40th International Chemistry Olympiad

Preparatory Problems

2008

Budapest, Hungary

Preparatory problems for the 40th International Chemistry Olympiad

Editor: Gábor Magyarfalvi

Contents

Problem Authors

Zoltán Fekete	University of Szeged
Sarolta Igaz	Okker Education Ltd.
Dávid Komáromy	Eötvös Loránd University
András Kotschy	Servier Research Institute for Medicinal Chemistry, Budapest
György Kóczán	Enzix LLC
Gábor Lente	University of Debrecen
Gábor Magyarfalvi	Eötvös Loránd University
Attila Nagy	Eötvös Loránd University
István Pálinkó	University of Szeged
András Stirling	Chemical Research Center of the Hungarian Academy of Sciences
László Túri	Eötvös Loránd University
Judit Zádor	Eötvös Loránd University, currently at Sandia National Laboratories, USA

Preface

We have developed this set of problems with the intention of making the preparation for the Olympiad easier for both students and mentors. Our intention was to shift the focus of the problems from current research topics to interesting applications of basic chemical principles that are easily accessible at the level of secondary education.

We aimed to comply with the presently valid IChO syllabus, but the Olympiad exams and the preparatory problems were prepared with a restructured syllabus in mind. We recommend the use of the version of the syllabus found at the end of this booklet during the preparations.

We restricted ourselves to the inclusion of only a few topics that are not usually covered in secondary schools. There are six such advanced topics that we expect the participants to be familiar with. These fields are listed explicitly and their application is demonstrated in the problems. In our experience each of these topics can be introduced to well-prepared students in 2-3 hours.

The official solutions are only available to the future mentors of each country at the time of publication of this set, Solutions will be published in May 2008 on the web.

We welcome any comments, corrections or questions about the problems via email at gmagyarf@chem.elte.hu.

We have enjoyed preparing the problems and we hope that you will also enjoy solving them. See you in Budapest!

Acknowledgement

Budapest, 20 January 2008

Gábor Magyarfalvi
editor

Constants and Formulae

Avogadro constant:	$N_A = 6.022 \cdot 10^{23}$ mol^{-1}	Ideal gas equation: $pV = nRT$
Gas constant:	$R = 8.314$ J K^{-1} mol^{-1}	Gibbs energy: $G = H - TS$
Faraday constant:	$F = 96485$ C mol^{-1}	$\Delta_r G^o = -RT \ln K = -nFE^o_{cell}$
Planck constant:	$h = 6.626 \cdot 10^{-34}$ J s	Nernst equation: $E = E^o + \dfrac{RT}{zF} \ln \dfrac{c_{ox}}{c_{red}}$
Speed of light:	$c = 3.000 \cdot 10^8$ m s^{-1}	Arrhenius equation: $k = A \exp\left(-\dfrac{E_A}{RT}\right)$
Zero of the Celsius scale:	273.15 K	Lambert-Beer law: $A = \log \dfrac{I_0}{I} = \varepsilon c l$

In equilibrium constant calculations all concentrations are referenced to a standard concentration of one mole per dm^3.

Periodic table with relative atomic masses

1																	18
1 H 1.008	2											13	14	15	16	17	2 He 4.003
3 Li 6.94	4 Be 9.01											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.30	3	4	5	6	7	8	9	10	11	12	13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.87	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.38	31 Ga 69.72	32 Ge 72.64	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.96	43 Tc -	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.90	54 Xe 131.29
55 Cs 132.91	56 Ba 137.33	57-71	72 Hf 178.49	73 Ta 180.95	74 W 183.84	75 Re 186.21	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po -	85 At -	86 Rn -
87 Fr -	88 Ra -	89-103	104 Rf -	105 Db -	106 Sg -	107 Bh -	108 Hs -	109 Mt -	110 Ds -	111 Rg -							

57 La 138.91	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm -	62 Sm 150.36	63 Eu 151.96	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.05	71 Lu 174.97
89 Ac -	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np -	94 Pu -	95 Am -	96 Cm -	97 Bk -	98 Cf -	99 Es -	100 Fm -	101 Md -	102 No -	103 Lr -

Fields of Advanced Difficulty

Theoretical

Relation between equilibrium constants, electromotive force and standard Gibbs energy;

Inorganic electrochemistry, redox titrations and redox equilibria;

Integrated rate law for first-order reactions, half-life, Arrhenius equation, determination of activation energy, analysis of moderately complex reaction mechanisms;

Solid state structures;

Stereoselective transformations (diastereoselective, enantioselective), optical purity;

Monosaccharides, equilibrium between linear and cyclic forms, pyranoses and furanoses, Haworth projection and conformational formulae, glycosides;

Practical

Advanced inorganic qualitative analysis;

Basic synthesis techniques: filtration, drying of precipitates, thin layer chromatography;

Theoretical problems

Problem 1

During a new construction at 221 Baker Street, an amazing discovery was made. A small cabinet was found containing previously unknown documents. They revealed that Dr. Watson kept notes about his adventures with Mr. Sherlock Holmes into the 1950s. An interesting, but incomplete story read as follows:

....and was able to spring into a cab and drive to Baker Street, half afraid that I might be too late to assist at the *dénouement* of the little mystery. I found Sherlock Holmes alone, however, half asleep, with his long, thin form curled up in the recesses of his arm-chair. A formidable array of bottles and test-tubes, with the pungent smell of hydrochloric acid, told me that he had spent his day in the chemical work which was so dear to him. It was obvious to me that my companion had already examined the carefully closed metal box we had found in a recess behind a sliding panel just above the right bell-pull in poor Browning's sitting-room.

'No doubt the murderers were after this box,' said he. 'They searched the house from cellar to garret. I would have been at a loss myself if I had not met Irene Adler some time ago...'

My attention was captured by the open box on the mantelpiece. It was empty.

'HOLMES WAS WORKING HARD OVER A CHEMICAL INVESTIGATION.'

'It is far better to keep the contents of the box in mineral oil,' Holmes explained and showed me a bottle. 'This will keep it safe from air but also makes it more flammable.'

The yellowish liquid in the bottle covered a few thumb-sized pellets.

'Is this a dangerous poison?' I asked.

'Not at all, Watson. Have you ever seen a poison in so big a pellet? It would hardly be healthy to swallow, but that is not the point. Now look at this.'

He took out a pellet, dried it with great care, and dropped it into a bowl of water. Instead of slowly dissolving or sinking, the pellet began a strange dance on the surface of the water, hissed ominously, gave out bubbles and some malodorous product. The acrid fumes took me by the throat and set me coughing.

'Holmes, this will kill us both,' I screamed.

'You should have seen the reaction with hydrochloric acid. Anyway, I told you it is not particularly poisonous,' said Holmes coughing. With dramatic suddenness he struck a match, and as he held the match nearer, the bubbles caught fire and gleamed with the most beautiful crimson flame I have ever seen.

'Magnificent, is it not? One ounce of this substance when reacting with water or hydrochloric acid gives more than three cubic feet of gas. To be precise, 3.068 cubic feet at 80.0 degrees and atmospheric pressure.'

'You measured this?' I cried.

'Of course I measured it,' said Holmes with an impatient gesture. He took a small bottle labelled phenolphthalein and put a few drops of its contents into the bowl of water, which turned pink immediately, its colour resembling the gleam of the flames.

'Is this why this substance is so precious?'

'Not really,' murmured Holmes. 'The Powers of Evil created these pellets, Watson, or I am very much mistaken. The murder of Browning was nothing but a trifle in this case.'

Half crazy with fear, I looked at the marble-like pellets in the bottle.

'I do not really understand, Holmes.'

'I made accurate measurements. I dissolved exactly one ounce of this substance in water, then boiled away the water. The remaining white solid I could not dry completely, so I re-dissolved it in water and added some hydrofluoric acid until the colour of phenolphthalein was gone. I boiled away the water again, and drying the white residue was not a problem this time. Its mass was precisely three and one eighth ounces. Three and one eighth. Do you see, Watson?'

'I am still in the dark,' I answered with some embarrassment.

'I do not wish to make a mystery,' said he, laughing. 'The matter is elementary; simplicity itself. You remember our little adventure with Professor Urey?'
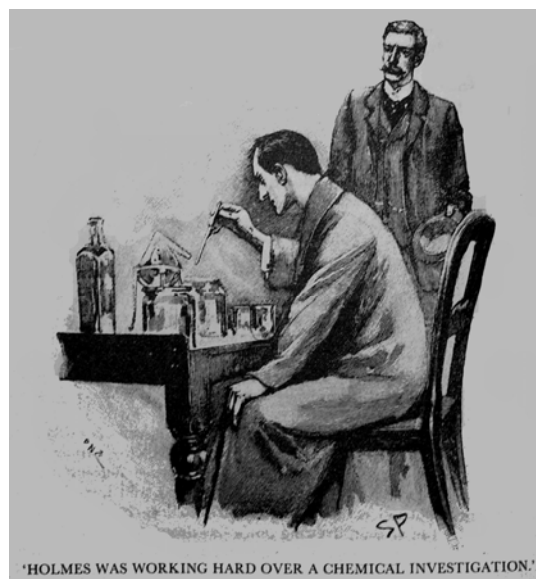
The notes end here. Sherlock Holmes uses imperial units of measurement: 1 foot equals 30.48 cm, 1 ounce is 28.350 g, the atmospheric pressure has been constant (101325 Pa) over the last few centuries. The temperature is measured in degrees Fahrenheit (°F): 0 °C equals 32 °F, whereas 100 °C is 212 °F.

Help Watson figure out what was in the box. What could it possibly have been intended for?

Problem 2

Compound **A** is a stable salt of metal **H**. It contains 11.97 % N, 3.45 % H and 41.03 % O (mass fractions), besides the metal. The following chart describes some reactions starting from **A** and **H** (Δ signifies heating). Above the arrows the necessary reactants are displayed. All substances tagged with a letter contain the metal, but none of the by-products do. (When a substance is labeled as dissolved in water, then it is ionic and you have to show only the ion containing the metal.)
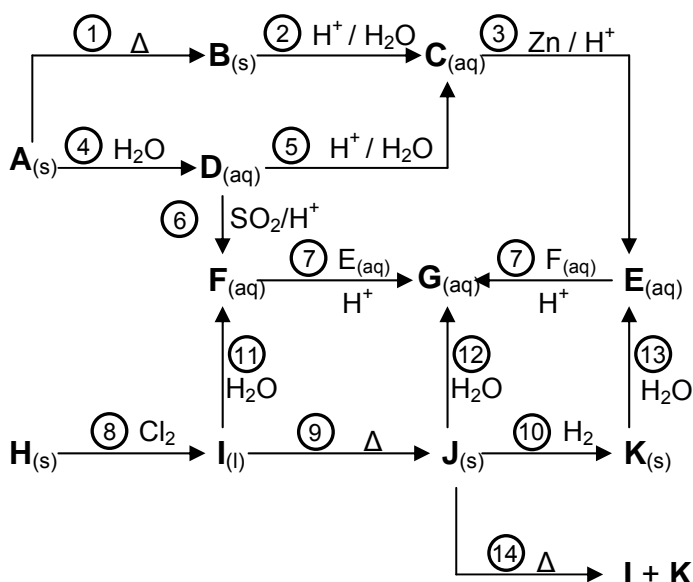
a)   Identify the substances **A**-**K** and write down all the equations 1-14.

b)   Select the redox processes from the reactions.

c)   Select those compounds from **A**-**K** that are not expected to have unpaired electrons.

d)   On the basis of the above chart propose a reaction to obtain **G** starting from **F**, but without using **E**.

e)   Compound **B** is industrially very important. Show a reaction where its presence is indispensable. What role does it play?

f)   What percentage of product **I** contains ^{35}Cl if chlorine gas containing 99 % ^{37}Cl and 1 % ^{35}Cl is used in reaction 8?

g)   What percentage of **J** produced from this sample of **I** contains ^{35}Cl?

Problem 3

The metallic radius of chromium is estimated to be 126 pm. The density of chromium is 7.14 g/cm^3. Solid chromium belongs to the regular cubic crystal system.

a)   Determine the lattice type of chromium using only the data given above.

A test for the presence of Cl^- ions used to be the following: a dry mixture of the unknown material and potassium dichromate is heated with concentrated H_2SO_4. The gases produced are passed into NaOH solution, where the appearance of a yellow color indicates the presence of chlorine.

b)   What is the volatile chromium compound produced in the reaction? Draw its structure. Note that neither Cr nor Cl changes oxidation state during the reaction.

Acidifying a solution of potassium chromate gives rise to the formation of the orange dichromate ion, then the deeper red tri- and tetrachromate ions. Using concentrated sulfuric acid we obtain a red precipitate not containing potassium.

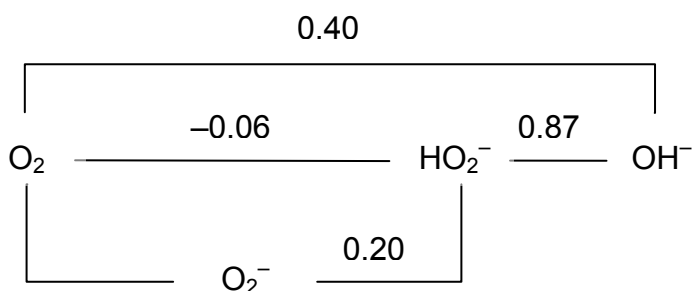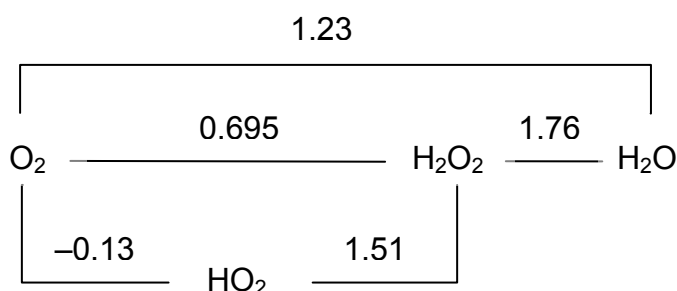**c)**   Write the equations and draw the structure of the ions. Can you propose a structure for the precipitate?

The Latimer diagrams for a series of chromium species in acidic (pH=0) and basic (pH=14) media is given below:
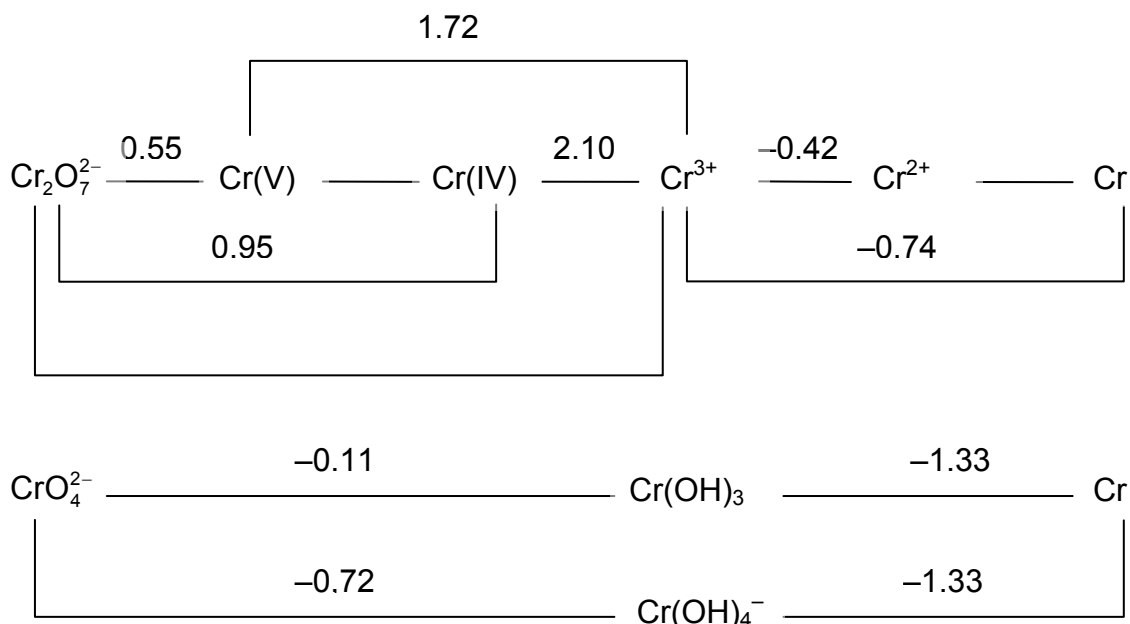
d)   Find the missing three values.

e) Are Cr(V) and Cr(IV) stable with respect to disproportionation? <u>Identify</u> a simple criterion based on the Latimer diagram. <u>What</u> is the equilibrium constant for the disproportionation of Cr^{2+}?

f) <u>Calculate</u> the solubility constant of chromium(III) hydroxide and the overall stability constant of tetrahydroxo-chromate(III) anion.

The Latimer diagram of a series of oxygen-related species in acidic (pH=0) and basic (pH=14) media is the following:

```
                        1.23
        ┌─────────────────────────────────────┐
               0.695                1.76
    O₂  ─────────────────  H₂O₂  ───────  H₂O
        │                          │
        │ −0.13           1.51     │
        └──────────  HO₂  ─────────┘
```

$$\begin{array}{c}
\text{1.23}\\
O_2 \;\underset{\text{HO}_2}{\overset{0.695}{\longrightarrow}}\; H_2O_2 \;\overset{1.76}{\longrightarrow}\; H_2O
\end{array}$$

O₂ — 0.695 — H₂O₂ — 1.76 — H₂O (top span 1.23)
O₂ — −0.13 — HO₂ — 1.51 — H₂O₂

```
                        0.40
        ┌─────────────────────────────────────┐
               −0.06               0.87
    O₂  ─────────────────  HO₂⁻  ───────  OH⁻
        │                          │
        │                  0.20    │
        └──────────  O₂⁻  ─────────┘
```

O₂ — −0.06 — HO₂⁻ — 0.87 — OH⁻ (top span 0.40)
O₂ — O₂⁻ — 0.20 — HO₂⁻

g) <u>What will happen</u> if the pH of a solution containing chromate(VI), Cr(III) and hydrogen peroxide is set to 0? What will happen if we set the pH to 14? <u>Write down</u> the reactions and the corresponding standard cell potential.

Problem 4

Silica and silica glass is held together by single covalent Si-O bonds.

a) <u>What</u> is the coordination number of the Si and O atoms in the structure?

The density of silica glass is 2.203 g/cm³.

b) <u>What</u> is the average volume of a SiO_2 unit? <u>How many</u> bonds are there on the average in such a volume?

A frequent crystal defect in silica glass is oxygen vacancy: oxygen atoms in the lattice are missing and the neighboring Si atoms of the missing oxygen stabilize by forming a Si-Si bond. An amorphous silica sample is characterized by the formula $SiO_{1.9}$.

c) <u>What percentage</u> of the total number of the bonds are Si-Si bonds?

d) Give an expression for the n_{Si-Si}/n_{Si-O} ratio of a SiO_x sample, as a function of x, where n_{Si-Si} is the number of Si-Si bonds and n_{Si-O} is the number of Si-O bonds. Give the value of x where, on the average, all Si atoms form one Si-Si bond.

Problem 5

Pyrite (FeS_2) forms NaCl-type crystals with Fe^{2+} ions occupying the positions of Na^+, and S_2^{2-} ions occupying the positions of the Cl^- ions. The directions of the S-S bonds are alternating body-diagonal.

a) Fe is octahedrally coordinated by sulfur atoms. What is the coordination of the sulfur atoms?

b) The density (ρ) of an ideal pyrite crystal is 5.011 g/cm^3. Calculate the lattice constant of the smallest cubic unit cell.

It has been found that the lattice constant does not depend on the stoichiometry of the crystal, i.e., the lattice remains stable if the y in the formula FeS_y deviates slightly from 2 within a small range (1.95–2.05).

c) Find the equation which gives the dependence of the density on y, assuming that only the iron content varies. Find a similar equation for the case when only the S content varies.

d) Plot the two curves in the same y-ρ coordinate system. Identify the following regions in the graphs: vacancies (Fe, or S deficiencies), interstitials (Fe, or S excess), perfect lattice.

In a natural pyrite sample it was found that only 99% of the iron positions are occupied, and 1 % additional sulfur atoms are in interstitial positions.

e) Calculate the composition of the crystal. Find the corresponding point in the previously constructed y-ρ diagram.

Problem 6

Until the end of the 20th century, only two species (one molecule and one anion) were known that are composed only of nitrogen atoms.

a) What are the empirical formulae of these two species?

The first inorganic compound containing a nitrogen-only species different from the above was synthesized by Christe and co-workers in 1999.
The starting material of the synthesis is an unstable liquid **A** that is a weak, monoprotic acid. It was liberated from its sodium salt (that contains 35.36 % sodium by mass) with a large excess of stearic acid.

b) Determine the molecular formula of **A** and draw two resonance structures of the molecule. (Show all bonding and non-bonding valence electron pairs.)

The other starting material (**B**) was prepared from the cis-isomer of a nitrogen halogenide that contains 42.44 % nitrogen by mass.

c) Determine the empirical formula of this halogenide. Draw the Lewis structure of the cis-isomer. Show all bonding and non-bonding valence electron pairs.

This nitrogen halogenide was reacted with SbF_5 (a strong Lewis acid) in a 1:1 ratio at –196 °C. The resulting ionic substance (**B**) was found to comprise three types of atoms. Elemental analysis shows that it contains 9.91 % N and 43.06 % Sb by mass; further, it contains one cation and one anion. The shape of the latter was found to be octahedral.

d) Determine the empirical formula of the ionic substance **B**.

e) Determine the empirical formula of the cation found in **B** and draw its Lewis structure. Show resonance structures, if there are any. Show all bonding and non-bonding electron pairs. Predict the bond angles expected in the contributing structures (approximately).

B reacts violently with water: 0.3223 g of the compound gave 25.54 cm^3 (at 101325 Pa and 0 °C) of a color- and odorless nitrogen oxide that contains 63.65 % nitrogen by mass.

f) Identify the nitrogen oxide formed in the hydrolysis reaction and draw its Lewis structure. Show resonance structures, if there are any. Show all bonding and non-bonding electron pairs.

g) Give the chemical equation for the reaction of **B** with water.

In the experiment described by Christe and co-workers, **A** was mixed with **B** in liquid hydrogen fluoride at –196 °C. The mixture was shaken for three days in a closed ampoule at –78 °C, finally it was cooled down again to –196 °C. A compound **C** was obtained, that contained the same octahedral anion as **B** and the expected, V-shaped cation composed only of N-atoms. **C** contained 22.90 % N by mass.

h) Determine the empirical formula of **C**.

i) The cation of **C** has many resonance structures. Show these structures, indicating all bonding and non-bonding electron pairs. Predict the bond angles expected in the contributing structures (approximately).

j) Give the chemical equation for the formation of **C**. The formation of which compound makes the process thermodynamically favorable?

The cation of **C** is a very strong oxidizing agent. It oxidizes water; the reaction gives rise to the formation of two elemental gases. The resulting aqueous solution contains the same compounds as in the case of hydrolysis of **B**.

k) Give the chemical equation for the hydrolysis of **C**.

In 2004, a further step was made. The ionic compound **E** was synthesized, whose nitrogen content was 91.24 % by mass! The first step in the synthesis of **E** was the reaction of the chloride of a main group element with an excess of the sodium salt of **A** (in acetonitrile, at –20 °C), giving rise to the formation of the compound **D** and NaCl. Gas evolution was not observed. In the second step, **D** was reacted with **C** in liquid SO_2 at –64 °C, giving **E** as the product. The cation : anion ratio in **E** is also 1:1 and it contains the same cation as **C**. **D** and **E** contain the same complex anion, whose central atom is octahedrally coordinated.

l) Determine the empirical formula of **E**, given that it contains two types of atoms.

m) <u>Determine</u> the empirical formula of **D** and <u>identify</u> the main group element used.

E is supposed to be a potential fuel for future space travel because of its extremely high endothermic character. (It is a so-called "high energy density material"). A further advance is that the products of the decomposition of **E** are not toxic, so they do not pollute the atmosphere.

n) <u>What</u> are the reaction products of the decomposition of **E** in air?

Problem 7

<u>Calculate</u> the analytical concentration for each of the following solutions:

a) HCl solution, pH = 4.00 (solution A),

b) acetic acid solution, pH = 4.00 (solution B),

c) sulfuric acid solution, pH = 4.00 (solution C),

d) citric acid solution, pH = 4.00 (solution D).

<u>Calculate</u> the pH for each of the following mixtures:

e) equal volumes of solution A and NaOH solution (pOH = 4),

f) equal volumes of solution B and NaOH solution (pOH = 4),

g) equal volumes of solution C and NaOH solution (pOH = 4),

h) equal volumes of solution D and NaOH solution (pOH = 4).

i) equal volumes of solution A and B,

j) equal volumes of solution A and C.

Acetic acid: pK_a = 4.76
Sulfuric acid: pK_{a2} = 1.99
Citric acid: pK_{a1} = 3.10, pK_{a2} = 4.35, pK_{a3} = 6.39

Problem 8

Numerous inorganic compounds undergo autodissociation in their liquid state. In liquid hydrogen fluoride (density, ρ = 1.002 g/cm^3) the following equilibrium can describe the autoprotolysis:

$$3\ HF \rightleftharpoons H_2F^+ + HF_2^-$$
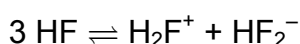
The corresponding equilibrium constant is $8.0 \cdot 10^{-12}$.

a) <u>Calculate</u> what fraction of the fluorine is present in the cationic species in liquid HF, supposing that only these three species are present in the system.

Various reactions can take place in liquid HF.

b) <u>Write</u> the equation of the reactions of liquid HF with the following substances: H_2O, SiO_2, acetone.

In water HF behaves as a medium-strength acid and dissociates only partially. The most important reactions determining the equilibrium properties of the solution are the following:

$$HF + H_2O \rightleftharpoons H_3O^+ + F^- \qquad (1)$$

$$HF + F^- \rightleftharpoons HF_2^- \qquad (2)$$
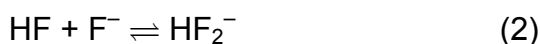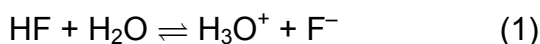
The equilibrium constants of the two equilibria are

$$K_1 = 1.1 \cdot 10^{-3}$$
$$K_2 = 2.6 \cdot 10^{-1}$$

c) <u>Calculate</u> the analytical concentration of HF in a solution having a pH = 2.00.

In early studies of aqueous HF, equilibrium (2) was not considered. However, pH measurements, assuming only equilibrium (1) led to contradictions.

d) <u>Show</u> that, assuming only equilibrium (1), pH measurements can indeed lead to a concentration-dependent equilibrium constant for (1).

Two chemists wanted to determine the acidity constant of HF (K_1) from one and the same solution with a known concentration. They measured the pH of the solution and then obtained a K_1 value by calculation. However, the better chemist knew about equilibrium (2), while she knew that the other did not. So, she was surprised when they both obtained the same K_1 value.

e) <u>What was</u> the concentration of the HF solution?

f) <u>Calculate</u> the equilibrium constant of the following equilibrium:

$$2\ HF + H_2O \rightleftharpoons H_3O^+ + HF_2^-$$
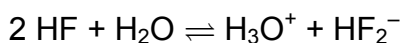
The dissociation equilibrium of a solute in a solvent can be significantly shifted by the addition of a suitable substance into the solution.

g) <u>Propose</u> three different inorganic compounds for increasing the dissociation of HF in water.

Suitable compounds can also shift the autodissociation equilibrium of HF in its liquid state by orders of magnitudes. A well-known such substance is SbF_5.

h) <u>Show</u> how SbF_5 shifts the autodissociation equilibrium of liquid HF.

The shift in the autodissociation also implies an important change in the Brønsted acidity of the solvent. In fact, the degree of solvation of the proton produced from the autodissociation essentially affects the Brønsted acidity of the solvent.

i) <u>How</u> is the Brønsted acidity of a given solvent determined by the extent of proton solvation?

The mixture of HF-SbF$_5$ belongs to the family of superacids, owing to their very high acidity. These acids are able to protonate very weak bases and thus have enabled the preparation of exotic protonated species. These, in turn, have opened new synthetic routes.

j) <u>Formulate</u> reaction equations for the reaction of methane and neopentane with the HF-SbF$_5$ superacid. Note that in both cases there is a gaseous product.

Problem 9

Ammonium sulfide ($(NH_4)_2S$) is a widely used reagent in qualitative analytical chemistry. To prepare the reagent, hydrogen sulfide gas is bubbled through a 4-5 mol/dm^3 ammonia solution, and then some water is added. The solution prepared in this way is almost never pure. It can contain either ammonia or ammonium hydrogen sulfide in excess when a lower or higher than stoichiometric amount of gas is absorbed.

- 10.00 cm^3 of an ammonium sulfide reagent solution was diluted to 1.000 dm^3. 10.00 cm^3 of the resulting stock solution was transferred into a distillation flask and ~40 cm^3 of water was added. Then, 25.00 cm^3 of 0.1 mol/dm^3 cadmium nitrate solution was added into the collector flask (where the distilled components would condense). Moreover, 20.00 cm^3 of a 0.02498 mol/dm^3 solution of sulfuric acid was added into the distillation flask.

- Approximately one half of the solution in the distillation flask was distilled into the collector flask. (In the collector flask, the formation of a yellow precipitate could be seen.)

- The content of the distillation flask was washed completely into a titration flask. After adding a few drops of methyl red indicator it was titrated with 0.05002 mol/dm^3 NaOH solution. The volume of the titrant used to reach the equivalence point was 10.97 cm^3.

- Bromine water was added to the solution in the collector flask (the precipitate dissolved), and the excess of bromine was removed by boiling the solution for 15 minutes. Bromine oxidizes all sulfur containing anions into sulfate ions. The hydrogen ions formed in the reactions in the collector flask were neutralized by 14.01 cm^3 of 0.1012 mol/dm^3 NaOH.

<u>Calculate</u> the exact composition of the reagent ammonium sulfide solution.

Problem 10

According to the website of the Hungarian Central Bank, the silvery white Hungarian 2 forint coin is composed of an alloy containing only copper and nickel. A curious chemist (who did not know that it is illegal to destroy money in Hungary) weighed a 2-Ft coin (3.1422 g) and dissolved it completely in concentrated nitric acid in about 4 hours under a fume hood. A brown gas was produced during this process and no other gaseous products were formed.

a) <u>What</u> are the chemical equations for the dissolution reactions?

Our hero diluted the solution to 100.00 cm^3 in a volumetric flask. To determine the composition of the coin, he devised a clever plan. First, he prepared a $Na_2S_2O_3$ solution by dissolving 6 g of $Na_2S_2O_3 \cdot 5H_2O$ in 1.0 dm^3 of water. Then he weighed 0.08590 g KIO_3, dissolved it in water and prepared 100.00 cm^3 stock solution in a volumetric flask. He measured 10.00 cm^3 of this stock solution, added 5 cm^3 20 % hydrochloric acid and 2 g solid KI. The solution turned brown immediately. Then he titrated this sample with the

$Na_2S_2O_3$ solution. In a number of parallel measurements the average for the equivalence point was 10.46 cm^3.

b) <u>Write</u> down the equations of all the reactions that have taken place and <u>determine</u> the concentration of the $Na_2S_2O_3$ solution. <u>What</u> could our hero have used as an indicator?

When our hero began to wash up, he noticed that some white precipitate appeared in the first sample. He remembered clearly that he added more $Na_2S_2O_3$ solution to this sample than was necessary to reach the end point.

c) <u>What</u> is the chemical equation of the process producing the precipitate?

Next, our hero returned to the greenish blue stock solution he prepared first. He measured 1.000 cm^3 of this solution into a titration flask, added 20 cm^3 of 5 % acetic acid and 2 g solid KI. He waited about 5 minutes. The solution became brown and a light-colored precipitate appeared.

d) <u>What</u> is the chemical equation of the process producing the colored species and the precipitate? <u>Why</u> did our hero have to wait? <u>Why</u> would it have been a mistake to wait hours rather than minutes?

Our hero then titrated the sample with his $Na_2S_2O_3$ solution. The average for the equivalence point was 16.11 cm^3. Now he could calculate the composition of the 2-Ft coin.

e) <u>What</u> is the mass percent composition of the coin?

As a good analytical chemist, he was not satisfied with one method and tried to determine the composition of the coin with complexometry. In this measurement he did not take into account the results obtained in the iodometric titration. First, he dissolved 3.6811 g $Na_2EDTA \cdot 2H_2O$ (M = 372.25 g/mol) to make 1.0000 dm^3 solution. Then he measured 0.2000 cm^3 of the original greenish blue stock solution, added 20 cm^3 of water and 2 cm^3 of 25 % ammonia solution. The color of the solution became an intense violet.

f) <u>Which</u> species are responsible for this color? <u>What</u> is the purpose of the addition of ammonia?

The equivalence point was 10.21 cm^3 as calculated from the average of a few parallel experiments.

g) <u>Did this experiment confirm</u> the earlier conclusion about the composition of the coin?

Our hero was still not satisfied and also began to suspect that he made an error when he weighed the coin, so he turned on the old spectrophotometer in the lab. The lab he worked in was very well maintained so he found recently prepared and standardized 0.1024 mol/dm^3 $CuCl_2$ and 0.1192 mol/dm^3 $NiCl_2$ solutions in the lab. First, he measured the absorbance spectrum of the $CuCl_2$ solution using a 1.000-cm quartz cell and made notes of the absorbance values at a few wavelengths he thought suitable:

λ / nm	260	395	720	815
A	0.6847	0.0110	0.9294	1.428

Then he measured the absorbances of the $NiCl_2$ solution at the same wavelengths in the same cell:

λ / nm	260	395	720	815
A	0.0597	0.6695	0.3000	0.1182

He diluted 5.000 cm^3 of his original greenish blue stock solution to 25.00 cm^3 in a volumetric flask and measured the absorbances. He obtained readings of 1.061 at 815 nm and 0.1583 at 395 nm.

h) <u>Why</u> did he dilute the solution? <u>What</u> is the composition of the coin based on these spectrophotometric data alone?

Next, he measured the absorbance at 720 nm and obtained 0.7405.

i) Is this value in agreement with the previous conclusions?

Finally, he tuned the instrument to 260 nm. He was surprised to see a reading of 6.000.

j) <u>What</u> was his expected reading?

He decided to measure the absorbance at this wavelength in a smaller, 1.00-mm quartz cell as well. Again, he obtained a reading of 6.000.

k) <u>Suggest</u> a possible explanation for this finding and a method to confirm it using chemicals and equipment that have already been used by our hero.

Problem 11

On January 30 in 2000, a dam failure in a gold mine spilled about 100 000 m^3 of cyanide-containing waste water into the river Szamos. The pollution wave, which later reached the Central European rivers Tisza and Danube, killed massive amounts of fish. On February 15, a popular Hungarian TV news show presented a simple experiment: first a NaCN solution was prepared, the concentration of which was similar to those measured in the pollution wave. Fish were killed in this solution but survived when ferrous sulfate was also added. The TV show suggested that ferrous sulfate should have been used to lower the environmental impact of the cyanide solution. However, when the same experiment was repeated with an actual sample from the pollution wave, fish were killed even after ferrous sulfate was added. Unfortunately, this second experiment was not covered in any evening news.
To clarify the underlying chemistry, an expert designed a detailed series of experiments in which the use of a cyanide selective combination electrode was an important element. He first calibrated the electrode using 3 different concentrations at 3 different pH values. The temperature was 25 °C in all experiments. The instrumental readings were as follows:

	1.00 ppm NaCN	10.0 ppm NaCN	100 ppm NaCN
0.01 mol/dm^3 NaOH	497.3 mV	438.2 mV	379.1 mV
0.001 mol/dm^3 NaOH	497.7 mV	438.6 mV	379.5 mV
pH = 7.5 buffer	598.9 mV	539.8 mV	480.7 mV

a) <u>Calculate</u> the acid dissociation constant of HCN based on these measurements.

To 100 cm^3 of a test solution, which contained 49.0 mg/dm^3 NaCN and was buffered to pH = 7.5, 40.0 mg of solid FeSO$_4$·7H$_2$O has been added. At this pH, the reaction between aqueous iron(II) and dissolved oxygen is quantitative under all conditions and gives an

iron(III) hydroxide precipitate. Ignore possible complexation reactions between the precipitate and cyanide ions.

b) <u>Write</u> the balanced equation for this redox reaction.

All the solutions used in the experiments initially contained 8.00 mg/dm^3 dissolved oxygen. The electrode reading in this solution was 585.9 mV. Iron(II) only forms one complex with cyanide ion, which has a coordination number of 6.

c) <u>Write</u> the ionic equation describing the formation of this complex. <u>Estimate</u> the stability constant of the complex.

The following toxicity data (LC_{50}: median lethal concentration for 24-hour exposure) for fish can be found in tables:

	LC_{50}
cyanide ion*	2.1 mg/dm^3
$Na_4[Fe(CN)_6] \cdot 3H_2O$	$6 \cdot 10^3$ mg/dm^3

* total noncomplexed cyanide = $[HCN] + [CN^-]$

The loss of dissolved oxygen is not a major problem for fish in the very small volume of the experiment, but it would probably be under natural conditions.

d) <u>Are</u> the experimental results and the toxicity data in agreement with the result of the experiment shown on the TV news show?

A little known fact about the pollution wave was that it also contained metals, primarily copper (which is hardly surprising for a gold mine). Copper is often present in our environment as copper(II), but it was present as copper(I) in the pollution wave because of the presence of cyanide ions.

e) <u>Write</u> the chemical equation for the reaction between copper(II) and cyanide ion.

An actual sample from the pollution wave had a pH of 7.5, its total cyanide content (including complexed, uncomplexed and protonated cyanide ions) was determined to be 26 ppm, its total copper content 21 ppm. The cyanide selective electrode gave a reading of 534.6 mV in this solution, and an electrochemical method showed that the concentration of free copper(I) is about $2 \cdot 10^{-15}$ mol/dm^3. Copper(I) forms complexes with cyanide ion in a stepwise manner up to a coordination number of 3. The formation constant of [CuCN] is negligible compared to that of the other two complex ions. Dissolved oxygen, the concentration of which was 8.00 mg/dm^3, coexists with cyanocopper(I) complexes.

f) <u>Is there</u> any copper(I)-cyanide precipitate in the solution? ($L_{CuCN} = 3.5 \cdot 10^{-19}$)

g) <u>Determine</u> the coordination number(s) of copper(I) complex(es) dominating in the sample studied. <u>Estimate</u> the stability constant(s) of the cyanocopper(I) complex(es).

The toxicity of copper(I) cyano complexes is very similar to that of NaCN; $[Cu(CN)_2]^-$ has an LC_{50} value of 4.5 mg/dm^3. To 100 cm^3 of the sample from the pollution wave, 40.0 mg of solid $FeSO_4 \cdot 7H_2O$ was added. The cyanide selective electrode gave a reading of 592.3 mV in this solution.

h) <u>Estimate</u> the concentrations of various complexes in this sample. Is this solution expected to be toxic? Does this expectation agree with the experiment *not* shown on TV?

20

Problem 12

The Fe^{3+}/Fe^{2+} and the H_3AsO_4/H_3AsO_3 systems are important redox systems in analytical chemistry, because their electrochemical equilibrium can be shifted by complex formation or by varying the pH.

a) Calculate the standard redox potential, E^o_3 of the reaction $Fe^{3+} + e^- \rightarrow Fe^{2+}$.

The standard redox potential of the Fe^{3+}/Fe^{2+} system in 1 mol/dm^3 HCl is 0.710 V.

b) Give an estimate for the stability constant of the complex $[FeCl]^{2+}$.

Both Fe^{3+} and Fe^{2+} ions form a very stable complex with CN^- ions.

c) Calculate the ratio of the cumulative stability constants for the formation of $[Fe(CN)_6]^{3-}$ and $[Fe(CN)_6]^{4-}$ ions.

d) H_3AsO_4 and $K_4Fe(CN)_6$ are dissolved in water in a stoichiometric ratio. What will the $[H_3AsO_4]/[H_3AsO_3]$ ratio be at equilibrium if pH = 2.00 is maintained?

e) Are the following equilibrium concentrations possible in an aqueous solution? If yes, calculate the pH of the solution.

$[H_3AsO_4] = [H_3AsO_3] = [I_3^-] = [I^-] = 0.100$ mol/dm^3.

Fe^{2+}/Fe	$E^o_1 = -0.440$ V
Fe^{3+}/Fe	$E^o_2 = -0.036$ V
$[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$	$E^o_4 = +0.356$ V
H_3AsO_4 /H_3AsO_3	$E^o_5 = +0.560$ V
$I_3/3\ I^-$	$E^o_6 = +0.540$ V

Problem 13

The solubility product of silver chloride is $2.10 \cdot 10^{-11}$ at 9.7 °C and $1.56 \cdot 10^{-10}$ at room temperature (25 °C).

a) Estimate the solubility product and the solubility (in mg/dm^3) of AgCl at 50 °C.

Although AgCl is practically insoluble in water, it dissolves in solutions containing complexing agents. For example, in the presence of a high excess of Cl^- ions, a part of the AgCl precipitate dissolves forming $[AgCl_2]^-$ ions.

The equilibrium constant of the reaction $Ag^+(aq) + 2\ Cl^-(aq) \rightleftharpoons AgCl_2^-(aq)$ is $\beta = 2.50 \cdot 10^5$ at 25 °C.

b) Calculate the concentration of a KCl solution (at room temperature), in which the solubility of AgCl is equal to its solubility in water at 50 °C.

If a substance is present in a solution in various oxidation states, it cannot be determined directly by a redox titration. In this case, the sample has to be first reduced. For this purpose, so-called reductors are used. A reductor is a column, containing a strong reducing agent in the solid phase. An acidified sample is passed through the reductor, collected, and titrated with a strong oxidizing titrant of known concentration (for example $KMnO_4$). The most common version is the so-called Jones-reductor that contains amalgamated zinc granules.

c) What reaction would take place if the zinc was not amalgamated?

d) Give the reactions that take place when the following solutions are passed through a Jones-reductor:

0.01 mol/dm^3 $CuCl_2$
0.01 mol/dm^3 $CrCl_3$
0.01 mol/dm^3 NH_4VO_3 (pH =1)

e) Estimate the equilibrium constants of these reactions using the redox potentials in the table.

When a milder reducing agent is required, sometimes the Ag/HCl-reductor (containing porous silver granules and aqueous HCl) is used. This might seem surprising, since Ag metal is not a good reducing agent. Considering only the standard potentials, the reduction of Fe^{3+} to Fe^{2+} by Ag is not a spontaneous reaction.

f) Consider a silver rod that is immersed in a 0.05 mol/dm^3 $Fe(NO_3)_3$ solution. Calculate the equilibrium concentration of the various metal ions. What percentage of Fe^{3+} ions has been reduced?

Now let us suppose that the reduction of Fe^{3+} with Ag is carried out in a solution that also contains 1.00 mol/dm^3 HCl.

g) What reaction takes place in this case? Calculate the equilibrium constant of the reaction.

h) Calculate $[Fe^{3+}]$ at equilibrium if the initial concentration of Fe^{3+} was 0.05 mol/dm^3.

i) Which of the following substances are reduced in an Ag/HCl reductor?

0.01 mol/dm^3 $CrCl_3$
0.01 mol/dm^3 $TiOSO_4$ (c_{HCl} = 1 mol/dm^3)

	$E°$ / V		$E°$ / V
Cu^{2+}/Cu	0.34	Cr^{3+}/Cr	−0.74
Cu^{2+}/Cu^+	0.16	Cr^{2+}/Cr	−0.90
VO_2^+/VO^{2+}	1.00	Zn^{2+}/Zn	−0.76
VO^{2+}/V^{3+}	0.36	TiO^{2+}/Ti^{3+}	0.10
V^{3+}/V^{2+}	−0.255	Ag^+/Ag	0.80
V^{2+}/V	−1.13	Fe^{3+}/Fe^{2+}	0.77

Problem 14

An experience dating back to antiquity and passed on by the great alchemists is that the fumes produced when heating proteins (e.g., slaughterhouse waste) with lime stain an acid-impregnated wooden stick deep red. The compound responsible for this interesting reaction (**B**) can be produced as follows (several of its typical reactions are indicated as well):

protein $\xrightarrow{\text{H}_2\text{O, heat}}$ H₂N-CH(C₂H₄-COOH)-COOH $\xrightarrow{\text{heat, } -\text{H}_2\text{O}}$ **A** $\longrightarrow$

glutamic acid   pyroglutamic acid

1. Ca(OH)₂
2. heat $\longrightarrow$ **B**
$\xrightarrow{\text{K (metal)}}$ **C**
$\xrightarrow{\text{Br}_2 \text{ (4 eq)}}$ **D**
$\xrightarrow{\text{H}_2/\text{Pd}}$ **E**
$\xrightarrow{\text{HCl/H}_2\text{O}}$ multiple products (red)
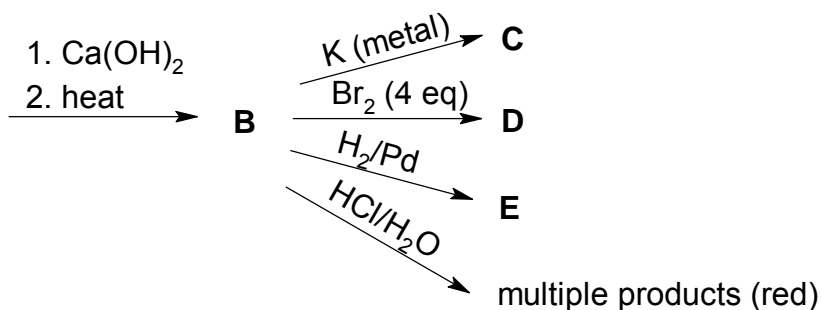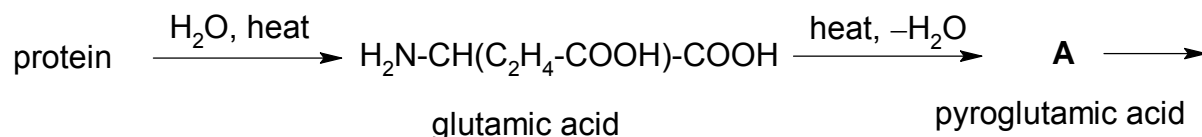
A-**E** are all colorless (white) compounds. **B** and **E** are liquids with a characteristic odor.

a) Draw the structures of **A**-**E**.

b) Explain the stability of **B** against bases and its rapid decomposition with acids.

c) Compare the basicity of **B** and **E**. Explain.

d) Suggest a reaction scheme for the acidic decomposition of **B**. Explain why the products are colored.

Problem 15

Aromaticity is an important concept in organic chemistry. Compounds containing aromatic rings exhibit characteristic physico-chemical properties and reactivities. A simple rule, the Hückel rule helps us to identify aromatic structures. This rule postulates that a cyclic conjugated system is aromatic if the number of p electrons participating in the delocalized π-bonds is $4n+2$, where n is a nonnegative integer. The rule can be extended to cover polycyclic and fused ring systems.

a) Give examples for aromatic structures, where n = 0, 1, 2.

The Hückel rule is also applicable to fused ring systems, as a sufficient condition for their aromaticity.

b) Show that linearly fused, originally aromatic rings (where the individual rings are added stepwise to the chain via 2 carbon atoms) are Hückel aromatic. Example:
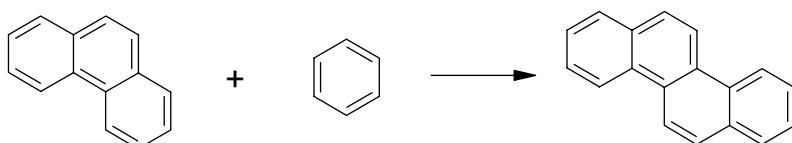
c) Show that fusion of two such fused chains via 2 carbon atoms also results in Hückel aromatic structures. Example:
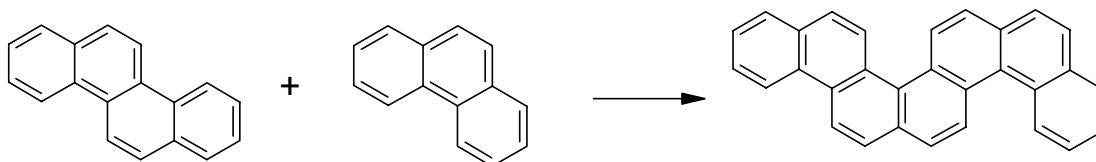
d) Give a criterion for a general fusion of two aromatic hydrocarbons to yield a Hückel aromatic system. Example:
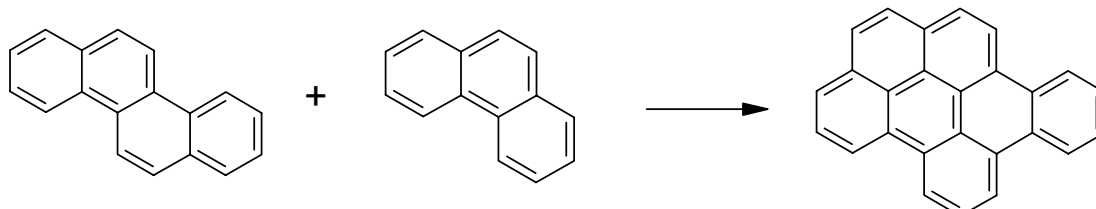
e) Show with a counterexample that the Hückel rule is not a necessary condition for aromaticity.

Aromaticity can be a very strong driving force in chemical processes, although not always. Let us consider the following examples:

f) Cyclopentadiene has pK_a = 18, cyclopentene has pK_a = 45. Explain the difference!

g) Tautomerism may also result in aromatic structures. Show how the following compound may undergo interconversion to yield an aromatic structure.
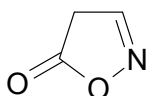
h) However, some of the following aromatic structures prefer to rearrange into structures *not* featuring an aromatic ring. Find these structures. Where do these non-aromatic structures have essential roles? Give additional examples of tautomerism, where the molecule prefers to lose its aromatic character.
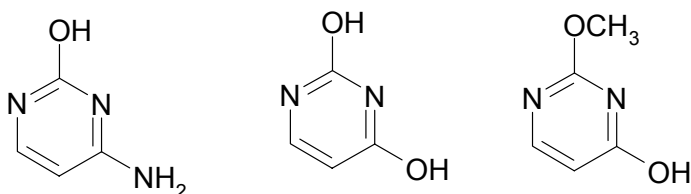
Problem 16

The porphin molecule is the simplest member in the family of porphyrins. Its structure, which contains four pyrrole rings, is completely planar. All its carbon and nitrogen atoms are sp^2 hybridized. A conjugated double-bond system can therefore be found in the molecule. The sigma-skeleton of porphin is depicted below:
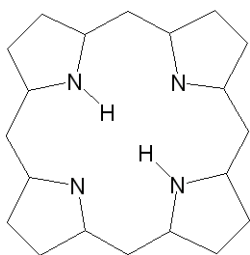
a) <u>How many</u> electrons participate in the conjugated double bond system? Is the molecule aromatic? <u>Draw</u> a porphin structure indicating the double bonds forming the conjugated double-bond system.

Two of the central nitrogen atoms have a hydrogen substituent. These hydrogens are slightly acidic and under normal conditions, the protons can easily migrate to a neighboring N atom, as shown below:
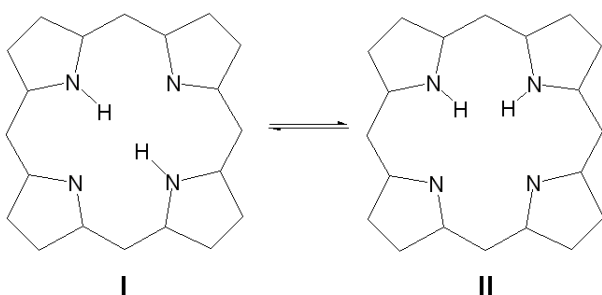
b) <u>What kind</u> of isomers are I and II? <u>How</u> does the migration process affect the conjugated double bond system: do less or more π electrons participate in isomer II than in isomer I? <u>Draw</u> a porphin structure for II indicating the double bonds.

The hydrogen atoms bound to the carbon atoms of the porphin molecule can be substituted by other groups. Suppose that we introduce a methyl group onto the porphin ring. Under normal conditions, the inner-nitrogen H migration is unaffected by this substitution and takes place continuously in solvent.

c) <u>How many</u> different monomethyl porphins can be produced?

We further introduce another methyl group into the porphin ring.

d) <u>How many</u> isomers can be isolated in this case?

Metal complexes of porphin can be easily prepared. An important compound of this kind is the magnesium complex which is a synthetic model of chlorophyll. Its sigma-structure is displayed below:
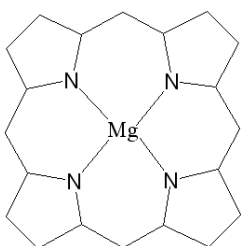
e) <u>How many</u> electrons of the organic ring system participate in the conjugated bond system in this case? <u>What</u> is the number of independent methyl-Mg-porphins having one methyl substituent on the organic ring?

Numerous iron-porphin derivatives (P) can be synthesized. Such salts all feature the heterocyclic macrocycle of porphin, but they contain additional substituents on the organic macrocycle as well. They are able to bind two additional ligands, coordinating them axially to the two sides of the iron atom. This complexation is a two-step process: the originally four-coordinated iron binds a ligand (L) and becomes five-coordinated (PL), and then binds a second ligand to become six-coordinated (PL_2). It was found in various cases that the reaction rapidly yields the PL_2 complex, whereas the PL complex was very difficult to obtain. For the complexation of a given iron-porphin derivative with pyridine in inert organic solvent, scientists were able to show employing spectroscopic methods that the two steps can be characterized via the following equilibria:

P + L = PL K_1=1500

PL + L = PL_2 K_2=19000

f)   We see an atypical $K_1 < K_2$ relation. <u>Why</u> does such a relation between two consecutive dissociation constants of a polyprotic acid never occur?

Assume that we perform this complexation reaction and reach an equilibrium concentration of 0.1 mol/dm^3 for ligand L.

g)   <u>Show</u> that the five-coordinated intermediate is indeed present in negligible quantity.

Suppose we are able to generate PL *in-situ* in a solvent and due to its kinetic stability we reach a concentration of 0.1 mol/dm^3 PL. After a given time however the system reaches equilibrium.

h)   <u>How</u> does temperature affect the kinetic stability?

i)   <u>What</u> will the concentrations of P, PL, PL_2 and L be at equilibrium?

Problem 17

a)   <u>How many</u> stereoisomers do the following compounds have?
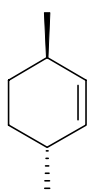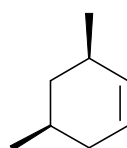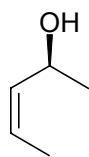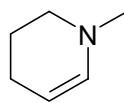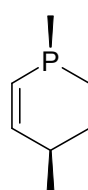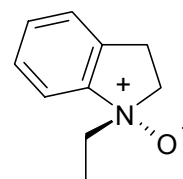
A   B   C   D   E   F

b)   <u>What</u> is the most likely product of the following reactions following work up? <u>How many</u> other stereoisomers might be formed?
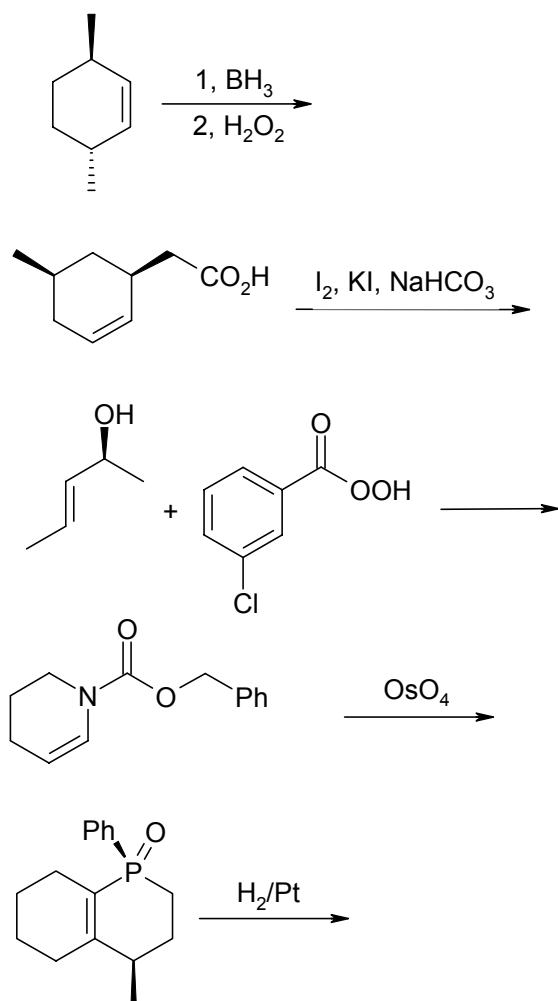
Problem 18

Ascaridol (**A**) is a natural organic compound that has an exotic structure. It can be found in the volatile oil of the goosefoot (*Chenopodium album*) and many other plants. The following information is available:

- Pure **A** can only be distilled in high vacuum because at elevated temperatures it explodes.

- The ^{13}C NMR spectrum shows the presence of only one C=C double bond in **A**.

- A solution of **A** (in diethyl ether) does not react with sodium. Reduction with $LiAlH_4$ leads to **B**.

- If **B** is reacted with $NaBH_4$ in the presence of acetic acid, then reacted with H_2O_2 in basic solution, the product is a mixture of two structural isomers.

- Reaction of **B** with one equivalent of hydrogen gas in the presence of a metal catalyst leads to **C**. **A** reacts with twice as much hydrogen as **B** in the same reaction, and also yields **C**. **C** does not react with chromic acid in acetone.

- The dehydration of **C** leads to the elimination of two equivalents of H_2O and two organic compounds **D** and **E** are formed. Treatment of **D** with ozone followed by a reductive workup (Zn/H_2O) leads to one equivalent of glyoxal (ethanedial) and one equivalent of 6-methyl-heptane-2,5-dione. The same reaction with **E** leads to one equivalent of 3-oxo-butanal and the same amount of 4-methyl-3-oxo-pentanal.

- It is assumed that under natural conditions **A** forms via the reaction of **D** and **F** catalyzed by chlorophyll in the presence of light.

Determine the structure of **A**-**F**.

Problem 19

2,7-dimethylnaphtalene can be prepared by the reaction of a Grignard reagent **A** and an acetal (**B**).
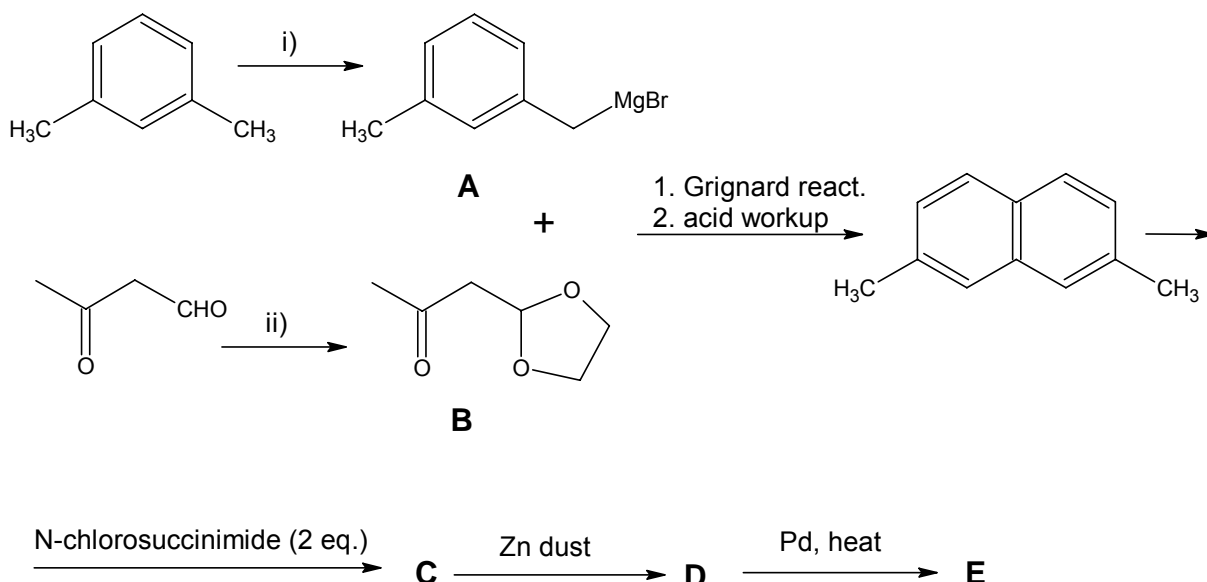
a) Suggest reaction conditions for the preparation of **A** and **B**.

b) Explain with a mechanism the formation of 2,7-dimethylnaphtalene.

c) 2,7-dimethylnaphtalene is converted to **E** via the indicated reactions. (**E** is a fancy compound with molecular formula $C_{24}H_{12}$.) Identify **C**, **D** and **E**.

Problem 20

a) Suggest a mechanism for the following transformation (Robinson-anellation).
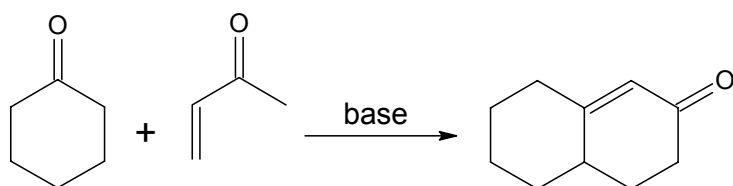
b) <u>Rationalise</u> the build-up of the gonane skeleton.
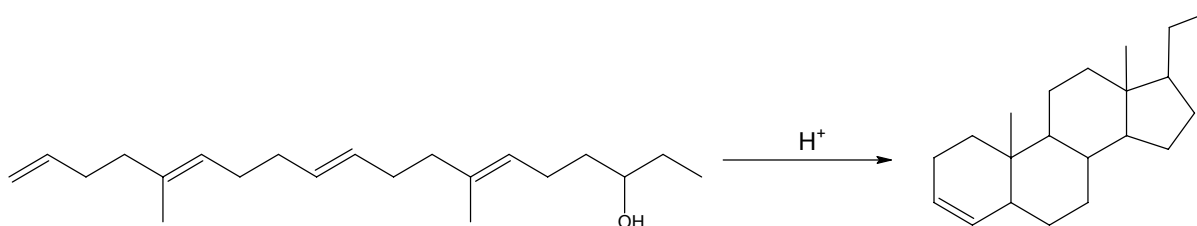
A prochiral α-chloro ketone was reduced to halohydrins enzimatically (R is an alkyl group). One alcohol dehydrogenase enzyme (*Rhodococcus ruber*) produces the R isomer, and another (*Lactobacillus brevis*) gives the S isomer. Under basic conditions enantiopure epoxides were produced from the halohydrins.

c) <u>Give</u> the stereostructures of the halohydrin intermediates and those of the epoxides. <u>Detail</u> the mechanism of the ring closure reaction.
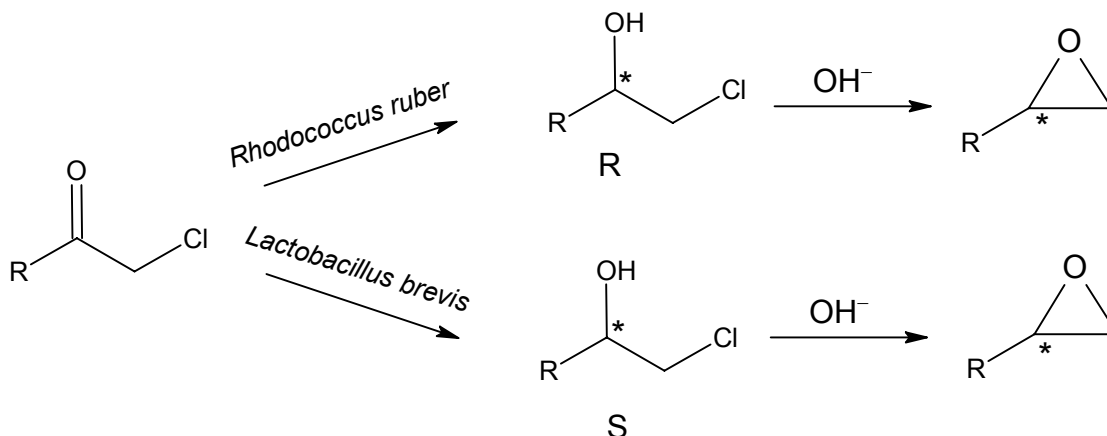
Problem 21

Ketoses are a special group of sugars. D-ribulose derivatives play a vital role in photosynthesis. An α-methyl glycoside of D-ribulose (**A**) can be prepared from D-ribulose on treatment with methanol and an acid catalyst. Heating **A** in acetone with HCl leads to **B**, a propylidene derivative. Acetone forms acetals with vicinal diols, if the orientation of the two OH groups is suitable.

D-ribulose

F
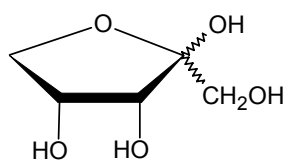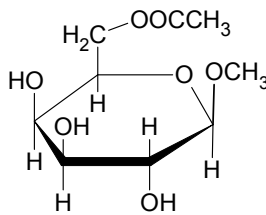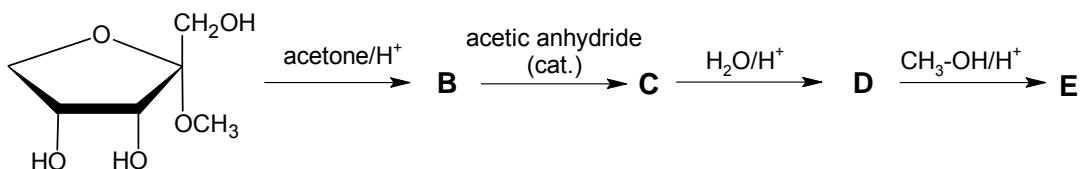
1-O-methyl-α-D-ribulose<2.5>

A

a) During the synthesis of **B** two possible products can form. <u>Draw</u> their structures. <u>Which</u> is the main product?

B is reacted with acetic anhydride (with catalyst) to obtain **C**. **D** is formed from **C** on heating in dilute aqueous acid. **D** reacts with methanol and acid to form **E**.

b) <u>Draw</u> the structures of **C**-**E**.

c) <u>Is it possible</u> to predict the conformation around carbon atom C1 of **E**?

Although acetonide formation is a versatile method for the temporary protection of OH groups that are close enough, in many cases it gives multiple products (or the product composition is highly dependent on the reaction conditions). In general, this is the case with sugars with 6-membered rings.
It has been shown that no acetonide can be formed when the neighbouring OH groups are both axial. However, both diequatorial and axial-equatorial vicinal diols react with acetone/HCl.

d) <u>Draw</u> the two chair conformers of 1-O-methyl-6-O-acetyl-β-D-galactose<1.5> (**F**). <u>Designate</u> the OH groups as axial (a) or equatorial (e). <u>Mark</u> the more stable conformer.

e) <u>How many</u> acetonide isomers can form from this compound? <u>How many</u> different chair conformers of these acetonides exist?

f) <u>Draw</u> the Haworth projection of L-galactose <1.5>

Problem 22

At present, fossil fuels are the most important energy sources for humankind. Their use is generating two major concerns. First, energy production from fossil fuels releases a lot of carbon dioxide into the atmosphere, which is now understood to contribute to global warming. In addition, natural supplies of fossil fuels are expected to be exhausted at the

present rate of use in a relatively short time on a historical scale. Many experts believe that alternative sources, like hydrogen or methanol could find widespread use as environmentally friendly substitutes for fossil fuels.

Hydrogen is not a primary energy source; it would have to be produced using another source of power, e.g. nuclear or solar power. The best way would be to produce hydrogen from water, a process popularly called water splitting.

a) Calculate how many kWh of electricity is needed to produce 1 kg hydrogen if the electrolysis operates at a voltage of 1.6 V and 90 % efficiency. Evaluate this process economically based on current industrial electricity and hydrogen prices (use average prices of 0.10 euro/kWh for electricity and 2 euro/kg for H_2).

In addition to production, storage and transport of hydrogen also presents some challenges. In this respect, volumetric and gravimetric energy densities are central concepts. The volumetric energy density is the recoverable energy from a source divided by its total volume. The gravimetric energy density is the recoverable energy from a source divided by its mass.

b) Calculate the volumetric and gravimetric energy density of hydrogen at atmospheric pressure and 298 K. (Assume that hydrogen follows the ideal gas law under these conditions.)

Hydrogen is often transported in cylinders which are normally filled to 200 bar. A typical big gas cylinder, made of steel (density 7.8 g/cm³) has a useful volume of 50 dm³ and weighs 93 kg when empty. At this high pressure, hydrogen no longer follows the ideal gas law. A better description can be obtained from the van der Waals equation:

$$\left(p + \frac{a}{V_m^2}\right)(V_m - b) = RT$$

where p is the pressure, V_m is the molar volume, R is the gas constant, T is the thermodynamic temperature, a and b are gas-specific constants. For hydrogen, $a = 2.48 \cdot 10^{-2}$ Pa m⁶mol⁻² and $b = 2.66 \cdot 10^{-5}$ m³mol⁻¹. Compressed hydrogen cannot be transported without a cylinder.

c) Estimate the volumetric and gravimetric energy density of compressed hydrogen.

Hydrogen can also be transported in the form of metal hydrides. $NaBH_4$ is a promising substance in this respect, as it reacts with water in the presence of a catalyst to give hydrogen.

d) How many moles of hydrogen can be produced from 1 mol of $NaBH_4$?

As water is a ubiquitous substance, it does not have to be transported together with the metal hydride.

e) Estimate the volumetric and gravimetric energy density of $NaBH_4$ as a hydrogen source. Its density is 1.07 g/cm³.

It is also important to compare these data with those of more conventional energy sources.

f) To put the previously calculated energy densities in perspective, determine the volumetric and gravimetric energy densities of the following energy sources:

   i. Graphite as a model of coal. Calculate the density based on the fact that the bond length in graphite is 145.6 pm and the interlayer distance is 335.4 pm.

ii. n-Octane (C_8H_{18}) as a model of gasoline. Its density is 0.70 g/cm^3.
iii. Methanol, the use of which instead of hydrogen was proposed by the 1994 Nobel laureate György Oláh. Its density is 0.79 g/cm^3.
iv. A Ni-MH rechargeable AA battery with a capacity of 1900 mAh and voltage of 1.3 V, which is shaped like a cylinder (diameter: 14.1 mm, height: 47.3 mm, weight: 26.58 g).
v. Water as a source of hydrogen in an imaginary fusion reactor simply converting ^{1}H into ^{4}He. The relative atomic masses are: $A_r(^1H) = 1.00782$, $A_r(^4He) = 4.00260$

Hydrogen could also be stored as a cryogenic liquid at very low temperatures. The density of liquid hydrogen at its boiling point (−253 °C) is 0.071 g/cm^3.

g) Estimate the volumetric and gravimetric energy density of liquid hydrogen.

h) What is the advantage of using liquid methanol instead of hydrogen in a hypothetical future economy?

Methanol can also be used in methanol fuel cells. The net reaction of the fuel cell is:

CH_3OH (l) + 1.5 O_2 (g)→ CO_2 (g)+ 2 H_2O (l)
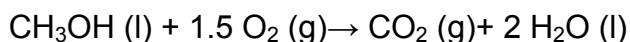
i) Write down the cathode and the anode reactions.

j) Calculate the maximum voltage of the methanol fuel cell at 25 °C.

k) The methanol fuel cell operates best at 120 °C. At this temperature, the cell reaction potential is 1.214 V. Compare this number with your calculated data.

Thermodynamic parameters at 298 K:

H_2O(l)	$\Delta_fH° = -286$ kJ/mol	O_2(g)	$S° = 205$ J mol^{-1} K^{-1}
H_2O(g)	$\Delta_fH° = -242$ kJ/mol	CO_2(g)	$\Delta_fG° = -394.4$ kJ/mol
H_2O(l)	$S° = 70$ J mol^{-1} K^{-1}	C_8H_{18}(l)	$\Delta_fG° = 6.4$ kJ/mol
H_2O(g)	$S° = 189$ J mol^{-1} K^{-1}	CH_3OH(l)	$\Delta_fG° = -166.3$ kJ/mol
H_2(g)	$S° = 131$ J mol^{-1} K^{-1}		

Problem 23

Most elements react with oxygen to form oxides in which the oxidation number of O is –2. At first sight it seems a striking contradiction that some alkali metals, the strongest reducing agents themselves, burn in air to give peroxides or superoxides with fairly strong oxidizing properties. Why is the oxygen only partially reduced in these reactions? To find out, we must start from some basic properties of the elements.

Alkali metals	Li	Na	K
$\Delta_{vap}H$	148 kJ/mol	99 kJ/mol	79 kJ/mol
Ionization energy	520 kJ/mol	496 kJ/mol	419 kJ/mol
Ionic radius for M^+	76 pm	102 pm	138 pm

a)   Explain the trend in the ionization energies of the metals.

Oxygen anions	O^{2-}	O_2^{2-}	O_2^-
$\Delta_f H$	904 kJ/mol	553 kJ/mol	–43 kJ/mol
Ionic radius	140 pm	173 pm	158 pm

b)   The enthalpy of formation of the free ions dramatically increases in the sequence superoxide → peroxide → oxide. Why?

We know the energy required to convert the elements into separated ions. How much energy is released when these ions combine to form ionic crystals? The lattice energy of an ionic solid can be estimated by the Kapustinskii equation. In its simplest form,

$$\Delta U(\text{lattice}) = -107000 \frac{\nu |z_+||z_-|}{r_+ + r_-}$$

where ν is the total number of ions in the empirical formula, z_+ and z_- are the charges of the individual ions, r_+ and r_- are the ionic radii in pm, and the result is given in kJ/mol.

c)   Calculate the molar lattice energies of the oxides, peroxides, and superoxides of the three lightest alkali metals.
Calculate the amount of energy released in each of the nine possible reactions leading to the oxides, peroxides, or superoxides of the elements. Always assume that 2 mols of a solid alkali metal react with oxygen to form a single product.

This simplified approach is by no means expected to give accurate estimates of the enthalpy of formation. It does, however, correctly reflect the main factors influencing the course of these reactions even without considering entropy changes. If your calculations were error-free, your conclusions will be in line with the experimental observations.

d)   For the reaction of each alkali metal with an excess of oxygen, which is the energetically most favoured product?

e)   Rationalize your results and try to explain, in terms of basic factors, why the composition of the most favoured product changes as we move down Group IA. What products do you expect from the reaction of Rb and Cs with oxygen?

f)   Does this mean that peroxides and superoxides, which are powerful oxidizers, cannot be reduced by one of the most powerful reducing agents, metallic potassium?

Let's now turn to the rest of the periodic system. Most other elements that form ionic oxides have multiply charged cations of relatively smaller size – properties that are generously rewarded in lattice energies.

g)   The alkali metals do not have this option. Why?

h)   Consider a metal that forms a cation M^{2+} with a radius of 100 pm (the cations of most metals are smaller than this). Compare the lattice energies of its oxide and peroxide. What products do you expect from the reaction of such metals with oxygen?

i) Only one of the non-radioactive Group IIA metals can form a peroxide when heated in air at atmospheric pressure. Which one? Estimate a limit for the size of its cation on the basis of our model.

j) In conclusion, you can see that the extremely strong reducing ability of the alkali metals and the fact that some do not completely reduce oxygen when they burn in air have a common underlying reason. What is this?

Problem 24

Let us examine three galvanic cells:

$Pt(s) | H_2(g) | HCl(aq) | Cl_2(g) | Pt(s)$

$Pb(s) | PbCl_2(s) | HCl(aq) | H_2(g) | Pt(s)$

$Pb(s) | PbSO_4(s) | K_2SO_4(aq) || KNO_3(aq) || KCl(aq) | PbCl_2(s) | Pb(s)$
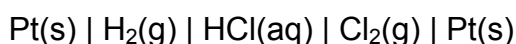
a) Write down the equation for the cell reactions.

b) Estimate the standard cell reaction potential of the galvanic cells at 25 °C based on thermochemical data.

c) Write down the cathode and the anode reactions in the galvanic cells if the measured electromotive force equals the standard cell reaction potential.

d) Calculate the equilibrium constant for the cell reactions.

e) How do the electromotive forces change with temperature?

Let us define a 'thermal efficiency' parameter as the theoretical maximum of the ratio between the electrical work and the enthalpy change in the cell.

f) What are the values of this parameter for these cells? What can we conclude from these numbers?

Thermochemical data at 25 °C:

	$\Delta_f H^\circ$ /kJ mol^{-1}	S°/J mol^{-1} K^{-1}
$Cl_2(g)$	0.0	223.1
$H_2(g)$	0.0	130.7
$HCl(aq)$	−167.2	56.5
$K_2SO_4(aq)$	−1414.0	225.1
$KCl(aq)$	−419.5	159.0
$Pb(s)$	0.0	26.4
$PbCl_2(s)$	−359.4	136.0
$PbSO_4(s)$	−920.0	148.5

Problem 25

You lead an interstellar expedition to a remote planet, inhabited by aliens. Unfortunately, the arrival of your spaceship initiates a reaction causing the atmosphere to decompose by a first-order rate law with a half-life of 13 hours. Everyone will have to leave by the time when only 13 % of the original atmosphere remains.

a) <u>How much time</u> do you have until then?

Ethyl-propionate hydrolyzes in aqueous alkaline solution:

$$C_2H_5COOC_2H_5(aq) + OH^-(aq) = C_2H_5COO^-(aq) + C_2H_5OH(aq)$$
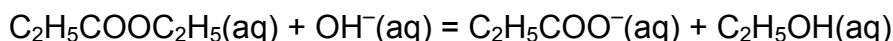
Initial rate data were collected for different concentrations, as shown in the Table:

$[C_2H_5COOC_2H_5]$	$[OH^-]$	Initial rate (mmol dm^{-3} s^{-1})
0.045	0.300	1.09
0.090	0.300	2.15
0.090	0.150	1.11

b) <u>Determine</u> the partial orders of reaction, its kinetic equation and rate coefficient.

The initial rate of the reaction above doubles when the temperature is raised from 25 °C to 42 °C, with the same initial concentrations.

c) <u>What</u> is the Arrhenius activation energy?

The reaction

$$2\ NO(g) + O_2(g) = 2\ NO_2(g)$$
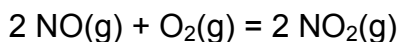
obeys the following kinetic equation:

$$r = k\,[NO]^2\,[O_2]$$

d) <u>Explain</u> how the rate of the reaction changes when the following concentration changes are made:

  i. $[O_2]$ is quadrupled
  ii. $[NO]$ is quadrupled
  iii. $[NO]$ is halved
  iv. $[O_2]$ is halved and $[NO]$ is quadrupled
  v. $[NO]$ is halved and $[O_2]$ is quadrupled

The initial rate of the above reaction remains the same when the temperature is raised from 460 °C to 600 °C, with all the initial concentrations halved.

e) <u>What</u> is the Arrhenius activation energy?

The first-order decay of a compound was followed spectrophotometrically. After loading a solution with an initial concentration 0.015 mol/dm^3 into a cuvette with a path-length of 0.99 cm, its absorbance (at a wavelength where only this species absorbs light) was recorded as a function of time.
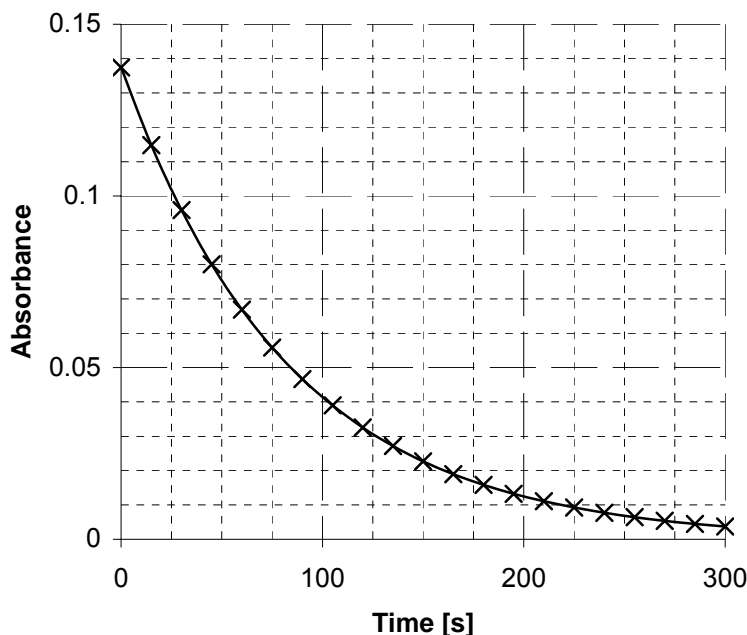
f) From this plot:

    i. Estimate the molar absorption coefficient.
    ii. Estimate the initial rate and the rate constant.
    iii. Estimate the half-life from the rate constant.
    iv. Discuss whether the estimated half-life is consistent with the plot.
    v. Calculate the time required to consume 99 % and 99.99 % of the compound.

Problem 26

Upper atmospheric (stratospheric) ozone protects us from harmful ultraviolet radiation coming from the Sun. On the other hand, ozone in the lower atmosphere (troposphere) damages the human respiratory system as well as crops and other plants, since ozone is a strong oxidizing agent.
Ozone formation in urban areas can be attributed mainly to the two-step reaction mechanism:

$$NO_2 + h\nu \rightarrow NO + O \qquad k_1 \qquad (1)$$

$$O + O_2 \rightarrow O_3 \qquad k_2 \qquad (2)$$

The first step is the photolysis of NO_2, which is a common air pollutant in cities. (N.B.: k_1 includes the intensity of the solar radiation on an average sunny day.) The second step is the reaction of the O atom formed with atmospheric oxygen. Under atmospheric conditions reaction (2) is orders of magnitudes faster than reaction (1).
Let us suppose that a small amount of NO_2 (e.g. 10^{-7} mole fraction of air) is introduced into the atmosphere and only reactions (1) and (2) take place.

a) Which species is going to be in a quasi steady-state? Write down the algebraic equation to calculate its concentration after an initial (so-called induction) period.

b) Write down the differential and integral rate equations describing ozone formation.

The rate coefficient of reaction (1) is 0.0070 s^{-1}. The initial NO_2 concentration is $2.5 \cdot 10^{12}$ molecule cm^{-3}.

c) <u>What</u> is the ozone concentration after 1 minute?

d) <u>What</u> is the half-life of NO_2?

e) <u>What</u> effect does temperature have on the rate of ozone formation? <u>Why</u>?

Ozone is not only formed but also removed from the troposphere, mainly by its reaction with NO:

   $NO + O_3 \rightarrow NO_2 + O_2$ k_3 (3)

Assuming reactions (1-3), O_3, NO and NO_2 will be in equilibrium.
$k_3 = 1.8 \cdot 10^{-14}$ cm^3 molecule^{-1} s^{-1}

f) <u>What</u> is the [NO]/[NO_2] ratio, if the equilibrium ozone concentration is $9 \cdot 10^{11}$ molecule cm^{-3}?

g) Assuming the same equilibrium ozone concentration, <u>how</u> does the above ratio change if we raise the temperature from 10 °C to 25 °C? The activation energy of reaction (3) is 10.8 kJ/mol.

Problem 27

The reaction of acetone with bromine produces bromoacetone.

a) <u>Give</u> the chemical equation of the reaction assuming that acetone is in excess.

In a mechanistic study, the reaction was followed in several kinetic experiments at 25 °C in aqueous solution by measuring the concentration of Br_2 using a spectrophotometric method. The following kinetic curve was recorded when the initial concentrations were $[Br_2]_0 = 0.520$ mmol/dm^3, $[C_3H_6O]_0 = 0.300$ mol/dm^3, and $[HClO_4]_0 = 0.050$ mol/dm^3.

t (min)	0	2	4	6	8	10	12	14
[Br_2] (μmol/dm^3)	520	471	415	377	322	269	223	173

t (min)	16	18	20	22	24	26	28	30
[Br_2] (μmol/dm^3)	124	69	20	0	0	0	0	0

b) <u>Which</u> is the limiting reagent in this experiment?

c) <u>What</u> is the order of reaction with respect to the limiting reagent?

The time where the characteristic break point occurs on the kinetic curve is called the reaction time and was determined in aqueous solution at 25 °C. The following table gives the reaction time in several different experiments (′ denotes minutes, ″ denotes seconds):

$\frac{[Br_2]_0}{mmol/dm^3}$	$\frac{[C_3H_6O]_0}{mmol/dm^3}$	$\frac{[HClO_4]_0}{mmol/dm^3}$	reaction time
0.151	300	50	5'56"
0.138	300	100	2'44"
0.395	300	100	7'32"
0.520	100	100	30'37"
0.520	200	100	15'13"
0.520	500	100	6'09"
0.520	300	200	4'55"
0.520	300	400	2'28"

d) <u>Determine</u> the orders of reaction with respect to all three components.

e) <u>What</u> is the rate equation of the process?

f) <u>What</u> is the value and unit of the rate constant?

A different, electrochemical method allowed detection of much smaller concentrations of Br_2. A kinetic curve, the initial concentrations for which were $[Br_2]_0 = 1.80$ µmol/dm³, $[C_3H_6O]_0 = 1.30$ mmol/dm³, and $[HClO_4]_0 = 0.100$ mol/dm³, is given in the following table:

t (s)	0	10	20	30	40	50	60	70
$[Br_2]$ (µmol/dm³)	1.80	1.57	1.39	1.27	1.06	0.97	0.82	0.73

t (s)	80	90	100	110	120	130	140	150
$[Br_2]$ (µmol/dm³)	0.66	0.58	0.49	0.45	0.39	0.34	0.30	0.26

g) <u>Which</u> is the limiting reagent in this experiment?

h) <u>What</u> is the order of reaction with respect to the limiting reagent?

The half life of the limiting reagent was determined in a few experiments, and is independent of the concentration of the limiting reagent:

$[Br_2]_0$ (µmol/dm³)	$[C_3H_6O]_0$ (mmol/dm³)	$[HClO_4]_0$ (mol/dm³)	$t_{½}$ (s)
1.20	3.0	0.100	24
1.50	3.0	0.100	23
1.50	1.0	0.100	71
1.50	0.4	0.100	177
1.50	3.0	0.030	23
1.50	3.0	0.400	24

i) <u>Determine</u> the order of reaction with respect to all three components.

j) <u>What</u> is the rate equation of the process?

k) <u>What</u> is the value and unit of the rate constant?

l) <u>Suggest</u> a detailed mechanism to interpret the experimental findings.

Problem 28

Chlorine dioxide is a somewhat exceptional molecule because it contains an unpaired electron.

a)   Draw the Lewis structure of chlorine dioxide.

b)   Name at least two other stable molecules which do not contain metals but have an odd number of electrons.

Chlorine dioxide is increasingly used in water treatment. In one study, the reaction of chlorine dioxide with iodine was studied in aqueous solution. Light accelerated the process greatly. Chloride and iodate ions were detected as final products.

c)   Write the expected balanced equation for the process.

The ratio of the decreases in chlorine dioxide and iodine concentration was experimentally determined to be 2.3.

d)   What side reactions can cause this deviation from the expected stoichiometry?

e)   Suggest a method to detect the possible side reactions.

Quantitative measurements on the photochemical reaction were carried out using a very intense halogen lamp. Between the lamp and the photoreactor, an interference filter was also used, which excluded all light with the exception of the 455–465 nm wavelength region. This wavelength band is sufficiently narrow to consider the light beam as monochromatic 460 nm light. Iodine has a molar absorption of $\varepsilon = 740$ $dm^3\,mol^{-1}\,cm^{-1}$ at 460 nm, whereas the molar absorption of chlorine dioxide is immeasurably low at this wavelength. A 25.00 cm^3 photoreactor with a 5.00 cm long light path length was used in all of the experiments. The reaction was studied in an acidic solution with initial concentrations $[I_2]_0 = 5.1 \cdot 10^{-4}$ mol/dm^3 and $[ClO_2]_0 = 4.0 \cdot 10^{-4}$ mol/dm^3. Reference experiments were also carried out in the absence of selected reagents. When the solution contained chlorine dioxide but no iodine, no change was observable.

f)   Does this prove that chlorine dioxide does not photodecompose?

When the solution contained iodine but no chlorine dioxide, a very slow decay of iodine was observed, but it was orders of magnitude smaller than in the presence of chlorine dioxide. In the remaining experiments, the solution contained both reagents. In each experiment, the initial rate of the loss of chlorine dioxide (v_0) was determined. The first experiment was carried out using the described experimental setup. In later experiments, a grey filter was inserted into the light beam before the photoreactor. The absorbance of this grey filter at 460 nm was measured in an independent experiment. In the final experiment, a steel sheet was inserted into the light beam that did not let any light through. The initial rates were determined in all of these experiments:

	no filter	filter 1 $A_{460} = 0.125$	filter 2 $A_{460} = 0.316$	filter 3 $A_{460} = 0.582$	steel sheet
v_0 (nmol dm^{-3} s^{-1})	2.51	1.97	1.40	0.93	0.37

g)   Why doesn't the rate fall to 0 in the experiment with the metal sheet?

The intensity of the light beam was determined by ferrioxalate actinometry. A 0.00600 mol/dm^3 solution of $K_3[Fe(C_2O_4)_3]$ was prepared in 0.05 mol/dm^3 H_2SO_4. 25.00 cm^3 of this solution was measured into the photoreactor. Previously, the absorbance of this solution was measured to be 1.41 at 460 nm in a 1.000 cm quartz cell. The sample was illuminated for 30.00 minutes. The following process takes place in the solution:

$$2\ [Fe(C_2O_4)_3]^{3-} + h\nu \rightarrow 2\ Fe^{2+} + 2\ CO_2 + 5\ C_2O_4^{2-}$$
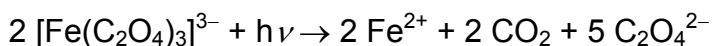
The quantum yield for the formation of iron(II) is 1.12.

After illumination, a 1.000 cm^3 sample from the solution was measured into a 5.000 cm^3 volumetric flask, which was then filled with a solution that contained 0.0100 mol/dm^3 1,10-phenanthroline and 0.50 mol/dm^3 1:1 acetate/acetic acid buffer. The absorbance of this solution at 510 nm was measured in a 1.000-cm cell, the absorbance reading was 0.3823. The molar absorption coefficient of the complex $Fe(phen)_3^{2+}$ is $\varepsilon = 1.10\cdot10^4$ dm^3 mol^{-1} cm^{-1} at 510 nm and nothing else absorbs light in this solution at this wavelength.

h) <u>What</u> is the concentration of the iron(II) complex in the cell?

i) <u>How much</u> iron(II) formed during the illumination?

j) <u>What</u> is the intensity of the 460 nm light in mol photon/s and W units?

k) <u>Determine</u> the quantum yield in the reaction of chlorine dioxide with iodine for both the loss of chlorine dioxide and iodine.

Problem 29

The following table displays energy data for selected atoms and diatomics in kJ/mol:

	1st excitation (E_{ex})	1st ionization (E_I)	2nd ionization (E_{II})	Electronaffinity (EA)
Na	51.1	496	4564	53.1
Hu*	100.0	200	500	250.0
Cl	29.0	1251	1148	348.0
NaCl		860		70.1

*hypothetical atom

The interaction energy of two point charges (q_1 and q_2) separated by a distance R is

$$E = -\frac{kq_1q_2}{R}$$

where $k = 8.99\cdot10^9$ m/F. The charge of the electron (e) is $1.602\cdot10^{-19}$ C.

a) Na and Cl atoms are approaching each other in the gas phase. <u>Find</u> the minimal distance at which they still do not react.

b) Is this distance smaller or larger if the Na atom is in its first excited state? <u>Show</u> your calculations.

Considering all the elements, the electron affinities vary between 4.6–348 kJ/mol, and the ionization energies vary between 375–2374 kJ/mol.

c)   Is it possible to make a diatomic molecule dissociate into a stable state containing two ions? <u>Show</u> your calculation.

d)   A neutral Hu atom and a Hu^+ ion are approaching each other in the gas phase. Will they react? <u>Prove</u> it with calculations.

Practical Problems

The participants of the Olympiad must be prepared to work in a chemical laboratory aware of necessary rules and safety procedures. The organizers will enforce the safety rules given in the Appendix A of the IChO Regulations during the Olympiad.

The Preparatory Problems are designed to be carried out only in properly equipped chemical laboratories under competent supervision. We did not include specific and detailed safety and disposal instructions as regulations are different in each country. Mentors must carefully adapt the problems accordingly.

The safety (S) and risk (R) phrases associated with the materials used are indicated in the problems. See the Appendix B of the Regulations for the meaning of the phrases. The Regulations are available from http://www.icho.sk.

Materials marked with a dagger, † will not be used at the Olympiad.

Problem 30

You have twelve unknown aqueous solutions, each containing one, and only one, of the following compounds (all of which are used):

$H_2Cr_2O_7$	CaS	$(NH_4)_2CO_3$	CH_3COONa	KBr	KI
NaOH	$BaCl_2$	$Ca(H_2PO_4)_2$	$MgSO_4$	$Al(NO_3)_3$	$FeCl_3$
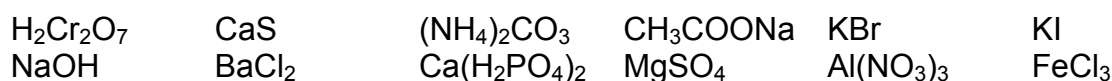
You have no additional reagents, only test tubes. <u>Identify</u> the compound in each solution.

Compound name	Formula	R phrases	S phrases
Aluminium nitrate	$Al(NO_3)_3$	8-36/38	17-26-36
Ammonium carbonate	$(NH_4)_2CO_3$	22-36/37/38	
Barium chloride	$BaCl_2$	20-25	1/2-45
Bichromic acid (solution)†	$H_2Cr_2O_7$	8-21-24/25-26-34-35-42/43-45-46-48/23-49-50/53-60-61-62	22-26-28-45-53-60-61
Calcium dihydrogenphosphate	$Ca(H_2PO_4)_2$	36/37/38	26-36/37
Calcium sulfide	CaS	31-36/37/38-50	28-61
Iron(III) chloride	$FeCl_3$	22-34	26-28
Magnesium sulfate	$MgSO_4$		22-25
Potassium bromide	KBr	36/37/38	26-36
Potassium iodide	KI	36/38-42/43-61	26-36/37/39-45
Sodium acetate	CH_3COONa		22-24-25
Sodium hydroxide	NaOH	35	26-37/39-45

Problem 31

You have three mixtures consisting of powdered inorganic solids on your desk. They could contain the following compounds:

a) $(NH_4)_2CO_3$, $AgNO_3$, $BaCl_2 \cdot 2H_2O$, NH_4NO_3, $NiCl_2 \cdot 2H_2O$

b) ZnO, KI, $Pb(NO_3)_2$, $BaSO_4$, MnO_2, Mg

c) $CaCO_3$, NH_4I, $FeSO_4 \cdot 7H_2O$, TiO_2, $CuCl_2 \cdot 2H_2O$

You can use distilled water, 2 mol/dm^3 HCl, 2 mol/dm^3 HNO$_3$, 2 mol/dm^3 NH$_3$, 2 mol/dm^3 NaOH solution, pH paper, test tubes and a Bunsen burner.

<u>Determine</u> which compounds are present in the mixture and which are not. <u>Note</u> your experimental findings in detail. <u>Explain</u> every conclusion (positive or negative). <u>Include</u> reaction equations where possible.

(not all of the compounds listed are present in the unknown samples)

Compound name	Formula	R phrases	S phrases
Ammonium carbonate	$(NH_4)_2CO_3$	22-36/37/38	
Ammonium iodide	NH_4I	26	
Ammonium nitrate	NH_4NO_3	8-36/37/38	17-26-36
Barium chloride	$BaCl_2$	20-25	1/2-45
Barium sulfate	$BaSO_4$		22-24/25
Calcium carbonate	$CaCO_3$	37/38-41	26-36/37/39
Copper(II) chloride dihydrate	$CuCl_2 \cdot 2H_2O$	22-36/37/38-50/53	26-60-61
Iron(II) sulfate heptahydrate	$FeSO_4 \cdot 7H_2O$	22	
Lead(II) nitrate	$Pb(NO_3)_2$	8-20/22-33-50/53-61-62	53-45-60-61
Magnesium	Mg	15-17	43-7/8
Manganese(IV) oxide	MnO_2	20/22	25
Nickel(II) chloride dihydrate†	$NiCl_2 \cdot 2H_2O$	23/24/25-36/37/38-42/43-45	53-26-27-28-36/37/39-45
Potassium iodide	KI	36/38-42/43-61	26-36/37/39-45
Silver nitrate	$AgNO_3$	34-50/53	26-45-60-61
Titanium(IV) oxide	TiO_2		
Zinc oxide	ZnO	50/53	60-61
Reagent	**Concentration**	**R phrases**	**S phrases**
Hydrochloric acid	2 mol/dm^3	34	26-36/37/39-45
Nitric acid	2 mol/dm^3	35	23-26-36-45
Sodium hydroxide	2 mol/dm^3	35	26-37/39-45
Ammonia	2 mol/dm^3	34-50	26-36/37/39-45-61

Problem 32

You have moderately concentrated (5-6 % by mass) aqueous solutions containing water-soluble compounds of the following cations with one of the most common anions (chloride, sulfate or nitrate):

NH_4^+, Li^+, Na^+, Mg^{2+}, Al^{3+}, K^+, Ca^{2+}, Cr^{3+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Sr^{2+}, Ag^+, Sn^{2+}, Sn^{4+}, Sb^{3+}, Ba^{2+}, Pb^{2+}, Bi^{3+}.
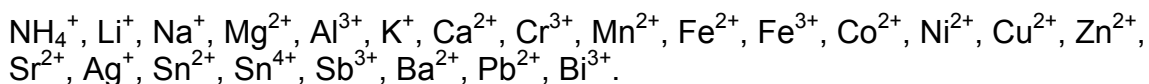
a) Observe the color and the pH of the solutions.

b) Study the reactions of these cations with the anions used in systematic qualitative analysis: chloride, sulfide, carbonate, and hydroxide. Note that some sulfides can be precipitated even from acidic solutions, others are soluble in dilute strong acids, some are soluble in water, and some would react with water. Most cations will give a precipitate with CO_3^{2-}. What happens if you use HCO_3^- instead?

Whenever you observe no reaction at ambient temperature, try to predict whether boiling the solution would bring about a detectable change.

c) Learn which cations react with some common anions: nitrate, nitrite, phosphate, sulfate, perchlorate, bromide, and iodide. Throughout this problem, use solutions in the same concentration range (approximately 5-6 % by mass).

d) Which two cations in the list above cannot be distinguished from each other on the basis of their reactions with the anions mentioned so far?

e) Using the reactions you have learned, identify five unknown aqueous solutions. Every solution was made from a single compound which may contain any of the cations and anions you have encountered in this problem.

Problem 33

In this problem you will identify a metal using complexometric titrations. EDTA (the disodium salt of ethylene-diamine-tetraacetic acid) forms stable complexes with most di- and trivalent metal ions.

$$M^{2+} + H_2Y^{2-} = MY^{2-} + 2 H^+ \qquad M^{3+} + H_2Y^{2-} = MY^- + 2 H^+$$
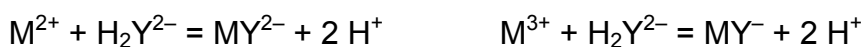
where M is the metal and Y^{4-} is the anion formed from EDTA.
While there is an excess of uncomplexed metal ions present, they bond to the indicator molecules. At the end of the reaction all ions form an EDTA complex and the indicator molecules will be liberated bringing about a change in color. Thus the end point of the reaction is when addition of EDTA does not change the hue of the solution. One has to titrate until a steady color is reached. A previously titrated sample can be used for comparison.
First a metal sample is dissolved in nitric acid. After setting the pH of the resulting solution to approximately 2, it is titrated with EDTA. In another measurement the oxide of the metal is dissolved and the solution is titrated again with EDTA. (The oxide was prepared previously by evaporating the nitric acid solution of the metal and calcining the residue.) Many solutions used are very acidic, treat them with due caution.

Titration of the metal

Weigh accurately about 150 mg of the unknown metal into a titration flask. Carefully add 3 cm^3 conc. nitric acid using working under the hood. Complete dissolution may take 10 minutes. Dilute the solutions to 50 cm^3 and then return to your desk. First add 8 cm^3 5 % ammonia solution, then continue adding the ammonia solution dropwise until the contents of the flask start to opalize from the hydroxide precipitate. Add immediately 5 cm^3 10 % nitric acid. Add two pinches of solid methylthymol blue indicator. Titrate with 0.0500 mol/dm^3 EDTA until a steady yellow color is attained. Repeat as necessary.

Titration of the metal oxide

Weigh accurately about 1.000 g of the oxide, dissolve it in 5 cm^3 conc. nitric acid and then dilute to 100 cm^3 in a volumetric flask. Transfer 20.00 cm^3 portions into a titration flask and dilute to 50 cm^3. Start adding 5 % ammonia dropwise until the appearance of the precipitate. Immediately add 5 cm^3 10 % nitric acid solution. Add two pinches of solid methylthymol blue indicator. Titrate with 0.0500 mol/dm^3 EDTA until a steady yellow color is attained. Repeat as necessary.

a) Identify the metal based on calculations.

b) Give the formula of the oxide.

Caveat: The best marks are not necessarily awarded to results reproducing the theoretically expected values.

Reagent	Concentration	R phrases	S phrases
EDTA disodium salt	0.05 mol/dm^3	36/38	26-36
Nitric acid	65 %	35	23-26-36-45
Nitric acid	10 %	35	23-26-36-45
Ammonia	5 %	34-50	26-36/37/39-45-61
Methylthymol blue			

Problem 34

The isolation of vitamin C was carried out by monitoring the reducing properties of green pepper extracts (1931, Szent-Györgyi). The determination of ascorbic acid can also be based on its reducing properties. This is often more convenient than titration as an acid, especially in the case of real life samples containing other acidic substances, e.g., citric acid.

A possible oxidizer is potassium bromate. Its use in direct titrations was suggested in 1872 by Győry. In strongly acidic solutions $KBrO_3$ reacts with KBr to form bromine. This will oxidize ascorbic acid ($C_6H_8O_6$) to dehydroascorbic acid ($C_6H_6O_6$) in this titration. The end point of the reaction can be followed by a suitable redox indicator.
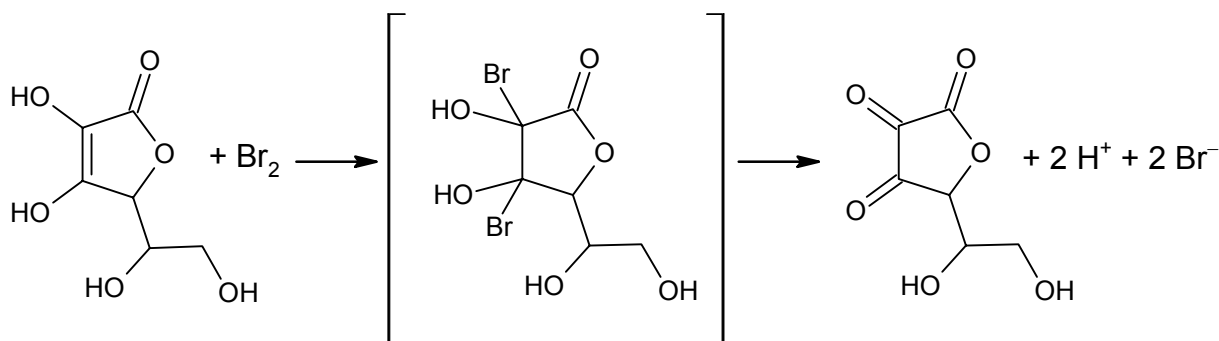
Crush the vitamin C tablet with a few drops of water in a mortar. Wash the soluble parts of the mixture through a folded filter paper into a 200 cm^3 Erlenmeyer flask. Do not use more than 60 cm^3 of distilled water. Add 10 cm^3 of 20 % (by mass) HCl and approx. 0.2 g of KBr to the sample . Titrate it immediately with the 0.02 mol/dm^3 KBrO$_3$ titrant in the presence of 2 drops of p-ethoxychrysoidine indicator (0.2 % in ethanol). The red solution will change to colorless (very light yellow) at the end point.

a)   <u>Write</u> the equation for bromine formation from bromate and bromide ions.

b)   <u>Give</u> the vitamin C content of the tablet in milligrams.

Reagent	Concentration	R phrases	S phrases
Hydrochloric acid	20 %	34	26-36/37/39-45
Potassium bromate†	0.02 mol/dm^3	45	45-53
Potassium bromide	solid	36/37/38	26-36
Para-ethoxychrysoidine	0.2% in ethanol		

Problem 35

Ascorbic acid (C$_6$H$_8$O$_6$) is a fairly good reducing agent (E^o = + 0.39 V). Due to this property, it is widely used in volumetric analysis. It can be used for the determination of various cations (e.g., Au^{3+}, Ag$^+$, Hg^{2+}) and anions (e.g., ClO$_3^-$, BrO$_3^-$, IO$_3^-$ VO$_4^{3-}$, Fe(CN)$_6^{3-}$). During the titration it is oxidized via loss of 2 electrons forming dehydroascorbic acid (C$_6$H$_6$O$_6$) – as shown in the previous problem.

Preparation of 0.05 mol/dm^3 ascorbic acid solution

Weigh approximately 8.9 g ascorbic acid and dissolve it in a small amount of water. Do not use metal vessels or spoons. Transfer the solution to a standard volumetric flask and dilute to 1.000 dm^3 with freshly prepared cold distilled water.

Preparation of 0.00833 mol/dm^3 potassium hydrogen iodate solution

Weigh accurately 3.2492 g KH(IO$_3$)$_2$ in a 50 cm^3 beaker and dissolve it in 50 cm^3 distilled water. Transfer the solution in a standard volumetric flask and dilute to 1000 cm^3 with freshly prepared distilled water.

Standardization of the 0.05 mol/dm^3 ascorbic acid solution

Pipette 20.00 cm^3 0.00833 mol/dm^3 KH(IO$_3$)$_2$ solution into a clean conical flask. Add approx. 1 g KI and 5 cm^3 2 mol/dm^3 HCl solution. Titrate the liberated iodine with 0.05 mol/dm^3 ascorbic acid solution. When the colour has faded to pale yellow, add 10 drops of Variamine Blue indicator (hydrogen sulfate, 0.2 % by mass solution in water). Slowly add 20 % sodium acetate solution until the deep violet colour of the indicator

appears, then add 2 cm^3 more. Titrate the solution slowly until the deep violet colour disappears. Repeat the procedure as necessary.

Determination of the silver content of the unknown

Dilute the given sample solution to 100 cm^3 in a volumetric flask using distilled water. Pipette 10.00 cm^3 of the unknown solution into a clean conical flask. Dilute the sample to 50-70 cm^3 with distilled water. Heat the solution to 60 °C. Add 1 cm^3 of Variamine Blue indicator and titrate rapidly with 0.05 mol/dm^3 ascorbic acid solution. The solution must be thoroughly shaken during the titration. If the temperature falls under 40 °C, reheat to 60 °C. When the blue or violet colour of the indicator has disappeared and the greyish-white colour of the precipitated silver metal has become apparent, add 20% sodium acetate solution to re-establish the colour of the indicator. Then titrate slowly adding titrant dropwise, until the colour of the indicator fades away. Repeat the procedure as necessary.

Variamine Blue has the structure shown below:
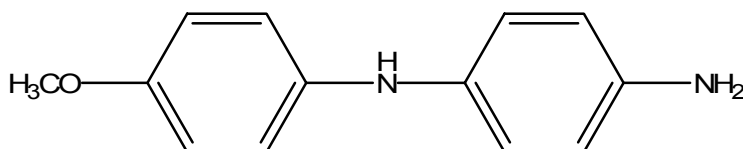
a)   Write a balanced equation for the formation of iodine and the titration of iodine with ascorbic acid solution in Procedure 2.

b)   Calculate the concentration of the ascorbic acid solution prepared.

c)   Variamine Blue is shown in its reduced form. Draw the structure of the oxidized form given that it is oxidized with the loss of 2 electrons. Which form is responsible for the blue-violet colour?

d)   Write a balanced equation of the reaction between ascorbic acid and silver ions.

e)   Determine the silver content of the unknown.

Reagent	Concentration	R phrases	S phrases
Unknown sample (containing Ag$^+$ ions)		34-51/53	26-36/37/39-45-61
Ascorbic acid	0.05 mol/dm^3		
Potassium hydrogen iodate	Solid	63-36/38-42/43	26-36/37/39-45
Potassium iodide	Solid	63-36/38-42/43	26-36/37/39-45
Hydrochloric acid	2 mol/dm^3	34	26-36/37/39-45
Sodium acetate	20 %		22-24-25
Variamine Blue	0.2 % in water	23/24/25	36/37/39-45

Problem 36

You will carry out a simple synthesis of N-benzyl-3-nitroaniline according to the reaction scheme:
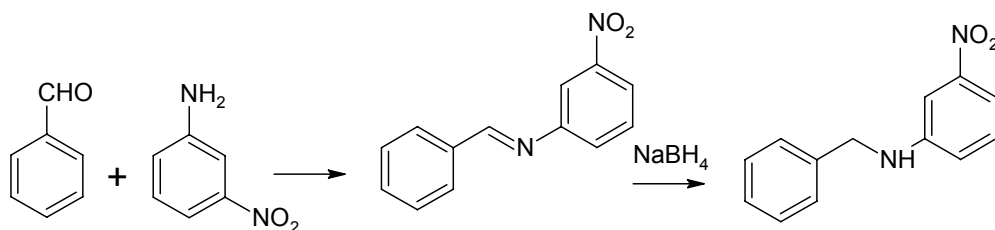
Dissolve 1.1 g *meta*-nitroaniline in 10 cm^3 ethanol in a 25 cm^3 Erlenmeyer flask and add 1.5 cm^3 benzaldehyde to this mixture. Let the flask stand for 20 minutes with occasional shaking. Transfer the flask to an ice-water bath. On cooling a solid material precipitates. Collect it on a sintered glass funnel. You can use the filtrate to wash the solid remaining in the flask onto the filter. Since the product is moderately soluble in alcohol, do not wash it on the filter, just dry it with suction. Set aside a small sample for thin-layer chromatography (TLC).
Place the solid substance into a 100 cm^3 Erlenmeyer flask and dissolve it in 20 cm^3 of ethanol. Slowly add to this solution 0.5 g of NaBH$_4$ in small portions with constant shaking. Continue shaking the flask for an additional 15 minutes, and then pour its content into 50 cm^3 of ice-cold water. Collect the precipitate on a sintered glass funnel and wash with cold water. Dry the product in air and weigh it.

Compare the chromatographic properties of the starting materials, the intermediate and the product. Make a thin layer chromatogram on a silica plate with hexane/ethyl acetate = 4:1 as eluent. Suggest a method for visualization of the spots. Comment on the purity of the intermediate and the product.

		R phrases	S phrases
Meta-nitroaniline	solid	23/24/25-33-52/53	28-36/37-45-61
Benzaldehyde	solid	22	24
NaBH$_4$	solid	15-24/25-34	22-26-36/37/39-43-45
Ethanol	abs.	11	7-16
Hexane		11-38-48/20-51/53-62-65-67	9-16-29-33-36/37-61-62
Ethyl acetate		11-36-66-67	16-26-33

Problem 37

Before highly efficient methods like chromatography or genetic engineering revolutionalized the elucidation of protein structure the analysis of protein hydrolizates was very complicated. Several reagents were developed to selectively precipitate individual amino acids from mixtures often containing 20 or more different compounds. One such widely used reagent was rhodanilic acid or its salts, which contain the rhodanilic complex ion ([Cr(SCN)$_4$(PhNH$_2$)$_2$]$^-$). This problem demonstrates the use of this reagent.

Ammonium rhodanilate

In a 100 cm^3 flask mix 5 g hydrated chromium(III) potassium sulfate, 5.8 g potassium thiocyanate and 5 cm^3 water and heat it in a 80 °C water bath for 10 minutes. Under the

hood add 5 cm^3 aniline and continue heating for an additional 60 minutes. Dilute the product with 50 cm^3 water and add 10 cm^3 glacial acetic acid. Keep the mixture in an ice-water bath for 10 minutes with occasional scratching using a glass rod. Filter off the purple precipitate on a sintered glass filter and wash it with water.

In a flask dissolve the product in 20 cm^3 methanol. Filter out any insoluble impurities. To the solution add 10 cm^3 of concentrated ammonia solution and 50 cm^3 water. Collect the precipitate with filtration, wash it with water and dry on an open Petri dish.

The reaction of ammonium rhodanilate with amino acids

Dissolve 0.35 g proline in 15 cm^3 0.25 mol/dm^3 aqueous HCl in a beaker. In a separate beaker dissolve 1.5 g ammonium rhodanilate in 20 cm^3 methanol. Mix the two solutions. Filter the precipitate on a glass filter. Wash with three 10 cm^3 portions of distilled water. Dry the product in an open Petri dish.

TLC experiments

Dissolve appr. 10 mg samples of alanine, proline, phenylalanine and glutamic acid (separately) in 1 cm^3 of water. Additionally, make a sample mixing the four standard solutions. In a separate test tube mix 0.1 cm^3 samples of these solutions with 0.1 cm^3 ammonium rhodanilate solution (5 % in methanol). Filter the solutions on paper using a small funnel.

Analyze the solutions by TLC on silica plates. Find an appropriate eluent by mixing 50% acetic acid and *n*-butanol. Visualise the spots with ninhydrin*. Summarize your results. Explain your findings!

		R phrases	S phrases
$KCr(SO_4)_2 \cdot 12H_2O$	solid		22-24/25
KSCN	solid	20/21/22-32-52/53	13-61
Aniline†		23/24/25-40-41-43-48/23/24/25-50-68	26-27-36/37/39-45-46-61-63
L-Alanine	solid		
L-Phenylalanine	solid		
L-Proline	solid		22-24/25
L-Glutamic acid	solid		
Methanol	abs.	11-23/24/25-39/23/24/25	7-16-36/37-45
Ninhydrin	0.5% (in acetone)	11-22-36/37/38-66-67	9-16-26
n-butanol		10-22-37/38-41-67	13-26-37/39-46-7/9
NH$_3$	conc.	34-50	26-36/37/39-45-61
Acetic acid	100%	10-35	23-26-45
Acetic acid	50%	34	23-26-45
HCl	0.25 mol/dm^3	34-37	26-36/37/39-45

---

* Ninhydrin is a selective reagent for amino acids. Dip the developed and dried plates in a 0.5% acetone solution of ninhydrin, dry the plates and heat them for a short time with a heat-gun. Contact of the reagent with skin should be avoided since it produces a rather long-lasting purple discoloration. Use forceps!

Worked Solutions

Problem 1

80.0 °F = 26.67 °C = 299.82 K

3.068 cubic feet = $3.068 \cdot (30.48)^3$ cm^3 = 86.876 dm^3

$$n = \frac{101325 \text{ Pa} \cdot 0.086876 \text{ m}^3}{R \cdot 299.82 \text{ K}} = 3.531 \text{ mol}$$

This is the amount of the gas produced from 28.35 g of the unknown substance. Thus, 1 mol of gas is produced when 8.028 g of the substance reacts with water. Together with the flammability of the gas and the color of the flame, this leads us to conclude that the substance is lithium hydride:

LiH + H$_2$O = LiOH + H$_2$
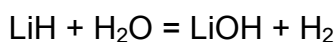
On subsequent neutralization with HF, one would expect the formation of 7 g + 19 g = 26 g LiF from 8 g LiH, i.e. 3.25 times the original mass. But Holmes had only observed a 3.125-fold mass increase, i.e. only 25 g LiF had formed from 1 mol of LiH. This cannot be explained if all elements were present in their naturally occurring isotopic composition. The mass of 1 mol of LiF is, however, 25 g if it contains the pure stable isotope ^{6}Li, which accounts for approximately 7 % of naturally occurring lithium (^{19}F is the only stable isotope of fluorine). Since the molar mass of the substance is still 8 g/mol, it must be a compound of ^{6}Li with deuterium. ^{6}Li deuteride used to be (and still probably is) the principal fusion fuel in thermonuclear weapons. After the capture of neutrons produced by a fission chain reaction, the following processes take place:

$$^6_3\text{Li} + {}^1_0\text{n} \rightarrow {}^3_1\text{H} + {}^4_2\text{He}$$

$$^3_1\text{H} + {}^2_1\text{H} \rightarrow {}^4_2\text{He} + {}^1_0\text{n}$$
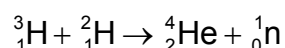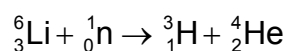
Problem 2

a) The composition of **A**:

n(N) : n (H) : n (O) = (11.97 / A_r(N)) : (3.45 / A_r(H)) : (41.03 / A_r(O)) = 1 : 4 : 3
From these molar ratios it is clear that **A** contains ammonium ions.
The amount of the metal **H** in 100 g **A** is 43.55 g. Supposing that one mol of **A** contains one mol of both **H** and nitrogen, the molar mass of **H** is 43.55 g / 0.8550 mol = 50.94 g/mol. That is vanadium. From here, the compounds (species) **A-K** are the following:

A: NH$_4$VO$_3$ **H**: V
B: V$_2$O$_5$ **I**: VCl$_4$
C: VO$_2$$^+$ **J**: VCl$_3$
D: VO$_3$$^-$ **K**:VCl$_2$
E: V^{2+}
F: VO^{2+}
G: V^{3+}
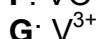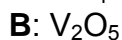
The reactions are:

1. $2 NH_4VO_3(s) \rightarrow 2 NH_3(g) + V_2O_5(s) + H_2O(g)$

2. $V_2O_5(s) + 2 H_3O^+(aq) \rightarrow 2VO_2^+(aq) + 3 H_2O(l)$

3. $2 VO_2^+(aq) + 3 Zn(s) + 8 H_3O^+(aq) \rightarrow 2 V^{2+}(aq) + 3 Zn^{2+}(aq) + 12 H_2O(l)$

4. $NH_4VO_3(s) \rightarrow NH_4^+(aq) + VO_3^-(aq)$

5. $VO_3^-(aq) + 2 H_3O^+(aq) \rightarrow VO_2^+(aq) + 3 H_2O(l)$

6. $2 VO_3^-(aq) + SO_2(g) + 4 H_3O^+(aq) \rightarrow 2 VO^{2+}(aq) + SO_4^{2-}(aq) + 6 H_2O(l)$

7. $VO^{2+}(aq) + V^{2+}(aq) + 2 H_3O^+(aq) \rightarrow 2 V^{3+}(aq) + 3 H_2O(l)$

8. $V(s) + 2 Cl_2(g) \rightarrow VCl_4(l)$

9. $2 VCl_4(l) \rightarrow 2 VCl_3(s) + Cl_2(g)$

10. $2 VCl_3(s) + H_2(g) \rightarrow 2 VCl_2(s) + 2 HCl(g)$

11. $VCl_4(l) + 3 H_2O(l) \rightarrow VO^{2+}(aq) + 4 Cl^-(aq) + 2H_3O^+$

12. $2 VCl_3(s) \rightarrow 2 V^{3+}(aq) + 6 Cl^-(aq)$

13. $VCl_2(s) \rightarrow V^{2+}(aq) + 2 Cl^-(aq)$

14. $2 VCl_3(s) \rightarrow VCl_2(s) + VCl_4(l)$

b) 3, 6, 7, 8, 9, 10, 14

c) Since V has an $4s^23d^3$ configuration, the loss of 2, 3 or 4 electrons leads to species having unpaired d electrons. Only compounds in the +5 oxidation state do not have these: **A**, **B**, **C**, **D**.

d) The reduction of VO^{2+} ions with zinc in acidic medium can be stopped at V^{3+}:

$2 VO^{2+}(aq) + Zn(s) + 4 H_3O^+(aq) \rightarrow 2 V^{3+}(aq) + Zn^{2+}(aq) + 6 H_2O(l)$

e) Production of SO_3, then sulfuric acid: $2 SO_2 + O_2 = 2 SO_3$. V_2O_5 is a catalyst.

f) The probability of no ^{35}Cl atoms being in a VCl_4 molecule is $0.99^4 = 96.06$ %. Thus the probability of ^{35}Cl being present, i.e. the mole fraction of ^{35}Cl containing products is 3.94 %.

g) The same reasoning gives the probability of a ^{35}Cl atom being present in a VCl_3 molecule as 2.97 %.

Problem 3

a) In the cubic system we can have simple cubic, face-centered cubic (fcc) and body-centered cubic (bcc) lattices. These unit cells contain 1, 4 or 2 atoms, respectively. We can determine how the lattice constant depends on the metallic radius utilizing the fact that in each lattice the atoms touch each other. We obtain for simple cubic $a = 2R$; for fcc: $a = 2R\sqrt{2}$; for bcc $a = 4R/\sqrt{3}$.

If the lattice is simple cubic, then we have 1 atom in a unit cell. Using the density value we obtain $M(Cr)/(\rho \cdot N_A) = 1.209 \cdot 10^7$ pm^3 for the volume of a unit cell. The lattice

constant is therefore $(1.209 \cdot 10^7 \text{ pm}^3)^{1/3} = 229.5$ pm. However, this value does not agree with the 252 pm ($a = 2R$) expected for a simple cubic lattice.

If the lattice is fcc, then we have 4 atoms in a unit cell. Using the density value we obtain $4 \cdot M(Cr)/(\rho \cdot N_A) = 4.838 \cdot 10^7 \text{ pm}^3$ for the volume of a unit cell. The lattice constant is therefore $(4.838 \cdot 10^7 \text{ pm}^3)^{1/3} = 364.4$ pm. For fcc, a should be $2R\sqrt{2} = 356$ pm. Again, this does not agree with the density.

If the lattice is bcc, then we have 2 atoms in a unit cell. Using the density value we obtain $2 \cdot M(Cr)/(\rho \cdot N_A) = 2.419 \cdot 10^7 \text{ pm}^3$ for the volume of a unit cell. The lattice constant is therefore $(2.418 \cdot 10^7 \text{ pm}^3)^{1/3} = 289.2$ pm. For bcc, $a = 4R/\sqrt{3} = 291$ pm, which is reasonably close. Hence the lattice of chromium is body-centered cubic.

b) CrO_2Cl_2, chromyl chloride. Its structure is:

c) The reaction equations:

$$2\ CrO_4^{2-} + 2\ H^+ = Cr_2O_7^{2-} + H_2O$$

$$3\ CrO_4^{2-} + 4\ H^+ = Cr_3O_{10}^{2-} + 2\ H_2O$$

$$4\ CrO_4^{2-} + 6\ H^+ = Cr_4O_{13}^{2-} + 3\ H_2O$$
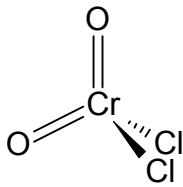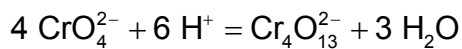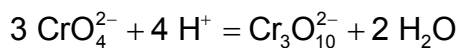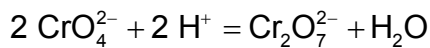
The structure of the polychromate ions:
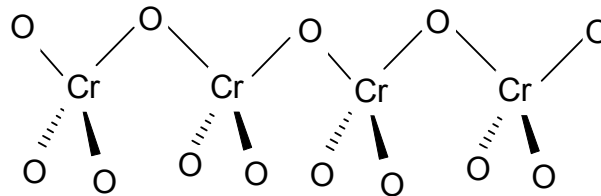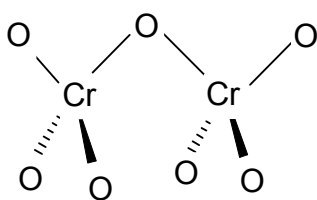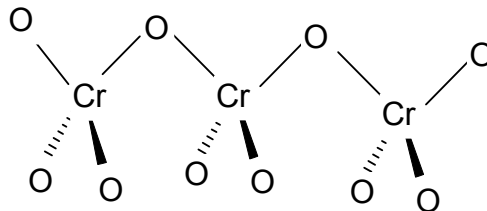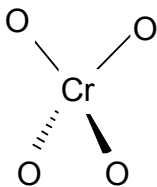
CrO_3 is a polymeric chain derived from the polychromate ions.

d) The formula to be used is

$$E^o = \frac{n_1 E_1^o + n_2 E_2^o}{n_1 + n_2}$$

From this we obtain $E^o = 1.35$ V for the Cr(V)-Cr(IV) process, $E^o = 1.33$ V for the $Cr_2O_7^{2-}$-Cr^{3+} process, $E^o = -0.90$ V and for the Cr^{2+}-Cr process.

e) The criterion for disproportionation is: $E^{ox} < E^{red}$, where E^{ox} is the redox potential for the oxidation process and E^{red} is the redox potential for the reduction. A species is prone to disproportionate if there is a larger number on the Latimer diagram on its right side than on its left side. It follows that both Cr(V) and Cr(IV) are unstable with respect to disproportionation.

For the 3 Cr^{2+} = 2 Cr^{3+} + Cr process the equilibrium constant can be calculated from standard redox potential values: $\Delta_r G^o = -2 \cdot F \cdot (-0.90\ V - (-0.42\ V)) = 93$ kJ/mol. From $\Delta_r G^o$ we obtain the equilibrium constant by using the formula

$K = \exp(-\Delta_r G^o / RT) = 5.91 \cdot 10^{-17}$

f) In order to calculate the solubility constant of $Cr(OH)_3$ we turn to the Latimer diagram for pH = 14. Comparing the standard potentials in volts for the Cr(III) → Cr(0) processes for pH = 0 and pH = 14 we can write:

$$-1.33 = -0.74 + \frac{0.059}{3} \lg\left(\frac{L}{[OH^-]^3} \right)$$

This gives pL = 30.
Similarly for the overall stability constant of the tetrahydroxo-chromate(III) anion we can write:

$$-1.33 = -0.74 + \frac{0.059}{3} \lg\left(\frac{[Cr(OH)_4^-]}{K[OH^-]^4} \right)$$

Substituting 1.0 for $[Cr(OH)_4^-]$ and $[OH^-]$ we obtain: pK = −30.

g) The highest possible standard cell potential belonging to these species in acidic conditions is 1.33 V − 0.695 V = 0.635 V. Thus in acidic solution hydrogen peroxide is oxidized to O_2 and Cr(VI) is reduced to Cr(III). The reaction equation is:

$Cr_2O_7^{2-} + 3\ H_2O_2 + 8\ H^+ = 2\ Cr^{3+} + 3\ O_2 + 7\ H_2O$
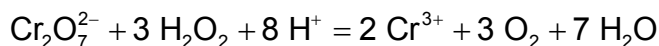
In basic solution OH^- formation and the oxidation of Cr(III) to Cr(VI) is associated with the highest standard cell potential: 0.87 V − (−0.72 V) = 1.59 V. The reaction equation is:

$2\ [Cr(OH)_4]^- + 3\ HO_2^- = 2\ CrO_4^{2-} + 5H_2O + OH^-$
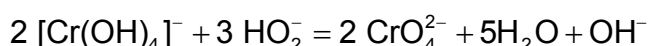
Problem 4

a) 4 and 2

b) In 1 cm^3 we have $\rho \cdot N_A / M(SiO_2) = 2.208 \cdot 10^{22}$ SiO_2 units. For 1 unit we obtain a volume of $4.53 \cdot 10^{-23}$ cm^3.

Every Si atom forms 4 Si-O bonds. Hence a volume element having 1 SiO_2 unit has 4 Si-O bonds.

c) Let us denote the number of Si atoms in the sample by n. We have $1.9n$ O atoms which form $3.8n$ Si-O bonds. The $4n$ and $3.8n$ valence electrons contributed by the Si and O atoms form $(2 + 1.9)n$ bonds (Si-O and Si-Si together). The remaining $3.9n - 3.8n$ bonds are the Si-Si bonds. Their ratio is

$$\frac{3.9n - 3.8n}{3.9n} = \frac{0.1}{3.9} = 0.0256 \,.$$

So 2.56 % of the bonds are Si-Si bonds.

d) In general the required formula can be written as:

$$\frac{n_{\text{Si-Si}}}{n_{\text{Si-O}}} = \frac{2n - nx}{2nx} = \frac{1}{x} - 0.5 \,.$$

The question implies that the $\dfrac{n_{\text{Si-Si}}}{n_{\text{Si-O}}}$ ratio is 1/6. It follows that x is 1.5 in this case.

Problem 5

a) The sulfur atoms are coordinated by one sulfur atom and three Fe^{2+} ions in a distorted tetrahedral arrangement.

b) The smallest unit cell with a lattice constant of a_0 contains 4 Fe and 8 S atoms. This leads to

$$\rho = \frac{4 \cdot M(\text{Fe}) + 8 \cdot M(\text{S})}{N_A a_0^3} = 5.011 \,\text{g/cm}^3$$

From this equation we obtain a_0 = 541.8 pm.

c) For varying iron content the calculations can be done as follows:

One mole of the crystal contains 8 mol S and 8/y mol Fe. Hence the relationship between the density of the crystal and the composition in the case of varying iron content is:

$$\rho = \frac{8 \cdot M(\text{S}) + 8 \cdot M(\text{Fe})/y}{N_A a_0^3} = \left(2.679 + \frac{4.667}{y}\right) \text{g/cm}^3$$

For varying S content: one mole of the crystal contains 4 mol Fe and 4y mol S. Thus the dependence of density on y is:

$$\rho = \frac{4 \cdot M(\text{Fe}) + 4y \cdot M(\text{S})}{N_A a_0^3} = \left(2.332 + 1.339y\right) \text{g/cm}^3$$

d)
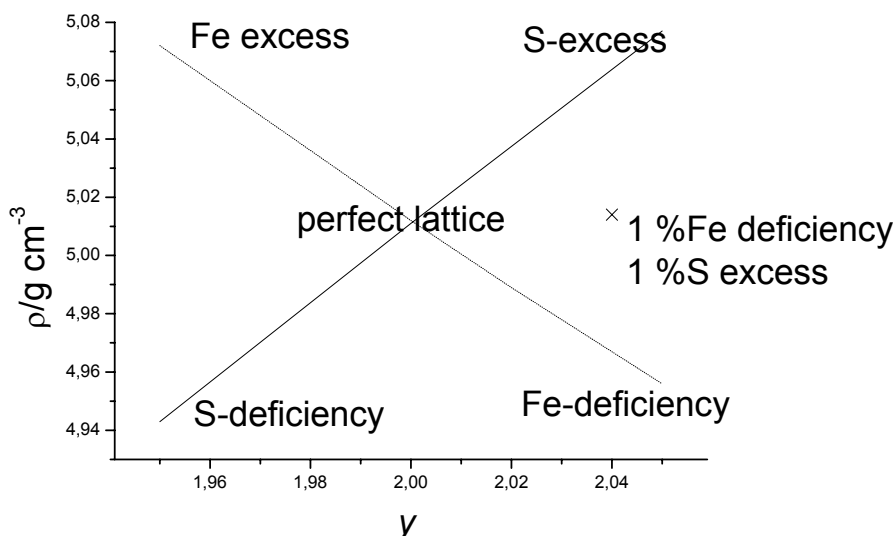
e)   In the unit cell of the natural pyrite sample, there is 4·0.99 = 3.96 mol Fe and 8·1.01 = 8.08 mol S. This gives y = 8.08/3.96 = 2.04. This is within the region where the unit cell parameter does not depend on the composition; therefore the density can be calculated from the available data.

$$\rho = \frac{3.96 \cdot M(\text{Fe}) + 8.08 \cdot M(\text{S})}{N_A a_0^3} = 5.014 \ \text{g/cm}^3$$

The (2.04, 5.014) point is given in the previous figure.

Problem 6

a) N_3^-, N_2

b)   The sodium salt of **A** contains one mol sodium per mole, hence its molar mass is $M(\text{Na})/0.3536$ = 65.02 g/mol. The molar mass of the anion is 42.03 g/mol, this implies N_3^-. **A** is hydrogen azide. The Lewis structures are:
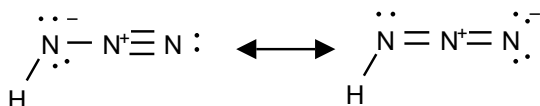
c)   If the formula of the halogenide is N_aX_b (X denotes the unknown halogen), the following equation can be written:

$$\frac{aM(\text{N})}{aM(\text{N}) + bM(\text{X})} = 0.4244$$

From this, $bM(\text{X}) = 19a$. Therefore X is fluorine, and $b = a$. Since NF does not exist, and the maximum number of covalent bonds formed by nitrogen is 4, the halogenide is N_2F_2. The molecular shape is:
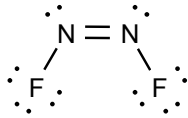
d) Since SbF_5 is a strong Lewis-acid, the formula of the anion of **B** is SbF_6^-. Since it contains one anion, **B** contains only one Sb atom. Hence the molar mass of the compound is $M(Sb)/0.4306 = 282.75$ g/mol. The nitrogen content is 282.75 g$\cdot 0.0991$ = 28 g, the rest (133 g) is fluorine. From these data, the empirical formula is SbN_2F_7.

e) The anion of **B** is SbF_6^-, so the molecular formula of **B** is $[N_2F^+][SbF_6^-]$. The resonance structures of the cation are:
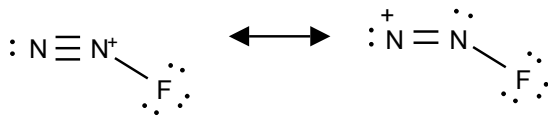
The bond angle would be 180° in the first and less than 120° in the second individual contributing structure.

f) If the formula of the nitrogenous oxide is N_aO_b, the following equation can be written:

$$\frac{aM(N)}{aM(N)+bM(O)} = 0.6365$$

From here $a = 2b$, so the molecular formula of the nitrogenous oxide is N_2O.

g) The amount of N_2O formed is 1.14 mmol. The amount of **B** is 0.3223 g / 282.75 g mol^{-1} = 1.14 mmol. The oxygen atom comes from the water molecule; this leaves two hydrogen atoms which can form HF with fluoride ions:

$$[N_2F^+][SbF_6^-] + H_2O \rightarrow N_2O + 2\ HF + SbF_5$$
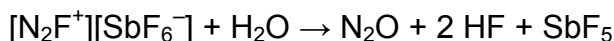
SbF_5 undergoes hydrolysis in dilute aqueous solution, but the reaction can lead to various products: e.g., $SbF_5 + H_2O \rightarrow SbOF_3 + 2HF$

h) The anion of **C** is SbF_6^-. If **C** contains n anions per cation and the cation contains x N atoms, then the nitrogen and antimony content is:

$$\frac{xM(N)}{xM(N)+nM(SbF_6)} = 0.2290$$

$$\frac{nM(Sb)}{xM(N)+nM(SbF_6)} = 0.3982$$

Dividing the first equation by the second, we obtain $n = 5x$. From this the formula of **C** is $[N_5^+][SbF_6^-]$.

i)
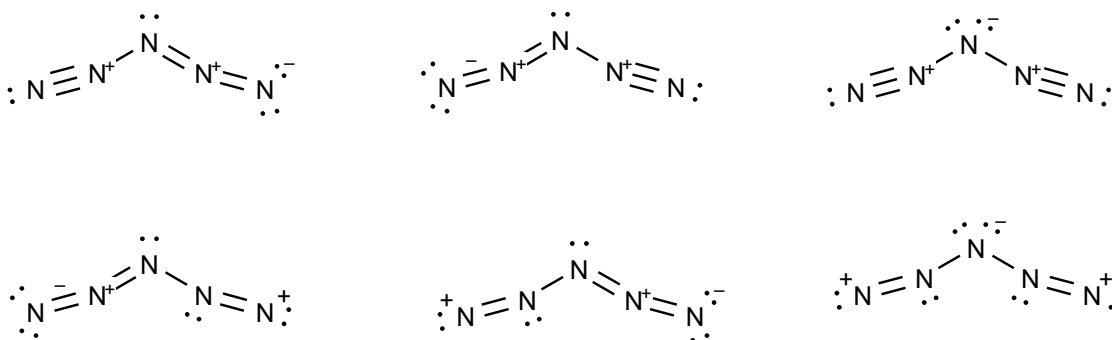
The central bond angle is smaller than 120° in all structures due to the presence of one or two non-bonding electron pairs on the central nitrogen. The other two bond angles would be equal to 180° in the resonance structures of the first row but less than 180° in the resonance structures of the second row due to the presence of non-bonding electron pairs on the relevant nitrogen atoms(s).

j) $[N_2F^+][SbF_6^-] + HN_3 \rightarrow [N_5^+][SbF_6^-] + HF$

The reaction is thermodynamically favorable because of the high stability of HF.

k)   If **C** oxidizes water, and two elemental gases are formed, one of them must be oxygen. The other is nitrogen, due to the instability of the cation of **C**. Therefore, the reaction equation for the hydrolysis is:

$4\ [N_5^+][SbF_6^-] + 2\ H_2O \rightarrow 10\ N_2 + O_2 + 4\ HF + 4\ SbF_5$.

l)   As the anion of **D** is octahedrally coordinated and it contains N_3^- ions (since it is formed from **A**), the only possibility is that the central atom of **D** (and therefore, that of **E**) is surrounded by six N_3^- ions. As the cation of **E** is N_5^+ and the cation:anion ratio is 1:1, the formula of **E** is $[N_5^+][X(N_3)_6^-]$, thus XN_{23} (where X is the unidentified main group element). The nitrogen content, expressed in terms of the relative atomic masses, is:

$$\frac{23 \cdot M(N)}{23 \cdot M(N) + M(X)} = 0.9124$$

From here, $M(X) = 30.9$ g/mol. This is phosphorus. The formula of **E** is therefore: $[N_5^+][P(N_3)_6^-]$

m)   The oxidation number of the atoms in Na^+ and Cl^- ions does not change, and gas evolution was not observed, indicating that the N_3^- ions did not decompose during the synthesis. Therefore, the formation of **E** is not a redox reaction; phosphorus has the same oxidation number in the chloride as in **E**. The chloride is PCl_5.

D contains $[P(N_3)_6]^-$ as anion. As cation it can contain only Na^+. Therefore the formula of **D** is $Na[P(N_3)_6]$

n)   Nitrogen is the gaseous product. As oxygen is present in the atmosphere, the phosphorus content is oxidized to P_2O_5. The chemical equation of the decomposition is:

$4\ [N_5^+][P(N_3)_6^-] + 5\ O_2 \rightarrow 46\ N_2 + 2\ P_2O_5$.
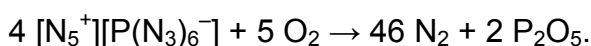
Problem 7

a) $[H_3O^+] = 10^{-4}$ mol/dm^3

$[HCl]_{total} = [H_3O^+] = 10^{-4}$ mol/dm^3

b) $[H_3O^+] = 10^{-4}$ mol/dm^3

Material balance: $[HAc]_{total} = [Ac^-] + [HAc]$
Charge balance: $[H_3O^+] = [Ac^-]$

$$K_a = \frac{[H_3O^+]\cdot[Ac^-]}{[HAc]} = \frac{[H_3O^+]^2}{[HAc]_{total} - [H_3O^+]}$$

$[HAc]_{total} = 6.75\cdot10^{-4}$ mol/dm^3

c) $[H_3O^+] = 10^{-4}$ mol/dm^3

Material balance: $[H_2SO_4]_{total} = [HSO_4^-] + [SO_4^{2-}]$
Charge balance: $[H_3O^+] = [HSO_4^-] + 2[SO_4^{2-}]$

$$K_{2a} = \frac{[H_3O^+]\cdot[SO_4^{2-}]}{[HSO_4^-]} = \frac{[H_3O^+]\cdot([H_3O^+]-[H_2SO_4]_{total})}{2[H_2SO_4]_{total} - [H_3O^+]}$$

$[H_2SO_4]_{total} = 5.024\cdot10^{-5}$ mol/dm^3

d) $[H_3O^+] = 10^{-4}$ mol/dm^3

Material balance: $[H_3A]_{total} = [H_3A] + [H_2A^-] + [HA^{2-}] + [A^{3-}]$
Charge balance: $[H_3O^+] = [H_2A^-] + 2[HA^{2-}] + 3[A^{3-}]$

$$K_{1a} = \frac{[H_3O^+]\cdot[H_2A^-]}{[H_3A]}$$

$$K_{2a} = \frac{[H_3O^+]\cdot[HA^{2-}]}{[H_2A^-]}$$

$$K_{3a} = \frac{[H_3O^+]\cdot[A^{3-}]}{[HA^{2-}]}$$

$[H_3A]_{total} = 8.29\cdot10^{-5}$ mol/dm^3

e) In the mixture $[HCl]_{total} = 5.00\cdot10^{-5}$ mol/dm^3 and $[NaOH]_{total} = 5.00\cdot10^{-5}$ mol/dm^3, so this is a neutral solution with <u>pH = 7.00</u>.

f) In the mixture $[HAc]_{total} = 3.375\cdot10^{-4}$ mol/dm^3 and $[NaOH]_{total} = 5.00\cdot10^{-5}$ mol/dm^3.

Material balance: $[HAc]_{total} = [Ac^-] + [HAc]$ and $[NaOH]_{total} = [Na^+]$
Charge balance: $[H_3O^+] + [Na^+] = [Ac^-]$

$$K_a = \frac{[H_3O^+]\cdot[Ac^-]}{[HAc]}$$

$[H_3O^+] = 4.46\cdot10^{-5}$ mol/dm^3 \qquad\qquad <u>pH = 4.35</u>

g) In the mixture $[H_2SO_4]_{total} = 2.512\cdot10^{-5}$ mol/dm^3 and $[NaOH]_{total} = 5.00\cdot10^{-5}$ mol/dm^3, so this solution is nearly neutral.

58

Material balance: $[H_2SO_4]_{total} = [HSO_4^-] + [SO_4^{2-}]$, and $[NaOH]_{total} = [Na^+]$

Charge balance: $[H_3O^+] + [Na^+] = [HSO_4^-] + 2[SO_4^{2-}] + [OH^-]$

$K_w = [H_3O^+] \cdot [OH^-] = 10^{-14}$

$$K_{2a} = \frac{[H_3O^+] \cdot [SO_4^{2-}]}{[HSO_4^-]}$$

$[H_3O^+] = 2.76 \cdot 10^{-7}$ mol/dm^3 pH = 6.56

h)   In the mixture $[H_3A]_{total} = 4.145 \cdot 10^{-5}$ mol/dm^3 and $[NaOH]_{total} = 5.00 \cdot 10^{-5}$ mol/dm^3, so this solution contains: $[NaH_2A]_{total} = 3.29 \cdot 10^{-5}$ mol/dm^3 and $[Na_2HA]_{total} = 8.55 \cdot 10^{-6}$ mol/dm^3

$$K_{2a} = \frac{[H_3O^+] \cdot [HA^{2-}]}{[H_2A^-]} = \frac{[H_3O^+] \cdot ([Na_2HA]_{total} + [H_3O^+])}{[NaH_2A]_{total} - [H_3O^+]}$$

$[H_3O^+] = 2.00 \cdot 10^{-5}$ mol/dm^3 pH = 4.70

i)   In the mixture $[HAc]_{total} = 3.375 \cdot 10^{-4}$ mol/dm^3 and $[HCl]_{total} = 5.00 \cdot 10^{-5}$ mol/dm^3,

Material balance: $[HAc]_{total} = [Ac^-] + [HAc]$ and $[HCl]_{total} = [Cl^-]$

Charge balance: $[H_3O^+] = [Ac^-] + [Cl^-]$

$$K_a = \frac{[H_3O^+] \cdot [Ac^-]}{[HAc]}$$

$[H_3O^+] = 9.99 \cdot 10^{-5}$ mol/dm^3 pH = 4.00

j)   In mixture $[H_2SO_4]_{total} = 2.512 \cdot 10^{-5}$ mol/dm^3 and $[HCl]_{total} = 5.00 \cdot 10^{-5}$ mol/dm^3

Material balance: $[H_2SO_4]_{total} = [HSO_4^-] + [SO_4^{2-}]$ and $[HCl]_{total} = [Cl^-]$

Charge balance: $[H_3O^+] = [HSO_4^-] + 2[SO_4^{2-}] + [Cl^-]$

$$K_{2a} = \frac{[H_3O^+] \cdot [SO_4^{2-}]}{[HSO_4^-]}$$

$[H_3O^+] = 1.00 \cdot 10^{-4}$ mol/dm^3 pH = 4.00

Problem 8

a)   From the ionic product: $[HF_2^-] = [H_2F^+] = \sqrt{8.0 \cdot 10^{-12}} = 2.8 \cdot 10^{-6}$ mol/dm^3

$[HF] = \rho / M(HF) = 50.1$ mol/dm^3.

The autodissociation causes a negligible change in [HF], hence the requested fraction is $[H_2F^+]/[HF] = 5.65 \cdot 10^{-8}$.

b) $2 HF + H_2O = H_3O^+ + HF_2^-$

$SiO_2 + 6 HF = SiF_6^- + 2 H_3O^+$

$CH_3COCH_3 + 2 HF = [CH_3{-}COH{-}CH_3]^+ + HF_2^-$
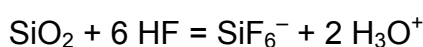
c)   The equations describing the system are:

$[HF]_{total} = [HF] + [F^-] + 2 \cdot [HF_2^-]$ (fluorine balance)

$[F^-] + [HF_2^-] = [H_3O^+]$ (charge balance)

From the charge balance: $[F^-] = [H_3O^+] - [HF_2^-]$.
Substituting into the fluorine balance: $[HF] = [HF]_{total} - [H_3O^+] - [HF_2^-]$.
The equilibrium constants:

$$K_1 = \frac{[H_3O^+][F^-]}{[HF]} = \frac{[H_3O^+]([H_3O^+] - [HF_2^-])}{[HF]}$$

$$K_2 = \frac{[HF_2^-]}{[HF][F^-]} = \frac{[HF_2^-]}{[HF]\cdot([H_3O^+] - [HF_2^-])}$$

$[H_3O^+] = 0.01$ mol/dm^3

Solving the equations we obtain: $[HF] = 0.0889$ mol/dm^3, $[HF]_{total} = 0.0991$ mol/dm^3.

d) Expressing the equilibrium constant for (1) as a function of $[H_3O^+]$, $[HF]_{total}$, and $[HF_2^-]$ gives:

$$K_1 = \frac{[H_3O^+]([H_3O^+] - [HF_2^-])}{[HF]_{total} - [H_3O^+] - [HF_2^-]}$$

Not considering equilibrium (2) the calculation goes as:

$$K_1' = \frac{[H_3O^+]^2}{[HF]_{total} - [H_3O^+]}$$

Clearly, the two expressions will be equal only in very special cases, i.e. the measurements can indeed indicate non-constant K_1'.

e) The two values for the equilibrium constant were found to be the same:

$$\frac{[H_3O^+]([H_3O^+] - [HF_2^-])}{[HF]_{total} - [H_3O^+] - [HF_2^-]} = \frac{[H_3O^+]^2}{[HF]_{total} - [H_3O^+]}$$

From this equation $[HF]_{total} = 2[H_3O^+]$
Substituting this into the expressions for K_1, we obtain $K_1 = [H_3O^+]$.
That is, $[HF]_{total} = 2K_1 = 0.0022$ mol/dm^3.

f) $K = K_1 \cdot K_2 = 2.86 \cdot 10^{-4}$.

g) E.g. NaOH, CaCl$_2$, Na$_2$CO$_3$, FeCl$_3$, AlCl$_3$, etc.

h) $2\,HF + SbF_5 = SbF_6^- + H_2F^+$

i) The weaker the solvation the greater the acidity.

j) $CH_4 + HSbF_6 = [CH_5^+][SbF_6^-] \rightarrow [CH_3^+][SbF_6^-] + H_2$
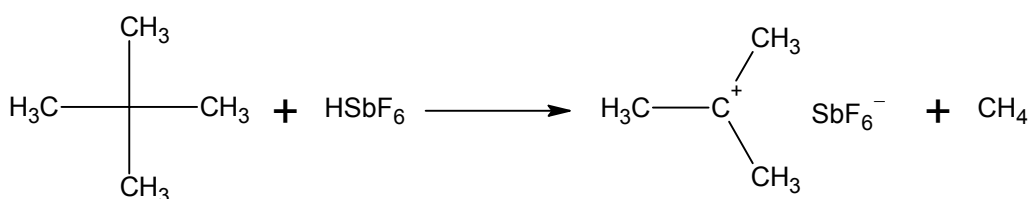
Problem 9

Sulfuric acid acidifies the solution, so all the sulfide and hydrogen sulfide ions are converted to H_2S which is distilled into the cadmium nitrate solution.
The amount of sulfuric acid added is 0.4996 mmol. The amount of NaOH that reacted with the excess sulfuric acid is 0.5487 mmol. So, the amount of the hydrogen ions that reacted is 0.4505 mmol.
Hydrogen ions from sulfuric acid can react in two ways:

$S^{2-} + 2 H_3O^+ = H_2S + 2 H_2O$

$NH_3 + H_3O^+ = NH_4^+ + H_2O$ (in the case of excess ammonia)
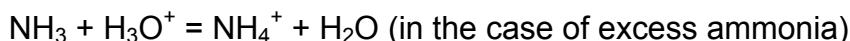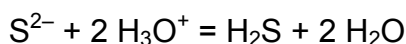
To decide between the two cases let us see what happens in the collector flask:

$Cd^{2+} + H_2S + 2 H_2O = \underline{CdS} + 2 H_3O^+$

$CdS + 4 Br_2 + 12 H_2O = Cd^{2+} + SO_4^{2-} + 8 Br^- + 8 H_3O^+$
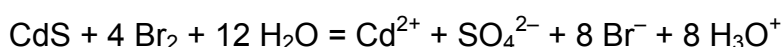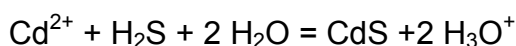
So, 1 mol of H_2S causes the formation of 10 moles of H_3O^+ (2 moles from the first and 8 moles from the second reaction).
NaOH reacts with the hydrogen ions formed in the reactions. The amount of NaOH used is 1.418 mmol. This means that there was 1.418 mmol / 10 = 0.1418 mmol of hydrogen sulfide in the collector flask.
Since the hydrogen ion equivalent of 0.1418 mmol hydrogen sulfide (0.2836 mmol) is much less than the hydrogen ions that reacted from the sulfuric acid (0.4505 mmol), we can conclude that some of the sulfuric acid reacted with excess of ammonia.
The amount of ammonia in 10.00 cm^3 of the stock solution is 0.1669 mmol.
So, the ammonia concentration of the reagent solution (which is 100 times greater than that of the stock solution) is 1.669 mol/dm^3.
Finally, the ammonium sulfide concentration in the reagent solution is 1.418 mol/dm^3.

Problem 10

a) $Cu + 4 HNO_3 \rightarrow Cu(NO_3)_2 + 2 NO_2 + 2 H_2O$

      $Ni + 4 HNO_3 \rightarrow Ni(NO_3)_2 + 2 NO_2 + 2 H_2O$

b) $IO_3^- + 5 I^- + 6 H^+ \rightarrow 3 I_2 + 3 H_2O$

      $I_2 + I^- \rightleftharpoons I_3^-$

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

      $I_3^- + 2 S_2O_3^{2-} \rightarrow 3 I^- + S_4O_6^{2-}$
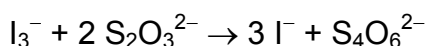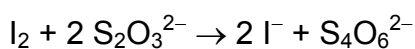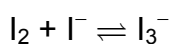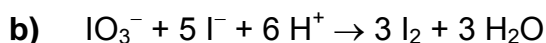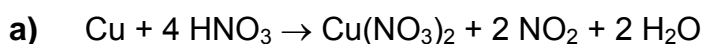
      $n(IO_3^-) = \dfrac{0.0895 \text{ g}}{214.00 \text{ g mol}^{-1}} \dfrac{10.00 \text{ cm}^3}{100.00 \text{ cm}^3} = 4.014 \cdot 10^{-5}$ mol

      $n(I_2) = 3 \cdot n(IO_3^-) = 1.2042 \cdot 10^{-4}$ mol
      $n(S_2O_3^{2-}) = 2 \cdot n(I_2) = 2.4084 \cdot 10^{-4}$ mol
      $c = n(S_2O_3^{2-}) / V(S_2O_3^{2-}) = 2.4084 \cdot 10^{-4}$ mol / 0.01046 dm^3 = 0.02302 mol/dm^3
      Starch solution.

c) $S_2O_3^{2-} + H^+ \rightarrow HSO_3^- + S$

d) $2\ Cu^{2+} + 4\ I^- \rightarrow 2\ CuI + I_2$

$I_2 + I^- \rightleftharpoons I_3^-$
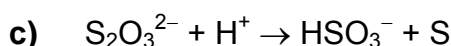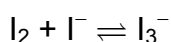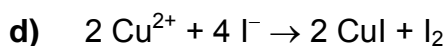
The redox reaction between Cu^{2+} and I^- is not instantaneous. Under the described conditions, 5 minutes is sufficient to ensure that the reaction is complete. Waiting hours would be a mistake, because oxygen in the air also slowly oxidizes I^-.

e) $n(S_2O_3^{2-}) = c \cdot V = 0.02302\ mol/dm^3 \cdot 0.01611\ dm^3 = 3.7085 \cdot 10^{-4}\ mol$

$n(Cu^{2+})$ (in 1.000 cm^3 stock solution) $= 2 \cdot n(I_2) = n(S_2O_3^{2-}) = 3.709 \cdot 10^{-4}\ mol$
$m(Cu) = 3.709 \cdot 10^{-2}\ mol \cdot 63.55\ g/mol = 2.357\ g$
The copper content of the 2-Ft coin is 2.357 g / 3.1422 g = 75.01 % by mass

f)   The color of the ammine complexes of both Cu^{2+} and Ni^{2+} are violet. (In reality, the color of the Cu^{2+} ammine complex is much more intense.)

Ammonia is needed to adjust the pH to a suitable value to ensure practically complete complex formation with EDTA.

g) $n(EDTA) = \dfrac{3.6811\ g}{372.25\ g\ mol^{-1}} \dfrac{10.21\ cm^3}{1000.00\ cm^3} = 1.010 \cdot 10^{-4}\ mol$

$n(Cu) + n(Ni) = 1.010 \cdot 10^{-4}\ mol \cdot 100.0\ cm^3 / 0.2000\ cm^3 = 0.05048\ mol$
From the mass of the coin:

$M(Cu) \cdot n(Cu) + M(Ni) \cdot n(Ni) = 3.1422\ g$

Solving the simultaneous equations for $n(Cu)$ and $n(Ni)$:
$n(Ni) = 0.0136\ mol \quad \Rightarrow \quad m(Ni) = 0.796\ g$
$n(Cu) = 0.0369\ mol \quad \Rightarrow \quad m(Cu) = 2.35\ g$
This result agrees with the composition calculated earlier based on the iodometric titration.

h)   The undiluted stock solution would give absorbance values higher than 2.0, which cannot be measured reliably.

The molar absorption coefficients for Cu^{2+}:
$\varepsilon(260\ nm) = 0.6847 / (0.1024\ mol \cdot dm^{-3} \cdot 1.000\ cm) = 6.687\ dm^3 mol^{-1} cm^{-1}$
$\varepsilon(395\ nm) = 0.0110 / (0.1024\ mol \cdot dm^{-3} \cdot 1.000\ cm) = 0.107\ dm^3 mol^{-1} cm^{-1}$
$\varepsilon(720\ nm) = 0.9294 / (0.1024\ mol \cdot dm^{-3} \cdot 1.000\ cm) = 9.076\ dm^3 mol^{-1} cm^{-1}$
$\varepsilon(815\ nm) = 1.428 / (0.1024\ mol \cdot dm^{-3} \cdot 1.000\ cm) = 13.95\ dm^3 mol^{-1} cm^{-1}$
 The molar absorption coefficients for Ni^{2+}:
$\varepsilon(260\ nm) = 0.0597 / (0.1192\ mol \cdot dm^{-3} \cdot 1.000\ cm) = 0.501\ dm^3 mol^{-1} cm^{-1}$
$\varepsilon(395\ nm) = 0.6695 / (0.1192\ mol \cdot dm^{-3} \cdot 1.000\ cm) = 5.617\ dm^3 mol^{-1} cm^{-1}$
$\varepsilon(720\ nm) = 0.3000 / (0.1192\ mol \cdot dm^{-3} \cdot 1.000\ cm) = 2.517\ dm^3 mol^{-1} cm^{-1}$
$\varepsilon(815\ nm) = 0.1182 / (0.1192\ mol \cdot dm^{-3} \cdot 1.000\ cm) = 0.9916\ dm^3 mol^{-1} cm^{-1}$

The concentrations of the diluted stock solution can be obtained by solving the following simultaneous equations:
$A\ (815\ nm) = (\varepsilon(815\ nm, Cu) \cdot c(Cu) + \varepsilon(815\ nm, Ni) \cdot c(Ni)) \cdot 1.000\ cm$
$A\ (395\ nm) = (\varepsilon(395\ nm, Cu) \cdot c(Cu) + \varepsilon(395\ nm, Ni) \cdot c(Ni)) \cdot 1.000\ cm$

$c(Cu) = 0.07418\ mol/dm^3 \quad c(Ni) = 0.02677\ mol/dm^3$ for the diluted solution

The concentrations of the stock solution are five times greater.
$c(Cu) = 0.3709$ mol/dm^3 $c(Ni) = 0.1338$ mol/dm^3
For the total volume of the stock solution (100.0 cm^3):
$n(Cu) = 0.03709$ mol $n(Ni) = 0.01338$ mol
This composition is in agreement with the titration results.

i) The expected absorbance value at 720 nm:

A (720 nm) = $(\varepsilon(720$ nm,Cu$)\cdot c(Cu) + \varepsilon(720$ nm,Ni$)\cdot c(Ni))\cdot 1.000$ cm = 0.7404
This is in agreement with the measured value.

j) The expected absorbance value at 260 nm:

A (260 nm) = $(\varepsilon(260$ nm,Cu$)\cdot c(Cu) + \varepsilon(260$ nm,Ni$)\cdot c(Ni))\cdot 1.000$ cm = 0.5093
This does not agree with experimental observations.

k) The spectrophotometer reading of 6.000 means that practically no light goes through the sample. This is unchanged in a shorter cell.

The molar absorbances of Cu^{2+} and Ni^{2+} were measured using $CuCl_2$ and $NiCl_2$ solutions. Nitric acid was used to dissolve the coin, so the concentration of the nitrate ion is high in the stock solution. The observations can be explained if the nitrate ion absorbed at 260 nm. This can be confirmed by recording the UV-VIS spectrum of a sample of dilute nitric acid.

Problem 11

a) The electrode gives a Nernstian response with a slope of 59.1 mV/decade at all three pH values used for the calibration. The electrode potential in millivolts is:

$$E = E° - 59.1\cdot \lg[CN^-]$$

The equilibrium concentration of CN^- can be given as a function of the analytical concentration and pH:

$$[CN^-] = \frac{[CN^-]_{total}}{1 + \dfrac{[H^+]}{K_a}}$$

Applying these two equations for a pair of points with identical analytical concentration of cyanide gives:

$$K_a = \frac{[H^+]_{pH1} - X[H^+]_{pH2}}{X - 1} \qquad \text{where} \quad X = 10^{\frac{E_{pH1} - E_{pH2}}{59.1 \text{ mV}}}$$

Applying this equation for pH1 = 12 and pH2 = 7.5 gives (at all three NaCN concentrations $E_{pH1} - E_{pH2} = -101.6$ mV):

$K_a = 6.15\cdot 10^{-10}$

b) $4\ Fe^{2+} + O_2 + 10\ H_2O \rightarrow 4\ Fe(OH)_3 + 8\ H^+$

c) $Fe^{2+} + 6\ CN^- \rightarrow [Fe(CN)_6]^{4-}$

The concentration of the NaCN solution is 0.0010 mol/dm^3. From the calibration of the electrode it follows that $E^o = 220.1$ mV and:

$$[CN^-]_{eq} = 10^{\frac{E^o - E}{59.1\,mV}}$$

The electrode reading is 585.9 mV at pH = 7.5. From this:

$[CN^-]_{eq} = 6.46 \cdot 10^{-7}$ mol/dm^3 $\Rightarrow$ $[HCN]_{eq} = [H^+]_{eq}[CN^-]_{eq}/K_a = 3.32 \cdot 10^{-5}$ mol/dm^3

The concentration of complexed cyanide is then:

$[CN^-]_{compl} = [CN^-]_{total} - [CN^-]_{eq} - [HCN]_{eq} = 9.66 \cdot 10^{-4}$ mol/dm^3

All complexed cyanide is in the hexacyano iron(II) complex, therefore its concentration is:

$[Fe(CN)_6{}^{4-}]_{eq} = [CN^-]_{compl}/6 = 1.61 \cdot 10^{-4}$ mol/dm^3

The total amount of iron(II) added is $1.44 \cdot 10^{-4}$ mol
The amount of iron(II) that reacts with O_2 is $1.00 \cdot 10^{-4}$ mol
The amount of iron(II) present as the hexacyano complex is $1.61 \cdot 10^{-5}$ mol
The concentration of free iron(II) is $2.78 \cdot 10^{-4}$ mol/dm^3
The stability product is:

$$\beta_6 = [Fe(CN)_6{}^{4-}]_{eq}/([Fe^{2+}]_{eq}[CN^-]_{eq}{}^6) = 7.99 \cdot 10^{36}$$

d) The concentrations of free CN^- and HCN are $[CN^-]_{eq} = 6.46 \cdot 10^{-7}$ mol/dm^3 and $[HCN]_{eq} = 3.32 \cdot 10^{-5}$ mol/dm^3, respectively. This corresponds to a total noncomplexed cyanide concentration of 0.88 mg/dm^3, which is less than half of the LC_{50} value. The concentration of practically non-toxic $[Fe(CN)_6]^{4-}$ is high. These data are in agreement with the presented experiment, although prolonged exposure to these conditions would probably cause adverse health effects in fish.

e) $2\,Cu^{2+} + 2\,CN^- \rightarrow 2\,Cu^+ + (CN)_2$

$Cu^+ + n\,CN^- = [Cu(CN)_n]^{(n-1)-}$ (n = 2-3)
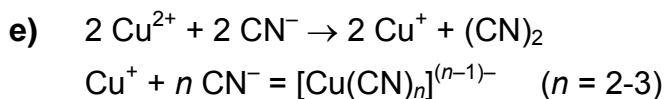
f) From the electrode reading and the pH $[CN^-]_{eq} = 4.77 \cdot 10^{-6}$ mol/dm^3

Since $[Cu^+] = 2 \cdot 10^{-15}$ mol/dm^3, the product of the two concentrations is $< L_{CuCN}$, therefore there is no precipitation of CuCN.

g) $[Cu^+]_{tot} = 0.021$ g/dm^3 / 63.55 g/mol $= 3.30 \cdot 10^{-4}$ mol/dm^3, practically all complexed.

$[CN^-]_{total} = 0.026$ g/dm^3 / 26.02 g/mol $= 1.00 \cdot 10^{-3}$ mol/dm^3

The concentration of cyanide ions:

$[CN^-]_{eq} = 4.77 \cdot 10^{-6}$ mol/dm^3 $\Rightarrow$ $[HCN]_{eq} = 2.45 \cdot 10^{-4}$ mol/dm^3

$[CN^-]_{compl} = [CN^-]_{total} - [CN^-]_{eq} - [HCN]_{eq} = 7.50 \cdot 10^{-4}$ mol/dm^3

The average number of ligands in cyanocopper complexes:

$[CN^-]_{compl}/[Cu^+]_{tot} = 2.27$

This means that the mixture contains $[Cu(CN)_2]^-$ and $[Cu(CN)_3]^{2-}$ complexes.

$[Cu(CN)_3{}^{2-}]_{eq} = [CN^-]_{compl} - 2 \cdot [Cu^+]_{tot} = 8.9 \cdot 10^{-5}$ mol/dm^3

$[Cu(CN)_2{}^-]_{eq} = ([CN^-]_{compl} - 3 \cdot [Cu(CN)_3{}^{2-}]_{eq})/2 = 2.4 \cdot 10^{-4}$ mol/dm^3

Therefore:

$\beta_2 = [Cu(CN)_2^-]_{eq}/([Cu^+]_{eq}[CN^-]_{eq}^2) = 5.3 \cdot 10^{21}$

$\beta_3 = [Cu(CN)_3^{2-}]_{eq}/([Cu^+]_{eq}[CN^-]_{eq}^3) = 4.1 \cdot 10^{26}$

h)   From the electrode reading and the pH:

$[CN^-]_{eq} = 5.04 \cdot 10^{-7}$ mol/dm^3 $\Rightarrow$ $[HCN]_{eq} = 2.59 \cdot 10^{-5}$ mol/dm^3

$[CN^-]_{compl} = [CN^-]_{total} - [CN^-]_{eq} - [HCN]_{eq} = 9.74 \cdot 10^{-4}$ mol/dm^3

The total amount of iron(II) added is $1.44 \cdot 10^{-4}$ mol, of this $1.00 \cdot 10^{-4}$ mol reacts with O_2. The total iron(II) concentration remaining in the solution is therefore $4.4 \cdot 10^{-4}$ mol/dm^3.

From the definition of β_6 and conservation of mass:

$\beta_6[CN^-]_{eq}^6 = [Fe(CN)_6^{4-}]_{eq}/([Fe^{2+}]_{tot} - [Fe(CN)_6^{4-}]_{eq})$

Solving this equation gives
$[Fe(CN)_6^{4-}]_{eq} = 5.04 \cdot 10^{-5}$ mol/dm^3 and $[Fe^{2+}]_{eq} = [Fe^{2+}]_{tot} - [Fe(CN)_6^{4-}]_{eq} = 3.9 \cdot 10^{-4}$ mol/dm^3

Combining the two complex formation reactions gives the following:

$3\ [Cu(CN)_2]^- + Fe^{2+} = 3\ Cu^+ + [Fe(CN)_6]^{4-}$
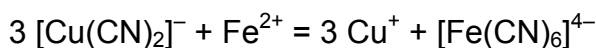
$K_{R1} = \beta_6/\beta_2^3 = 5.34 \cdot 10^{-29}$

From this process the following ratio can be calculated:

$$\frac{[Cu^+]_{eq}}{[Cu(CN)_2^-]_{eq}} = \sqrt[3]{K_{R1}\frac{[Fe^{2+}]_{eq}}{[Fe(CN)_6^{4-}]_{eq}}} = 7.43 \cdot 10^{-10}$$

This means that practically all the copper is complexed in the solution.
The concentration of cyanide complexed in copper complexes:

$[CN^-]_{Cu,compl} = [CN^-]_{compl} - 6 \cdot [Fe(CN)_6^{4-}]_{eq} = 6.73 \cdot 10^{-4}$ mol/dm^3

Therefore the concentrations of cyanocopper complexes are:

$[Cu(CN)_3^{2-}]_{eq} = [CN^-]_{Cu,compl} - 2 \cdot [Cu^+]_{tot} = 1 \cdot 10^{-5}$ mol/dm^3

$[Cu(CN)_2^-]_{eq} = ([CN^-]_{Cu,compl} - 3 \cdot [Cu(CN)_3^{2-}]_{eq})/2 = 3.2 \cdot 10^{-4}$ mol/dm^3

Precipitation of CuCN is possible, and this should be checked for:

$[Cu^+]_{eq} = 7.45 \cdot 10^{-10} \cdot [Cu(CN)_2^-]_{eq} = 2.4 \cdot 10^{-13}$ mol/dm^3

$[Cu^+]_{eq}[CN^-]_{eq} = 1.2 \cdot 10^{-19} < L_{CuCN}$

This solution contains toxic $[Cu(CN)_2]^-$ in high concentration relative to the lethal concentration (37 mg/dm^3 > LC$_{50}$), so it is toxic in agreement with the experiment not shown on TV.

Problem 12

a) $E^o_3 = (3\ E^o_2 - 2\ E^o_1) = 0.772$ V

b) $E_3 = E^o_3 + 0.059\ lg([Fe^{3+}]/[Fe^{2+}]) = 0.710$ V

$([Fe^{3+}]/[Fe^{2+}]) = 0.0890$

A very rough estimate:

$$K_{st} = \frac{[FeCl^{2+}]}{[Fe^{3+}][Cl^-]} = \frac{0.911}{0.089 \cdot 0.089} = 115$$

c)　　$E^o_4 = 0.356$ V

$$\beta_6(FeIII) = \frac{[Fe(CN)_6^{3-}]}{[Fe^{3+}] \cdot [CN^-]^6}$$

$$\beta_6(FeII) = \frac{[Fe(CN)_6^{4-}]}{[Fe^{2+}] \cdot [CN^-]^6}$$

$E^o_4 = E^o_3 + 0.059 \, lg(\beta_6(FeII)/\beta_6(FeIII))$

$\beta_6(FeII)/ \beta_6(FeIII) = 10^{-7.05} = 8.90 \cdot 10^{-8}$

d)　　$E = \dfrac{n_5 E_5^{o\prime} + n_6 E_6^o}{n_5 + n_6}$

$H_3AsO_4 + 2H^+ + 2e^- = H_3AsO_3 + H_2O$
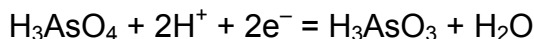
$E^o_5{}' = E^o_5 + (0.059/2) \, lg \, [H_3O^+]^2 = E^o_5 - 0.059 \, pH = 0.442$ V

$E = (2 \cdot 0.442 + 0.356)/3 = 0.413$ V

$0.413 = 0.442 + 0.059/2 \, lg([H_3AsO_4]/[H_3AsO_3])$

$[H_3AsO_4]/[H_3AsO_3] = 0.107$

e)　　$E_6 = E^o_6 + 0.059/2 \, lg([I_3^-]/ [I^-]^3) = 0.540 + (0.059/2) \cdot 2 = 0.599$ V

$E_5 = 0.599$ V $= 0.560 - 0.059 \, pH$

$pH = -0.66$

Problem 13

a)　　$T_1 = 282.85$ K and $L_1 = 2.10 \cdot 10^{-11}$. Therefore $\Delta_r G^o_1 = -RT_1 \ln L_1 = 57.8$ kJ/mol.

　　$T_2 = 298.15$ K and $L_2 = 1.56 \cdot 10^{-10}$. Therefore $\Delta_r G^o_2 = -RT_2 \ln L_2 = 56.0$ kJ/mol.

Using $\Delta G = \Delta H - T\Delta S$ gives $\Delta_r S^o = 119$ J mol^{-1} K^{-1} and $\Delta_r H^o = 91.3$ kJ mol^{-1}, if we assume that $\Delta_r H^o$ and $\Delta_r S^o$ are independent of temperature in this limited range.

Extrapolating to 50 °C $\Delta_r G^o_3$ is 53.0 kJ/mol, thus $L_3 = \exp(-\Delta_r G^o/RT) = 2.71 \cdot 10^{-9}$. The solubility is $c = \sqrt{L_3} = 5.2 \cdot 10^{-5}$ mol/dm^3, that is 7.5 mg/dm^3.

b)　　Let us suppose that the concentration of Cl$^-$ ions is relatively high at equilibrium. This means that [Ag$^+$] is relatively low and it can be neglected in comparison with [AgCl$_2^-$].

$[AgCl]_{total} = 5.2 \cdot 10^{-5}$ mol/dm^3 = $[AgCl_2^-] + [Ag^+] \approx [AgCl_2^-]$

$$\beta = \frac{[AgCl_2^-]}{[Ag^+][Cl^-]^2} = \frac{[AgCl]_{total}}{L[Cl^-]}$$

Therefore $[Cl^-] = \dfrac{[AgCl]_{total}}{L\beta} = 1.34$ mol/dm³.

$[KCl]_{total} = [Cl^-] + 2[AgCl_2^-] \approx [Cl^-] = 1.34$ mol/dm³.

c) $Zn + 2 H^+ \rightarrow Zn^{2+} + H_2$
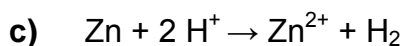
d) <u>Cu^{2+} ions</u>:

Since $E^o(Cu^{2+}/Cu) > E^o(Cu^{2+}/Cu^+) >> E^o(Zn^{2+}/Zn)$, the preferred reaction is:

$Cu^{2+}(aq) + Zn(Hg) \rightarrow Cu(s) + Zn^{2+}(aq)$
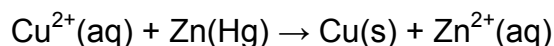
<u>Cr^{3+} ions</u>:

$E^o(Cr^{3+}/Cr^{2+}) = \dfrac{3 \cdot (-0.74\ V) - 2 \cdot (-0.90\ V)}{1} = -0.42$ V

Since $E^o(Cr^{3+}/Cr^{2+}) > E^o(Cr^{3+}/Cr) >> E^o(Zn^{2+}/Zn) > E^o(Cr^{2+}/Cr)$, the preferred reaction is:
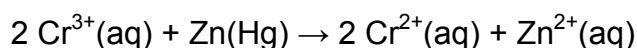
$2\ Cr^{3+}(aq) + Zn(Hg) \rightarrow 2\ Cr^{2+}(aq) + Zn^{2+}(aq)$

<u>$VO_2^{\pm}$ ions</u>:

$VO_2^+ + 2H^+ + e^- \rightarrow VO^{2+} + H_2O$

At pH = 1 $E^{o'}(VO_2^+/VO^{2+}) = 1.00$ V + 0.059 V·lg $0.1^2 = 0.88$ V.

$VO^{2+} + 2H^+ + e^- \rightarrow V^{3+} + H_2O$
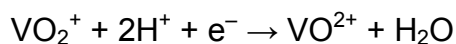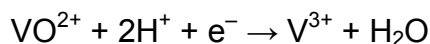
At pH = 1, $E^{o'}(VO^{2+}/V^{3+}) = 0.36$ V + 0.059 V·lg $0.1^2 = 0.24$ V.

$E^o(V^{3+}/V^{2+}) = -0.255$ V

Since all three half-reactions have a standard potential higher than the Zn^{2+}/Zn system, vanadium reaches an oxidation number of +2. The standard potential for further reduction is lower; therefore the preferred reaction is:

$2\ VO_2^+(aq) + 3\ Zn(Hg) + 8\ H^+(aq) \rightarrow 2\ V^{2+}(aq) + 3\ Zn^{2+}(aq) + 4\ H_2O(l)$
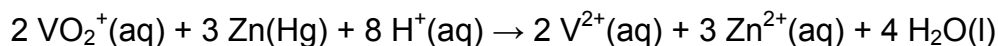
e) Amalgamation supposedly does not change the zinc potential.

$Cu^{2+}(aq) + Zn(Hg) \rightarrow Cu(s) + Zn^{2+}(aq)$
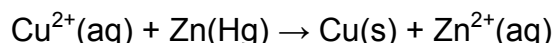
The number of electrons is $n = 2$.

$E^o{}_{cell} = 0.34$ V − (−0.76 V) = 1.10 V.

$K_1 = e^{\frac{nFE^o_{cell}}{RT}} = 1.6 \cdot 10^{37}$

$2\ Cr^{3+}(aq) + Zn(Hg) \rightarrow 2\ Cr^{2+}(aq) + Zn^{2+}(aq)$
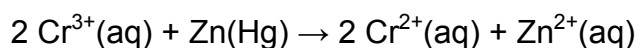
The number of electrons is $n = 2$.

$E^o{}_{cell} = -0.40$ V − (−0.76 V) = 0.36 V.

$K_2 = e^{\frac{nFE^o_{cell}}{RT}} = 1.5 \cdot 10^{12}$

$2\ VO_2^+ + 3\ Zn + 8\ H^+ \rightarrow 2\ V^{2+} + 3\ Zn^{2+} + 4\ H_2O$
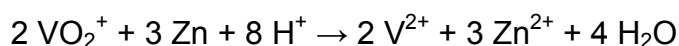
The number of electrons is $n = 6$.

For the half reaction $VO_2^+ + 4H^+ + 3e^- \rightarrow V^{2+} + 2H_2O$:

$$E^o = \frac{1.00V + 0.36V - 0.255V}{3} = 0.368V$$

At pH = 1, $E^{o'} = 0.368V + \frac{0.059V}{3} \cdot \lg 0.1^4 = 0.290$ V

$E^o{}_{cell} = 0.290$ V $- (-0.76$ V$) = 1.05$ V.

$$K_3 = e^{\frac{nFE^o_{cell}}{RT}} = 2.9 \cdot 10^{106}$$

f) The reaction that takes place is:

$Fe^{3+}(aq) + Ag(s) \rightleftharpoons Fe^{2+}(aq) + Ag^+(aq)$
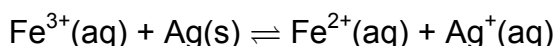
$E^o{}_{cell} = 0.77$ V $- 0.80$ V $= -0.03$ V

$$K_4 = e^{\frac{nFE^o_{cell}}{RT}} = 0.31$$

If $[Ag^+] = [Fe^{2+}] = x$, $[Fe^{3+}] = 0.05 - x$, thus:

$$\frac{x^2}{0.05 - x} = 0.31$$

From here $x = [Ag^+] = [Fe^{2+}] = 4.4 \cdot 10^{-2}$ mol/dm^3 and $[Fe^{3+}] = 6 \cdot 10^{-3}$ mol/dm^3.
Thus 88 % of the Fe^{3+} ions are reduced.

g) The reaction taking place is:

$Fe^{3+}(aq) + Ag(s) + Cl^-(aq) \rightleftharpoons Fe^{2+}(aq) + AgCl(s)$
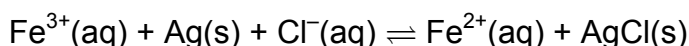
The potential of the half reaction $AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq)$ is:

$$E^{o'} = 0.80 \text{ V} + 0.059 \text{ V} \cdot \lg \frac{L_2}{[Cl^-]} = 0.22 \text{ V}$$

$E^o{}_{cell} = 0.77V - 0.22$ V $= 0.55$ V.

$$K_5 = e^{\frac{nFE^o_{cell}}{RT}} = 1.99 \cdot 10^9$$

h) If $[Fe^{3+}] = y$, $[Fe^{2+}] = 0.05 - y \approx 0.05$ mol/dm^3, $[Cl^-] = 1 - y \approx 1$ mol/dm^3 (since the equilibrium constant is relatively high).

$$K_5 = \frac{[Fe^{2+}]}{[Fe^{3+}][Cl^-]} = \frac{0.05}{y} = 1.99 \cdot 10^9 .$$

From here, $y = [Fe^{3+}] = 2.51 \cdot 10^{-11}$ mol/dm^3.

i) Both reactions have a standard potential under 0.22 V, so the cations are not reduced.

Problem 14

a)

| A | B | C | D | E |
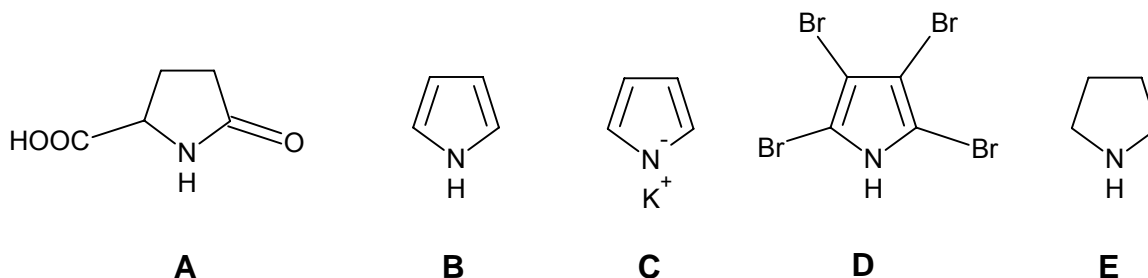
b) The pyrrole anion is aromatic; the pyrrole cation has two conjugated double bonds, and is non aromatic, thus less stable.

c) **E** is a stronger base having a localized lone pair on the N.

d) Polymerization occurs by reaction at the conjugated double bonds. The resulting polymeric compounds have several conjugated π systems.

Problem 15

a)

$n = 0$ $n = 1$ $n = 2$
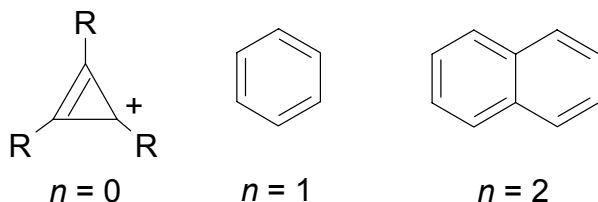
b) Fusion of an aromatic ring with 6 π electrons to a linear, aromatic chain, which has $4n+2$ π electrons implies that we will lose two aromatic carbon atoms, hence the total number of π electrons is: $4n + 2 + 6 - 2 = 4(n + 1) + 2$, i.e., the Hückel condition is satisfied.

c) Fusion of two linear chains of fused aromatics via 2 carbon atoms means that the total number of π electrons is $4n_1 + 2 + 4n_2 + 2 - 2 = 4(n_1 + n_2) + 2$, consequently the structure is aromatic according to Hückel.

d) A possible criterion can be that the fusion should involve $4n+2$ aromatic carbon atoms, where n is a nonnegative integer.

e) For example coronene.
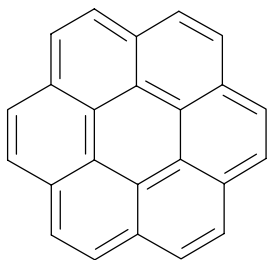
f) The conjugate base of cyclopentadiene is aromatic.

g)
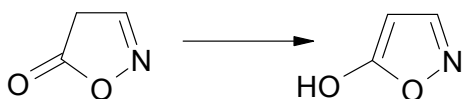
h)
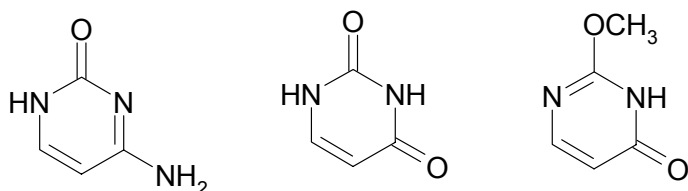
The first is cytosine, the second is uracil. The essential role of these tautomeric forms is to participate in the hydrogen bonds of the nucleic acid chains. The aromatic tautomers would form fewer hydrogen bonds within the DNA base-pairs.
Additional examples are guanine and thymine. (Adenine remains aromatic.)

Problem 16

a) $26 = 4 \cdot 6 + 2$, hence it is aromatic.
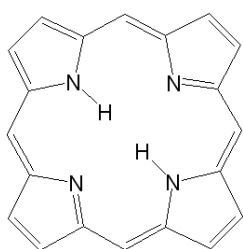
b)　　They are constitutional isomers or tautomers.

The number of π electrons is not affected by the rearrangement.
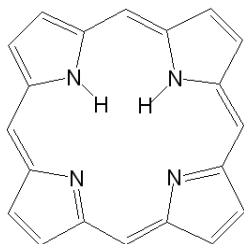
c)　We have two constitutional isomers. The migration of the proton (and the subsequent rearrangement of the aromatic electrons) is so fast that the different tautomers cannot be isolated.

d)　We can isolate 11 constitutional isomers.

e)　The number of π electrons is the same: 26.

With one methyl substituent one can form 2 constitutional isomers.

f)　For electrostatic reasons

g)　The equilibrium concentrations can be derived from:

$$\frac{[PL_2]}{[PL]} = K_2[L] = 1900 \text{ and } \frac{[PL_2]}{[P]} = K_1 K_2[L]^2 = 285000$$

Thus $[PL_2]$ = 1900 [PL] and $[PL_2]$ = 285000 [P]. Clearly, both [PL] and [P] are negligible compared to $[PL_2]$.

h)　Kinetic stability decreases as the temperature increases. (In other words the significance of the kinetic stability diminishes with increasing temperature.)

i)　The following net reaction can be postulated:

$$PL + PL \rightleftharpoons P + PL_2$$
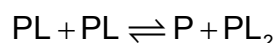
This follows from the fact that both ligand association equilibria are strongly shifted toward the ligand-uptake direction. The above equilibrium can also be derived from the original equilibria and subsequently the corresponding equilibrium constant can be written as follows:

$$\frac{K_2}{K_1} = \frac{[P][PL_2]}{[PL]^2} = 12.67$$

Assuming that x mol/dm^3 from the original [PL] concentration is transformed into P and PL_2 the equilibrium [P] and $[PL_2]$ concentrations are $x/2$ mol/dm^3. [PL] is $0.1 - x$. Solving this equation the equilibrium concentrations are:

[P] = $[PL_2]$ = 0.0438 mol/dm^3　　　　　　　　[PL] = 0.0123 mol/dm^3

$$[L] = \frac{[PL_2]}{[PL] \cdot K_2} = 0.000187 \text{ mol/dm}^3$$

Problem 17

a)

enantiomer   diastereomer

A
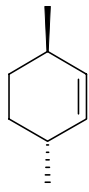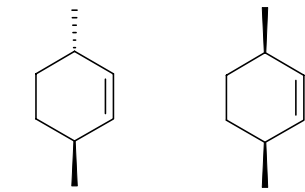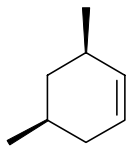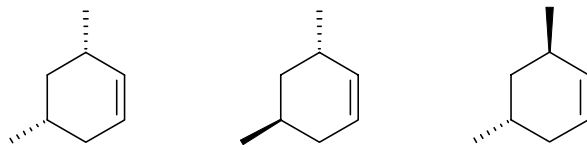
enantiomer   diastereomer-1   diastereomer-2

B
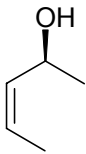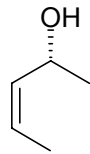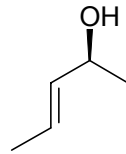
enantiomer   diastereomers according to definition

C
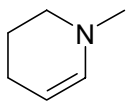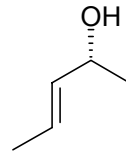
no stereoisomer due to the facile
racemization at the pyramidal N atom
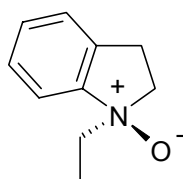
D
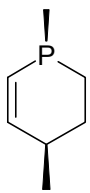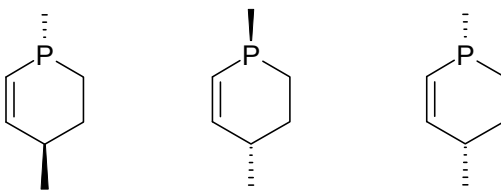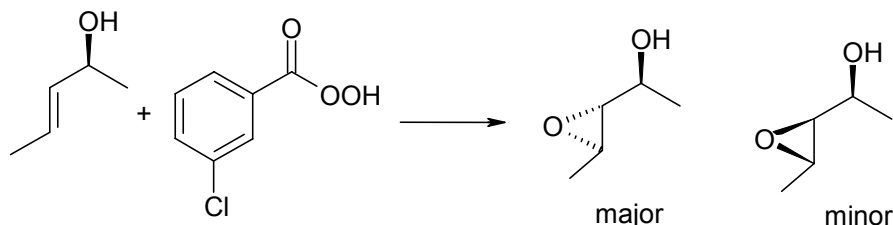

diastereomer-1   diastereomer-2   enantiomer

E

enantiomer

F
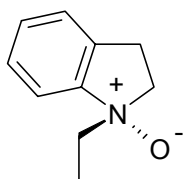
b) The primary step in the process is hydroboration of the olefin. This is a *syn-*addition and can give rise to two intermediates of which the one shown is favored for steric reasons. Reaction of the intermediate with hydrogen peroxide proceeds with the retention of chirality giving a major product with good diastereoselectivity. A little of the hydroboration might proceed from the other face of the molecule giving rise to a minor product after oxidative work up.

major
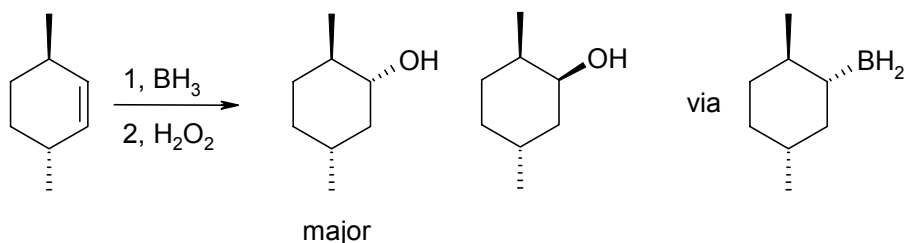
The so-called iodolactonization of olefins starts with the activation of the double bond by the electrophilic iodine giving the depicted intermediate. Since the top face of the double bond is sterically more hindered, attack is preferentially from the bottom. Intramolecular nucleophilic attack by the carboxylate ion on the iodonium species leads to diastereoselective formation of the depicted (sole) product.
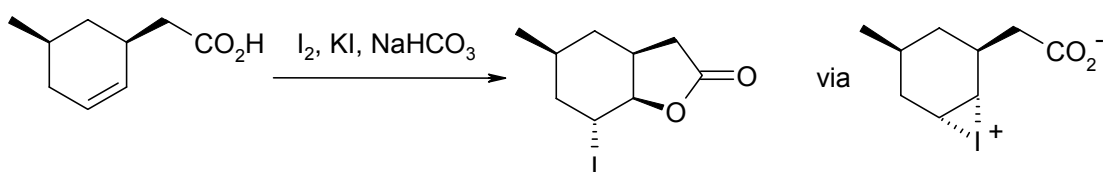
Epoxidation of the double bond by meta-chloroperbenzoic acid is directed by steric factors. The predominant site of attack is the sterically less hindered side of the double bond giving the "threo" compound as the major product. Attack from the other face is less facile and only small amounts of the „erythro" product are formed.

major   minor

Cis-dihydroxylation of the starting material by osmiumtetroxide gives rise to diastereoselective formation of the depicted product which exists as a mixture of enantiomers.
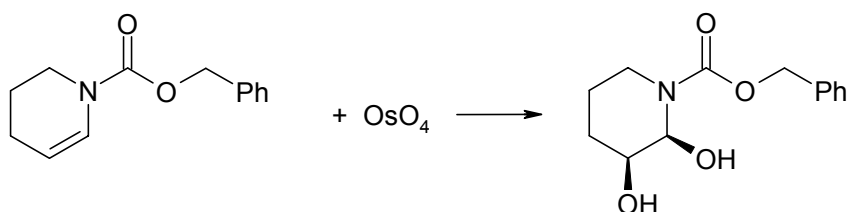
Catalytic hydrogenation proceeds on the surface of platinum and is a *syn*-addition of the hydrogen to the double bond. The preferred approach of the molecule to the catalyst surface is with the side bearing the smaller substituents. Since the steric demand of the phenyl and methyl groups exceeds that of the oxygen the reduction is diastereoselective and a single product is formed.
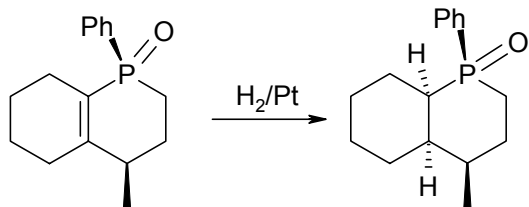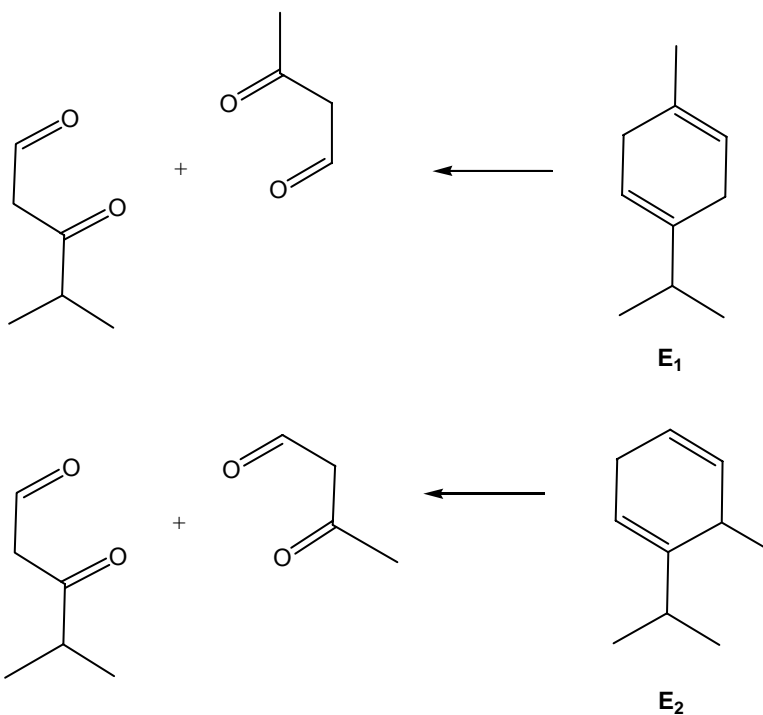

Problem 18

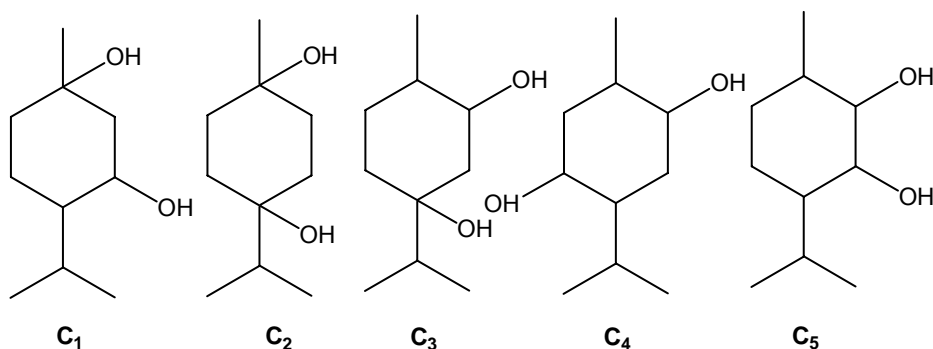As glyoxal is symmetric the structure of **D** can be determined:
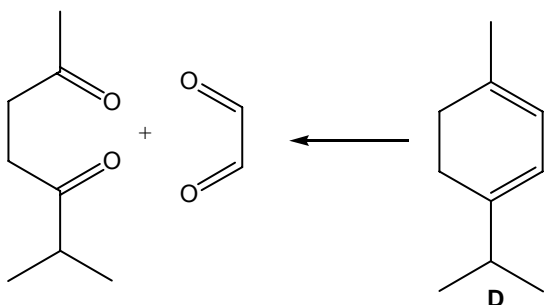
Based on its ozonolysis products, **E** has two possible structures:

As **D** and **E** are formed on dehydration of the same alcohol, both have the same carbon skeleton. Therefore, E_1 is the correct structure:

Possible structures of **C** are:

C_1 C_2 C_3 C_4 C_5

Dehydration of C_4 and C_5 only produces **E** and **D**, respectively, thus neither of these structures are correct. As **C** cannot be oxidized by chromic acid, it does not contain any secondary hydroxyl groups. C_2 is therefore the correct structure.

**B** contains one double bond. It can be either in the ring or in the isopropyl group:

B_1 B_2
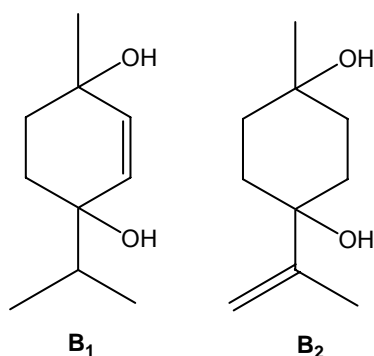
Hydroboration of B_1 leads to two structural isomers; that of B_2 to a single product, so the former is the right alternative.
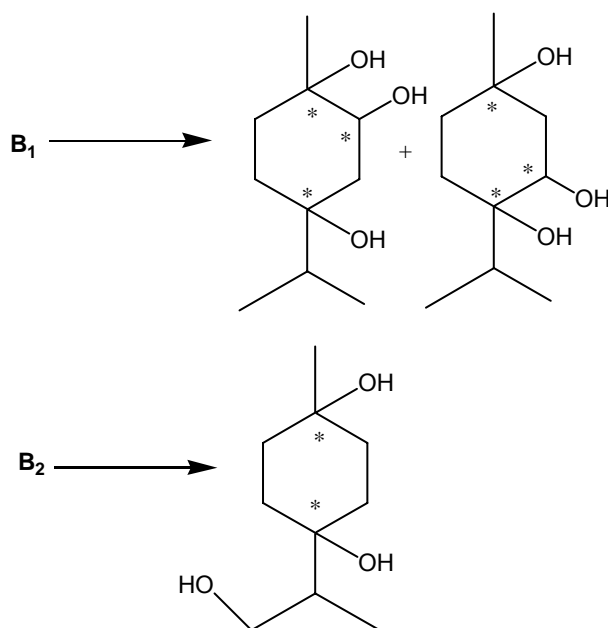
The composition of **B** is $C_{10}H_{18}O_2$, while that of **A** is $C_{10}H_{16}O_2$. The NMR spectrum shows that **A** contains only one double bond. As **A** does not react with sodium, it does not have any hydroxyl groups. The elemental composition precludes the possibility that **A** contains an ether and a hydroxyl group. Thus, in **A**, neither of the

oxygen atoms are bonded to a hydrogen atom, despite this **A** contains only two hydrogen atoms less than **B**. This is only possible if the two oxygen atoms are bonded to each other, i.e., **A** contains a peroxide bond. This finding explains its reduction by LiAlH$_4$ and hydrogen to a diol, as well as its explosive property.


A
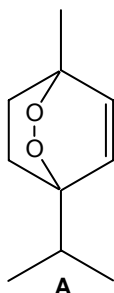
Formally **A** can be formed via an addition reaction from **D** and oxygen (**F**). This reaction indeed happens on irradiation in the presence of a photosensitiser (e.g., chlorophyll). It can be shown that reaction occurs with the excited (singlet) state of oxygen, not the triplet ground state. The reaction is a Diels–Alder type addition with singlet oxygen as a dienophile.
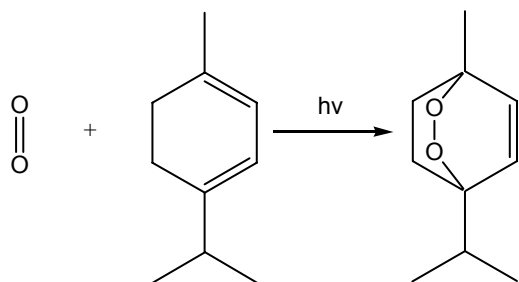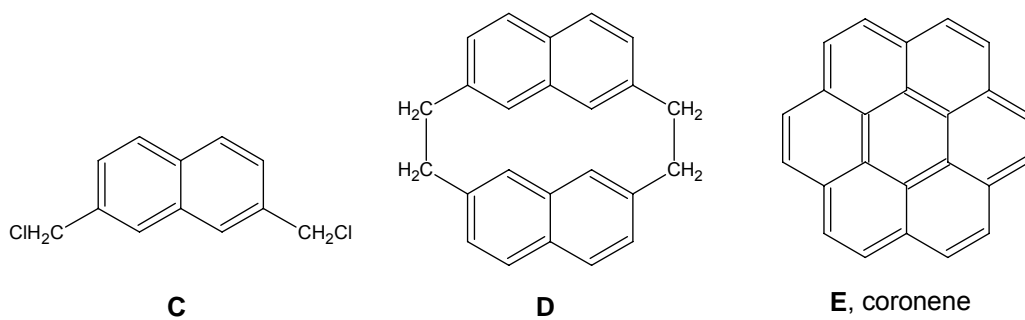

Problem 19

a) i. Radical bromination: Br$_2$/UV or N-bromosuccinimide, then Mg + diethyl ether (iodine as catalyst)
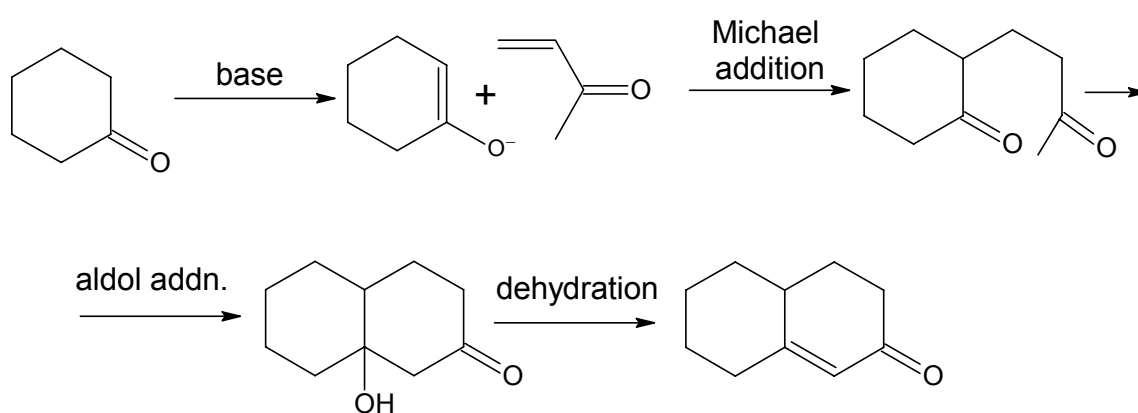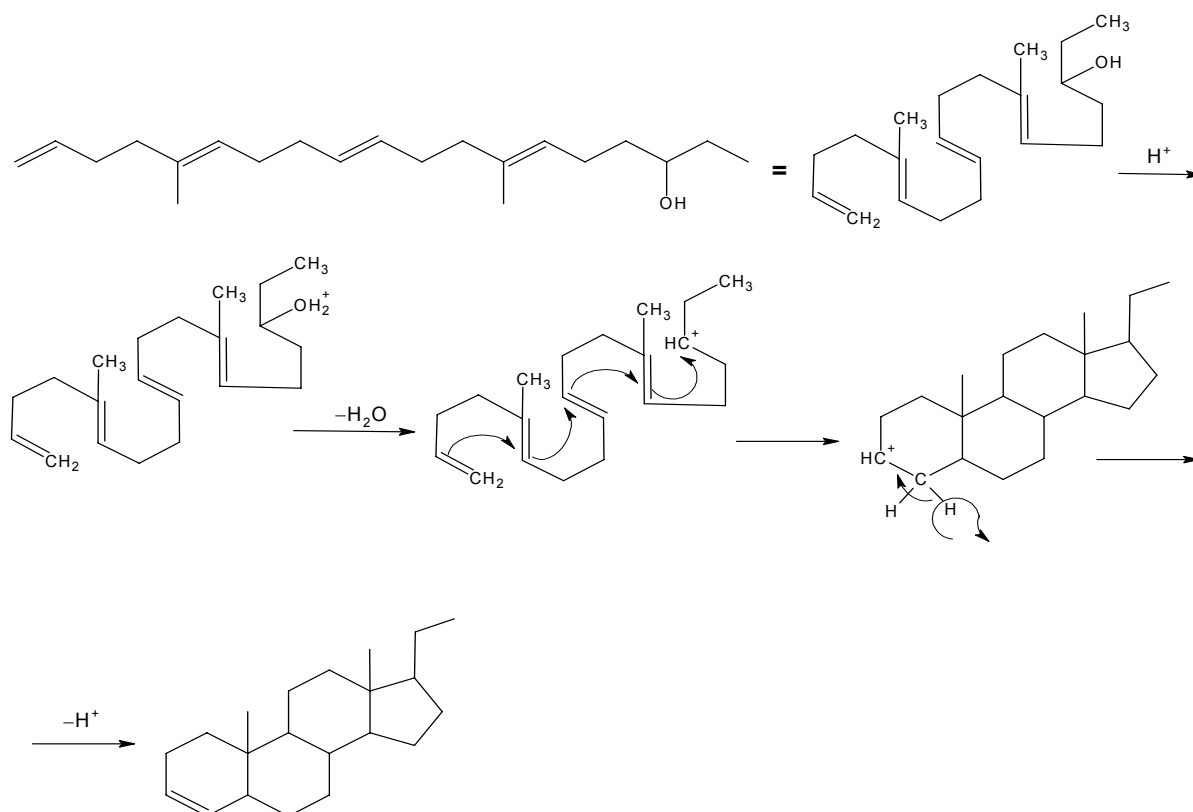
ii. ethylene glycol, acid catalysis

b)

c)

C   **D**   **E**, coronene

Problem 20

a)

b)

c)
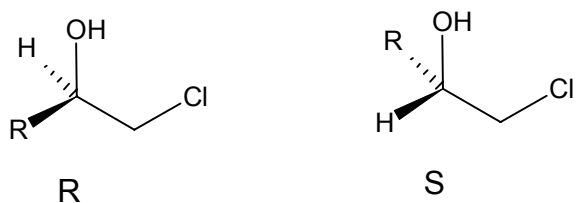
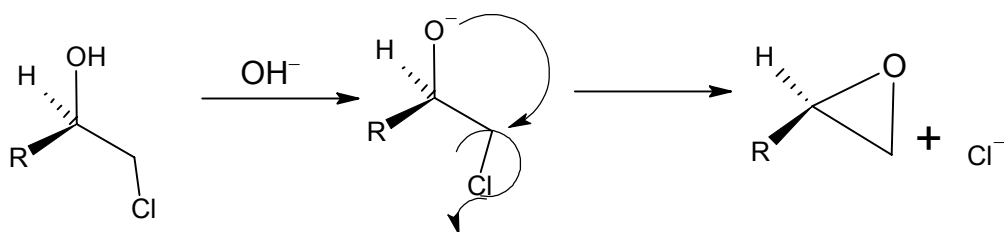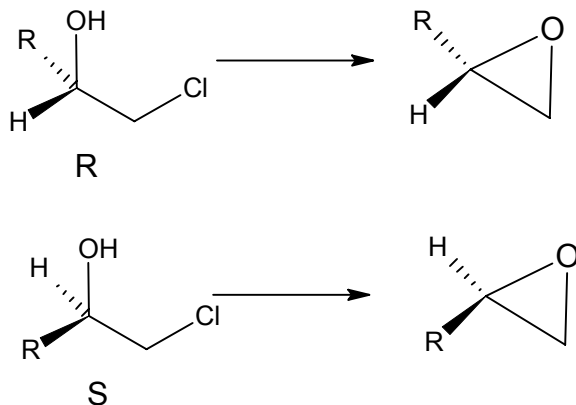

R   S
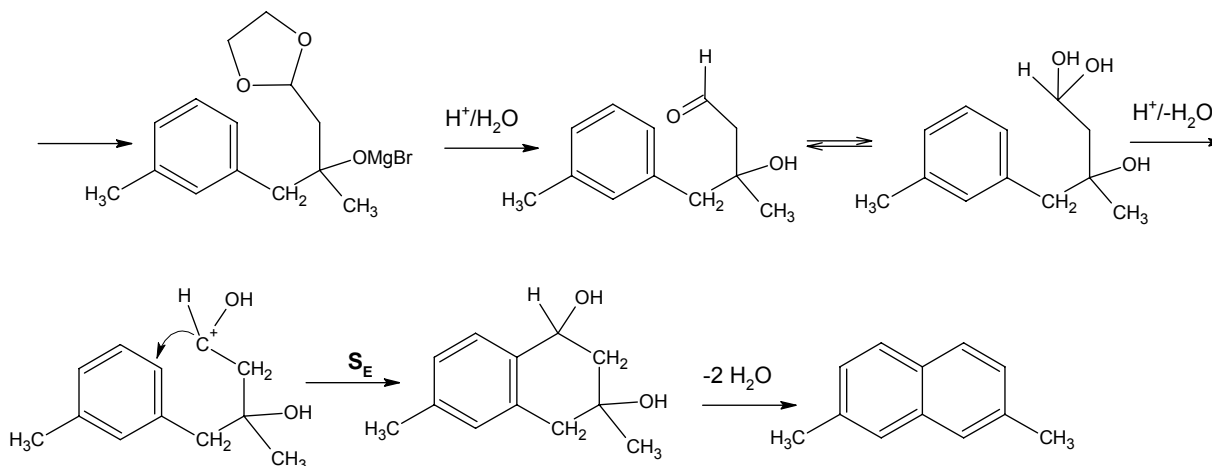
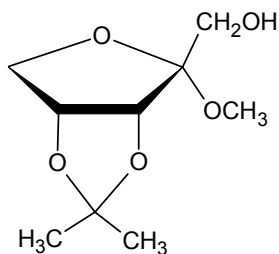The mechanism for the ring closure:

The reaction does not alter the configuration around the chiral center; thus the products are:
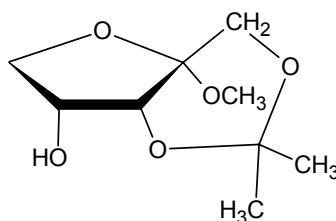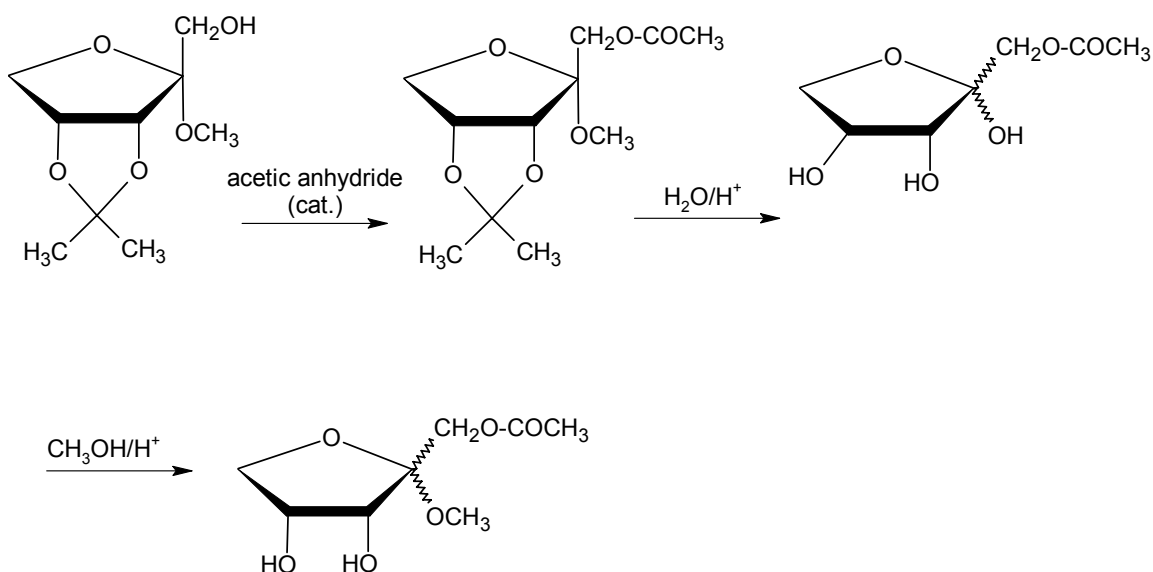

R

S

Problem 21

a)

3,4-acetonide   1,3-acetonide
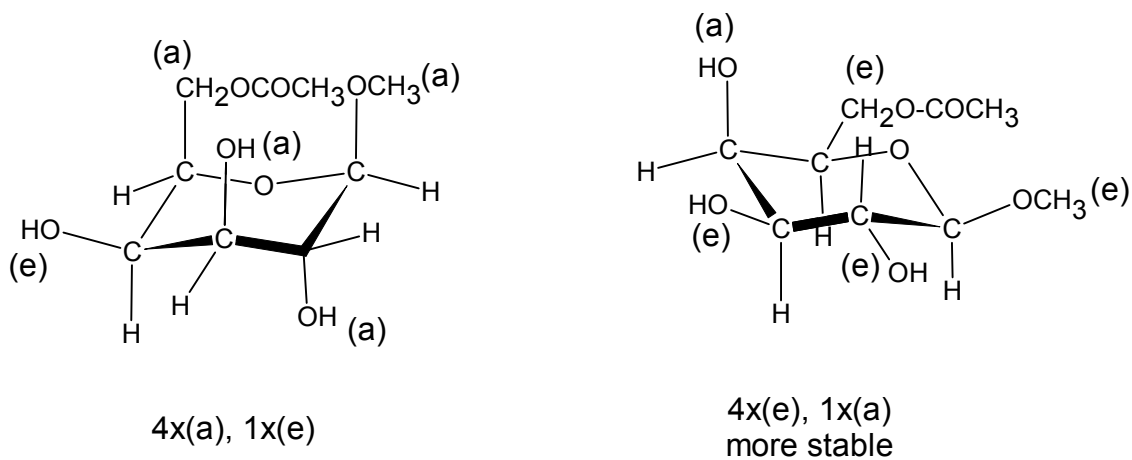
The formation of the 1,3 isomer is less likely (trans anellation of a 5 and 6-membered ring). The main product is the 3,4-acetonide.

78

b)

c)   No. **D** has an unblocked glycosidic OH group, so during the synthesis of **E** both α and β isomers can be formed. The isomeric composition depends on the reaction conditions.

d)

4x(a), 1x(e)

4x(e), 1x(a)
more stable

e)

3,4-acetonide   2,3-acetonide
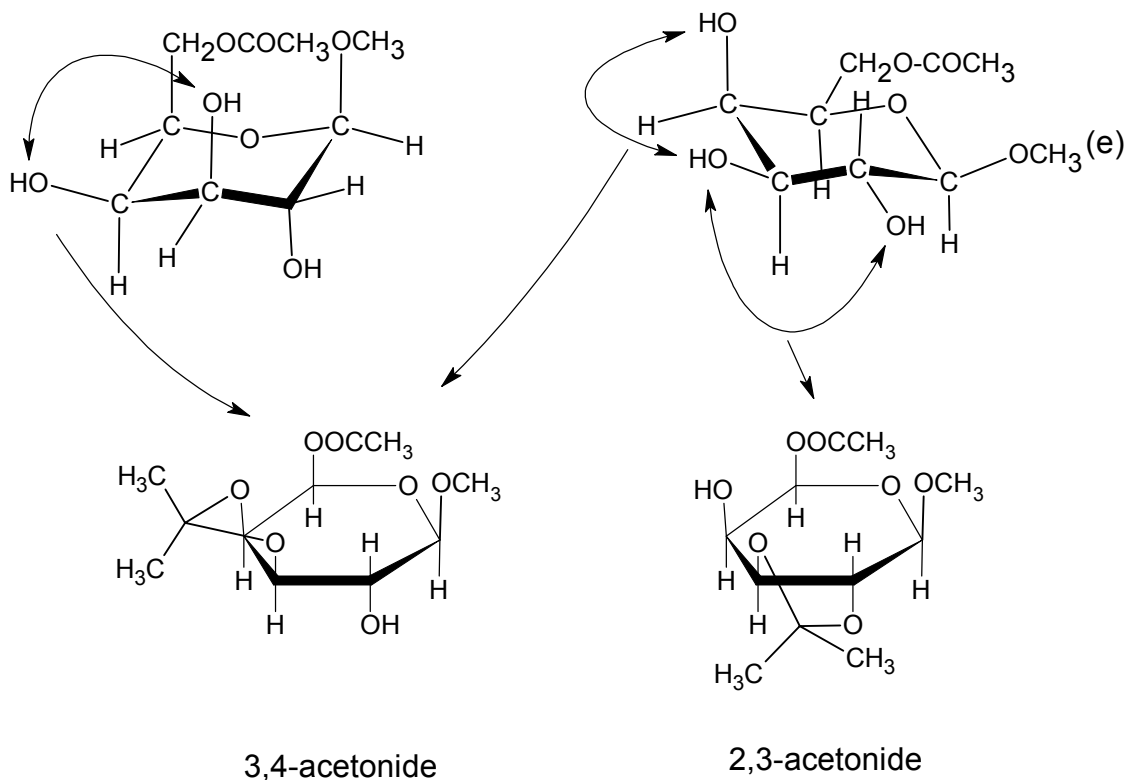
The 3,4-acetonide isomer has two different chair conformers, the 2,3 isomer has only one:

f)

Problem 22

a)   Water splitting by electrolysis:

Anode: $2\ H_2O \rightarrow 4\ H^+ + O_2 + 4\ e^-$

Cathode: $4\ H_2O + 4\ e^- \rightarrow 2\ H_2 + 4\ OH^-$
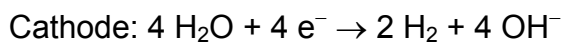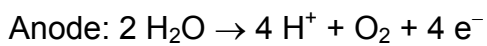
Therefore a charge of 4 mol e$^-$ is necessary to produce 2 mol H_2.
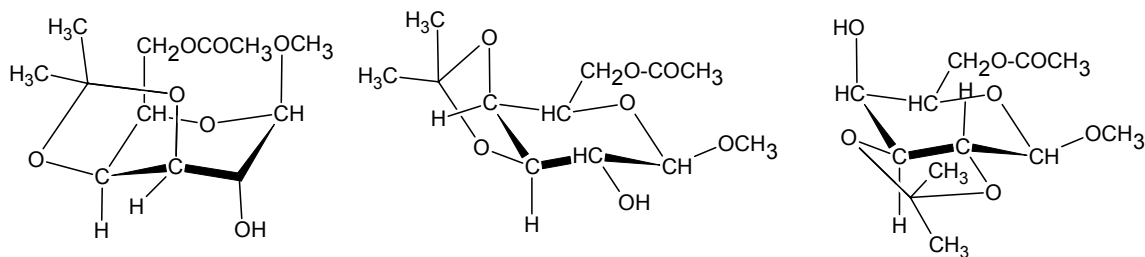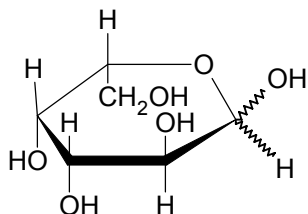For 1 kg hydrogen: $2 \cdot 1000$ g/ $M(H_2)$ = 992 mol e$^-$, $9.55 \cdot 10^7$ C charge is needed.

E = 1.6 V$\cdot 9.55 \cdot 10^7$ C = $1.5 \cdot 10^8$ J

The electricity necessary taking the efficiency into account:

$1.5 \cdot 10^8$ J $/(0.90 \cdot 3.6 \cdot 10^6$ J/kWh) = 47 kWh

The cost of electricity for producing 1 kg hydrogen is therefore
47 kWh$\cdot 0.10$ euro/kWh = 4.7 euro, which is more than the present industrial price of
1 kg hydrogen (2 euro), so electrolysis does not seem economical.

b) The free energy of hydrogen burning at 298 K: $H_2(g) + 0.5\ O_2(g) \rightarrow H_2O(l)$

$\Delta_r G° = \Delta_f H°(H_2O) - T(S°(H_2O) - S° (H_2) - 0.5\ S°(O_2)) = -237$ kJ/mol

The gravimetric energy density: 237 kJ/mol / 0.00202 kg/mol = $\underline{1.17 \cdot 10^5}$ kJ/kg
The molar volume of hydrogen can be estimated from the ideal gas law:

$V_m = RT/p = R \cdot 298$ K / 101325 Pa = 0.02445 m^3/mol

The volumetric energy density: 237 kJ/mol / 0.02445 m^3/mol = $\underline{9.69 \cdot 10^3}$ kJ/m^3

c) Rearranging the van der Waals equation gives:

$$V_m = (b + \frac{RT}{p}) - \frac{a}{pV_m} + \frac{ab}{pV_m^2}$$

Using this as an iterative formula to find V_m for p = 200 bar at T = 298 K.

$$V_M(i+1) = 1.50 \cdot 10^{-4} \text{m}^3\text{mol}^{-1} - \frac{1.24 \cdot 10^{-9}\text{m}^6\text{mol}^{-2}}{V_m(i)} + \frac{3.30 \cdot 10^{-14}\text{m}^9\text{mol}^{-3}}{V_m^2(i)}$$

If one starts the iteration with $V_m(0) = 1 \cdot 10^{-2}$ m^3 mol^{-1}

$V_m(1) = 1.50 \cdot 10^{-4}$ m^{3}mol^{-1}; $V_m(2) = 1.43 \cdot 10^{-4}$ m^{3}mol^{-1}; $V_m(3) = 1.43 \cdot 10^{-4}$ m^{3}mol^{-1}

Therefore $V_m = 1.43 \cdot 10^{-4}$ m^3 mol^{-1} under these conditions. The volume of the cylinder
is 0.050 m^3, so it contains 0.050 m^3 / $1.43 \cdot 10^{-4}$ m^3 mol^{-1} = 350 mol H_2.
The total mass of the cylinder is therefore 93 kg + 350 mol$\cdot 0.00202$ kg/mol = 93.7 kg.
The gravimetric energy density: 350 mol$\cdot 237$ kJ/mol / 93.7 kg = $\underline{8.85 \cdot 10^2}$ kJ/kg
The volume of the filled cylinder is 50 dm^3 + 93 kg / 7.8 kg/dm^3 = 62 dm^3
The volumetric energy density: 350 mol$\cdot 237$ kJ/mol / 0.062 m^3 = $\underline{1.3 \cdot 10^6}$ kJ/m^3

d) 1 mol $NaBH_4$ gives 4 mol H_2.. A greatly simplified chemical equation of the reaction is
given. (The actual chemical form of borate ions is much more complicated.)

$NaBH_4 + 2H_2O \rightarrow NaBO_2 + 4H_2$
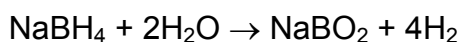
e) The gravimetric energy density: 4 mol$\cdot 237$ kJ/mol / 0.03784 kg = $\underline{2.51 \cdot 10^4}$ kJ/kg

The volumetric energy density: $2.51 \cdot 10^4$ kJ/kg$\cdot 1070$ kg/m^3 = $\underline{2.68 \cdot 10^7}$ kJ/m^3

f) i. Burning of graphite: $C(s, gr) + O_2(g) \rightarrow CO_2(g)$

$\Delta_r G° = \Delta f G°(CO_2) = -394.4$ kJ/mol

The gravimetric energy density: 394.4 kJ/mol / 0.01201 kg/mol = $\underline{3.28 \cdot 10^4}$ kJ/kg

The structure of graphite consists of regular hexagons in one layer. The area of one hexagon is: $6 \cdot \sqrt{3} \cdot (1.456 \cdot 10^{-10}$ m$)^2 / 4 = 5.508 \cdot 10^{-20}$ m^2

The volume of a hexagon-based prism found between two layers:

$5.508 \cdot 10^{-20}$ m$^2 \cdot 3.354 \cdot 10^{-10}$ m $= 1.847 \cdot 10^{-29}$ m^3

In this cell (which is easy to imagine, but not the unit cell of graphite), there is one carbon atom in each vertex, and each vertex is common to six cells. The cell thus contains $12 \cdot 1/6 = 2$ C atoms.

The density is therefore $2 \cdot M(C)/ (N_A \cdot 1.847 \cdot 10^{-29}$ m$^3) = 2160$ kg/m^3

The volumetric energy density: $3.28 \cdot 10^4$ kJ/kg $\cdot 2160$ kg/m^3 = $\underline{7.08 \cdot 10^7}$ kJ/m^3

ii. Burning of n-octane: $C8H18(l) + 12.5\ O2(g) \rightarrow 8\ CO2(g) + 9\ H2O(l)$

$\Delta_r G° = 8\ \Delta_f G°(CO_2) + 9\ \Delta_f G°(H_2O) - \Delta_f G°(C_8H_{18}) = -5295$ kJ/mol

The gravimetric energy density: 5295 kJ/mol / 0.11426 kg/mol = $\underline{4.63 \cdot 10^4}$ kJ/kg
The volumetric energy density: $4.63 \cdot 10^4$ kJ/kg $\cdot 700$ kg/m^3 = $\underline{3.24 \cdot 10^7}$ kJ/m^3

iii. Burning of methanol: $CH_3OH(l) + 1.5\ O_2(g) \rightarrow CO_2(g) + 2\ H_2O(l)$

$\Delta_r G° = \Delta_f G°(CO_2) + 2\ \Delta_f G°(H_2O) - \Delta_f G°(CH_3OH) = -702$ kJ/mol

The gravimetric energy density: 702 kJ/mol / 0.03205 kg/mol = $\underline{2.19 \cdot 10^4}$ kJ/kg
The volumetric energy density: $2.19 \cdot 10^4$ kJ/kg $\cdot 790$ kg/m^3 = $\underline{1.73 \cdot 10^7}$ kJ/m^3

iv. The energy of the battery: $E = 1.9$ A$\cdot 3600$ s$\cdot 1.3$ V $= 8.9 \cdot 10^3$ J
The gravimetric energy density: 8.9 kJ / 0.02658 kg = $\underline{3.3 \cdot 10^2}$ kJ/kg
The volume of the battery: $(7.05$ mm$)^2 \cdot \pi \cdot 47.3$ mm $= 7386$ mm^3
The volumetric energy density: 8.9 kJ / $7.386 \cdot 10^{-6}$ m^3 = $\underline{1.2 \cdot 10^6}$ kJ/m^3

v. The mass change associated with the nuclear reaction is:

$\Delta m = 4 \cdot 1.00782 - 4.00260 = 0.02868$ g/mol

$\Delta E = \Delta m c^2 = 2.868 \cdot 10^{-5}$ kg/mol$\cdot(3.000 \cdot 10^8$ m/s$)^2 = 2.581 \cdot 10^{12}$ J/mol

Each molecule of water contains 2 hydrogen nuclei.
The gravimetric energy density: $2.578 \cdot 10^{12}$ J/mol / $(2 \cdot 0.01802$ kg/mol$) = \underline{7.15 \cdot 10^{10}}$ kJ/kg
The volumetric energy density: $7.15 \cdot 10^{10}$ kJ/kg $\cdot 1000$ kg/m^3 = $\underline{7.15 \cdot 10^{13}}$ kJ/m^3

g) The gravimetric energy density of liquid hydrogen is the same as that of gaseous hydrogen: $\underline{1.17 \cdot 10^8}$ J/kg

The volumetric energy density: $1.17 \cdot 10^8$ J/kg $\cdot 71$ kg/m^3 = $\underline{8.3 \cdot 10^9}$ J/m^3
However, it should be noted that cooling involves a lot of extra cost not reflected directly by the energy density.

h) The volumetric and gravimetric energy densities of methanol are high. There is no need for liquification.

i) $CH_3OH + H_2O \rightarrow CO_2 + 6\ H^+ + 6\ e^-$ on the anode and

$1.5\ O_2 + 6\ H^+ + 6\ e^- \rightarrow 3\ H_2O$ on the cathode.

j) $\Delta_r G° = -zFE°$, $\Delta_r G° = -702$ kJ/mol, $z = 6$, $E°_{cell} = 1.213$ V

k) It is practically the same, but the efficiency of the fuel cell is higher at higher temperature.

Problem 23

a) The atoms have analogous valence electron configurations, therefore the ionization energy decreases with increasing size.

b) The superoxide ion is easily (and exothermically) formed by the addition of an electron to a neutral molecule. To form a peroxide ion, another electron must be added to this negative ion which requires considerable energy. In the oxide ion, the double negative charge must be accommodated by a single atom and, in addition, the O-O bond must also be broken.

c) The results are summarized in the following table. All values are in kJ/mol.

	Energy required for the formation of			Lattice energy	$\Delta_r H$ (reaction)
Product	metal ions	oxygen ions	total		
Li_2O	1336	904	2240	−2972	−732
Li_2O_2	1336	553	1889	−2578	−689
2 LiO_2	1336	−86	1250	−1829	−579
Na_2O	1190	904	2094	−2653	−559
Na_2O_2	1190	553	1743	−2335	−592
2 NaO_2	1190	−86	1104	−1646	−542
K_2O	996	904	1900	−2309	−409
K_2O_2	996	553	1549	−2064	−515
2 KO_2	996	−86	910	−1446	−536

d) Li_2O, Na_2O_2, KO_2.

e) The energy required for the formation of the anion from O_2 steeply increases in the sequence $O_2^- \rightarrow O_2^{2-} \rightarrow O^{2-}$ and so does the lattice energy released during the formation of the corresponding ionic compound. (Peroxide has a greater charge than superoxide, and oxide is smaller in size than peroxide.) The smaller the cation, the greater are the lattice energies and also the differences between those of oxide, peroxide, and superoxide. In the case of Li, the difference between the lattice energies is large enough to compensate for the higher energy required to form the oxide ion, thus Li_2O is the most stable product. For larger cations, the lattice energy differences are smaller and do not cover this energy requirement, so the anions with progressively lower formation energies become preferred.

The preferred product in the reaction of Rb or Cs with O_2 should be the superoxide, even more so than for K. Indeed, this is actually the case.
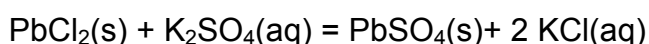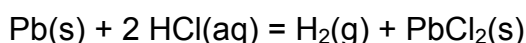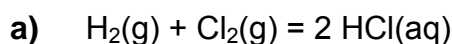
f) Of course not. Our calculations have identified the most stable compound when oxygen is in excess. Should we compare the reactions of 1 mol O_2 with various amounts of metals, the oxide would always be at the top. Potassium peroxide and superoxide are easily reduced by an excess of metallic potassium, e.g.:

$KO_2 + 3 K = 2 K_2O$

g) For the alkali metals to form a cation M^{2+} would require the removal of an electron from an inner electron shell which needs disproportionately large amounts of energy (on the order of 3000-5000 kJ/mol).

h) MO: –3567 kJ/mol, MO_2: –3136 kJ/mol. The difference is greater than in the case of Li. Clearly the oxide is the favoured product.

i) Barium, which has the largest cation. According to our model, the peroxide is stable if the difference between the lattice energies of the oxide and the peroxide is smaller than the difference between the enthalpies of formation of O^{2-} and O_2^{2-}, i.e., 351 kJ/mol.

$$107000\frac{8}{r_+ +140} - 107000\frac{8}{r_+ +173} < 351$$

Hence we obtain $r_+ > 127.7$ pm, which is in good agreement with the experimental findings: the ionic radius of Sr^{2+} is 118 pm, that of Ba^{2+} is 135 pm.

j) The relatively small attraction force that the outer electrons experience from the core in the atoms of alkali metals. This results, on the one hand, in low ionization energies and, on the other hand, in cations of large size. As we have shown, peroxides and superoxides are formed if the counterions are large enough.

Problem 24

a) $H_2(g) + Cl_2(g) = 2 HCl(aq)$

$Pb(s) + 2 HCl(aq) = H_2(g) + PbCl_2(s)$

$PbCl_2(s) + K_2SO_4(aq) = PbSO_4(s) + 2 KCl(aq)$

b) For the first cell:

$\Delta_r H^o = -334.4$ kJ/mol, $\Delta_r S^o = -240.8$ J mol^{-1}K^{-1}, $\Delta_r G^o = -262.6$ kJ/mol

$E^o_{cell} = -\Delta_r G^o/(n \cdot F) = 1.361$ V

For the second cell:

$\Delta_r H^o = -25$ kJ/mol, $\Delta_r S^o = 127.3$ J mol^{-1}K^{-1}, $\Delta_r G^o = -62.9$ kJ/mol

$E^o_{cell} = 0.326$ V

For the third cell:

$\Delta_r H^o = 14.4$ kJ/mol, $\Delta_r S^o = 105.4$ J mol^{-1}K^{-1}, $\Delta_r G^o = -17.0$ kJ/mol

$E^o_{cell} = 0.088$ V

c)   For the first cell:

     Anode: $H_2 = 2 H^+ + 2 e^-$

     Cathode: $Cl_2 + 2 e^- = 2 Cl^-$

     For the second cell:

     Anode: $Pb + 2 Cl^- = PbCl_2 + 2 e^-$

     Cathode: $2 H^+ + 2 e^- = H_2$

     For the third cell:

     Anode: $Pb + SO_4^{2-} = PbSO_4 + 2 e^-$
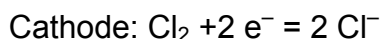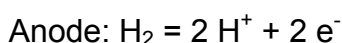
     Cathode: $PbCl_2 + 2 e^- = Pb + 2 Cl^-$
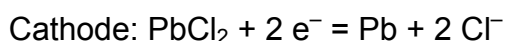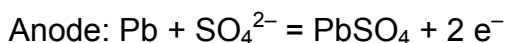
d) $K = \exp\left(-\dfrac{\Delta_r G^0}{RT}\right)$

     For the first cell: $K = 1.02 \cdot 10^{46}$
     For the second cell: $K = 1.05 \cdot 10^{11}$
     For the second cell: $K = 952$

e)   If we suppose that the thermodynamic data are independent of the temperature in a limited range, then the following expression

     $E_{cell} = -\dfrac{\Delta_r H}{nF} + \dfrac{\Delta_r S}{nF} T$

     shows that the temperature dependence of the cell potential is determined by the reaction entropy. For the first cell this is negative, therefore the electromotive force decreases with increasing temperature. For the other two cells the electromotive force increases with increasing temperature.

f) $\eta_{max} = \dfrac{\Delta_r G}{\Delta_r H}$

     For the first cell: $\eta_{max} = 78.5\ \%$
     For the second cell: $\eta_{max} = 252\ \%$
     For the third cell $\eta_{max} = -118\ \%$
     In the first cell, the strongly exothermic reaction proceeds, although there is a significant entropy decrease resulting from the disappearance of gases. This entropy decrease during the reaction necessarily means energy dissipation and efficiency less than 100 %
     In both the other two cells, there is an entropy increase associated with the reaction (a gas forms or the number of dissolved ions increases). The maximal work is thus larger than the reaction enthalpy. The difference must be taken from the environment, meaning that both cells could extract heat from the environment and convert it into electrical work.
     In the third cell an endothermic cell reaction is driven by the entropy increase. Energy from the environment for the operation of the galvanic cell dominates over the reaction enthalpy, so the efficiency parameter is ill-defined in this case.

Problem 25

a) Plugging the data into the integrated rate law gives the equation:

$$0.13 = \left(\frac{1}{2}\right)^{\frac{t}{13}}$$

$t = -13$ hr·ln(0.13)/ln(2) = 38.3 hours.

b) Inspection of the data shows a doubling of the rate upon doubling either of the concentrations. Therefore both partial orders are unity, i.e., the kinetic equation is:

$r = k\,[C_2H_5COOC_2H_5]\,[OH^-]$

The rate coefficient can then be calculated from any row of the table, e.g.:

$k = 0.00109$ mol·dm^{-3}·s^{-1} / (0.045 mol·dm^{-3}·0.300 mol·dm^{-3}) = 0.081 dm^3·mol^{-1}·s^{-1}

c) Taking the logarithm of the ratio for two Arrhenius expressions gives the equation:

$$\ln\left(\frac{k_2}{k_1}\right) = -\frac{E_A}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Rearranging and plugging in the data yields $E_A = 32$ kJ mol^{-1}.

d) **i.** The rate will increase by a factor of 4.

ii. The rate will increase by a factor of $4^2 = 16$.
iii- The rate will decrease by a factor of $2^2 = 4$.
iv. The rate will increase by a factor of $4^2/2 = 8$.
v. The rate will not change, because $(1/2)^2 \cdot 4 = 1$.

e) Since the overall reaction order is 3, halving all concentrations makes the product of the concentration terms in the kinetic equation smaller by a factor of $2^3 = 8$; in order to keep the rate unchanged, k must be increased by the same factor.

$$E_A = \frac{\ln(k_2/k_1)}{\frac{1}{T_1} - \frac{1}{T_2}}R = 79 \text{ kJ·mol}^{-1}$$

f) i. From the absorbance at $t = 0$: $\varepsilon = 0.138/ (0.015$ mol·dm^{-3}·0.99 cm) =
= 9.29 dm^3 mol^{-1} cm^{-1}

ii. Using, e.g., the change from 0 to 25 s:

$$r = \frac{0.138 - 0.102}{0.138} \cdot \frac{0.015\,\text{mol·dm}^{-3}}{25\text{ s}} = 1.57\cdot 10^{-4}\text{mol·dm}^{-3}\cdot\text{s}^{-1}$$

$k = \ln(0.138/0.102)/25$ s = $1.2\cdot10^{-2}$ s^{-1}

iii. $t_{1/2} = \ln(2)/k = 57$ s

iv. The estimated half-life is consistent with the plot, from which it can be seen that the absorbance (and concentration) drops roughly by half for each half-life interval.
v. $t(99\,\%) = \ln(1 - 0.99)/k = 381$ s

$t(99.99\,\%) = \ln(1 - 0.9999)/k = 762$ s

Problem 26

a) It is the O atom, because its formation is much slower than its removal, which fulfills the condition of being in a quasi steady-state.

$$\frac{d[O]}{dt} = k_1[NO_2] - k_2[O][O_2] = 0 \text{, which gives } [O] = \frac{k_1[NO_2]}{k_2[O_2]}.$$

b) Differential:

$$\frac{d[O_3]}{dt} = k_2[O][O_2]$$

Since [O] is in quasi steady-state, the problem simplifies to a zeroth order differential equation (the molecular oxygen concentration will stay approximately constant, only a small fraction of it will react). Initially there is no ozone, i.e. $[O_3]_0 = 0$.
The integral form (i.e. the solution) is:

$$[O_3] = k_2[O][O_2]t$$

c) Substituting into the integral form for ozone concentration the equation for O atom concentration we get:

$$[O_3] = k_2 \frac{k_1[NO_2]}{k_2[O_2]}[O_2]t = k_1[NO_2]t$$

and NO_2 decays in a first-order process:

$$[NO_2]_t = [NO_2]_0 \exp(-k_1 t) = 1.64 \cdot 10^{12} \text{ molecule cm}^{-3}$$

The oxygen atoms formed in the first reaction practically all form ozone:

$$[O_3] = [NO_2]_0 - [NO_2]_t = 8.6 \cdot 10^{11} \text{molecule cm}^{-3}$$

d) $\quad t_{1/2} = \dfrac{\ln 2}{k_1} = 99 \text{ s}$

e) We have shown that the ozone concentration is a function of NO_2 concentration and k_1. Since photolysis rates (such as k_1) are usually less sensitive to temperatures than thermal processes (such as the bimolecular reaction (2)), only small changes in the ozone concentration are expected.

f) Equilibrium means no net production or loss for any of the species:

$$\frac{d[NO_2]}{dt} = -k_1[NO_2] + k_3[NO][O_3] = 0$$

$$k_1[NO_2] = k_3[NO][O_3]$$
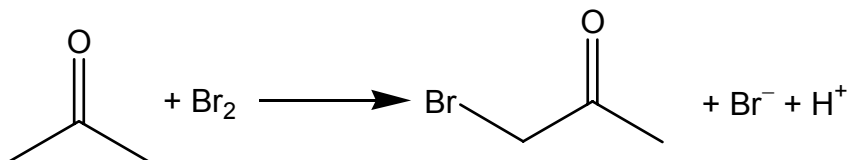
$$\frac{[NO]}{[NO_2]} = \frac{k_1}{k_3[O_3]} = 0.432$$

g) The ratio will decrease, since according to the Arrhenius expression, k_3 increases with temperature.

$$\frac{k_3(T_2)}{k_3(T_1)} = \frac{A\exp(-E_A/(RT_2))}{A\exp(-E_A/(RT_1))} = \exp\left[\frac{E_A}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right] = 1.26$$

The concentration ratio has to be multiplied by $1/1.26 = 0.79$, so the new value is 0.342.

Problem 27

a)

b) Br_2 is the limiting reagent.

c) The plot of the kinetic curve:
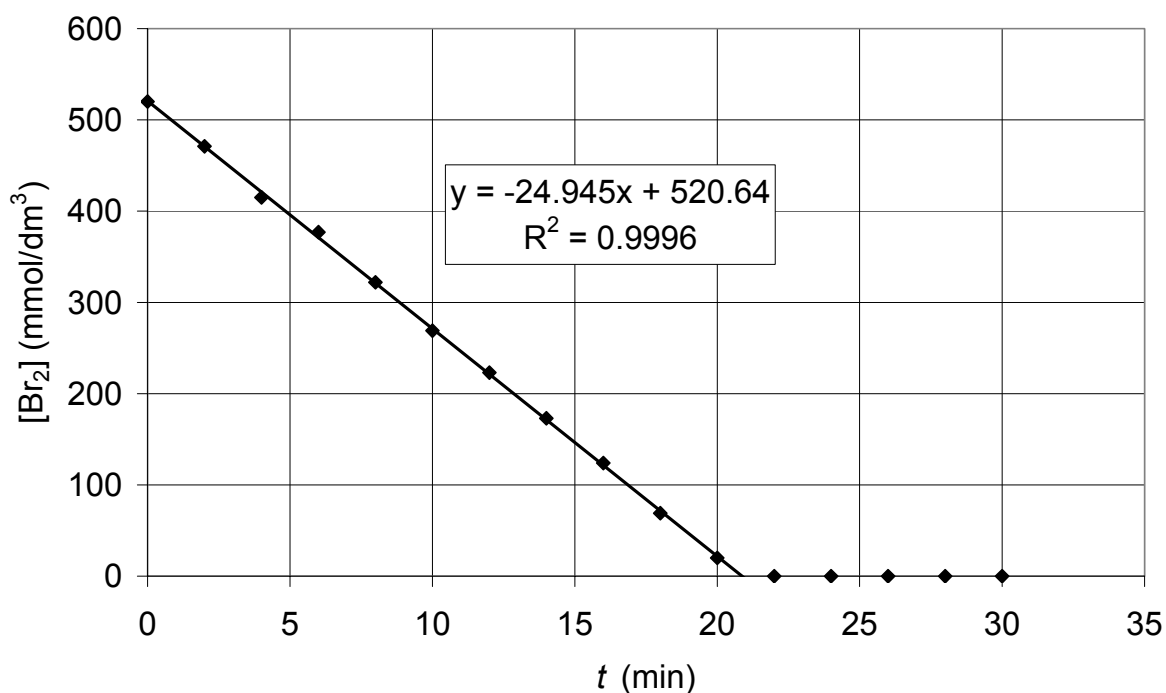
The kinetic curve is a straight line; therefore the process is zeroth-order with respect to Br_2.

d) As the process is zeroth-order with respect to Br_2, and all the other reagents are in large excess, the rate is constant in each experiment. It can be simply calculated as

$v = [Br_2]_0 / t_{break}$

where t_{break} is the reaction time. The dependence of the rate on the reagent concentrations can be studied directly using this formula. Plotting the rate as a function of acetone concentration at constant acidity (0.100 mol/dm^3) gives:
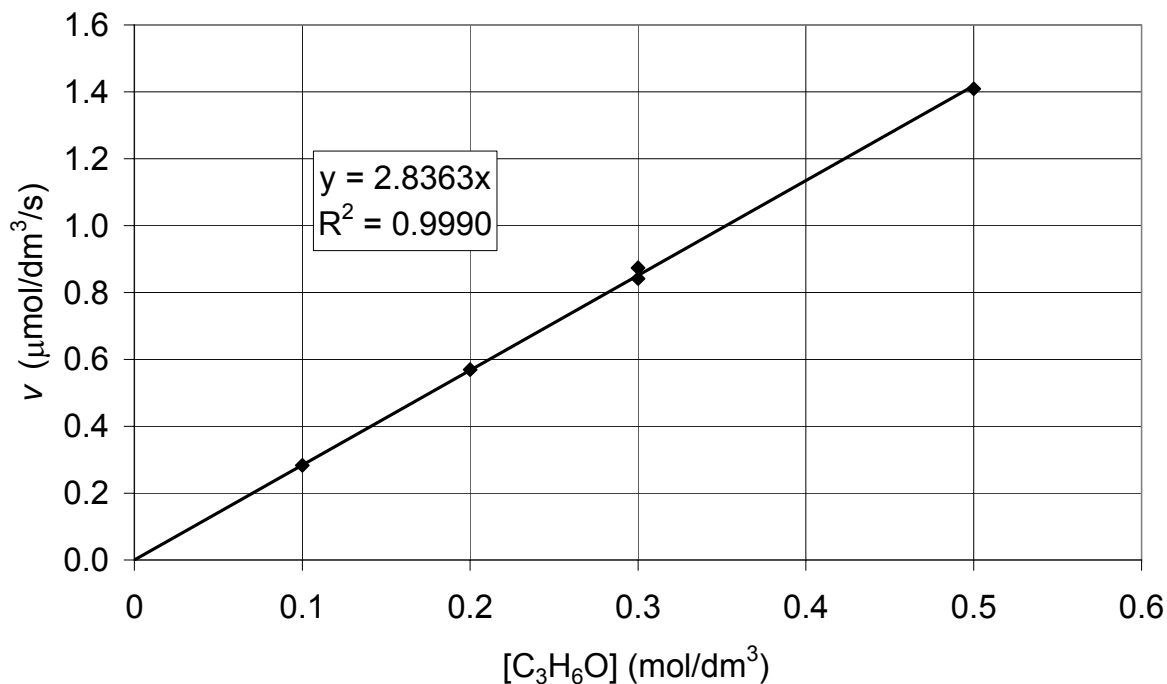
This is a straight line; therefore the reaction is first-order with respect to acetone. Plotting the rate as a function of acid concentration at constant acetone concentration (0.300 mol/dm^3) gives:
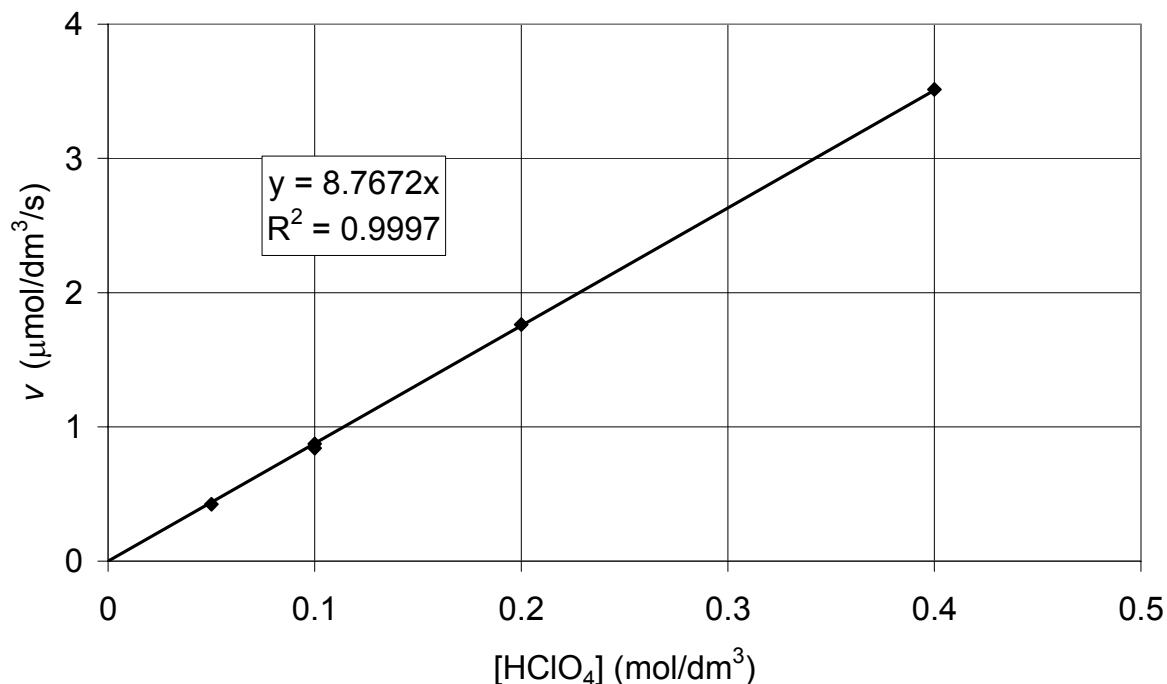
This is a straight line, therefore the reaction is first-order with respect to H$^+$.

e) $v = k_a[C_3H_6O][H^+]$

f)   The rate constant can be determined by dividing the rates calculated in each experiment with both the acetone and acid concentrations. From the average of the 8 measurements shown in the table:

$k_a = 2.86 \cdot 10^{-5}$ dm^{3}mol^{-1}s^{-1} (second-order rate constant with second order unit).

g) Br_2 is the limiting reagent.

h) The plot of the kinetic curve:
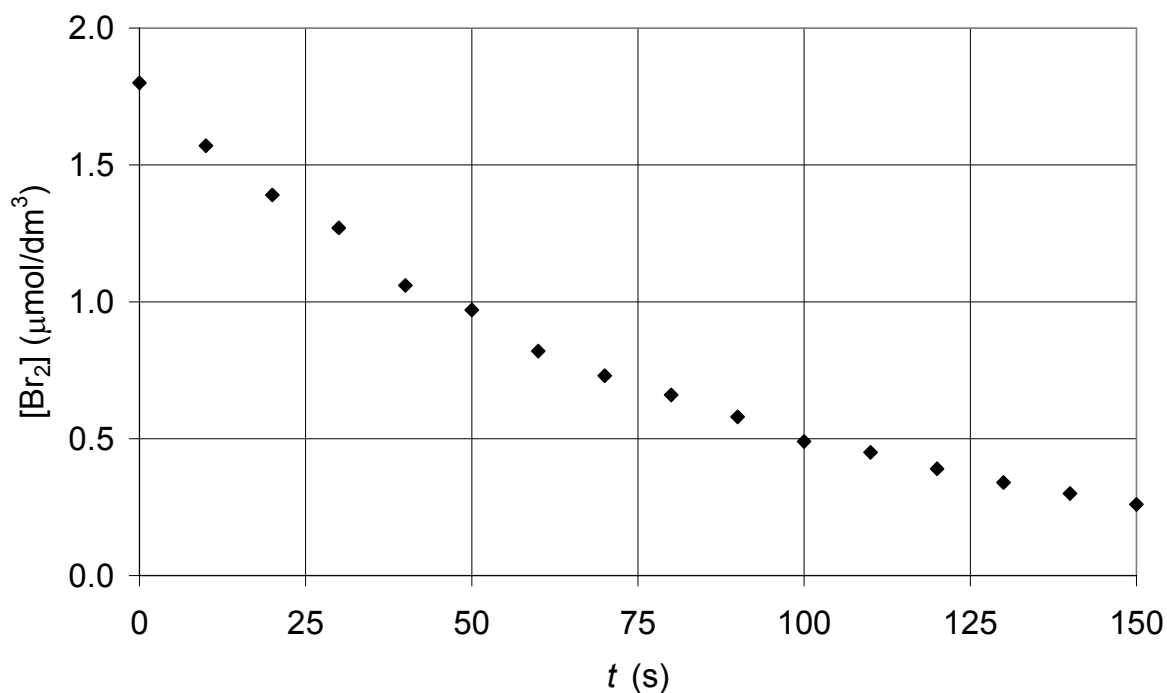
This is not a straight line; the process is not zeroth-order. Testing for first-order behavior is possible by constructing a semilogarithmic graph. This plot looks like:

$$y = -0.0128x + 0.0039$$
$$R^2 = 0.9992$$
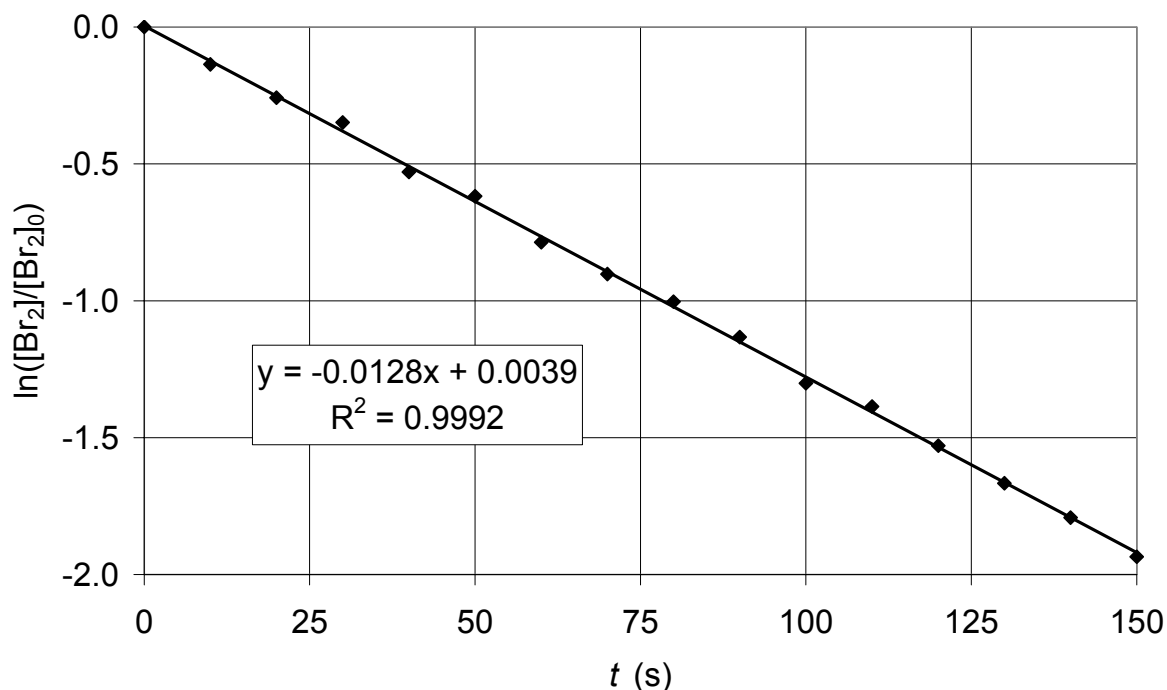
The points fit to a reasonably straight line. Thus, the process is first-order with respect to Br_2.
An alternative solution: estimating the half life from various concentration pairs in the dataset gives a constant value. Therefore the decay of Br_2 follows first-order kinetics.

i)   The process is first-order with respect to the limiting reagent Br_2. From the half-lives of the first order curves, a pseudo first-order rate constant (k_{obs}) can be calculated as follows:

$k_{obs} = \ln 2 / t_{\frac{1}{2}}$

The dependence of k_{obs} on the concentrations of reagents in large excess reveals the kinetic orders with respect to the remaining two reagents. The acetone concentration dependence at constant acidity (0.100 mol/dm^3):
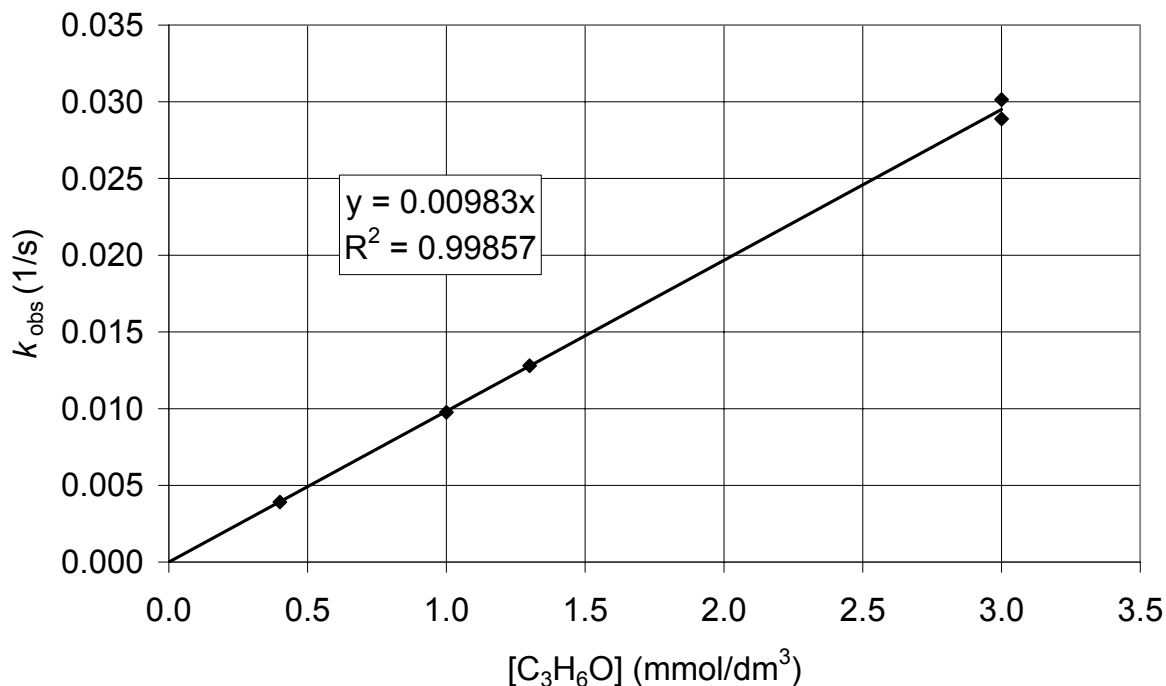
This is a straight line; therefore the reaction is first-order with respect to acetone. For the [H$^+$] dependence at constant acetone concentration (3.0 mmol/dm^3) we get:
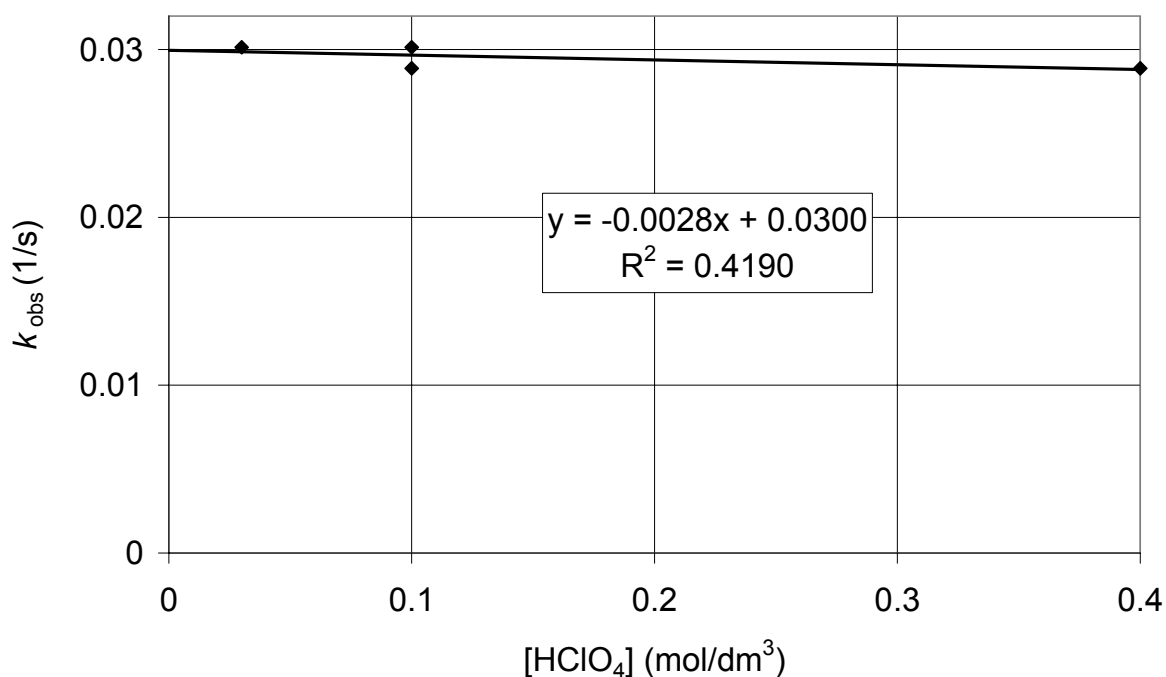
The pseudo first-order rate constant k_{obs} is practically independent of acidity, therefore the reaction is zeroth-order with respect to H^+.

j) $v = k_b[C_3H_6O][Br_2]$

k)   The rate constant can be determined by dividing the pseudo first-order rate constants calculated in each experiment by the acetone concentration. From the average of the 6 measurements shown in the table:

$k_b = 9.82 \text{ dm}^3\text{mol}^{-1}\text{s}^{-1}$ (second-order rate constant with second order unit)

l)   Step 1:
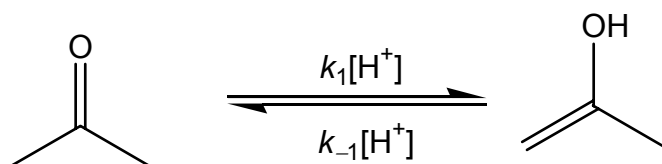
Step 2:
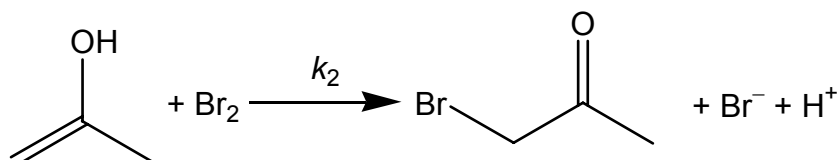
At high initial concentration of bromine, k_1 is rate determining, therefore

$k_a = k_1$

At low initial bromine concentrations, step 1 is a rapid pre-equilibrium, therefore

$$k_b = \frac{k_2 k_1}{k_{-1}}$$

Problem 28

a)

b)   NO, NO_2

c) $2 \text{ ClO}_2 + I_2 + 2 \text{ H}_2\text{O} \rightarrow 2 \text{ Cl}^- + 2 \text{ IO}_3^- + 4 \text{ H}^+$
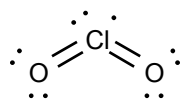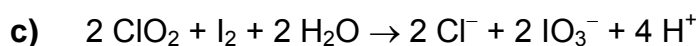
d)   The side reaction taking place is the disproportionation of ClO_2:

$6 \text{ ClO}_2 + 3 \text{ H}_2\text{O} \rightarrow \text{Cl}^- + 5 \text{ ClO}_3^- + 6 \text{ H}^+$
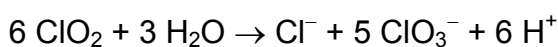
Other possibilities include a different disproportionation of ClO_2:

$8 \text{ ClO}_2 + 4 \text{ H}_2\text{O} \rightarrow 3 \text{ Cl}^- + 5 \text{ ClO}_4^- + 8 \text{ H}^+$
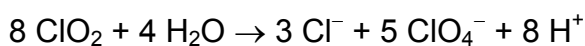
or the formation of periodate ion in the redox reaction:

$14\ ClO_2 + 5\ I_2 + 12\ H_2O \rightarrow 14\ Cl^- + 10\ IO_4^- + 24\ H^+$
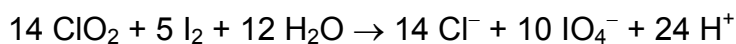
e) Qualitative analysis for chlorate, perchlorate, and periodate ions can be used to differentiate between possible side reactions.

f) No. At 460 nm, chlorine dioxide does not absorb light; therefore a 460 nm light beam cannot cause the photodecomposition. Lower wavelength light actually induces such a photodecomposition.

g) The reaction also takes place in the absence of light, so there are simultaneous photochemical and thermal pathways.

h) $c_{Fe(II)} = 0.3823/(1.10\cdot10^4\ dm^3\ mol^{-1}\ cm^{-1}\cdot1.000\ cm) = 3.48\cdot10^{-5}\ mol/dm^3$

i) The amount of iron(II) in the 5.000 cm^3 volumetric flask is $1.74\cdot10^{-7}$ mol.

This amount of iron(II) was present in 1.000 cm^3 of the illuminated solution whose overall volume was 25.00 cm^3. Therefore, the total amount of iron(II) formed is $4.35\cdot10^{-6}$ mol.

j) The quantum yield of the process producing iron(II) is 1.12. Therefore, in the 30.00 minute illumination period

$4.35\cdot10^{-6}$ mol / 1.12 = $3.88\cdot10^{-6}$ mol photon

photon caused photoreaction.
The absorbance of the solution in a 1.00 cm cell is 1.41. The photoreactor has an optical path length of 5.00 cm, therefore the absorbance is expected to be 7.05. This means the solution absorbs $(1 - 10^{-7.05})\cdot100 = 100.00$ % of the light (practically all of it). The light intensity from this and the illumination time is $3.88\cdot10^{-6}$ mol / 1800 s = $2.16\cdot10^{-9}$ mol/s.
The energy of a 460-nm photon is $h\nu$, where h is Planck's constant and the frequency of the photon can be calculated using the speed of light c as $\nu = c/\lambda$:

$I = 2.16\cdot10^{-9}$ mol/s$\cdot N_A\cdot h\cdot c$ / $\lambda = 5.62\cdot10^{-4}$ J/s = 0.562 mW.

k) The light intensity after the filter can be calculated as $10^{-A}\cdot I_0$

The absorbance of iodine in the photoreactor:

$5.1\cdot10^{-4}$ mol/dm$^3\cdot740$ dm^3 mol^{-1} cm$^{-1}\cdot5.00$ cm = 1.887

therefore $(1 - 10^{-1.887})\cdot100 = 98.7$ % of the light is absorbed by this solution at 460 nm.

	no filter	filter 1	filter 2	filter 3	steel sheet
filter absorbance	0	0.125	0.316	0.582	∞
light intensity after filter	$2.16\cdot10^{-9}$	$1.62\cdot10^{-9}$	$1.04\cdot10^{-9}$	$5.66\cdot10^{-10}$	0
absorbed by iodine	$2.13\cdot10^{-9}$	$1.60\cdot10^{-9}$	$1.03\cdot10^{-9}$	$5.59\cdot10^{-10}$	0
v_0 (mol dm^{-3} s^{-1})	$2.51\cdot10^{-9}$	$1.97\cdot10^{-9}$	$1.40\cdot10^{-9}$	$9.3\cdot10^{-10}$	$3.7\cdot10^{-10}$

A plot of initial rate as a function of light intensity:
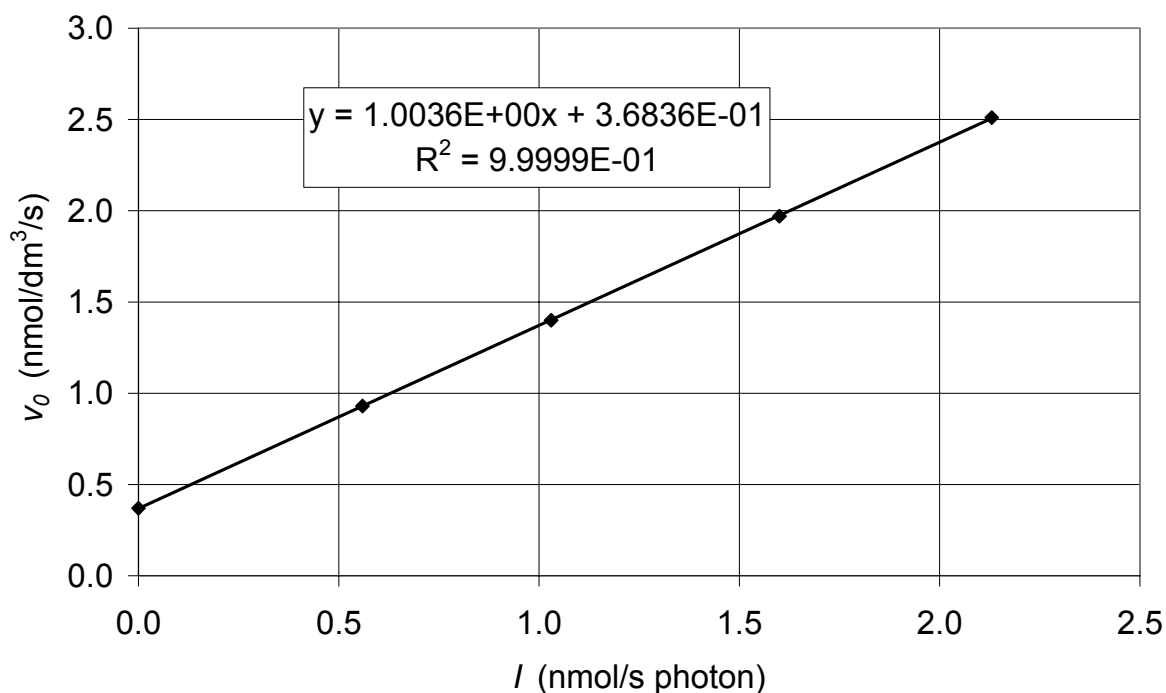
The slope of this plot is the quantum yield for the loss of ClO_2 (1.00). The intercept is the initial rate of the dark reaction.
The quantum yield for the loss of iodine is obtained by taking the stoichiometry into account is 1.00 / 2.30 = 0.43.

Problem 29

a) At a given Na–Cl distance an electron jumps from Na to Cl. At this point the energy gain arising from the electrostatic attraction and the electron affinity of the Cl atom is exactly equivalent to the energy necessary to ionize the Na atom.

$$E_I = EA + \frac{kq^2}{R}$$

where EA = 348 kJ/mol = $5.78 \cdot 10^{-19}$ J, E_I = 496 kJ/mol = $8.24 \cdot 10^{-19}$ J.
Rearranging the equation to solve for R we obtain R = 939 pm.

b) The distance will be larger as the excited Na atom can be ionized easier. In the equation above the ionization energy should be replaced with the value $E_I - E_{ex}$ = 445 kJ/mol. The distance is: 1432 pm.

c) The formula for R, the distance where the electron jump occurs:

$$R = \frac{kq^2}{E_I - EA}$$

This value increases as $E_I - EA$ decreases. However it always remains positive as the largest electron affinity of the elements is smaller than the smallest ionization energy. Therefore for all possible (ionic) diatomics there is a well-defined R value beyond which the dissociated ions are less stable than the dissociated atoms.

d)   We postulate the redox reaction:

$Hu^+ + Hu = Hu^{2+} + Hu^-$
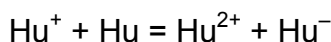
For the Coulomb interaction we have $q_1 = 2 \cdot 1.602 \cdot 10^{-19}$ C, EA(Hu) = 250 kJ/mol = $4.15 \cdot 10^{-19}$ J, $IE = IE_{II}$(Hu) = 500 kJ/mol = $8.30 \cdot 10^{-19}$ J. The reacting distance is: 1110 pm.

Problem 30

Ten solutions are colourless, $H_2Cr_2O_7$ is orange and $FeCl_3$ is yellow to brownish. The unknown solutions react with each other as follows (↓ = precipitate; ↑ = evolution of a colourless and odourless gas; – = no visible change):

	+ $H_2Cr_2O_7$	+ $FeCl_3$	Identified
CaS	↓ green	↓ black	☑
$(NH_4)_2CO_3$	↑ the solution turns lighter yellow	↑ ↓ brown	☑
NaOAc	– (the odor of HOAc may be detected)	reddish-brown solution	☑
KI	brown solution	brown solution	☑
NaOH	the solution turns lighter yellow	↓ brown	☑
KBr	–	–	
$BaCl_2$	– (↓ can slowly form)	–	
$Ca(H_2PO_4)_2$	–	–	
$MgSO_4$	–	–	
$Al(NO_3)_3$	–	–	

	KBr	$BaCl_2$	$Ca(H_2PO_4)_2$	$MgSO_4$	$Al(NO_3)_3$
+ $(NH_4)_2CO_3$	–	↓ white	↓white	–	↑, ↓ white
+ excess NaOH	–	–	–	↓ white	precipitate dissolves
Identified	☑			☑	☑

	$BaCl_2$	$Ca(H_2PO_4)_2$
+ NaOH	–	↓ white
Identified	☑	☑

Problem 31

The following compositions were handed out:

a) $AgNO_3$, $BaCl_2 \cdot 2H_2O$, NH_4NO_3 absent: $(NH_4)_2CO_3$, $NiCl_2 \cdot 2H_2O$

Colorless – no nickel.
No gas evolution observed with acids – no carbonate.
Sample does not dissolve in water – the precipitate must be AgCl. Indeed, the solution clears up on adding ammonia.
Heating the solution with NaOH produces ammonia, as seen on the indicator paper at the mouth of the test tube. (Or smelt.)

$Ag^+ + Cl^- = \underline{AgCl}$

$\underline{AgCl} + 2\ NH_3 = Ag(NH_3)_2^+ + Cl^-$

$NH_4^+ + OH^- = NH_3\uparrow + H_2O$
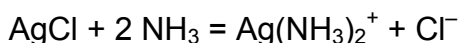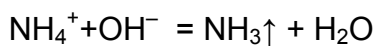
b) ZnO, $Pb(NO_3)_2$, Mg   absent: $BaSO_4$, KI, MnO_2

Grey powder consisting of a dark and white component – contains Mg or MnO_2
After adding water a grey, heterogeneous substance remains – ZnO or $BaSO_4$ might also be present.
Slowly dissolves without residue in nitric acid with gas evolution – Mg and ZnO is present.
A white precipitate remains in HCl – $Pb(NO_3)_2$ is present.
KI can be excluded as yellow PbI_2 was not seen.

$Mg + 2H^+ = Mg^{2+} + H_2\uparrow$

$Pb^{2+} + 2Cl^- = \underline{PbCl_2}$
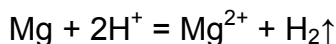
c) $CaCO_3$, $CuCl_2 \cdot 2H_2O$ absent: NH_4I, $FeSO_4 \cdot 7H_2O$, TiO_2

Sample dissolves completely in acids with gas evolution – TiO_2 absent, $CaCO_3$ present. $FeSO_4$ must also be absent because $CaSO_4$ is not formed.
The green powder dissolves in acid leaving a bluish solution. Ammonia gives a dark blue discoloration – $CuCl_2$
NH_4I cannot be present together with Cu^{2+} as iodine would be produced.

$Cu^{2+} + 4NH_3 = Cu(NH_3)_4^{2+}$
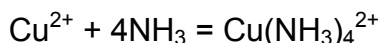
Problem 32

d) Ca^{2+}, Sr^{2+}

Problem 33

a) If m_1 is the mass of the metal and the volume of EDTA solution consumed is V_1, the following equation can be written for the molar mass of the metal Me:

$$M(Me) = \frac{m_1}{c_{EDTA}V_1}$$

b) Let n denote the oxidation number of the metal in the oxide. From here it follows that the formula of the oxide is M_2O_n. If m_2 is the mass of the oxide weighed and the volume of EDTA solution consumed is V_2 the following equation can be written:

$$\frac{m_2}{2M(Me) + nM(O)} \cdot 2 \cdot \frac{20.00}{100.00} = c_{EDTA}V_2$$

$$n = \frac{1}{c_{EDTA}M(O)}\left(\frac{0.4m_2}{V_2} - \frac{2m_1}{V_1}\right)$$

Bismuth is best used as the unknown. In this case the volumes consumed should be $V_1 = 14.36$ cm^3 and $V_1 = 17.17$ cm^3 to give $M(Me) = 208.9$ g/mol and $n = 3$. Actual volumes measured are reproducible and lower, but the identification of the metal and the formula of the oxide (Bi_2O_3) are unambiguous.

Problem 34

a) $BrO_3^- + 5\ Br^- + 6\ H^+ = 3\ Br_2 + 3\ H_2O$.

b)   If V cm^3 potassium bromate solution is consumed then the tablet contains $10.57V$ mg ascorbic acid, as the following equation can be written.

$$\frac{m}{M(C_6H_8O_6)} = 3c_{KBrO_3}V$$

Problem 35

a) $H(IO_3)_2^- + 10\ I^- + 11\ H^+ \rightarrow 6\ I_2 + 6\ H_2O$

       $C_6H_8O_6 + I_2 \rightarrow C_6H_6O_6 + 2\ HI$

b)   The amount of iodine liberated is 1 mmol. If V_1 cm^3 is the volume of the ascorbic acid solution consumed, its concentration is $1/V_1$ mol/dm^3.

c)   The oxidized form is shown below:
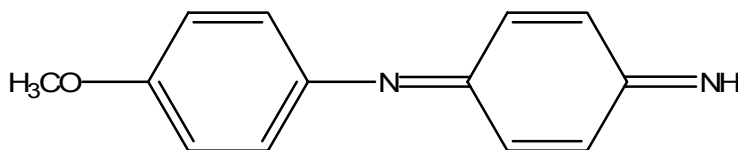
       The oxidized form is responsible for the blue-violet colour because of its non-aromatic (chinoidal) structure.

d) $C_6H_8O_6 + 2\ Ag^+ \rightarrow C_6H_6O_6 + 2\ Ag + 2\ H^+$

e)   If the consumption is V_2, the amount of silver in the unknown is $20V_2/V_1$ mmol.

       If consumption between 10 and 20 cm^3 is required, the AgNO$_3$ content in the unknown sample must be between 1.7–3.4 g.

Problem 37

       The students should find an eluent that is capable of separating all the amino acids (e.g. *n*-butanol : 50% acetic acid = 2:1).
       The plates show that unreacted amino acids are present in the filtrates with the exception of proline. Thus, the reagent selectively removes proline from the mixture.
       A precipitate is formed in every test tube, as the reagent itself precipitates.
       Note that proline produces a yellow discoloration with ninhydrin, while the other amino acids give purplish-blue spots. The mechanism of the chromophore generation is rather complex and is not needed to do the problem.

Restructured Syllabus

Rationale for the restructuring of the syllabus of the IChO

The Steering Committee of the IChO has begun to work on an updated version of the syllabus (found in the appendix of the IChO regulations). We would like to invite any comments and suggestions to Gabor Magyarfalvi at gmagyarf@chem.elte.hu. The new rules and the syllabus can then be discussed and voted upon by the International Jury at the 40th IChO in Budapest.

It has been the case that the implementation of the regulations/syllabus has not always been completely satisfactory with regard to keeping in line with the letter of the regulations with respect to the material the students are expected to know.

The primary reason for this seems to have been the balance the organizers tried to strike between incorporating the state of the art of chemistry into the tasks and keeping within the reach of the students. It is apparent that this inbalance should shift in favour of limiting the material at the olympiads which is not taught at secondary level education.

However, this poses a problem in that it is almost impossible to differentiate between the best students, especially if we define the knowledge that will be tested in the exams exactly. If the problem authors would stick to the letter of a set syllabus, then the problems would be repetitious and somewhat predictable. The best results would go to students who are good at reproducing exactly what they have learned, instead of the brightest and most creative students who take what they have learned and apply it to new situations.

The present syllabus might already be too restrictive in some aspects, so it is somewhat understandable that previous organizers have found it difficult to keep within the rules. E.g.: if there is a problem concerning the pH of a carbon dioxide solution, that would exhaust all possibilities for the organizers to include questions not explicitly listed as allowed. (pH of multiprotic acids, equilibrium constants in partial pressures and Henry's law are all listed as level 3.)

The purpose of the syllabus and the preparatory problems is twofold. They should limit the organizers to keep the questions within the reach of the students. On the other hand, the fact that the international jury have a free hand in editing the problems risks that the most interesting tasks could also be left out by majority vote perhaps unwisely.

The points listed in the present syllabus are typically of two kinds:
-skills and concepts that the students should be able to use,
-factual knowledge that is expected to be known.

The beauty of chemistry is that one needs both facts and concepts to solve problems and understand phenomena, but these two categories would require rather different rules.

The first type of required knowledge (concepts and skills) is much more easy to list and limit in the syllabus. We now attempt to list those the students are expected to know in Appendix C.

The number of new concepts or fields is definitely an area where the problem authors should be restricted from including too many in the exam. Our recommendation is no more than 8 such topics (6 theoretical and 2 practical) in a preparatory problem set. If each topic can be taught and example problems can be practiced in a few hours then this can be accomplished well within the two week period of special training allowed.
It would be better also that the preparatory problems can list these fields in their preamble explicitly.

We include a (not comprehensive) list of some possible new topics in the appendix.

The second type of knowledge (facts) is the more sensitive one. Luckily, if a problem is based on the knowledge of a fact, then it is usually a bad problem. There have been few of such problems at the Olympiads.

This is the aspect of the syllabus that needs to be confined strictly.

If the problem authors need to use facts possibly unfamiliar to many students, they should be conveyed explicitly in the problem itself, or alternatively they can be included and demonstrated in the preparatory problems, as the content and solutions of the preparatory problems is supposed to be known by all participants. Obviously the extent of the preparatory problems does not give much space to include lots of such 'facts'. We do not think that there could be explicit limits on these in the regulations if the 'fact' is expressed explicitly e.g. a specific equation or property. The authors should be aware that the International Jury will probably remove those questions from the exam if they are based on hidden information only.

Draft recommendations

Paragraph 10 of the regulations

(1) The organizer distributes a set of preparatory tasks written in English to all participating countries in the January of the competition year. The preparatory tasks are intended to give students a good idea of the type and difficulty of the competition tasks, including safety aspects (see §12 and Appendix "B"). SI units must be used throughout the preparatory tasks.

(2) Leave as it is.

(3) Appendix C of the regulations contains a list of concepts and skills expected to be mastered by the participants. Organizers may freely include questions and tasks in the theoretical or experimental competition based on the knowledge listed there.
The organizer can include problems in the exams based on the use of concepts and skills from not more than 6 theoretical and 2 practical fields outside this list, if a minimum of 2 tasks from each field is included and the necessary skills demonstrated in the set of preparatory problems. Examples of such external fields are also listed in Appendix C. Fields not already listed should have a breadth similar to the examples. These 6 theoretical and 2 practical fields must be stated explicitly at the beginning of the Preparatory problems. If an equation not covered by the listed fields is required for the solution of the exam questions, then this should be defined in the exam text.

(4) Appendix D contains an outline of the factual knowledge supposedly familiar to the competitors. If specific facts not included here are required for the solution of the exam questions, then these should be included in the exam text or in the preparatory problems and their solutions.

(5) Leave as it is

Appendix C

Concepts and skills expected to be known by all participants:
(predominantly equivalent to former number 1 and 2 topics)

Estimation of experimental errors, use of significant figures;

Nucleons, isotopes, radioactive decay and nuclear reactions (alpha, beta, gamma);
Quantum numbers (n,l,m) and orbitals (s,p,d) in hydrogen-like atoms;
Hund's rule, Pauli principle;
Electronic configuration of main group and the first row transition metal atoms and their ions;
Periodic table and trends (electronegativity, electronaffinity, ionization energy, atomic and ionic size, melting points, metallic character, reactivity);
Bond types (covalent, ionic, metallic), intermolecular forces and relation to properties;
Molecular structures and simple VSEPR theory (up to 4 e pairs);

Balancing equations, empirical formulae, mole concept and Avogadro's number, stoichiometric calculations, density, calculations with different concentration units;

Chemical equilibrium, Le Chatelier's principle, equilibrium constants in terms of concentrations, pressures and mole fractions;
Arrhenius and Bronsted acid-base theory, pH, self ionization of water, equilibrium constants of acid-base reactions, pH of weak acid solutions, pH of very dilute solutions and simple buffer solutions, hydrolyis of salts;
Solubility constants and solubility;
Complexation reactions, definition of coordination number, complex formation constants;

Basics of electrochemistry: Electromotive force, Nernst equation; Electrolysis, Faraday's laws;

Rate of chemical reactions, elementary reactions, factors affecting the reaction rate, rate law for homogeneous and heterogeneous reactions, rate constant, reaction order, reaction energy profile, activation energy, catalysis, influence of a catalyst on thermodynamic and kinetic characteristics of a reaction;

Energy, heat and work, enthalpy and energy, heat capacity, Hess' law, standard formation enthalpies, solution, solvation and bond enthalpies;

Definition and concept of entropy and Gibbs' energy, second law of thermodynamics, direction of spontaneous change;

Ideal gas law, partial pressures;

Principles of direct and indirect tiration (back titration);
Acidi and alkalimetry, acidimetric titration curves, choice and colour of indicators for acidimetry;
Redox titrations (permanganometric and iodometric);

Simple complexometric and precipitation titrations;

Basic principles of inorganic qualitative analysis for ions specified in factual knowledge, flame tests;

Lambert-Beer law;

Organic structure-reactivity relations (polarity, electrophilicity, nucleophilicity, inductive effects, relative stability)
Structure-property relations (boiling point, acidity, basicity);
Simple organic nomenclature;
Hybridization and geometry at carbon centers;
Sigma and pi bonds, delocalization, aromaticity, mesomeric structures;
Isomerism (constitutional, configuration, conformation, tautomerism)
Stereochemistry (*E-Z*, cis-trans isomers, chirality, optical activity, Cahn-Ingold-Prelog system, Fisher projections);
Hydrophilic and hydrophobic groups, micelle formation;
Polymers and monomers, chain polymerizations, polyaddition and polycondensation;

Laboratory skills

Heating in the laboratory, heating under reflux;
Mass and volume measurement (with electronic balance, measuring cylinder, pipette and burette, volumetric flask);
Preparation and dilution of solutions and standard solutions;
Operation of a magnetic stirrer;
Carrying out of test tube reactions;
Qualitative testing for organic functional groups (using a given procedure);
Volumetric determination, titrations, use of a pipette bulb;
Measurement of pH (by pH paper or calibrated pH meter);

Examples of concepts and skills allowed in the exam only if included and demonstrated in the preparatory problems

6 theoretical and 2 practical topics from these or other topics of similar breadth are allowed in a preparatory problem set. It is intended that a topic can be introduced and discussed in a lecture of 2-3 hours before a prepared audience.

- VSEPR theory in detail (with more than 4 ligands);
- Inorganic stereochemistry, isomerism in complexes;
- Solid state structures (metals, NaCl, CsCl) and Bragg's law;
- Relation of equilibrium constants, electromotive force and standard Gibbs energy;
- Integrated rate law for first order reactions, half-life, Arrhenius equation, determination of activation energy;
- Analysis of complex reactions using steady-state and quasi-equilibrium approximations, mechanisms of catalytic reactions, determination of reaction order and activation energy for complex reactions;
- Collision theory

- Simple phase diagrams and the Clausius-Clapeyron equation, triple and critical points;
- Stereoselective transformations (diastereoselective, enantioselective), optical purity
- Conformational analysis, use of Newman projections, anomeric effect
- Aromatic nucleophilic substitution, electrophilic substitution on polycyclic aromatic compounds and heterocycles
- Supramolecular chemistry
- Advanced polymers, rubbers, copolymers, thermosetting polymers. Polymerization types, stages and kinetics of polymerization;
- Amino acid side groups, reactions and separation of amino acids, protein sequencing;
- Secondary, tertiary and quaternary structures of proteins, non-covalent interactions, stability and denaturation, protein purification by precipitation, chromatography and electrophoresis;
- Enzymes and classification according to reaction types, active sites, coenzymes and cofactors, mechanism of catalysis;
- Monosaccharides, equilibrium between linear and cyclic forms, pyranoses and furanoses, Haworth projection and conformational formulae;
- Chemistry of carbohydrates, oligo and polysaccharides, glycosides, determination of structure;
- Bases, nucleotides and nucleosides with formulae, Functional nucleotides, DNA and RNA, hydrogen bonding between bases, replication, transcription and translation, DNA based applications;
- Complex solubility calculations (with hydrolysing anions, complex formation);
- Simple Schrödinger equations and spectroscopic calculations;
- Simple MO theory;
- Basics of mass spectrometry (molecular ions, isotope distributions);
- Interpretation of simple NMR spectra (chemical shift, multiplicity, integrals);
- Synthesis techniques: filtrations, drying of precipitates, thin layer chromatography.
- Synthesis in microscale equipment,;
- Advanced inorganic qualitative analysis;
- Gravimetric analysis;
- Use of a spectrophotometer;
- Theory and practice of extraction with immiscible solvents;
- Column chromatography;

Appendix D

Outline of the factual knowledge supposed to be known by the competitors:

Reactions of s-block elements with water, oxygen and halogens, their color in flame tests;
Stoichiometry, reactions and properties of binary non-metal hydrides;
Common reactions of carbon, nitrogen and sulfur oxides (CO, CO_2, NO, NO_2, N_2O_4, SO_2, SO_3);
Common oxidation states of p-block elements, stoichiometry of common halides and oxoacids (HNO_2, HNO_3, H_2CO_3, H_3PO_4, H_3PO_3, H_2SO_3, H_2SO_4, HOCl, $HClO_3$, $HClO_4$);
Reaction of halogens with water;
Common oxidation states of first row transition metals (Cr(III), Cr(VI), Mn(II), Mn(IV), Mn(VII), Fe(II), Fe(III), Co(II), Ni(II), Cu(I), Cu(II), Ag(I), Zn(II), Hg(I), and Hg(II)) and the color of these ions;
Dissolution of these metals and Al, amphoteric hydroxides ($Al(OH)_3$, $Cr(OH)_3$, $Zn(OH)_2$);
Permanganate, chromate, dichromate ions and their redox reactions;
Iodometry (reaction of thiosulphate and iodine);
Identification of Ag^+, Ba^{2+}, Fe^{3+}, Cu^{2+}, Cl^-, CO_3^{2-}, SO_4^{2-} ;

Organic:
Common electrophiles and nucleophiles
Electrophilic addition: addition to double and triple bonds, regioselectivity (Markovnikoff's rule), stereochemistry
Electrophilic substitution: substitution on aromatic rings, influence of substituents on the reactivity and regioselectivity, electrophilic species;
Elimination: E1 and E2 reactions at sp^3 carbon centers, stereochemistry, acid-base catalysis, common leaving groups;
Nucleophilic substitution: S_N1 and S_N2 reactions at sp^3 carbon centers, stereochemistry;
Nucleophilic addition: addition to carbon-carbon and carbon-hetero atom double and triple bonds, addition-elimination reactions, acid-base catalysis;
Radical substitution: reaction of halogens and alkanes;
Oxidations and reductions: switching between the different oxidation levels of common functional groups (alkyne – alkene – alkane – alkyl halide, alcohol – aldehyde, ketone – carboxylic acid derivatives, nitriles – carbonates)
Cyclohexane conformations;
Grignard reaction, Fehling and Tollens reaction;

Simple polymers and their preparation (polystyrene, polyethylene, polyamides, polyesters);
Amino acids and their classification in groups, isoelectric point, peptide bond, peptides and proteins;
Carbohydrates: open chain and cyclic form of glucose and fructose;
Lipids: general formulae of triacyl glycerides, saturated and unsaturated fatty acids;