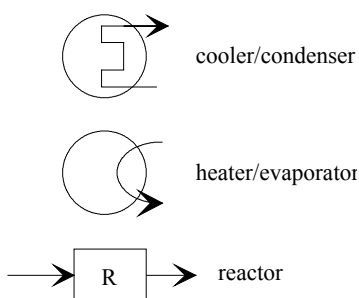


Fig. 5 Pieces of apparatus available

- Draw a flow diagram of the process in which all flows are given (flow sheet) and in which the starting materials are used as efficiently as possible using as few pieces of apparatus as possible.
- Express the equilibrium constant in terms of the degree of conversion and of total pressure for the case that the feed to the reactor is stoichiometric. What is the value of the degree of conversion when total pressure is 0.100 MPa?
- Number all flows. Calculate the composition of each flow in mol/s for a rate of production of 1 mole of C per second under the conditions of part b.
- In what respect can the reaction conditions influence the composition of the mixture that leaves the reactor? (Refer to question b)
- The process requires energy. For the conditions of b explain where energy should be supplied in the flow diagram drawn in part a. Derive an expression for the total energy needed.

IChO Veszprém - Budapest 1987

Treating waste water in a sewage plant, 45 % of its carbohydrate $(\text{CH}_2\text{O})_n$ is completely oxidized, 10 % undergoes anaerobic decomposition by fermentation (two components) and the rest remains in the sludge. The total gas formation is 16 m^3 per day (25°C , 100 kPa).

- What is the amount of carbohydrate remaining in the sludge measured in kg per day ?
- Given the heat of combustion of methane ($- 882 \text{ kJ / mol}$), calculate the amount of energy that can be produced by combustion of the methane formed.
- Knowing the concentration of the carbohydrate in the waste water to be 250 mg/ l, calculate the daily amount of waste water processed in the plant in m^3 of water per day.

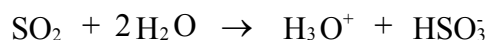
IChO Halle 89

Sulphur dioxide is removed from waste gases of coal power stations by washing with aqueous suspensions of calcium carbonate or calcium hydroxide. The residue formed is recovered.

- Write all reactions as balanced equations.
- How many kilograms of calcium carbonate are daily consumed to remove 95% of the sulphur dioxide if 10000 m³/h of waste gas (corrected to 0 °C and standard pressure) containing 0.15% sulphur dioxide by volume are processed? How many kilograms of gypsum are recovered thereby ?
- Assuming that the sulphur dioxide is not being removed and equally spread in an atmospheric liquid water pool of 5000 m³ and fully returned on earth as rain, what is the expected pH of the condensed water ?
- If a sodium sulphite solution is used for absorption, sulphur dioxide and the sulphite solution can be recovered. Write down the balanced equations and point out possible pathways to increase the recovery of sulphur dioxide from the liquid phase.

Information

Protolysis of sulphur dioxide in aqueous solution is described by:



The acidity constant K_a is equal to $K_a = 10^{-2.25}$ mol/l. Assume ideal gases and a constant temperature of 0 °C at standard pressure. $M[\text{CaCO}_3] = 100$ g/mol; $M[\text{CaSO}_4] = 172$ g/mol

IChO Paris 1990

Hydrogenation of benzene to cyclohexane is performed in continuous reactors. The reaction is as follows:



Two different types of reactors are examined: continuous plug flow reactor and continuous stirred reactor (Fig. 6): In the continuous plug flow reactor, reactants are introduced and mixed in the inlet of the reactor (F1, F2); each slice of reaction medium (grey shaded zone in the diagram) moves along the inside without mixing with the others and exits from the reactor (F3). When the flow has stabilized, concentrations and conditions are time-independent but dependent on the location in the reactor. In the continuous stirred reactor, stirring is perfect and instantaneous. When the flow is stabilized, concentration and conditions are time-independent and identical at every point of the reactor.

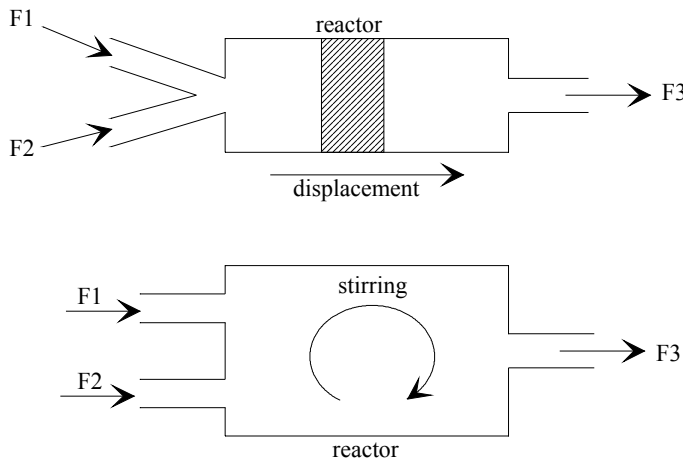


Fig. 6 Continuous plug flow and continuous stirred reactor

The differential yield of hydrogenation (Y) is given by

$$Y = - d([C_6H_{12}])/d([C_6H_6]).$$

The proportion of benzene already hydrogenated is given by $p = [C_6H_{12}]/([C_6H_{12}]+[C_6H_6])$. The relationship between p and Y is shown in Fig. 7.

The aim is to hydrogenate almost all the benzene, i.e. $0.9 \leq p \leq 1$ with the best mean yield

$$Y = - \Delta([C_6H_{12}])/ \Delta([C_6H_6]).$$

- What is the value of p in a continuous stirred reactor leading to the maximal mean yield of hydrogenation? What is the maximal value of Y?
- For a continuous plug flow reactor, give a rough value of Y for $0.9 \leq p \leq 1$:
Y = 0.97, 0.98, 0.99 or 1.00 ?
- Represent by grey shading the quantities of benzene lost in installation P (plug flow reactor) and installation MP (stirred reactor + plug flow reactor).
- Give the amount of benzene annually lost in installation P and MP assuming an annual consumption of 100000 tons of benzene.

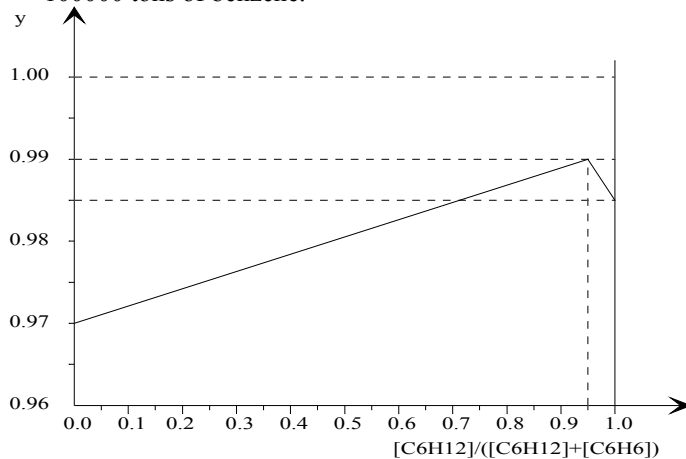


Fig. 7 relationship between p and Y

ICHO Lodz 1991

Sulphuric acid is produced by catalytic oxidation of SO_2 to SO_3 , absorption of SO_3 in concentrated sulphuric acid forming oleum (containing 20% SO_3 by mass) and appropriate dilution hereafter. The gas leaving the catalyst chamber contains nitrogen, oxygen, a trace of SO_2 and 10 % (by volume) of SO_3 . SO_3 is converted into sulphuric acid (98 % by mass) and/or oleum.

- Assuming that oleum is the only product formed, calculate the mass of water which is required for 1000 m^3 of gas leaving the catalyst chamber (273 K, 101.3 kPa) and determine the mass of oleum produced hereby.
- Assuming that only 98 % sulphuric acid is produced, calculate the necessary mass of water and the mass of product produced thereby.
- In the industry both 98 % sulphuric acid and oleum are produced in a mass ratio of $x = m_1/m_2$, where m_1 denotes the mass of oleum, m_2 the mass of 98 % sulphuric acid. Find an expression $y = f(x)$ to describe the relation between the mass of water consumed for 1000 m^3 gas. Show that the results of a) and b) are in good agreement with your mathematical expression.

5. Organic chemistry

ICHO Leiden 1986

The high efficiency of catalysis by enzymes is mainly due to an enzyme-reactant complex in which the reacting group is placed in a favourable position for the reaction with respect to the catalyzing groups of the enzyme. Studies are carried out with model compounds in which a catalyzing group has been introduced in the proximity of the reaction centre of the molecule. As an example we consider the hydrolysis of the amide bond in compound A. This reaction proceeds in water at 39 °C and pH = 2 more than a million times faster than the hydrolysis of compound B.

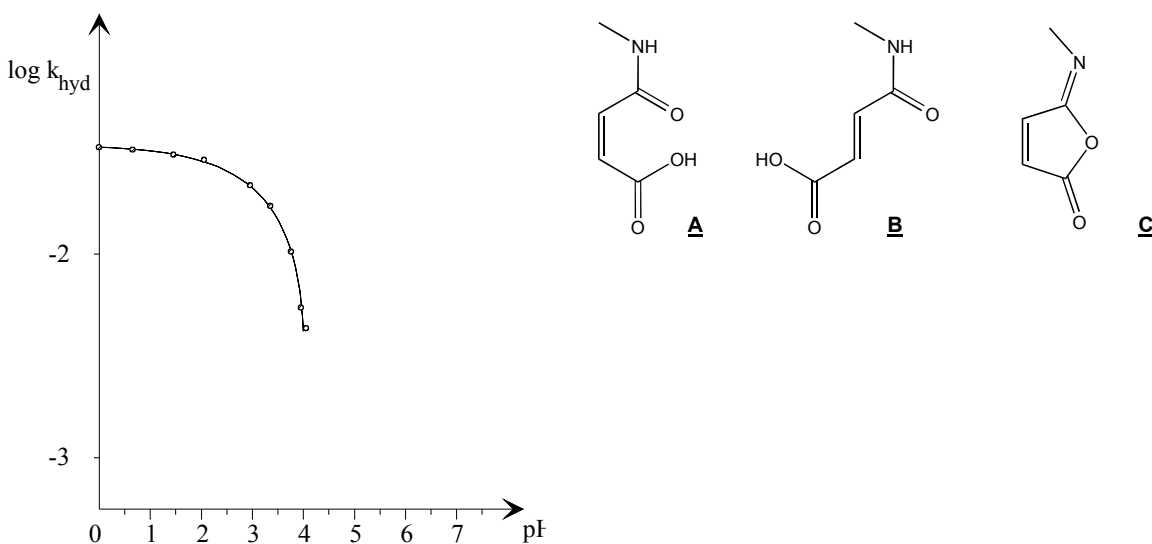


Fig. 8 Relation between the rate constant k_{hyd} and pH for the hydrolysis of A

The relation between the rate constant k_{had} and pH for the hydrolysis of A at 39 °C is shown in figure 8.

Further observations

Addition of water to the iso-imide C gives a rapid reaction, which initially yields A. Subsequently, hydrolysis of A occurs.

The amid carbonyl group in A is labelled with ^{13}C and the hydrolysis is allowed to take place in H_2^{18}O at $\text{pH} = 2$ and $39\text{ }^\circ\text{C}$. The diacid formed upon hydrolysis is isolated, converted into the di-silver salt and completely decarboxylated with bromine in an anhydrous reaction medium. The formed carbon dioxide is a mixture of particles of masses 44, 45, 46 and 47 which are formed in equal amounts.

- Why is the hydrolysis of A so much faster than that of B ?
- Explain why the rate of hydrolysis of A is independent of pH on the range between $\text{pH} = 0$ to $\text{pH} = 2$.
- Why does k_{hyd} decrease so rapidly at pH-values higher than 3.
- Give a detailed reaction mechanism for the hydrolysis of A. Indicate which step in the reaction is rate determining.
- Show that the observations further made are consistent with the reaction mechanism given under d.

IChO Leiden 1986

Bacterial conversion of saccharose leads to (S) - (+) - 2 - hydroxypropanoic acid (L - (+) - lactic acid), which forms a cyclic ester out of two molecules. This dilactide can be polymerized to a polylactide, which is used in surgery.

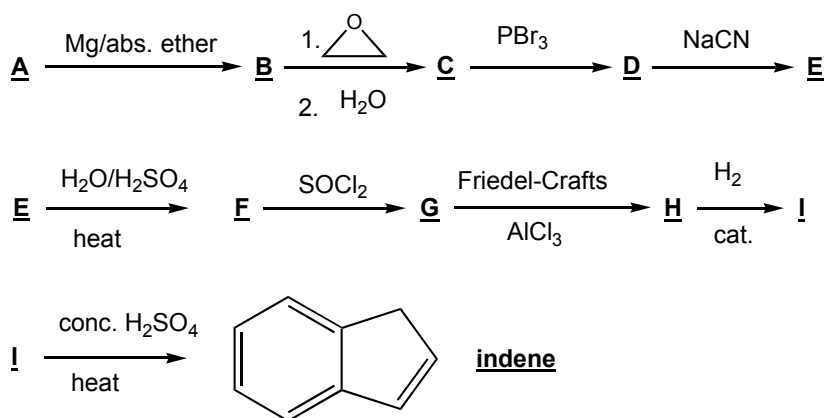
- Give the spatial structures and Fischer projection of L - (+) - lactic acid and its dilactide
- Sketch the structure of the polylactide discussed above (at least three units). What is its tacticity (iso-, syndio- or atactic) ?
- Draw the isomeric dilactides formed out of racemic lactic acid. Show the configuration of the chiral centres.

L - (+) - lactic acid is used for the preparation of the herbicide Barnon that is 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 is then submitted to a $\text{S}_{\text{N}}2$ - reaction with 3 - fluoro - 4 - chloro - phenylamine, where the methanesulfonate group leaves as CH_3SO_3^- . Finally a benzoyl group is introduced with the help of benzoyl chloride.

- Draw the Fischer projection of the various consecutive reaction products.

IChO Veszprém - Budapest 1987

Write the structural formulae of the compounds A to I in the following reaction sequence.



IChO Veszprem - Budapest 1987

- What ratio of primary / secondary / tertiary products can statistically be expected in the high temperature chlorination of methylbutane? Assume that the reaction rate of the substitution is equal for all C-H bonds.
- Which of the following alcohols: pentan-1-ol, pentan-2-ol and 2-methyl-butan-2-ol react with the following reagents listed below ?
1) cold, concentrated sulphuric acid; 2) $\text{CrO}_3/\text{H}_2\text{SO}_4$; 3) ZnCl_2/HCl ; 4) I_2/NaOH
- Which of the following aldohexose structures (Fig. 9) are 1) enantiomer pairs, 2) diastereomer pairs?
- Two hydrocarbon compounds of the same molecular formula C_4H_8 easily react with hydrogen in presence of a platinum catalyst. During ozonolysis only ethanal (acetaldehyde) is formed in both cases. The $^1\text{H-NMR}$ spectra of the two compounds show two types of protons in a ratio of 3 to 1. Draw the structures of the described compounds.
- Select the components of the group listed below that can be obtained during complete hydrolysis of lecithin (a phospholipid): serine, phosphoric acid, sphingosine, choline, glycerol, myo-inositol, phosphatidic acid and fatty acids). Which of the following carboxylic acid can be formed in the tricarboxylic acid cycle (Krebs' citric acid cycle): maleic acid (cis-butenedioic acid), mandelic acid (a-hydroxy-phenylethanoic acid), malic acid (2-hydroxy-butanedioic acid), tricarb-allylic acid (propane-1,2,3-tricarboxylic acid), oxalacetic acid (2-oxo-butanedioic acid), keto-glutaric acid (2-oxo-pentanedioic acid), fumaric acid (trans-butenedioic acid) and acetoacetic acid (3-oxo-butanoic acid).
- To which structures is the nicotinamide moiety (part) of NAD^+ converted during the uptake of hydrogen to form NADH (A, B or C) ?

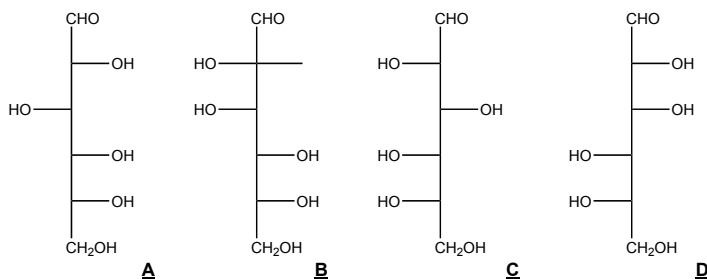
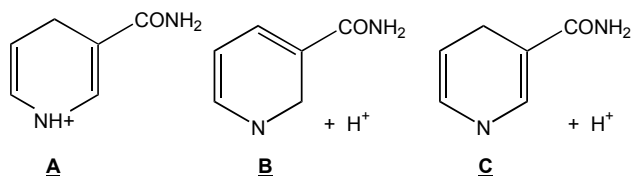


Fig. 9 Aldohexose structures



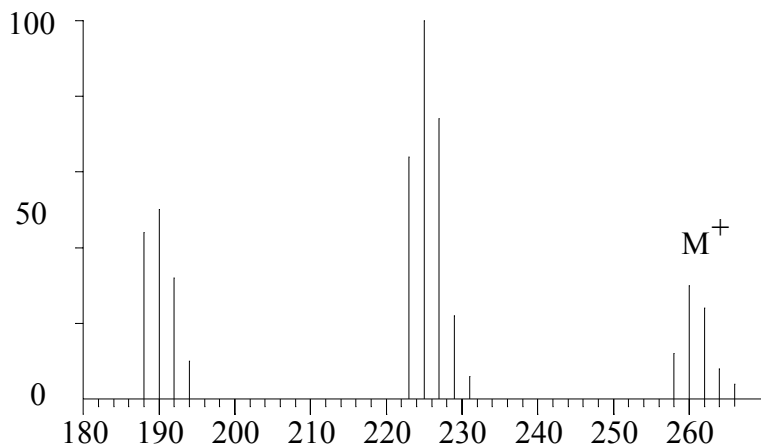
IChO Helsinki 1988

A common compound A is prepared from phenol and oxidized to compound B. Dehydration of A with H₂SO₄ leads to compound C and treatment of A with PBr₃ gives D. In the mass spectrum of D there is a very strong peak at m/e = 83 (base peak) and two molecular ion peaks at m/e 162 and 164. The ratio of intensities of the peaks 162 and 164 is 1.02. Compound D can be converted to an organomagnesium compound E which reacts with a carbonyl compound F in dry ether to give G after hydrolysis. G is a secondary alcohol with the molecular formula C₈H₁₆O.

- Outline all steps in the synthesis of G and draw the structural formulae of the compounds A - G.
- Which of the products A - G consist of configurational stereoisomeric pairs ?
- Identify the three ions in the mass spectrum considering isotopic abundances given in the text.

IChO Helsinki 1988

Upon analyzing sea mussels a new bioaccumulated pollutant X was found as determined by mass spectroscopy coupled to a gas chromatograph. The mass spectrum is illustrated in Fig 10. Determine the structural formula of X assuming that it is produced out of synthetic rubber used as insulation in electrolysis cells that are used for the production of chlorine. Give the name of the compound X. The isotopic abundances of the pertinent elements are shown in Fig. 11. Intensities of the ions m/e = 196, 233, 268 and 270 are very low and thus omitted. Peaks of the ¹³C containing ions are omitted for simplicity



Element	Mass	Abundance	Mass	Abundance	Mass	Abundance
H	1	100.0	2	0.015		
C	12	100.0	13	1.1		
N	14	100.0	15	0.37		
O	16	100.0	17	0.04		
P	31	100.0				
S	32	100.0	33	0.80	34	4.4
Cl	35	100.0			37	32.5
Br	79	100.0			81	98.0

Fig. 10 Mass spectrum and isotopic abundances

IChO Halle 1989

A chemically and biologically important class of organic compounds are carboxylic acids.

- Draw the structural formulae of all isomeric cyclobutanedicarboxylic acids and give the corresponding systematic names.
- There are three stereoisomers, I,II and III. Draw perspective stereoforulas of I, II and III indicating the relative configuration of each molecule.
- Which pairs of stereoisomers I,II and III are diastereoisomers and which are enantiomers of each other ?
- Which reaction can be used to determine the relative configuration of diastereoisomers?
- How may the enantiomers of cyclobutane-1,2-dicarboxylic acid be separated ?
- Indicate the absolute configuration of each asymmetric centre on the structures of the stereoisomers I, II and III using the Cahn-Ingold-Prelog rules (R,S system).

Fats (lipids) contain a non-polar (hydrophobic) and a polar (hydrophilic) group.

- Draw the structures of *Z*-octadec-9-enoic acid (oleic acid), octadecanoic acid (stearic acid) and hexadecanoic acid (palmitic acid). Using these three fatty acids draw a possible structure of a triacyl glyceride.
- Write the equations for the hydrolysis reactions of your triacyl glyceride in NaOH(aq). Give the corresponding mechanism.
- Which of the following fatty acids, $C_{21}H_{43}COOH$, $C_{17}H_{35}COOH$ or $C_5H_{11}COOH$ is the least soluble in water.
- Phospholipids are an important class of bio-organic compounds. Draw the structure of the phosphatic acid derived from your triacyl glyceride and mark the hydrophilic and hydrophobic groups.
- Draw two possibilities for the association of six identical molecules of phospholipids in water.
- Biomembranes consist of a phospholipid bi-layer. Draw such a structure. What other biomacromolecules are contained in such biomembranes?

IChO Paris 1990

Synthesis of Haloperidol, a powerful neuroleptic

- Give a simplified equation for the preparation of methyl 4 - chlorobenzoate starting from benzene and all necessary inorganic substances. Diazomethane must be used in your synthesis.
- How can γ -butyrolactone be converted into 4-hydroxybutanoic acid (K)? Convert K into 4-chlorobutanoyl chlorid (L)!

Methyl 4 - chlorobenzoate is treated with an excess of vinylmagnesiumbromide in anhydrous ether. M is obtained after hydrolysis. Treating M with an excess of HBr in anhydrous conditions in the presence of benzoyl peroxide, N is obtained. N reacts with ammonia to form 4-(4-chlorophenyl)-4-hydroxypiperidine (O).

- Write down the structure of M, N and O and indicate the mechanism of the reaction leading to M.
- In the presence of moderate amounts of aluminium chloride, L reacts with fluorobenzene to yield mainly a ketone P ($C_{10}H_{10}OFCl$). Sketch the structure of P and indicate the mechanism.
- Give a chemical and physical test method for the determination of the carbonyl group. How can you make sure that the carbonyl group does not belong to an aldehyde group?
- P reacts with O on a 1 to 1 mole basis, in basic media, to give H that contains only one chlorine atom on the aromatic ring. Give the structure of H which is haloperidol.

- g) State the multiplicity of each resonance in the ^1H NMR spectrum of K. Assume that all coupling constants between protons and adjacent carbons are identical.

IChO Lodz 1991

A polymer X contains 88.25% C and 11.75% H. In dilute solutions it reacts with bromine and ozone. The thermal degradation produces a volatile liquid Y in 58% yield. Y starts boiling at 34 °C and contains 88.24% C and 11.75% H. Some higher boiling products are formed both from the cracking of X and from Diels-Alder-type cyclization of Y. The vapour of Y was 34 times as dense as hydrogen. The product of bromination yields Y containing 82.5% bromine by mass. Ozonolysis of Y followed by mild reduction gave A and B in a molar ratio A:B = 2:1. Only compound B gave a positive result for the iodoform reaction.

- a) Determine the molecular formula and the molar mass of A, B and Y and show its structure.
b) Give an equation for the reaction of Y with bromine.

In the catalytic hydrogenation of 13.6 g of X, 0.2 mole of hydrogen was absorbed. Ozonolysis of X followed by mild reduction yielded compound Z (80.0% C, 8.0% H).

- c) Give the molecular formula of Z and the degree of unsaturation of X.

Compound Z gave a positive reaction with Fehling's solution. Mild oxidation of Z gave an acid C of which a solution was titrated with aqueous KOH. 0.116 g of C neutralized 0.001 mol KOH. In the iodoform probe 2.90 g of C yielded 9.85 g of iodoform. In addition the alkaline filtrate yielded compound E upon acidification.

- d) What is the molar mass of C and what functional groups are present in Z?

When heated, E loses water to form F. Both E and F react with an excess of acidified ethanol to G ($\text{C}_8\text{H}_{14}\text{O}_4$).

- e) Sketch the structures of C, E, F, G and Z and give an unbalanced reaction scheme for $\text{E} \rightarrow \text{F} \rightarrow \text{G}$.

X exists in isomeric forms which are stereoregular. Show the structure (containing at least 3 monomer units) for two possible stereoisomers of X.

IChO Lodz 1991

After passing 0.25 mol of hydrocarbon A over heated pumice (950 K) in an iron pipe, compound B in yield of 80 % (i.e. 15.4 g) and hydrogen, 2.4 l (295 K, 102 kPa) were obtained; B and hydrogen are the only products. A mixture of halogen derivatives C, D, E, F and G is produced from B by reaction with a halogen in presence of a Lewis acid. C to G contain each one halogen atom more than the preceding compound. For the compounds C to F only one of the possible isomers is formed. In compound G there is no such preference and its three isomers G1, G2 and G3 are found in the mixture. Compounds C to F easily racemize, so that no optical isomerism occurs. However racemization is difficult for G1, G2 and especially for G3. In the mass spectrum of E only three isotopic peaks were observed. Their relative intensity is 1: 1: 0.3.

Information:

- $k_{\text{ortho}} > k_{\text{para}}$ in compound B
- the effect of the first halogen in the ring: $k_{\text{para}} > k_{\text{ortho}}$

- compounds D and F have a center of symmetry
- the contribution of carbon and hydrogen isotopes in the mass spectrum of E are negligible
- natural abundance of halogen isotopes:

$$^{19}\text{F} = 100\%$$

$$^{35}\text{Cl} = 75.53\%$$

$$^{79}\text{Br} = 50.54\%$$

$$^{127}\text{I} = 100\%$$

$$^{37}\text{Cl} = 24.47\%$$

$$^{81}\text{Br} = 49.46\%$$

- Give the structural formulas of A, B, C, D, E, F, G1, G2 and G3. Explain your choice for the halogen.
- Draw and label stereo-formulas of the rotational isomers of D for $\varphi = 0, \pi/2, 3\pi/2$ where φ denotes the dihedral or torsional angle in radians and $\varphi = 0$ describes the configuration with maximal energy.
- Draw profiles of the energy changes as a function of the angle of rotation around the C-C bond for compounds C and D.
- Give G1, G2, G3 in their increasing difficulty of racemization. Explain your answer.
- Draw stereo-formulas of the enantiomers of G3.
- Suggest a chemical reaction or a biological method by which compounds like these can be destroyed.

IChO Pittsburgh 1992

Coniferyl alcohol which is not soluble in water or aqueous NaHCO_3 has the molecular formula $\text{C}_{10}\text{H}_{12}\text{O}_3$. It is isolated from pine trees. A solution of Br_2 in CCl_4 is decolorized when added to coniferyl alcohol forming A ($\text{C}_{10}\text{H}_{12}\text{O}_3\text{Br}_2$). Upon reductive ozonolysis vanillin (4-hydroxy-3-methoxybenzaldehyde) and B ($\text{C}_2\text{H}_4\text{O}_2$) are produced. Coniferyl alcohol reacts with benzoyl chloride ($\text{C}_6\text{H}_5\text{COCl}$) in the presence of a base to form C ($\text{C}_{24}\text{H}_{20}\text{O}_5$). This product rapidly decolorized KMnO_4 (aq) and is insoluble in dilute NaOH .

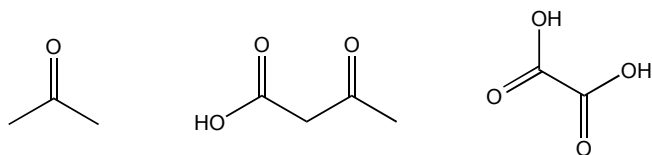
Coniferyl alcohol reacts with cold HBr to form D ($\text{C}_{10}\text{H}_{11}\text{O}_2\text{Br}$). Hot HI converting ArOR to ArOH and RI converts coniferyl alcohol to E ($\text{C}_9\text{H}_9\text{O}_2\text{I}$) and CH_3I . In an aqueous base CH_3I and coniferyl alcohol form F ($\text{C}_{11}\text{H}_{14}\text{O}_3$), which is not soluble in a strong base, but decolorizes Br_2/CCl_4 -solution.

- Draw the structures of compounds A-F including coniferyl alcohol.
- There are a number of stereoisomers of A. Draw Fischer projections of all stereoisomers labelling each chiral centre with the proper R or S designation giving the absolute configuration about the chiral centre.

IChO Pittsburgh 1992

Rose oil is obtained from steam distillation of roses. It contains a number of terpenes, one of which is geraniol, $\text{C}_{10}\text{H}_{18}\text{O}$ (A). Upon oxidation, geraniol can either give a ten-carbon aldehyde or a ten-carbon carboxylic acid. Reaction with two moles of bromine gives a tetrabromide ($\text{C}_{10}\text{H}_{18}\text{OBr}_4$) (B). Geraniol reacts with HBr to give two bromides of formula $\text{C}_{10}\text{H}_{17}\text{Br}$.

When geraniol is vigorously oxidized, three products are obtained:

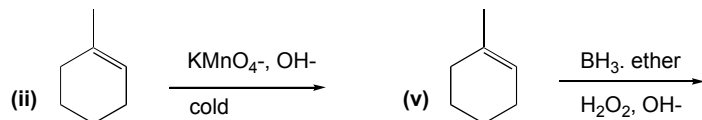
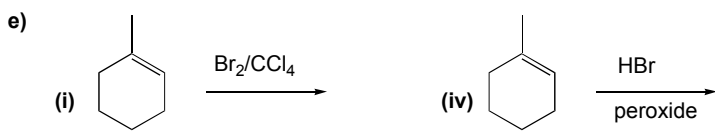
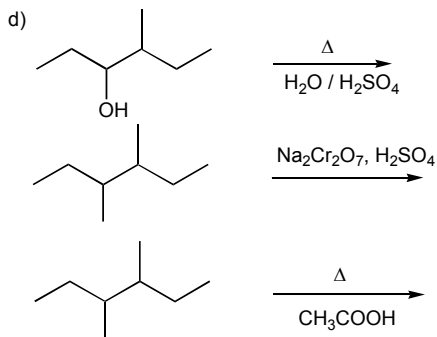
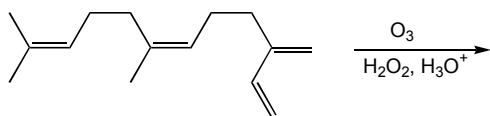
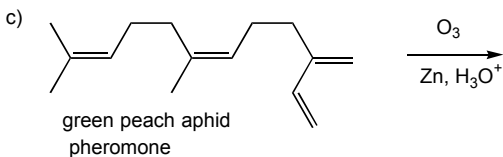
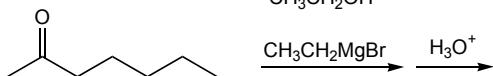
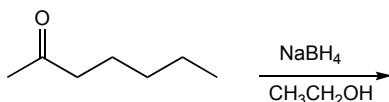
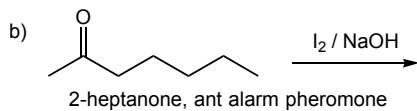
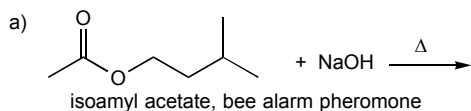


- Give the structure of geraniol (A), B and the two bromides of formula $\text{C}_{10}\text{H}_{17}\text{Br}$

b) Indicate which of the two bromides is formed in greater proportions.

IChO Pittsburgh 1992

Complete the following reactions and indicate their stereoselectivity (cis/trans) where appropriate.



ICHO Perugia 93

Frontalin is a pheromone of the western pine beetle with a composition C 67.58%, H 9.92%, O 22.50%. It is an acetal that can be prepared starting from sodium diethylmalonate and 3-chloro-2-methylpropene. The resulting product **A** is hydrolyzed by conc. potassium hydroxide and then decarboxylated by treatment with hot acetic acid to give a compound **B**. The latter reacts with aq. NaHCO_3 (gas evolution is observed) as well as with cold aq. KMnO_4 which turns to a brown color. The compound **B** is then converted by LiAlH_4 into **C** ($\text{C}_6\text{H}_{12}\text{O}$).

Treatment of **C** with *p*-toluenesulfonyl chloride in pyridine and then sodium cyanid in dimethylsulfoxide affords **D** ($\text{C}_7\text{H}_{11}\text{N}$). The subsequent reaction of **D** with methylmagnesium iodide, followed by hydrolysis, yields **E** ($\text{C}_8\text{H}_{14}\text{O}$). **E** shows IR absorption at ca. 1700 cm^{-1} . The epoxidation of **E** with metachloroperbenzoic acid then affords **F** ($\text{C}_8\text{H}_{14}\text{O}_2$) which, by treatment with diluted acids is converted to frontalin acetal **G**.

Question: Draw the structure of compounds **A-G**.

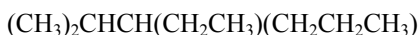
ICHO Perugia 93

By treatment with an optically active hydroborating agent (R_2^*BH) and subsequent oxidative work-up, 1-methylcyclopentene affords a mixture of alcohols that rotates the plane of polarized light. [H.C.Brown, *J.Org.Chem.*, 47, 5074, 1982]

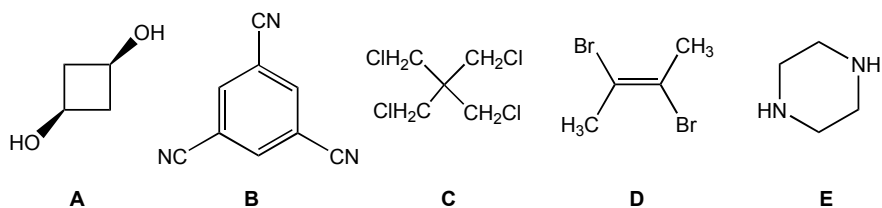
- Write the structures of the alcohols.
- Assign the configurations (*R,S*) to the chiral centers.
- Explain in a sentence why the obtained mixture of alcohols exhibits optical activity.

ICHO Oslo 1994

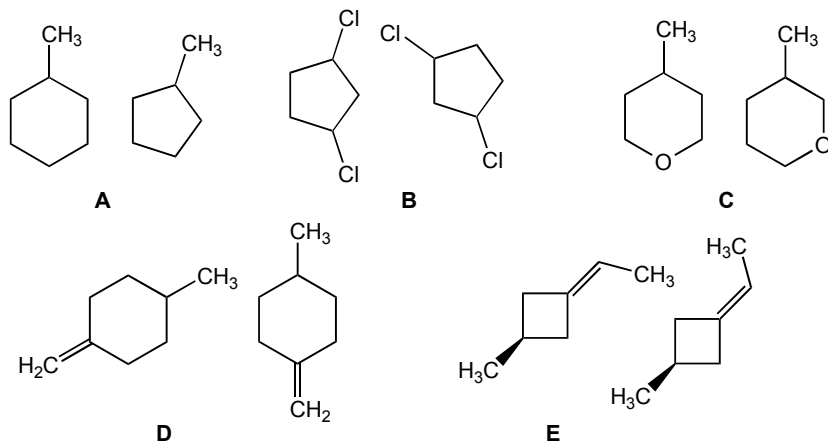
- What is the correct systematic name (IUPAC name) for the compound below?



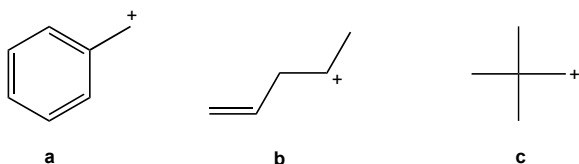
- 3-Isopropylhexane
 - 2-Methyl-3-propylpentane
 - Ethyl isopropyl propyl methane
 - 3-Hexylpropane
 - 3-Ethyl-2-methylhexane
- How many isomers, including stereoisomers, containing only saturated carbon atoms, are there for C_5H_{10} ?
 - Which one of the following compounds has a dipole moment significantly different from zero?



d) Which of the following is a pair of structural isomers?

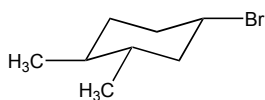


e) Which of the following five options is the correct order of relative stabilities of cations a, b and c as written below? Write the most stable first.



1. a > b > c
2. b > c > a
3. c > a > b
4. a > c > b
5. b > a > c

f) What is the correct stereochemical descriptor of the optically active compound drawn below?



g) All the molecules drawn below are neutral compounds. Which one does not contain a formal positive charge and a formal negative charge?

1. $(\text{CH}_3)_3\text{N}-\text{B}(\text{CH}_3)_3$
2. $(\text{CH}_3)_2\text{N}-\text{O}-\text{CH}_3$
3. $\text{CH}_2=\text{N}=\text{N}$
4. $(\text{CH}_3)_3\text{N}-\text{O}$
5. $\text{F}_3\text{B}-\text{O}(\text{CH}_3)_2$

h) Which one of the IR-spectra shown on the next page corresponds to that of benzaldehyde?

[Image]

ICHO Oslo 1994

An optically active compound A ($C_{12}H_{16}O$) has a strong IR-absorption at $3000-3500\text{ cm}^{-1}$, and two medium signals at 1580 and 1500 cm^{-1} . The compound does not react with 2,4-dinitrophenylhydrazine (2,4-DNP). Upon treatment with $I_2/NaOH$, A is oxidized and gives a positive iodoform reaction. Ozonolysis of A (a. O_3 ; b. Zn, H^+) gives B ($C_9H_{10}O$) and C ($C_3H_6O_2$).

Both B and C give precipitates when treated with 2,4-DNP, and only C gives a positive reaction with Tollen's reagent ($Ag(NH_3)^{2+}$). Nitration of B (HNO_3/H_2SO_4) may give two mono-nitro compounds D and E, but in practice, only D is formed. When the organic product from the Tollen's reaction is acidified and then heated, compound F ($C_6H_8O_4$) is formed. F gives no IR absorption above 3100 cm^{-1} .

- Based on the above information draw the structural formulae for the compounds A-F and give the overall reaction scheme, including the 2,4-DNP reaction and the products of the Tollen's and iodoform reactions.
- Draw C in an *R*-configuration. Transform this into a Fischer projection and state whether it is a D- or L-configuration.

6. Biochemistry

ICHO Leiden 1986

In recombinant DNA technology specific endonucleases can recognize and hydrolyse the phosphoric ester bound in each of both strands. Cla I for example hydrolyses the bond between two nucleotides in the sequence: 5'-pApT | pCpGpApT-3'

- Give the base sequence of the complementary strand in the 5' - 3' direction and indicate with arrows the location where the hydrolysis by Cla I would occur.
- How often on average will this sequence occur in one strand of DNA molecule of 10^5 base pairs? You can assume that the four bases occur equally often and that they randomly distribute in the two chains.

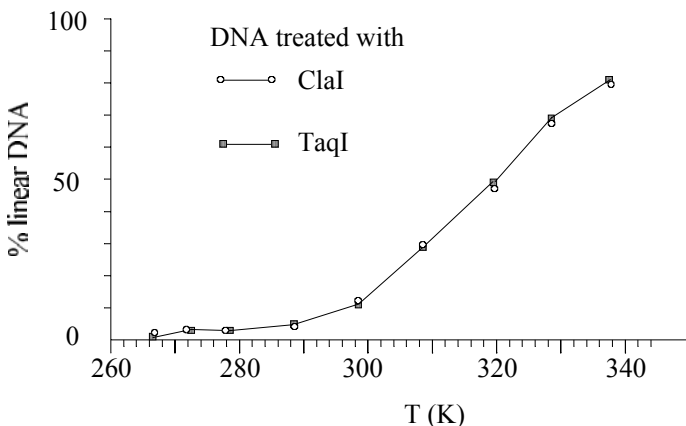


Fig. 111 Cleavage curve for DNA treated with ClaI and TaqI

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 treated by cleavage turns out to be a thymine(T)- and the 5' end a cytosine(C) -end.

- c) How long is the sequence recognized by Taq I ?
 d) Give the two possible base sequences (in the direction 5' - 3') which form the recognition pattern for Taq I (must obviously have some symmetry).

The DNA of a phage which occurs as a close circle contains only 5'- pApTpCpGpApT- 3' sequence in each of the two strands. After treatment with ClaI an equilibrium is established: circular DNA → linear DNA

- 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 Fig. 11 the percentage of linear DNA is given as a function of temperature, measured in a solution of 0.15 M NaCl buffered with citrate at pH = 6.5. With Taq I as cleavage enzyme, the same curve is obtained.
 f) Is the reaction as written endothermic or exothermic? Explain your answer.
 g) Show, considering the information given, which of the two base sequences of the answer to d) is the correct one.
 h) What would look the curve for Taq I like 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, purified and mixed 1:1 with phage DNA which was also cleaved with Cla I. Thereby recombinant molecules can be formed through the reaction: phage-DNA + fragment DNA → recombinant-DNA

- i) Would the enthalpy of this reaction be positive, negative or about zero ? Explain your answer.
 k) Which combination of temperature, DNA concentration and ionic strength (high or low in each case) will give the maximum percentage of recombinant molecules ?

ICHO Paris 1990

Stereochemistry of the dehydrogenation of succinate to fumarate

- a) Write down structures for all the possible stereoisomers obtained by catalytic deuteration of maleic and fumaric acid. How many isomers are there. Indicate those that are optically active. Establish a stereochemical relationship between them (compare the isomers two by two). Which is the most stable conformation ? Draw Newman projections.
 b) The proportion of dideuterated fumarate (obtained when each of the 2-3 dideuterated succinates is submitted to the enzymatic reaction) is 4 % when using fumaric acid as starting molecule, but 48.5 % when using maleic acid.
 c) On the basis of the Newman projections of the most stable conformations of each isomere, complete the following table:

2,3 dideuteriosuccinate	% of dideuterated fumarate syn dehydrogenation	% of dideuterated fumarate anti dehydrogenation
isomer I		
isomer II		
...		

Assume that the percentages of dideuterated fumarate are 0 or 50% respectively.

- d) Show the stereochemistry of the enzymatic dehydrogenation.
 e) The 2,3 - dideuterofumarate reacts with fumarase to (2S, 3S)-2,3-dideuteromalate (through addition of water). Show the stereochemical pathway of the reaction.

- f) The acetylcoenzyme A, CH_3COSCoA reacts with glyoxylate OHC-CO_2^- in the presence of malate synthase enzyme to (S)-malate.

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A similar reaction can proceed between an ester CH_3COOR and an aldehyde R. It leads to a β -hydroxy-ester. Write the steps of the mechanism.

- g) The enzymatic reaction is carried out using acetylcoenzyme A which is obtained from acetic acid CH_3COOH having R-configuration. The formed (S)-malate is dehydrated (the reverse reaction of question c) by an enzymatic reaction. What enzyme can be used? The major product is monotrinitiated fumarate (79%) with 21 % untrinitiated fumarate. Write down the Fischer projections of the two possible structures of the major product (S)-malate arising from the acetylcoenzyme A which has a labelled acetyl group with R-configuration. What would be the products if the starting material has a labelled acetyl group with S-configuration?