19th – 29th July 2018
Bratislava, SLOVAKIA
Prague, CZECH REPUBLIC

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PREPARATORY PROBLEMS: THEORETICAL

50th IChO 2018

International Chemistry Olympiad
SLOVAKIA & CZECH REPUBLIC

BACK TO WHERE IT ALL BEGAN

UPDATED 1st JUNE 2018

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Preface

We are happy to introduce the Preparatory Problems for the 50th International Chemistry Olympiad. These problems are intended to make the preparation for the Olympiad easier for both students and their mentors. The problems we prepared cover a wide range of challenging topics in modern chemistry. We based the problems on subjects typically covered in high school chemistry courses as well as six topics of advanced difficulty for the Theoretical part and two topics of advanced difficulty for the Practical part. These topics are listed under “Topics of Advanced Difficulty”, and their applications are shown in the preparatory problems. Based on our experience, each of these topics can be introduced to well-prepared students in two to three hours.

The solutions will be sent to the head mentor of each country by email by 15th February 2018 and will be published online on 1st June 2018. We welcome any comments, corrections and questions about the problems via email at info@50icho.eu.

We wish you a lot of fun solving the problems and we look forward to seeing you in July in Bratislava and Prague.

Acknowledgment

We would like to thank all the authors for their hard and dedicated work on both the preparatory and competition problems. We are also grateful to the reviewers for their valuable comments and suggestions.

Bratislava and Prague, 30th January 2018

On behalf of the Scientific Committee,

Petra Ménová and Martin Putala

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Fields of Advanced Difficulty

1. *Thermodynamics*: relation of equilibrium constants and standard Gibbs energy, van 't Hoff equation, weak acid-base equilibria
2. *Kinetics*: integrated rate law for first- and second-order reactions, half-life, Arrhenius equation, relaxation methods in chemical kinetics, kinetic isotope effects
3. *Electrochemistry*: electrochemical cells, Nernst-Peterson equation, Latimer, Frost and Pourbaix diagrams
4. *Inorganic complexes*: crystal field theory
5. *Stereochemistry*: organic stereochemistry, diastereoselective reactions
6. *DNA and RNA*: nucleobases, hydrogen bonding between bases and its thermodynamics

Notes

We do not expect students to get an advanced training in the following topics met in the preparatory problems as they WILL NOT appear in the exam set.

- Claisen rearrangement
- Chemistry of *N*-oxides
- Arrow-pushing mechanisms
- Use of spreadsheet software
- Solving cubic equations

Polymer chemistry will be covered only from the viewpoint of organic chemistry.

No further biochemistry of nucleic acids than covered in the preparatory problems.

Unless stated otherwise, the number of significant figures reported by the student will not be evaluated.

Physical Constants and Equations

Avogadro's constant:	$N_A = 6.022 \times 10^{23}$ mol^{-1}
Universal gas constant:	$R = 8.314$ J K^{-1} mol^{-1}
Speed of light:	$c = 2.998 \times 10^{8}$ m s^{-1}
Planck's constant:	$h = 6.626 \times 10^{-34}$ J s
Faraday constant:	$F = 9.6485 \times 10^{4}$ C mol^{-1}
Standard pressure:	$p = 1$ bar $= 10^{5}$ Pa
Normal (atmospheric) pressure:	$p_{atm} = 1.01325 \times 10^{5}$ Pa
Zero of the Celsius scale:	273.15 K
Mass of electron:	$m_e = 9.109 \times 10^{-31}$ kg
Unified atomic mass unit:	$u = 1.6605 \times 10^{-27}$ kg
Ångström:	1 Å $= 10^{-10}$ m
Electronvolt:	1 eV $= 1.602 \times 10^{-19}$ J

Ideal gas equation:	$pV = nRT$
The first law of thermodynamics:	$\Delta U = q + W$
Power input for electrical device:	$P = UI$ where U is voltage and I electric current
Enthalpy:	$H = U + pV$
Gibbs free energy:	$G = H - TS$ $\Delta G^{o} = -RT\ln K = -zF E^{o}_{cell}$ $\Delta G = \Delta G^{o} + RT\ln Q$
Reaction quotient Q for a reaction a A + b B $\rightleftharpoons$ c C + d D:	$Q = \dfrac{[C]^{c}[D]^{d}}{[A]^{a}[B]^{b}}$
Entropy change:	$\Delta S = \dfrac{q_{rev}}{T}$ where q_{rev} is heat for the reversible process
Heat change for temperature-independent c_m:	$\Delta q = nc_m\Delta T$ where c_m is molar heat capacity
Van 't Hoff equation:	$\dfrac{d\ln K}{dT} = \dfrac{\Delta_r H_m}{RT^2} \quad \Rightarrow \quad \ln\left(\dfrac{K_2}{K_1}\right) = -\dfrac{\Delta_r H_m}{R}\left(\dfrac{1}{T_2} - \dfrac{1}{T_1}\right)$

Henderson–Hasselbalch equation: $\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log \frac{[\mathrm{A}^-]}{[\mathrm{HA}]}$

Nernst–Peterson equation: $E = E^\mathrm{o} - \frac{RT}{zF} \ln Q$

Energy of a photon: $E = \frac{hc}{\lambda}$

Relation between E in eV and in J: $E/\mathrm{eV} = \frac{E/\mathrm{J}}{q_\mathrm{e}/\mathrm{C}}$

Lambert–Beer law: $A = \log \frac{I_0}{I} = \varepsilon l c$

Wavenumber: $\tilde{\nu} = \frac{\nu}{c} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$

Reduced mass μ for a molecule AX: $\mu = \frac{m_\mathrm{A}\, m_\mathrm{X}}{m_\mathrm{A} + m_\mathrm{X}}$

Arrhenius equation: $k = A\, \mathrm{e}^{-\frac{E_\mathrm{a}}{RT}}$

Rate laws in integrated form:

Zero order: $[\mathrm{A}] = [\mathrm{A}]_0 - kt$

First order: $\ln[\mathrm{A}] = \ln[\mathrm{A}]_0 - kt$

Second order: $\frac{1}{[\mathrm{A}]} = \frac{1}{[\mathrm{A}]_0} + kt$

PERIODIC TABLE OF ELEMENTS

50th IChO 2018
INTERNATIONAL CHEMISTRY OLYMPIAD
SLOVAKIA & CZECH REPUBLIC

50.942 — Standard relative atomic weight
V — Symbol
23 — Atomic number
1.50 — Electronegativity

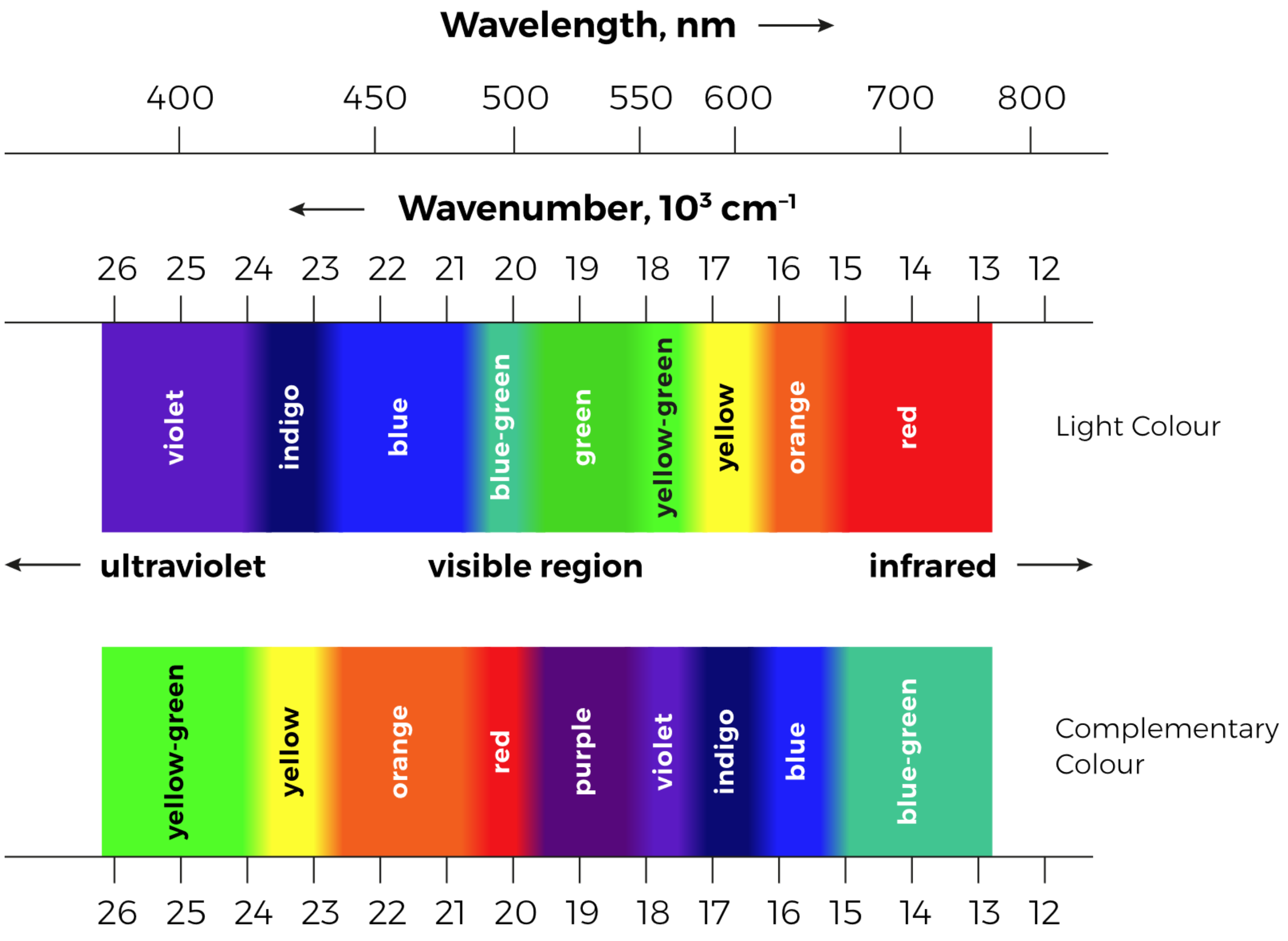
	1 I. A	2 II. A	3 III. B	4 IV. B	5 V. B	6 VI. B	7 VII. B	8 VIII. B	9 VIII. B
1	1.00794 **H** 1 2.20								
2	6.941 **Li** 3 0.97	9.0122 **Be** 4 1.50							
3	22.990 **Na** 11 1.00	24.305 **Mg** 12 1.20							
4	39.098 **K** 19 0.91	40.078 **Ca** 20 1.00	44.956 **Sc** 21 1.30	47.867 **Ti** 22 1.30	50.942 **V** 23 1.50	51.996 **Cr** 24 1.60	54.938 **Mn** 25 1.60	55.845 **Fe** 26 1.60	58.933 **Co** 27 1.70
5	85.468 **Rb** 37 0.89	87.62 **Sr** 38 0.99	88.906 **Y** 39 1.10	91.224 **Zr** 40 1.20	92.906 **Nb** 41 1.20	95.95 **Mo** 42 1.30	~98 **Tc** 43 1.40	101.07 **Ru** 44 1.40	102.91 **Rh** 45 1.40
6	132.91 **Cs** 55 0.86	137.33 **Ba** 56 0.97		178.49 **Hf** 72 1.20	180.95 **Ta** 73 1.30	183.84 **W** 74 1.30	186.21 **Re** 75 1.50	190.23 **Os** 76 1.50	192.22 **Ir** 77 1.50
7	~223 **Fr** 87 0.86	226.03 **Ra** 88 0.97		261.11 **Rf** 104	262.11 **Db** 105	263.12 **Sg** 106	262.12 **Bh** 107	270 **Hs** 108	268 **Mt** 109

	10 VIII. B	11 I. B	12 II. B	13 III. A	14 IV. A	15 V. A	16 VI. A	17 VII. A	18 VIII. A
1									4.0026 **He** 2
2				10.811 **B** 5 2.00	12.011 **C** 6 2.50	14.007 **N** 7 3.10	15.999 **O** 8 3.50	18.998 **F** 9 4.10	20.180 **Ne** 10
3				26.982 **Al** 13 1.50	28.085 **Si** 14 1.70	30.974 **P** 15 2.10	32.06 **S** 16 2.40	35.453 **Cl** 17 2.80	39.948 **Ar** 18
4	58.693 **Ni** 28 1.70	63.546 **Cu** 29 1.70	65.38 **Zn** 30 1.70	69.723 **Ga** 31 1.80	72.631 **Ge** 32 2.00	74.922 **As** 33 2.20	78.971 **Se** 34 2.50	79.904 **Br** 35 2.70	83.798 **Kr** 36
5	106.42 **Pd** 46 1.30	107.87 **Ag** 47 1.40	112.41 **Cd** 48 1.50	114.82 **In** 49 1.50	118.71 **Sn** 50 1.70	121.76 **Sb** 51 1.80	127.60 **Te** 52 2.00	126.90 **I** 53 2.20	131.29 **Xe** 54
6	195.08 **Pt** 78 1.40	196.97 **Au** 79 1.40	200.59 **Hg** 80 1.40	204.38 **Tl** 81 1.40	207.20 **Pb** 82 1.50	208.98 **Bi** 83 1.70	~209 **Po** 84 1.80	~210 **At** 85 1.90	~222 **Rn** 86
7	281 **Ds** 110	280 **Rg** 111	277 **Cn** 112	~287 **Nh** 113	289 **Fl** 114	~288 **Mc** 115	~289 **Lv** 116	~291 **Ts** 117	293 **Og** 118

6 LANTHANIDES	138.91 **La** 57 1.10	140.12 **Ce** 58 1.10	140.91 **Pr** 59 1.10	144.24 **Nd** 60 1.10	~145 **Pm** 61 1.10	150.36 **Sm** 62 1.10	151.96 **Eu** 63 1.00	157.25 **Gd** 64 1.10
7 ACTINIDES	227.03 **Ac** 89 1.00	232.04 **Th** 90 1.10	231.04 **Pa** 91 1.10	238.03 **U** 92 1.20	237.05 **Np** 93 1.20	{244} **Pu** 94 1.20	~243 **Am** 95 1.20	~247 **Cm** 96 1.20

6 LANTHANIDES	158.93 **Tb** 65 1.10	162.50 **Dy** 66 1.10	164.93 **Ho** 67 1.10	167.26 **Er** 68 1.10	168.93 **Tm** 69 1.10	173.05 **Yb** 70 1.10	174.97 **Lu** 71 1.10
7 ACTINIDES	~247 **Bk** 97 1.20	~251 **Cf** 98 1.20	~252 **Es** 99 1.20	~257 **Fm** 100 1.20	~258 **Md** 101 1.20	~259 **No** 102 1.20	~260 **Lr** 103 1.20

VISIBLE LIGHT SPECTRUM



Problem 1. Synthesis of hydrogen cyanide

Hydrogen cyanide (HCN) is a colourless liquid with a characteristic almond-like odour. It can be produced when sufficient energy is supplied to numerous systems containing hydrogen, nitrogen, and carbon. Today, only the processes starting from hydrocarbons and ammonia are of economic importance. Two main HCN production processes are:

- Degussa (BMA) process: $CH_4(g) + NH_3(g) \rightarrow HCN(g) + 3\ H_2(g)$
- Andrussow process: $CH_4(g) + NH_3(g) + 3/2\ O_2(g) \rightarrow HCN(g) + 3\ H_2O(g)$

Both processes take place at temperatures above 1 000 °C and at near standard pressure. Both of them require the use of special platinum catalysts.

1.1 Calculate a change in enthalpy $\Delta_r H_m$ at 1 500 K for the reactions which take place in the Degussa process (BMA process) and in the Andrussow process, respectively. Use the data on the enthalpy of formation $\Delta_f H_m$ given in the table below.

Compound	**$\Delta_f H_m$(1 500 K), kJ mol^{-1}**
$CH_4(g)$	−90.3
$NH_3(g)$	−56.3
$HCN(g)$	129.0
$H_2O(g)$	−250.1
$H_2(g)$	0
$O_2(g)$	0

1.2 Which process (Degussa BMA or Andrussow) requires the use of an external heater to keep the reaction system at 1 500 K? Why?

1.3 Calculate the equilibrium constant K of the reaction which takes place in the Degussa process (BMA process) at the temperatures of 1 500 K and 1 600 K. The standard change in Gibbs free energy for this reaction at 1 500 K is $\Delta_r G_m(1\ 500\ K) = -112.3$ kJ mol^{-1}. Assume that the reaction enthalpy at 1 500 K is constant over a temperature range from 1 500 K to 1 600 K. Is the result in accordance with Le Chatelier's principle?

1.4 Referring to the Le Chatelier's principle, estimate whether the equilibrium constant K of the reaction in the Andrussow process increases or decreases when the temperature changes from 1 500 K to 1 600 K.

Problem 2. Thermochemistry of rocket fuels

Common rocket engines that power spacecraft used for the transportation of space probes to Earth's orbit or to leave its gravitational field rely on simple nitrogen-based fuels. Methylhydrazine and 1,1-dimethylhydrazine (also known as unsymmetrical dimethylhydrazine) are commonly used in combination with nitrogen dioxide (or fuming nitric acid) for this purpose. Despite the relatively high toxicity of the given hydrazine derivatives, these compounds possess several beneficial characteristics which make them most suitable for powering rocket engines in the outer space. First, all hydrazine derivatives form hypergolic (spontaneously ignitable) mixtures with nitrogen dioxide, making it possible for the engine to work without any additional ignition system. Next, the melting temperatures of both methylhydrazine and 1,1-dimethylhydrazine are sufficiently low, so these species remain liquid even at extreme conditions.

To investigate the thermochemical properties of selected derivatives of hydrazine, the following calorimetric experiments were performed. Samples of liquid hydrazine, methylhydrazine, and 1,1-dimethylhydrazine, each weighing 1 gram, were combusted in an adiabatic bomb calorimeter operating at a constant volume, in a stoichiometric amount of oxygen. The temperature in the calorimeter was initially 298.15 K, and it increased by 8.25 K, 12.55 K and 14.76 K during the experiments with the respective individual compounds. By calibration, the heat capacity of the calorimeter was determined to be 2.04 kJ K^{-1}.

2.1 Assuming that all three hydrazine derivatives react with oxygen to yield molecular nitrogen, water vapour and, if relevant, carbon dioxide at 298.15 K and 101 325 Pa, calculate the enthalpies of combustion for the reactants at the given conditions. Consider all gaseous species participating in the reaction to behave as ideal gas, and neglect any differences between the enthalpy and internal energy of all condensed phases.

2.2 Calculate the reaction enthalpies for combustion reactions of the three selected fuels with dinitrogen tetroxide at 298.15 K and 101 325 Pa (again, water vapour is produced). Consider all of the reacting hydrazine species to be liquid, mimicking the chemical processes occurring in rocket engines. Dinitrogen tetroxide enters the reaction in gaseous state. Use the standard enthalpies of formation of gaseous water (−241.83 kJ mol^{-1}), carbon dioxide (−393.52 kJ mol^{-1}) and dinitrogen tetroxide (9.08 kJ mol^{-1}).

Extensive calorimetric experiments were performed for the relevant low-temperature phases of all chemical compounds present in the given systems at temperatures ranging from the vicinity of absolute zero up to ambient temperature. From these measurements, the absolute values of the standard molar entropies (at 298.15 K and 101 325 Pa) were evaluated according to the third law of thermodynamics:

Compound	**$S°$, J K^{-1} mol^{-1}**	**Compound**	**$S°$, J K^{-1} mol^{-1}**
N_2H_4 (l)	121.92	N_2 (g)	191.61
$CH_3N_2H_3$ (l)	166.35	CO_2 (g)	213.79
$(CH_3)_2N_2H_2$ (l)	199.60	H_2O (l)	69.95
N_2O_4 (g)	209.46		

2.3 Calculate standard reaction Gibbs energies for the three combustion reactions with dinitrogen tetroxide, estimate the corresponding equilibrium constants and predict qualitatively the extent of reactions occurring at 101 325 Pa and 298.15 K. Assume that the reactions start from stoichiometric amounts of reactants, and water is produced in its standard state – liquid. Use the given standard entropy values and the molar vaporization enthalpy of water at 298.15 K, which amounts to 40.65 kJ mol^{-1}.

2.4 In which direction do the total pressure and temperature affect the given chemical equilibria? In other words, does an increase in pressure or in temperature lead to an increase or a decrease in the extent of the reaction?

2.5 Within the adiabatic approximation, calculate the flame temperature for a 1:1:1 molar mixture of the three fuels reacting with 3.75 moles of N_2O_4 for the case when the reactants enter a combustion chamber at 298.15 K in the liquid state. The flame temperature can be calculated, assuming that the combustion reaction formally occurs at 298.15 K and all of the heat released by the reaction (enthalpy) is then consumed to warm up the gaseous products (including water vapour) to the resulting temperature of the flame. Approximate the isobaric heat capacities of the relevant compounds with the following constants.

Compound	**C_p, J K^{-1} mol^{-1}**
N_2 (g)	35.26
CO_2 (g)	59.83
H_2O (g)	52.29

2.6 Compare the calculated flame temperature obtained above for the mixture of fuels, using an analogous value corresponding to burning pure liquid 1,1-dimethylhydrazine in an oxygen atmosphere.

2.7 The critical temperature of oxygen is 154.6 K and the melting temperature of 1,1-dimethylhydrazine is 216.0 K. Is there a temperature range in which the same liquid–fuel engine could be used for this alternative fuel setup?

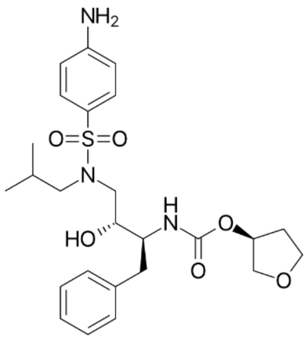
2.8 Explain the extraordinarily high thermodynamic efficiency of rocket engines when compared to the other representatives of thermal engines (e.g. steam or Diesel engine) and support your answer with a quantitative argument.

Problem 3. HIV protease

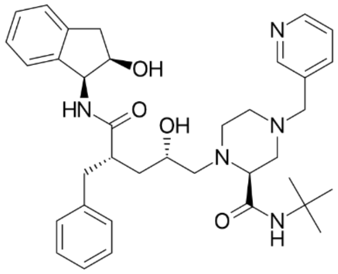
Human immunodeficiency virus (HIV) is a retrovirus that causes acquired immunodeficiency syndrome (AIDS). AIDS is a condition in which the afflicted patient's immune system fails progressively, allowing otherwise benign infections to be life-threatening. The life cycle of HIV relies on the enzyme HIV-1 protease. As this enzyme plays a crucial role in the replication of the virus, HIV-1 protease has been a prominent target for therapy, with drugs being designed to inhibit the action of the enzyme. An HIV-1 protease inhibitor binds to the active site of the enzyme more strongly than the substrate that it mimics, thus disabling the enzyme. Consequently, without active HIV-1 protease present, viral particles do not mature into infectious virions.

Several inhibitors of HIV-1 protease have been licensed as drugs for HIV therapy. A detailed thermodynamic and kinetic study of seven then-available inhibitors of HIV-1 protease was performed in 2003 in Uppsala (interested readers are referred to the original publication in *J. Mol. Recognit.* DOI: 10.1002/jmr.655). The molecular structures of six of them are shown below.

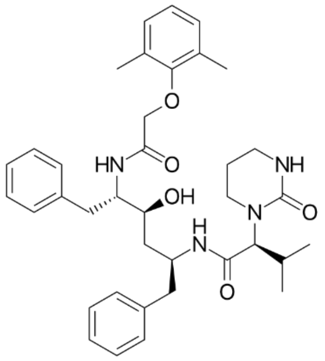
Amprenavir



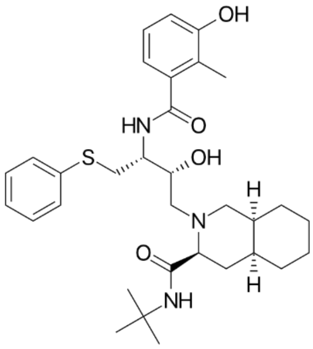
Indinavir



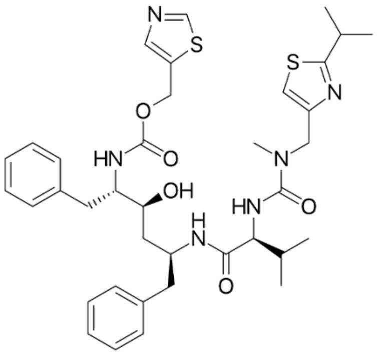
Lopinavir



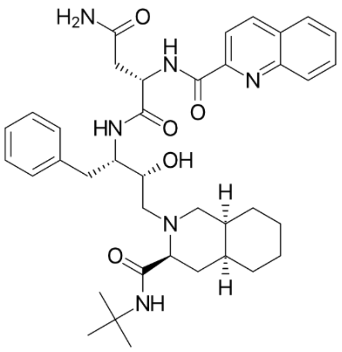
Nelfinavir



Ritonavir



Saquinavir



The affinity of the selected compounds to the HIV-1 protease was measured in terms of equilibrium constants for the dissociation of the protease–inhibitor complex, in a range of temperatures from 5 °C to 35 °C under otherwise identical conditions including pH. The obtained data are presented below; dissociation constants K_D are in units of nM, i.e. 10^{-9} mol dm^{-3}.

Temperature °C	**Amprenavir**	**Indinavir**	**Lopinavir**	**Nelfinavir**	**Ritonavir**	**Saquinavir**
5	1.39	3.99	0.145	6.83	2.57	0.391
15	1.18	2.28	0.113	5.99	1.24	0.320
25	0.725	1.68	0.101	3.67	0.831	0.297
35	0.759	1.60	0.0842	2.83	0.720	0.245

3.1 Which of the compounds binds most strongly to the protein at 35 °C?

3.2 Calculate the standard Gibbs energy of binding (i.e. association) for each compound at each temperature. It may be of advantage to use a spreadsheet application.

3.3 Use the temperature-dependent data to calculate the standard enthalpy and entropy of binding of each of the compounds. Consider the enthalpies and entropies to be independent of temperature in the interval 5–35 °C.

The dissociation rate constants k_D (in the units of $10^{-3}\,s^{-1}$) of the protease–inhibitor complexes for each inhibitor at two temperatures are presented below:

Temperature °C	**Amprenavir**	**Indinavir**	**Lopinavir**	**Nelfinavir**	**Ritonavir**	**Saquinavir**
5	1.85	1.88	0.506	0.912	1.93	0.146
25	4.76	3.44	0.654	2.17	2.59	0.425

3.4 Identify the inhibitor with the slowest dissociation from the protease at 25 °C.

3.5 Calculate the rate constants of association (i.e. binding) of the protein–inhibitor complexes, k_A, at 25 °C for all inhibitors. Which of the inhibitors exhibits the fastest association with the protease?

3.6 Using the Arrhenius equation, calculate the activation free energy of dissociation $\Delta G^{\ddagger}$ (or E_a) of Lopinavir as well as that of the slowest dissociating inhibitor from question 3.4, and the compound with the largest association rate constant (which were obtained in question 3.5). Assume that the activation free energy is constant in the respective temperature range.

3.7 Is the inhibitor with the largest activation energy for dissociation the same compound as the strongest binder which was identified in question 3.1? We may extrapolate this finding: What relationship is there between the strength of binding expressed by the dissociation constant and the rate of dissociation expressed by the activation energy of dissociation?

Problem 4. Enantioselective hydrogenation

The hydrogenation of acetophenone with chiral catalyst **(*R*)-CAT** (2 mol%) at −40 °C for 8 hours gives a crystalline solid, (*R*)-1-phenylethan-1-ol, in 70% yield and 90% enantiomeric excess (*ee*). The specific rotation $[\alpha]_D^{20}$ (*c* 1.00, EtOH) of the product was determined to be +45°.

4.1 Draw the structure of the product.

4.2 The rate constant of the reaction leading to the (*R*)-product is $k_R = 2.5 \times 10^{-5}\ \mathrm{s}^{-1}$ at −40 °C. What is the rate constant k_S of the reaction that leads to the the (*S*)-product at the same temperature?

4.3 The activation energy for the reaction leading to the (*S*)-product is $E_a(S) = 80\ \mathrm{kJ\ mol^{-1}}$. Provided that the pre-exponential factor A is the same for both reactions, what is the activation energy $E_a(R)$ for the reaction leading to the (*R*)-product?

4.4 What temperature is needed to obtain 99% *ee*? What is a potential drawback?

4.5 Determine the specific rotation $[\alpha]_D^{20}$ (*c* 1.00, EtOH) of the product if **(*S*)-CAT** (4 mol%), an optical antipode to the catalyst **(*R*)-CAT**, is used at 0 °C and the same machine and cuvette are used for the measurement.

4.6 How would you increase the optical purity of the final product after the reaction?

Problem 5. Ultrafast reactions

The rate of true neutralization reactions has proved to be immeasurably fast.
Eucken's Lehrbuch der Chemischen Physik, 1949

The main problem with studying ultrafast reactions is mixing the reactants. A smart way to circumvent this problem is the so-called relaxation technique.

Neutralization is a good example of an ultrafast reaction:

$$\mathrm{H^+ + OH^- \underset{\mathit{k_2}}{\overset{\mathit{k_1}}{\rightleftharpoons}} H_2O}$$

Here, k_1 and k_2 are the rate constants for the forward and backward reaction, respectively. The mean enthalpy for this reaction is −49.65 kJ mol^{-1} in the temperature range 298–373 K. The density of water is 1.000 g cm^{-3}.

5.1 Water has pH = 7.00 at 298 K. Calculate the apparent equilibrium constant $K = \frac{[\mathrm{H_2O}]}{[\mathrm{H^+}][\mathrm{OH^-}]}$ of the neutralization reaction shown above. Calculate also the entropy change for the reaction.

5.2 Estimate the pH of boiling water (T = 373 K).

Heavy water undergoes an analogous neutralization reaction, yet it is less dissociated than light water at the given temperature: $K_w(\mathrm{D_2O}) = 1.35 \times 10^{-15}$ at 298 K.

$$\mathrm{D^+ + OD^- \underset{\mathit{k_2}}{\overset{\mathit{k_1}}{\rightleftharpoons}} D_2O}$$

5.3 What is pD of heavy water at 298 K?

5.4 Write the rate law for the change of the concentration of D_2O in terms of the concentrations of D^+, OD^- and D_2O.

The composition of the equilibrium system depends on temperature. If we apply an external stimulus, for example a very fast heat pulse on the system, we disturb the equilibrium and observe a subsequent relaxation to the equilibrium composition. We can describe the relaxation with a new quantity x, a deviation from the equilibrium concentrations:

$$x = [\mathrm{D_2O}]_{\mathrm{eq}} - [\mathrm{D_2O}] = [\mathrm{OD^-}] - [\mathrm{OD^-}]_{\mathrm{eq}} = [\mathrm{D^+}] - [\mathrm{D^+}]_{\mathrm{eq}}$$

5.5 Express the time change $\frac{\mathrm{d}x}{\mathrm{d}t}$ in terms of x. Give both the exact equation and the equation in which you neglect the small terms of x^2.

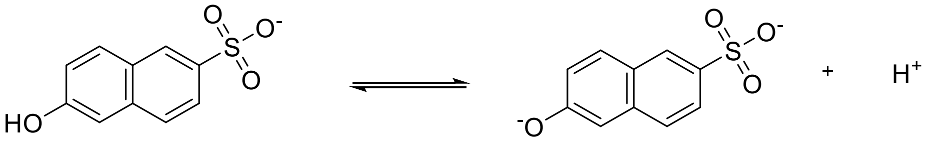
Solving the equation derived in 5.5, we get:

$$x = x(0) \times \exp(-t \times (k_1[\mathrm{D^+}]_{\mathrm{eq}} + k_1[\mathrm{OD^-}]_{\mathrm{eq}} + k_2))$$

where $x(0)$ is the deviation from equilibrium at the moment of perturbation.

5.6 For heavy water at 298 K, the relaxation time τ (time at which the deviation from equilibrium drops to $\frac{1}{e}$ of the initial value) was measured to be 162 μs. Calculate the rate constant for the forward and backward reaction. The density of heavy water is ρ = 1.107 g cm^{-3} and molar mass is M_r = 20.03.

Ultrafast reactions can also be triggered by a pH jump. Using an ultrafast laser pulse, we can induce a pH jump in a system with so-called photoacids. These compounds have dramatically different acid-base properties in the ground and excited electronic states. For example, the pK_a of 6-hydroxynaphthalene-2-sulfonate is 9.12 in the ground state and 1.66 in the excited state.



5.7 1 cm^3 of 5.0×10^{-3} mol dm^{-3} 6-hydroxynaphthalene-2-sulfonate solution was irradiated by light with the wavelength of 297 nm. The total absorbed energy was 2.228×10^{-3} J. Calculate the pH before and after irradiation. Neglect the autoprotolysis of water in both cases.

Note that the standard state for a solution is defined as c_0 = 1 mol dm^{-3} and assume that the activity coefficient is $\gamma_i = 1$ for all species. It may be of advantage to use an online cubic equation solver.

Problem 6. Kinetic isotope effects

Various isotopes of a given atom obey the same chemical principles, but their different masses cause different behaviour in a dynamic sense. The kinetic isotope effect refers to a phenomenon wherein isotopically substituted molecules react at different rates. It was postulated in 1933 by Eyring and Polanyi and since then kinetic isotope effects have provided detailed information about mechanisms of many organic and biochemical reactions.

Vibrational modes are quantized and we can use the harmonic oscillator approximation for the description of the stretching modes. The energy level E_v can be calculated as:

$$E_\mathrm{v} = \left(\mathrm{v} + \frac{1}{2}\right)\mathrm{h}\nu\,,$$

where v = 0, 1, 2, ... is the vibrational quantum number and ν the frequency which depends on the force constant k and the reduced mass μ:

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}\,.$$

Note for the following calculations: unless stated otherwise, round the isotopic mass in amu to the nearest integer.

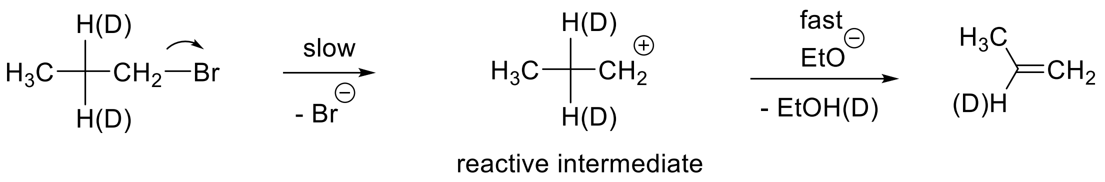
6.1 Let us start with a simple diatomic molecule ^{1}HF. Calculate its harmonic vibrational wavenumber in cm^{-1} and energies of the first two vibrational levels in J. The value of the harmonic force constant is k = 968 kg s^{-2}.

6.2 Isotopic substitution does not change the potential energy surface of a molecule. Therefore, k remains unaffected. Given the vibrational wavenumbers of $^{1}\mathrm{H}^{A}\mathrm{X}$ (2 439.0 cm^{-1}) and $^{2}\mathrm{D}^{A+2}\mathrm{X}$ (1 734.8 cm^{-1}), determine the unknown element X.

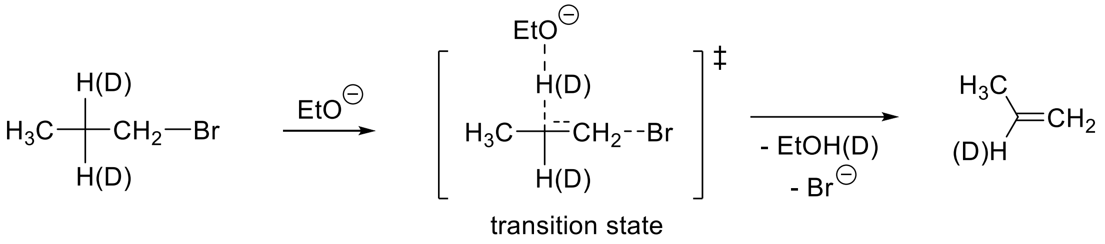
6.3 Zero-point vibrational energy is the key contributor to the kinetic isotope effect. If we assume that the bond is fully broken at the transition state and only the ground vibrational state is populated, the difference in activation energies has the same absolute value as the difference in zero-point vibrational energies. The wave numbers of the C−H and C−D stretches are 2 900 cm^{-1} and 2 100 cm^{-1}, respectively. Calculate the ratio of the rate constants k(C−H)/k(C−D) for the cleavage of the C−H/D bond at 300 K, taking into account only the difference in zero-point vibrational energies.

6.4 Kinetic isotope effects provide insight into the rate-determining step of a reaction mechanism. The ratio of $k_\mathrm{H}/k_\mathrm{D}$ for the formation of propene from 1-bromopropane and 1-bromo-2,2-dideuteriopropane in basic solution is 6.5. Does the reaction proceed by E1 or E2 mechanism? E1 takes place in two steps: formation of the carbocation intermediate followed by loss of H^{+}. E2 occurs in a single step involving removal of the halide at the same time as the neighbouring hydrogen.

E1



E2



6.5 Let us consider the formation of the corresponding alkene from 2-bromo-3,3--dideuterio-2-methylbutane and its light-hydrogen analogue upon heating in ethanol. How significant would the kinetic isotope effect be in this case?

Problem 7. Designing a photoelectrochemical cell

One of the most challenging issues for future technologies is to maximize the energy gain from renewable sources: solar, wind, hydropower, geothermal and biomass. Although they represent clean and highly abundant sources of energy with a tremendous physical potential, they are intermittent, which applies mainly to solar energy. This means that they are not available when and where needed, or at least not all the time: the sun sets, wind does not blow, etc. One of the possible solutions to this problem is to store energy in a medium that is long-lasting and dispatchable. Chemical bonds represent such a medium. In general, this is the concept of solar fuels.

Such a system is already readily available in nature: photosynthesis. Plants use sunlight to make fuel (carbohydrates) out of water and carbon dioxide. To be able to do that, however, plants need fertile soil, water and favourable climate. On the other hand, artificial photosynthetic systems are not limited by such constraints and are capable of producing a fuel with a higher energy density, like hydrogen. Photoelectrochemical (PEC) water splitting is a powerful, yet complex process. By completing the upcoming tasks, you will get a basic insight into photoelectrochemistry.

7.1 Which of the following half-reactions have reduction potentials dependent on pH?

a) $\mathrm{Br_2 + 2e^- \rightarrow 2Br^-}$
b) $\mathrm{NO_3^- + 3H^+ + 2e^- \rightarrow HNO_2 + H_2O}$
c) $\mathrm{ClO_3^- + 6H^+ + 6e^- \rightarrow Cl^- + 3H_2O}$
d) $\mathrm{Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O}$
e) $\mathrm{2CO_2 + 2e^- \rightarrow (COO)_2^{2-}}$
f) $\mathrm{2IO_3^- + 12H^+ + 10e^- \rightarrow I_2 + 6H_2O}$
g) $\mathrm{S_2O_8^{2-} + 2e^- \rightarrow 2SO_4^{2-}}$
h) $\mathrm{TiO^{2+} + 2H^+ + e^- \rightarrow Ti^{3+} + H_2O}$

7.2 Using the Nernst-Peterson equation and considering [$\mathbf{A}_{\mathrm{ox}}$] = [$\mathbf{A}_{\mathrm{red}}$], derive a formula for the dependence of the reduction potential of the following reaction on pH:

$$\mathbf{A}_{\mathrm{ox}} + ze^- + n\mathrm{H}^+ \rightarrow \mathbf{A}_{\mathrm{red}} + \frac{n}{2}\mathrm{H_2O}$$

What is the nature of this dependence (logarithmic, exponential, quadratic, etc.)?

7.3 Let us consider two possible reactions occurring in an electrolyte:

$$\mathbf{B}_{\mathrm{ox}} + 3\mathrm{e}^- \rightarrow \mathbf{B}_{\mathrm{red}} \qquad E^\circ_{\mathbf{B}} = +0.536\ \mathrm{V}$$
$$\mathbf{C}_{\mathrm{ox}} + 2\mathrm{e}^- \rightarrow \mathbf{C}_{\mathrm{red}} \qquad E^\circ_{\mathbf{C}} = +0.824\ \mathrm{V}$$

a) Which of the two possible reactions will occur under the conditions of $p = 1$ atm, $T = 298.15$ K? Will substance **B** oxidize **C** or will substance **C** oxidize **B**? Write a balanced chemical equation for the reaction between substances **B** and **C**.

b) Determine the standard potential for such a reaction.

c) Calculate the equilibrium constant for this reaction.

7.4 Now, let us consider the electrochemical system of two reactions that can occur in a cooled experimental cell, where one of them is pH-dependent and the other is not:

$$\mathbf{D}_{\mathrm{ox}} + \mathrm{e}^- \rightarrow \mathbf{D}_{\mathrm{red}} \qquad E_{\mathbf{D}} = +0.55\ \mathrm{V}$$
$$\mathbf{E}_{\mathrm{ox}} + \mathrm{e}^- + \mathrm{H}^+ \rightarrow \mathbf{E}_{\mathrm{red}} \qquad E_{\mathbf{E}} = +0.95\ \mathrm{V}$$

a) Calculate the change in potential (in millivolts) as a function of pH for the pH-dependent reaction. The given potentials correspond to pH = 0 and $T = 262$ K. The only parameter that can be changed during the experiment is the pH value of electrolyte.

b) Draw a straight line plot of the dependence of the reduction potentials (for both **D** and **E**) on pH in the range from 0 to 13.

c) Find the value of pH at which the equilibrium constant for the oxidation of substance **D** is $K = 2.56 \times 10^5$.

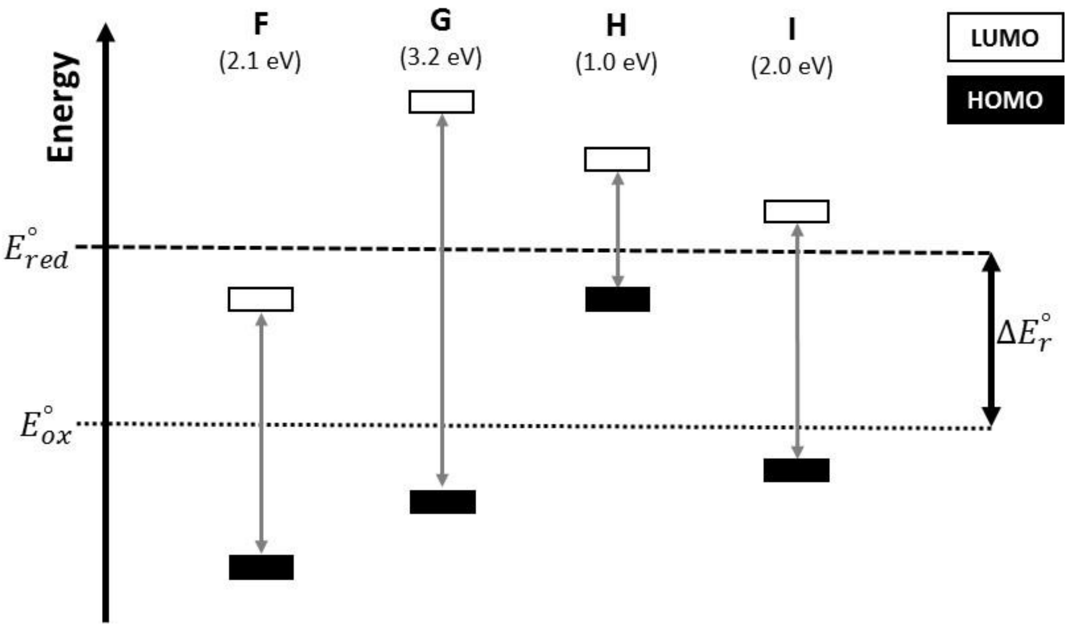
d) Show on the drawn plot the region of pH where **D** will oxidize **E**.

7.5 Calculate the time needed to electrolytically cover a 5 × 10 × 0.5 mm metallic plate fully immersed into 10 cm^3 of the solution of a gold precursor with $c(\mathrm{Au}^{3+}) = 5\ \mathrm{mmol\ dm}^{-3}$ with 5 mg of a gold protective film. Consider that only gold ($M_{\mathrm{Au}} = 197\ \mathrm{g\ mol}^{-1}$) is being deposited on the surface of the metallic plate, no side reactions occur, the surface area of the contacts with the electrode is negligible, and there is a constant current of 25 mA during the process.

Once the substrate for testing electrode is covered with a highly conducting and relatively non-reacting coating (e.g. gold), a photocatalyst can be added. Thanks to their chemical stability in aqueous environment, metal oxide-based semiconductors are suitable materials for photo-electrochemical applications. Recently, titanium dioxide has emerged as an excellent photocatalyst. It is an n-type semiconductor and can be used as a material for photoanodes. The whole complex mechanism of photoreactions occurring on irradiated n-type semiconductors can be simplified as follows. A photon with sufficient energy (wavelength) strikes the surface of a semiconductor and an electron from the highest occupied molecular orbital (HOMO) is excited to the lowest unoccupied molecular orbital (LUMO), leaving a positively charged hole (h^+) behind. When applying an external electric field, the excited electrons are driven through the system to the counter-electrode where they participate in reduction reactions while photogenerated holes participate in oxidation reactions. The observed flow of electrons is called net photocurrent.

Let us call E_{g} the difference between the energy levels of HOMO and LUMO. It denotes the minimum excitation energy (maximum wavelength) of irradiation. To choose the optimal photocatalyst for a redox reaction, two main presumptions exist: 1) the E_{g} of a semiconductor has to be “accurately” wider than the potential of a redox reaction; 2) the energy level of HOMO has to be below the energy level of the oxidation half-reaction while the energy level of LUMO has to be above the energy level of the reduction half-reaction.

7.6 In the following picture you can see a schematic view of an energy diagram comparing four materials (**F–I**) by positions of their HOMOs and LUMOs towards the investigated redox reaction.



a) Which materials could be used as photocatalysts for the reaction outlined in the diagram?

b) Calculate the maximum wavelengths (in nm) of irradiation sources needed to excite your chosen materials. Based on your results, decide whether you can or cannot use UV and/or VIS light for the irradiation.

Problem 8. Fuel cells

Let us consider a classical hydrogen cell with porous electrodes. Such electrodes are permeable to gases and the cathode also to liquid water. The cathode is fed with oxygen and the anode with hydrogen. The produced water is led out from the cathode compartment. The space between the electrodes is separated by a membrane which is permeable only to H^+ ions, so that they can conduct the electric current. Such a fuel cell is quite efficient as there is no other way for hydrogen and oxygen to react except for electron-transfer via electrodes and H^+ exchange through the membrane. Assume all gases behave as ideal. In this task, assume standard temperature 298 K and standard pressure 1 bar.

8.1 Determine the standard electromotive force (EMF) of the above described fuel cell working at 298 K with 1 bar hydrogen and 1 bar oxygen. Assume that water is produced in the liquid state.

8.2 Determine the standard EMF of the above described fuel cell working at 298 K with 1 bar hydrogen and 1 bar oxygen. Assume that water is produced in the gas state.

8.3 Calculate the ideal thermodynamic efficiency (thermodynamic or maximum or ideal efficiency is the ratio between the maximum extractible work and the heating value) of the fuel cells described in previous questions at (a) the standard temperature of 298 K and (b) 373 K. Neglect the enthalpy and entropy temperature dependence in all the calculations.

It is possible to construct a fuel cell very similar to the one described above, but working with butane and oxygen.

8.4 Write the balanced chemical equations for the cathode and anode half-reaction.

8.5 Calculate the EMF of the butane–oxygen fuel cell. Assume that butane is fed to the electrodes at the standard temperature and 1 bar and that it reacts with oxygen at 1 bar. Assume that water is produced in the liquid state.

8.6 Calculate the ideal thermodynamic efficiency of the butane fuel cell.

A modified construction of the butane fuel cell uses an oxide-conducting electrolyte, in which the following electrode half-reactions occur:

$$O_2 + 4\,e^- \rightarrow 2\,O^{2-}$$

$$4\,CO_2 + 5\,H_2O + 26\,e^- \rightarrow C_4H_{10} + 13\,O^{2-}$$

8.7 Determine the standard EMF of this modified butane fuel cell with an oxide-conducting electrolyte.

Another fuel cell works with the formal combustion of methanol. The EMF of such a cell at the standard temperature of 298 K is 1.21 V, and at 373 K it drops by 10 mV.

8.8 Write balanced chemical equations for the cathode and anode half-reaction. Write also the overall reaction that takes place in the methanol fuel cell.

8.9 Write down the Nernst equation for the EMF of this cell. Choose the appropriate standard states for the reactants and products.

8.10 Calculate the standard reaction enthalpy and entropy of the reaction taking place in the methanol fuel cell related to lowest integer coefficients in the chemical reaction involved in the fuel cell.
Hint: Use the van ’t Hoff equation.

Useful data:

$\Delta_f H°(H_2O(l)) = -286\ \text{kJ mol}^{-1}$

$\Delta_f H°(H_2O(g)) = -242\ \text{kJ mol}^{-1}$

$\Delta_f H°(CO_2(g)) = -393\ \text{kJ mol}^{-1}$

$\Delta_f H°(C_4H_{10}(g)) = -126\ \text{kJ mol}^{-1}$

$S°(H_2O(l)) = 70\ \text{J K}^{-1}\ \text{mol}^{-1}$

$S°(H_2O(g)) = 189\ \text{J K}^{-1}\ \text{mol}^{-1}$

$S°(H_2(g)) = 131\ \text{J K}^{-1}\ \text{mol}^{-1}$

$S°(O_2(g)) = 205\ \text{J K}^{-1}\ \text{mol}^{-1}$

$S°(C(s)) = 6\ \text{J K}^{-1}\ \text{mol}^{-1}$

$S°(CO_2(g)) = 214\ \text{J K}^{-1}\ \text{mol}^{-1}$

$\Delta_f G°(C_4H_{10}(g)) = -17\ \text{kJ mol}^{-1}$

Problem 9. Acid-base equilibria in blood

Acid-base homeostasis is one of the most strictly regulated systems in living organisms. Blood buffers are responsible for the short-term stability of pH. The most important one is the bicarbonate buffer, the components of which are further regulated by the lungs and kidneys.

9.1 The daily production of acids in our body is about 60 mmol released into 6 dm^3 of blood. For simplification, consider the blood bicarbonate buffer as a closed system initially containing only bicarbonate buffer with pH = 7.4. The partial pressure of CO_2 is $p(CO_2) = 5.3$ kPa. Calculate the pH at 37 °C, provided that the above-mentioned acidic burden is buffered by the bicarbonate buffer at physiological conditions.

9.2 However, blood is best considered to be an open system, taking into account that the partial CO_2 pressure is maintained at a constant level by respiration. Calculate the final pH for the bicarbonate buffer under the same conditions as described in task 9.1, assuming that $p(CO_2)$ does not change upon the addition of acids. Does the pH value fall into the physiologic range? Explain.

9.3 During cardiac surgery, patients are cooled down to hypothermia in order to prevent brain damage and to slow down their metabolism. Calculate pH at 20 °C (under the conditions of hypothermia), considering that $p(CO_2)$ and the concentration of bicarbonate remain unchanged.

The importance of pH regulation in a narrow window can be illustrated by its influence on other physiological networks, for example, oxygen transport mediated by red blood cells containing haemoglobin. Haemoglobin has lower affinity to oxygen in tissues with a lower value of pH.

9.4 During physical activity, pH in muscles decreases due to anaerobic metabolism. In lungs, on the other hand, CO_2 is removed from the bloodstream. How do these processes influence the haemoglobin-mediated oxygen transport?

Data for calculations:

Dissociation constants of dissolved carbon dioxide: pK_a (37 °C) = 6.1, pK_a (25 °C) = 6.35

Enthalpy of vaporization: $\Delta H_{vap}(CO_2, \text{blood}) = 19.95 \text{ kJ mol}^{-1}$

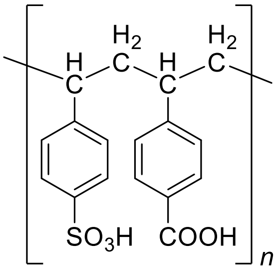
Henry's solubility of CO_2 in blood at 37 °C: $H^{cp}(CO_2, 37\ °C, \text{blood}) = 2.3 \times 10^{-4} \text{ mol m}^{-3} \text{ Pa}^{-1}$

Consider ideal behaviour and the concentration of carbonic acid $[H_2CO_3] = 0$.

Problem 10: Ion exchange capacity of a cation exchange resin

Ion exchange resins are porous materials, typically used in the form of small beads, with surface functional groups capable of ion exchange. As the binding of ions from a solution occurs, other ions are released from the resin. For example, the binding of cations from a sample of sea water is accompanied by the release of the corresponding amount of hydrogen ions originally bound to the sulfonyl acid groups on the surface of a cation exchange resin.

Let us have a look at the following cation exchange resin – catex **A**. Since *n* is very large, the terminal hydrogen atoms can be neglected in the following calculations.



Structure of catex **A**.

10.1 Calculate the mass percentage of sulfur and carbon.

10.2 Calculate the theoretical ion exchange capacities Q_m given separately by SO_3H groups (a strong catex) and COOH groups (a weak catex) in mmol g^{-1} of the dry catex.

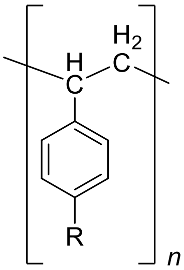
10.3 Calculate the total theoretical ion exchange capacity, $Q_{m,total}$, in mmol g^{-1}.

Frequently, ion-exchange resins become swollen when hydrated, i.e. the volume of the beads changes significantly due to the hydration of highly polar ion-exchange functional groups.

10.4 Calculate the total ion exchange capacity, $Q_{V,total}$, in mmol cm^{-3} of a swollen resin. The ratio of void volume to the total volume is $\varepsilon = 0.48$, the density of the swollen resin is $\rho = 1.28$ g cm^{-3} and the mass ratio of water bound to a resin is $w = 0.45$.

Problem 11. Weak and strong cation exchange resin

The total cation exchange capacity of catex **B** has been determined experimentally by the following procedure. The volume of 4 cm^3 of swollen catex was rinsed with the excess of sodium chloride solution to get a resin with sodium cations at all cation exchange sites. Afterwards, all unbound sodium cations were removed by rinsing with water. Next, the column was rinsed with a solution of acetic acid and all the effluent was collected in a 1 000 cm^3 volumetric flask which was then filled with water to the mark (solution A). During this procedure, H^+ ions were bound to all weak exchange sites and to some strong exchange sites. Subsequently, the column was rinsed with water to remove the excess acetic acid. In the next step, the column was rinsed with a neutral solution of $MgSO_4$ and all the effluent was collected in a 500 cm^3 volumetric flask which was then filled with water to the mark (solution B). In this case, Mg^{2+} was bound to all strong exchange sites.



Structure of catex **B** (R = H, COOH, SO_3H).

The amount of sodium ions in 100 cm^3 of solution A was determined by direct potentiometry with a sodium ion-selective electrode (ISE); the measured potential was $E_1 = -0.2313$ V, whereas the corresponding potentials of the electrode in the solutions of $c(Na^+) = 10.0$ mmol dm^{-3} and $c(Na^+) = 0.100$ mmol dm^{-3} were $E_2 = -0.2283$ V and $E_3 = -0.3466$ V, respectively.

The amount of sodium ions in 100 cm^3 of solution B was determined by the same procedure as described above. In this case, the measured potential of the electrode in solution B was $E_4 = -0.2534$ V. The concentration of hydrogen ions in 100 cm^3 of solution B was determined by alkalimetry. The volume of sodium hydroxide of $c = 0.1000$ mol dm^{-3} at the equivalence point was 12.50 cm^3.

All potentials were measured at a temperature of 298 K.

Hint: For the determination of sodium ion concentration use the equation $E = k + S \log_{10}[Na^+]$, where E is the potential of ISE and k and S are constants.

11.1 Calculate the ion exchange capacities of the catex, Q_V, which correspond to sulfonyl and carboxyl ion exchange groups, respectively. Provide the results in mmol cm^{-3}.

11.2 Calculate total ion exchange capacity, $Q_{V,total}$, in mmol cm^{-3}.

Problem 12: Uranyl extraction

Bis(2-ethylhexyl) hydrogen phosphate (di-(2-ethylhexyl)phosphoric acid, DEHPA) is used in the extraction of uranyl ions from an aqueous solution to an organic solvent. This water-to-kerosene extraction is known as the "Dapex process".

DEHPA (HA)

- Is a weak acid that is partially dissociated in water, with a dissociation constant

$$\mathrm{HA} \rightleftharpoons \mathrm{A}^- + \mathrm{H}^+ \qquad K_{\mathrm{a,HA}} = \frac{[\mathrm{A}^-]_{\mathrm{aq}} \times [\mathrm{H}^+]_{\mathrm{aq}}}{[\mathrm{HA}]_{\mathrm{aq}}} = 3.16 \times 10^{-4}$$

- Can be extracted to kerosene with a distribution constant

$$K_{\mathrm{D,HA}} = \frac{[\mathrm{HA}]_{\mathrm{org}}}{[\mathrm{HA}]_{\mathrm{aq}}} = 1.89 \times 10^{2}$$

- Forms a hydrogen-bonded dimer in non-polar organic solvents, with a dimerization constant

$$2\mathrm{HA} \rightleftharpoons (\mathrm{HA})_2 \qquad K_{\mathrm{p,HA}} = \frac{[(\mathrm{HA})_2]_{\mathrm{org}}}{[\mathrm{HA}]^2_{\mathrm{org}}} = 2.14 \times 10^{4}$$

- When dissociated in an aqueous solution, it forms a neutral compound with the uranyl ion in a ratio of 2:1 (Note: In real systems, the structure of the neutral compound can vary).

$$2\mathrm{A}^- + \mathrm{UO}_2^{2+} \rightleftharpoons \mathrm{UO_2A_2} \qquad \beta_{2,\mathrm{UO_2A_2}} = \frac{[\mathrm{UO_2A_2}]_{\mathrm{aq}}}{[\mathrm{A}^-]^2_{\mathrm{aq}} \times [\mathrm{UO}_2^{2+}]_{\mathrm{aq}}} = 4.31 \times 10^{11}$$

  This neutral compound can be extracted to kerosene with a distribution constant

$$K_{\mathrm{D,UO_2A_2}} = \frac{[\mathrm{UO_2A_2}]_{\mathrm{org}}}{[\mathrm{UO_2A_2}]_{\mathrm{aq}}} = 1.69 \times 10^{2}$$

Assume that:

- The concentration of DEHPA before the extraction: $c_{\mathrm{HA,org,0}}$ = 0.500 mol dm^{-3} and $c_{\mathrm{HA,aq,0}}$ = 0.000 mol dm^{-3}.
- $c_{\mathrm{UO}_2^{2+}} \ll c_{\mathrm{HA}}$, therefore it is possible to omit the concentration of $\mathrm{UO_2A_2}$ in the mass balance of HA in both the aqueous and organic phase.
- The volume ratio is $V_{\mathrm{org}}/V_{\mathrm{aq}}$ = 1.00.

Uranyl ions also form hydroxo complexes

$$\mathrm{UO}_2^{2+} + i\mathrm{OH}^- \rightleftharpoons [\mathrm{UO}_2(\mathrm{OH})_i]^{2-i} \quad \text{where } i = 1\text{–}4$$

$$\beta_{i,[\mathrm{UO}_2(\mathrm{OH})_i]} = \frac{[\mathrm{UO}_2(\mathrm{OH})_i^{2-i}]_{\mathrm{aq}}}{[\mathrm{UO}_2^{2+}]_{\mathrm{aq}} \times [\mathrm{OH}^-]^i_{\mathrm{aq}}}$$

Note: For clarity square brackets as a symbol for a complex were omitted in the numerator.

with decimal logarithms of the overall complexation constants log β_1 = 10.5, log β_2 = 21.2, log β_3 = 28.1, log β_4 = 31.5.

12.1 Considering that the pH of the aqueous phase after reaching equilibrium equals to 1.7, calculate the yield of uranyl ions extraction.

Hint: First, calculate the concentration of DEHPA in the organic phase after reaching the equilibrium with the aqueous phase, i.e. calculate $[HA]_{org}$. To do this, use the mass balance of HA. Consider the different forms of DEHPA in both the organic and aqueous solution.

12.2 Considering that the pH of the aqueous phase after reaching equilibrium equals to 10.3, calculate the yield of uranyl ions extraction.

Hint: Use the same procedure as in task 12.1.

In both cases, consider only the equilibria that have been mentioned so far.

Problem 13. Determination of active chlorine in commercial products

Traditional Czech and Slovak bleaching and disinfecting products include a commercially available solution called “SAVO”. The strength of products like SAVO is commonly expressed as the content of active (or free) chlorine. The active chlorine value determination is usually carried out by adding an excess of potassium iodide to a sample and titrating the equivalent of released iodine with the standard sodium thiosulfate solution.

13.1 Consider a reaction (i) between chlorine and water giving products **A** and **B** and a reaction (ii) between sodium hypochlorite and water giving products **A** and **C**. Write the chemical equations for both reactions. Which form of **A** will be dominant in an alkaline aqueous solution?

13.2 Commercial SAVO contains 22.4 g dm^{-3} of active chlorine. What is the corresponding molar concentration of sodium hypochlorite in SAVO?

13.3 For the determination of sodium hypochlorite, 10.00 cm^3 of SAVO (density 1.070 g cm^{-3}) were transferred into a 250 cm^3 volumetric flask, distilled water was added to the mark and the solution was mixed. An aliquot of 10.00 cm^3 of the solution was transferred into a titration flask and diluted with approx. 50 cm^3 of distilled water. After the addition of 5 g of potassium iodide, the released iodine was titrated by 10.15 cm^3 of 0.0503 mol dm^{-3} standard sodium thiosulfate solution to reach the equivalence point. Calculate the mass percentage of sodium hypochlorite in the original SAVO product.

Problem 14. Chemical elements in fireworks

Low explosive pyrotechnics used in fireworks contain inorganic elements in the fuel or as oxidizers or additives. Typical fuels are based on metal or metalloid powders and typical oxidizers are based on perchlorates, chlorates and nitrates with added alkali, alkaline earth and some transition metals. All these substances can easily be determined in an analytical laboratory.

14.1 Explain the principle of qualitative flame tests used for the detection of sodium, barium and lithium ions dissolved in aqueous solution. Which flame colours are associated with these elements?

Ions of alkaline earth metals and transition metals can by determined by complexometric titrations with EDTA, which is a weak acid with $\mathrm{p}K_{\mathrm{a1}} = 2.00$, $\mathrm{p}K_{\mathrm{a2}} = 2.67$, $\mathrm{p}K_{\mathrm{a3}} = 6.16$ and $\mathrm{p}K_{\mathrm{a4}} = 10.26$.

14.2 Sketch the structure of a metal–EDTA complex. Which forms of EDTA will be present in a solution with a pH = 10 at molar concentration higher than 0.5% of the total?

The determination of calcium, strontium and barium ions by the reaction with EDTA is often performed in the presence of an ammonium buffer, which keeps the pH of the solution around 10.

14.3 What is the chemical composition of an ammonium buffer? What is the role of an alkaline pH in these reactions?

A combustible mixture used in fireworks (containing zinc, magnesium, lead, and no other multivalent ions) in a paper cartridge was analyzed in the following three steps:

i. The sample (0.8472 g) was dissolved and an excess of cyanide was added to mask the zinc in solution. This mixture was titrated with 0.01983 mol $\mathrm{dm^{-3}}$ EDTA and $V_1 = 35.90\ \mathrm{cm^3}$ was required to reach the equivalence point.

ii. Next, 2,3-disulfanylpropan-1-ol (DMP) was added and the released EDTA was titrated with 12.80 $\mathrm{cm^3}$ of 0.01087 mol $\mathrm{dm^{-3}}$ of $\mathrm{Mg^{2+}}$ standard solution to reach the equivalence point.

iii. Finally, formaldehyde was introduced to release the zinc ions, which were subsequently titrated with $V_2 = 24.10\ \mathrm{cm^3}$ of 0.01983 mol $\mathrm{dm^{-3}}$ EDTA to reach the equivalence point.

14.4 Write both ionic equations for the masking and the releasing of the zinc ions.

14.5 Explain the role of the DMP addition.

14.6 Calculate the mass (in mg) of all three elements in 1 g of the original sample.

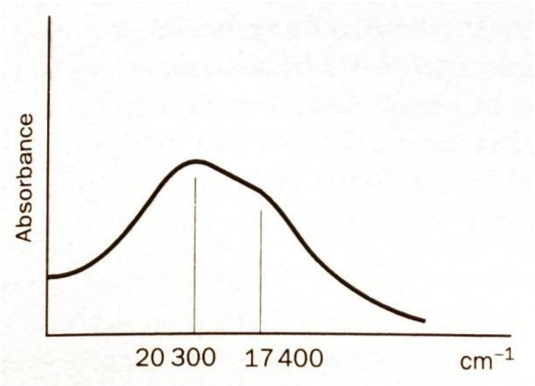
14.7 10.00 $\mathrm{cm^3}$ of 0.0500 mol $\mathrm{dm^{-3}}$ $\mathrm{Ca^{2+}}$ solution was mixed with 50.00 $\mathrm{cm^3}$ of 0.0400 mol $\mathrm{dm^{-3}}$ EDTA in a 100 $\mathrm{cm^3}$ volumetric flask and after the pH was set to 6, the flask was filled up to the mark with distilled water. Calculate the concentration of free $\mathrm{Ca^{2+}}$ ions in the solution. Decimal logarithm of the stability constant for the complex of $\mathrm{Ca^{2+}}$ ions with EDTA is 10.61. Consider only the equilibria that have been mentioned so far.

Problem 15. Colours of complexes

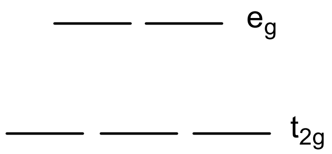
Due to the absorption of a part of the light in the visible region of the spectrum, transition metal complexes are often coloured. In this problem, we shall focus on simple cases in which this absorption is caused by d-d transitions.

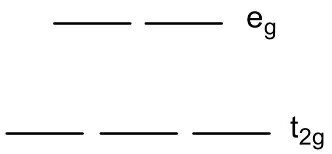
Titanium complex

Titanometry is a reductometric method that uses blue-violet aqueous solution of titanium(III) chloride. The colour of the solution is caused by the presence of octahedral particles $[Ti(H_2O)_6]^{3+}$. The spectrum features absorption band with a maximum at 20 300 cm^{-1}:



15.1 Draw the electron configuration of the ground and the excited state of the $[Ti(H_2O)_6]^{3+}$ ion into the schemes.



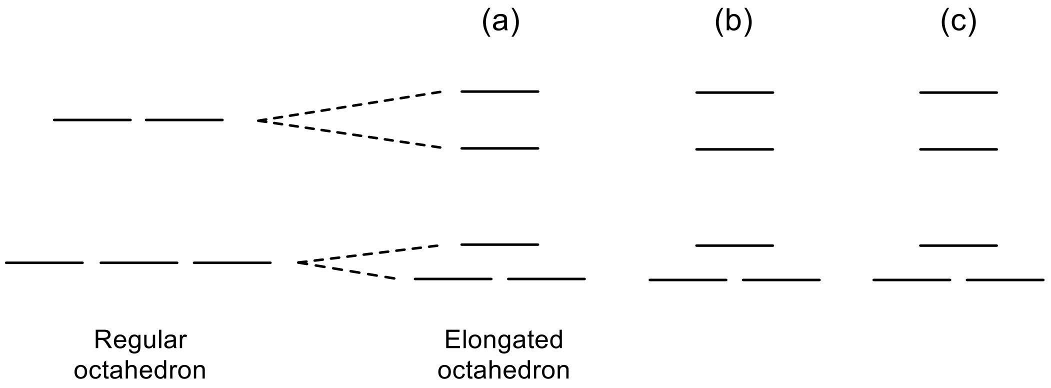


15.2 Predict the colour of the complex. Consider the absorption of the light at 20 300 cm^{-1}.

15.3 In fact, there is a second absorption band in the spectrum. This band shows itself as a shoulder at 17 400 cm^{-1}. Explain the colour of the complex based on the actual spectrum.

The presence of two bands in the spectrum is caused by the fact that the $[Ti(H_2O)_6]^{3+}$ particle is not a regular octahedron; it is rather an elongated octahedron. This elongation causes further splitting of the d-orbitals.

15.4 Draw the electron configuration of the ground (a) and the excited states (b) and (c) into the schemes.



Cobalt complexes

The $K_3[CoF_6]$ complex is a rare example of a high-spin cobalt(III) complex. The fluorination of cobalt(II) chloride yields cobalt(III) fluoride (1). Its reaction with potassium fluoride yields the $K_3[CoF_6]$ complex (2). This reaction is carried out in non-aqueous media (HF) because cobalt(III) fluoride oxidizes water (3).

15.5 Write the equations of reactions (1) to (3).

The $[Co(NH_3)_6]Cl_3$ complex is prepared by bubbling air through ammoniacal solution of cobalt(II) chloride and ammonium chloride under activated carbon catalysis.

15.6 Write the equation of reaction (4).

15.7 The common name of the $[Co(NH_3)_6]Cl_3$ complex is luteochloride. It has two absorption bands at the wavenumbers of 21 050 cm^{-1} and 29 400 cm^{-1} in the near UV and visible part of the spectrum. Predict the colour of the complex. Find the relation between the colour and its common name.

15.8 Explain why the $K_3[CoF_6]$ complex is high-spin and paramagnetic, while the $[Co(NH_3)_6]Cl_3$ complex is low-spin and diamagnetic.

High-spin complexes with the d^6 configuration have spectra like those of d^1 configuration. The $[CoF_6]^{3-}$ ion has the shape of an elongated octahedron.

15.9 Draw the electron configuration of the ground state and excited states provided that the net spin of the particle is not changed when excited.

15.10 The wavenumbers of the bands corresponding to these excitations are 11 400 cm^{-1} and 14 500 cm^{-1}. Predict the colour of the $[CoF_6]^{3-}$ ion.

Problem 16. Iron chemistry

For historical, political, economic, technological as well as biological and biochemical reasons, iron is one of the most important elements on the periodic table. In the following task some general aspects concerning the chemistry of iron will be discussed from the viewpoint of physical chemistry.

First, let us explore the available redox states of iron in detail.

16.1 Sketch the Latimer diagram for iron species (pH 0), using the following standard redox potentials: $E°(FeO_4^{2-}, H^+/Fe^{3+}) = 1.90$ V, $E°(Fe^{3+}/Fe^{2+}) = 0.77$ V, $E°(Fe^{2+}/Fe) = -0.44$ V. Calculate also the redox potentials for couples FeO_4^{2-}/Fe^{2+}, FeO_4^{2-}/Fe and Fe^{3+}/Fe and add them to the diagram.

16.2 Determine the voltage equivalents for individual redox states of iron and plot the Frost diagram. Decide whether the mixture of FeO_4^{2-} and Fe^{2+} at $pH = 0$ will interact spontaneously.

Another frequently used type of redox (and acid-base) equilibrium plot is the Pourbaix diagram. It involves individual pH-dependent redox potentials. Let us look into the problem more deeply.

For simplicity, activities will be replaced with equilibrium concentrations even though such description does not always adequately correspond to reality. Potentials are given in volts. The notation of the cationic species in the text and equations ignores the water molecules in the coordination sphere, i.e. Fe^{2+} means $[Fe(H_2O)_6]^{2+}$, $[Fe(OH)]^+$ means $[Fe(H_2O)_5(OH)]^+$, etc. Therefore, e.g. $[Fe(OH)_3]$ must not be considered as solid iron(III) hydroxide but it denotes dissolved neutral $[Fe(OH)_3(H_2O)_3]$ complex species.

Each line in the Pourbaix diagram originates from the assumption that the activities (concentrations) of both species participating in the given equilibrium are equal.

(a) If only redox equilibria are considered, the resulting plot contains horizontal lines (Figure 1a). A typical example is the redox pair Tl^+/Tl with $E° = -0.34$ V (in the pH range 0 to 12; in more basic solutions hydroxido complexes are formed). The mathematical expression of the given line is simple, eq. (1):

line a The potential at which activities/concentrations of Tl^+ and Tl(s) are equal, i.e. $a(Tl,s)/[Tl^+] = 1$:

$$(Tl^+/Tl): E = E° - (0.059 / n) \log(a(Tl,s) / [Tl^+]) = -0.34 - 0 = -0.34 \text{ V} \quad (1)$$

(b) When the same approach is applied to a system in which only protolytic (e.g. hydrolytic) processes occur (with no redox contribution within the selected potential limits) leads to vertical lines (Figure 1b). For instance, the stepwise hydrolysis of Ga^{3+} ion occurs according to four overall stability constants of complex hydroxido species, eq. (2–5).

$$Ga^{3+} + OH^- = [Ga(OH)]^{2+}, \log\beta_1 = [Ga(OH)^{2+}] / ([Ga^{3+}] \times [OH^-]) = 11.4 \quad (2)$$

$$Ga^{3+} + 2\ OH^- = [Ga(OH)_2]^+, \log\beta_2 = [Ga(OH)_2^+] / ([Ga^{3+}] \times [OH^-]^2) = 22.1 \quad (3)$$

$$Ga^{3+} + 3\ OH^- = [Ga(OH)_3], \log\beta_3 = [Ga(OH)_3] / ([Ga^{3+}] \times [OH^-]^3) = 31.7 \quad (4)$$

$$Ga^{3+} + 4\ OH^- = [Ga(OH)_4]^-, \log\beta_4 = [Ga(OH)_4^-] / ([Ga^{3+}] \times [OH^-]^4) = 39.4 \quad (5)$$

The final expressions (6–9) can be derived and calculated as follows:

line b pH at which concentrations of Ga^{3+} and $[Ga(OH)]^{2+}$ are equal, i.e. pH = pK_a of $[Ga(H_2O)_6]^{3+}$ leading to the formation of $[Ga(H_2O)_5OH]^{2+}$:

$$(Ga^{3+}/[Ga(OH)]^{2+}):\ pH = pK_w - \log\beta_1 = 14.0 - 11.4 = 2.6; \qquad (6)$$

and, analogously:

line c $([Ga(OH)]^{2+} / [Ga(OH)_2]^{+})$:

$$pH = pK_w - \log\beta_2 + \log\beta_1 = 14.0 - 22.1 + 11.4 = 3.3 \qquad (7)$$

line d $([Ga(OH)_2]^{+} / [Ga(OH)_3])$:

$$pH = pK_w - \log\beta_3 + \log\beta_2 = 14.0 - 31.7 + 22.1 = 4.4 \qquad (8)$$

line e $([Ga(OH)_3] / [Ga(OH)_4]^{-})$:

$$pH = pK_w - \log\beta_4 + \log\beta_3 = 14.0 - 39.4 + 31.7 = 6.3 \qquad (9)$$

(c) If both redox and protolytic equilibria are involved, the resulting line is sloping. One useful example is the oxygen reduction (10) and hydrated proton reduction (11), which is shown in Figure 1c. The analytical expressions of *lines f* (12) and *g* (13) have an identical slope value, i.e. both lines are parallel and they define the area of water redox stability with respect to the reduction affording $H_2(g)$ and oxidation to $O_2(g)$.

$$O_2 + 4\,H^+ + 4\,e^- \rightarrow 2\,H_2O,\ E° = 1.23\ V \qquad (10)$$

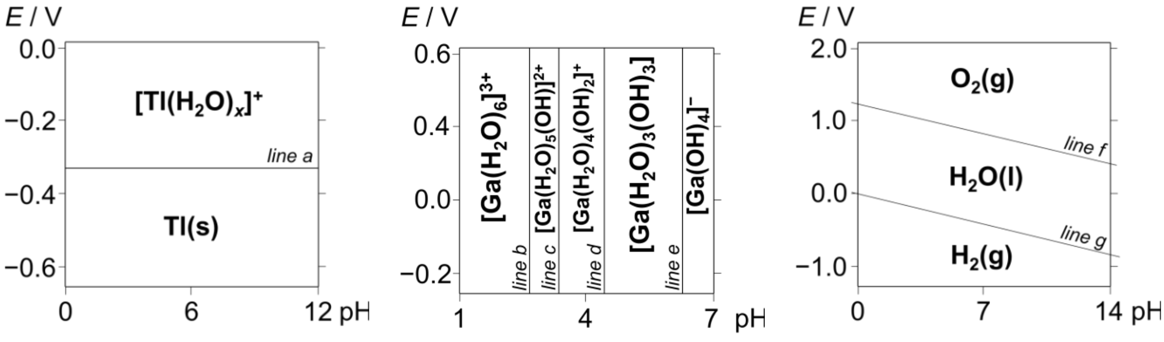
$$2\,H^+ + 2\,e^- \rightarrow H_2,\ E° = 0\ V\ (def.) \qquad (11)$$

line f $(O_2,H^+/H_2O)$:

$$E = E° - (0.059 / n) \times \log[a^2(H_2O,l) / (a(O_2,g) \times [H^+]^4)] = 1.23 - 0.059 \times pH \qquad (12)$$

line g (H^+/H_2):

$$E = E° - (0.059 / n) \times \log[a(H_2,g) / [H^+]^2] = -0.059 \times pH \qquad (13)$$



(a) **(b)** **(c)**

Figure 1. Pourbaix diagrams of **(a)** Tl^+/Tl system, **(b)** $Ga^{3+}/[Ga(OH)_n]^{(3-n)+}$ system and **(c)** $H_2/H_2O/O_2$ system.

Now, let us turn back to iron chemistry.

16.3 The construction of the Pourbaix diagram for all iron species is rather tedious. Thus, a rough form of the result valid for metallic iron and dissolved iron species between pH 0 and 14 is provided in Figure 2.

a) All the lines divide the area of the diagram into many zones. Deduce which species prevail in the individual zones in Figure 2 and fill the answers into the diagram.

b) Using the data from 16.1 together with Table 1, derive and write down the conditions for horizontal *lines 11* and *17*, and vertical *lines 2* and *5*.

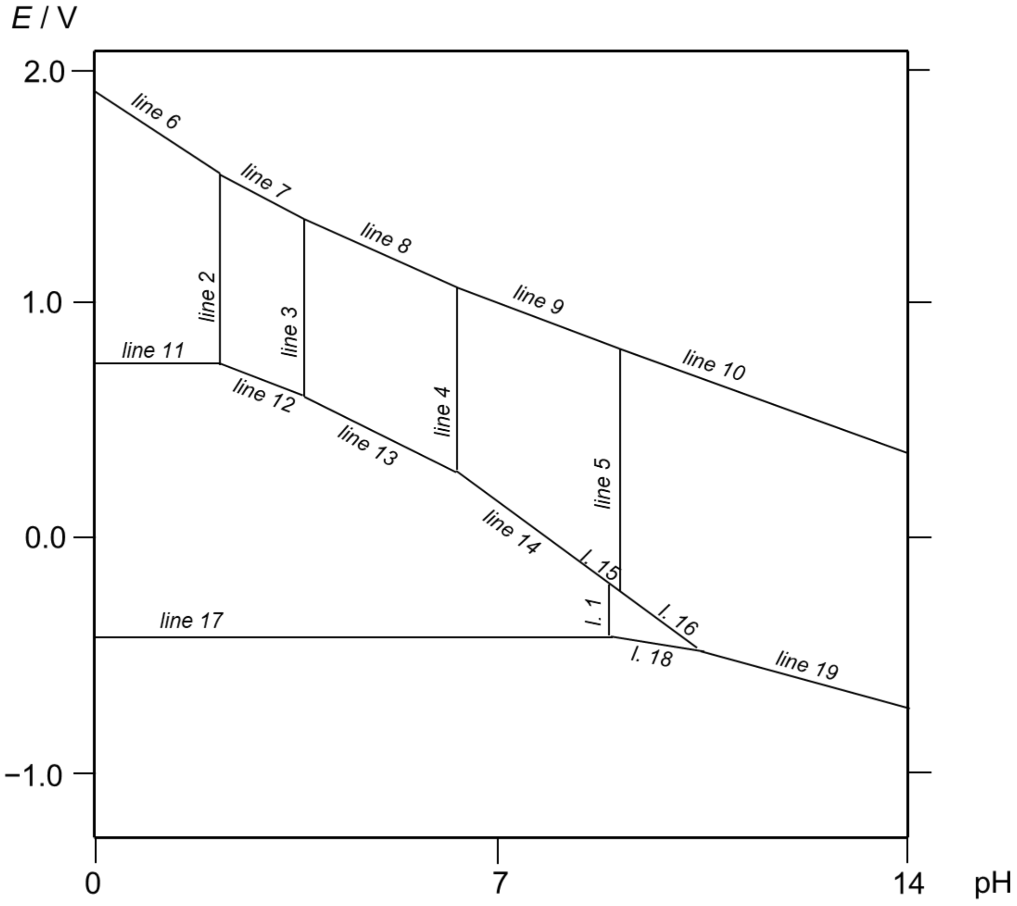


Figure 2. Pourbaix diagram for metallic iron and dissolved iron species in water.

Table 1: Overall stability constants β_n of ferrous / ferric hydroxido complexes.

	log β_n ($Fe^{2+} + n\ OH^-$)	log β_n ($Fe^{3+} + n\ OH^-$)
$n = 1$	4.5	11.8
$n = 2$	–	22.3
$n = 3$	–	30.0
$n = 4$	–	34.4

c) As an example of sloping lines, derive the equation for *line 6* and determine the coordinates [pH, *E*] of its intersection with *lines 2* and *7*.

d) Ferrate(VI) anion is a stronger oxidizing agent than oxygen itself (compare *line f* in Figure 1c with the stability region of the ferrate ion in Figure 2), and thus is stable only in an extremely basic region, in which the potentials of O_2/H_2O and $FeO_4^{2-}/[Fe(OH)_n]^{(3-n)+}$ are comparable. Thus, in general, the ferrate ion is not stable in aqueous solutions and oxidizes water to oxygen. Suggest a method for generating a ferrate ion. Write the corresponding stoichiometric equation.

It is generally known that ferric compounds tend to hydrolyze more readily than ferrous compounds.

16.4 Discuss all the species involved in the Pourbaix diagram (Figure 2) in terms ion size and surface charge density concept and explain which ligands would best match each metal-ion centre.

Thermodynamic, kinetic, spectroscopic and magnetic properties are closely related to the electronic structure of the individual species. Since iron is a d-block metal, crystal field and ligand field theories help us to understand the situation. Concerning the determination of the electron configuration in the frame of split d-orbital levels, the most useful qualitative concept is the spectrochemical series.

16.5 Write down the magnetic state of the following species (high/low-spin state): $[Fe(H_2O)_6]^{2+}$, $[Fe(CN)_6]^{4-}$, $[Fe(H_2O)_6]^{3+}$, $[Fe(H_2O)_5OH]^{2+}$, $[Fe(CN)_6]^{3-}$. In the approximation of O_h symmetry, calculate the LFSEs and express the results in the units of ligand field strength Δ_o and electron-pairing energy P.

16.6 Figure 3 below shows the UV-Vis spectra of an orange-brown solution of $FeCl_3$ containing a $[Fe(H_2O)_5OH]^{2+}$ cation and of a nanosuspension of the Prussian blue (which can be approximated as $Fe_4[Fe(CN)_6]_3$). The spectra are shown in an unknown order. Assign each compound to the respective spectrum.

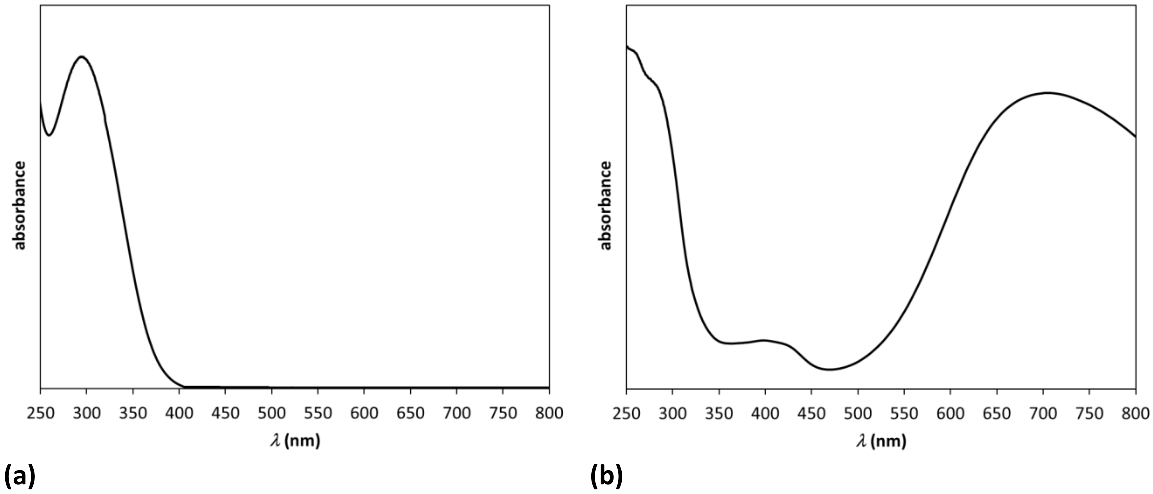


Figure 3. Spectra of $FeCl_3$ and $Fe_4[Fe(CN)_6]_3$ (in unknown order).

Problem 17. Cyanido- and fluorido-complexes of manganese

Manganese forms the highest number of oxidation states among the first-row transition metals. This task deals with the synthesis and electronic structure of manganese cyanido- and fluorido-complexes in oxidation states +I to +IV.

Oxidation state +I

Metallic manganese reacts only slowly with water. It dissolves readily in 2 M deaerated solution of NaCN to give colourless, diamagnetic $Na_5[Mn(CN)_6]$ (1).

17.1. Write a balanced equation (1).

17.2 Draw the splitting diagram for the complex anion and fill in the electrons.

Oxidation state +II

Soluble manganese(+II) compounds (e.g. chloride, nitrate, sulfate) are common starting materials for the preparation of manganese complexes. Mn^{2+}(aq) in deaerated aqueous solution reacts with excess CN^- to give a blue ion $[Mn(CN)_6]^{4-}$ with a magnetic moment corresponding to one unpaired electron.

17.3 Mn^{2+}(aq) ion can be considered as a high-spin hexaaqua-complex. Draw the splitting diagram, fill in the electrons and predict the number of unpaired electrons in the complex.

17.4 Draw the splitting diagram for $[Mn(CN)_6]^{4-}$ and fill in the electrons.

Oxidation state +III

Red $[Mn(CN)_6]^{3-}$ is an example of a rare low-spin manganese(+III) complex. It can be prepared by three different methods:

i. Stream of air is bubbled through the solution of a manganese(+II) salt and excess of cyanide (2).

ii. $[Mn(CN)_6]^{4-}$ is oxidized by 3% solution of hydrogen peroxide (3).

iii. Manganese(+II) chloride is oxidized by nitric acid in excess phosphoric acid (NO is formed) (4). The green-grey precipitate thus formed is filtered off and dissolved in potassium cyanide solution at 80 °C (non-redox reaction) (5).

17.5 Write balanced equations (2)–(5), (2) and (3) in an ionic form.

17.6 Draw the splitting diagram for $[Mn(CN)_6]^{3-}$ ion and fill in the electrons.

Violet complex $K_3[MnF_6]$ can be prepared by dissolving manganese dioxide in KHF_2 aqueous solution (6).

17.7 Write a balanced equation (6).

Other manganese(+III) fluorido-complexes exist with seemingly different coordination numbers: $Na_2[MnF_5]$, $Cs[MnF_4]$. In reality, the coordination number of Mn atom is 6 in both cases. Octahedral units $[MnF_6]^{oct}$ in the structure of these salts are interconnected by bridging F atoms.

17.8 Draw the splitting diagram for the octahedral species $[MnF_6]^{3-}$ and fill in the electrons.

17.9 Predict the structure of anionic 1D-chains present in $Na_2[MnF_5]$.

17.10 Predict the structure of anionic 2D-layers present in $Cs[MnF_4]$.

Oxidation state +IV

The oxidation of a $[Mn(CN)_6]^{3-}$ ion by nitrosyl chloride gives a $[Mn(CN)_6]^{2-}$ ion. When irradiated with sunlight, this ion undergoes reductive photolysis to give a tetrahedral $[Mn(CN)_4]^{2-}$ ion.

17.11 Draw the splitting diagram for $[Mn(CN)_6]^{2-}$ and fill in the electrons.

17.12 All the regular tetrahedral complexes are high-spin. Why? Draw the splitting diagram for $[Mn(CN)_4]^{2-}$ and fill in the electrons.

Yellow fluorido-complex $K_2[MnF_6]$ can be prepared by reducing $KMnO_4$ with hydrogen peroxide in the presence of KHF_2 and HF (7).

17.13 Write a balanced equation (7).

17.14 The electronic structure of $[MnF_6]^{2-}$ can be described qualitatively by the same splitting diagram as $[Mn(CN)_6]^{2-}$. Why?

Interestingly, complex $K_2[MnF_6]$ can be used for non-electrolytic fluorine preparation. Upon heating, it reacts with SbF_5 to give $K[SbF_6]$, MnF_2 and fluorine (8).

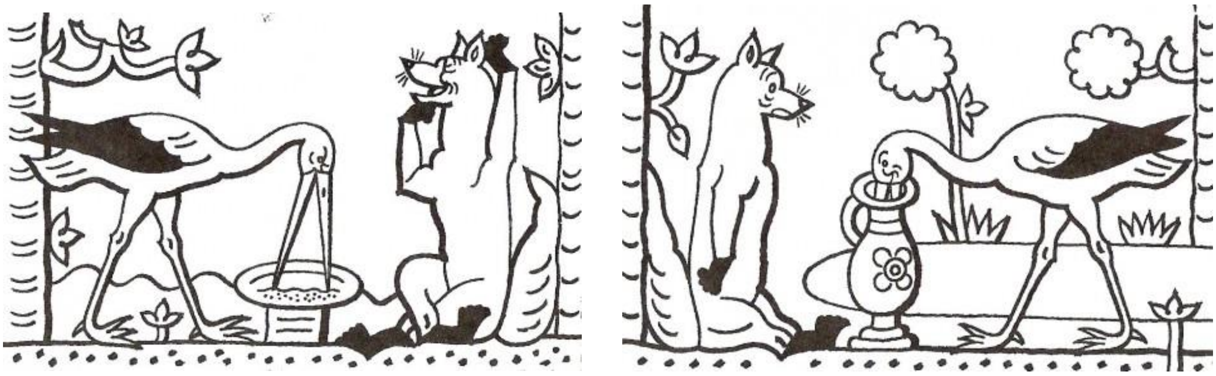
17.15 Write a balanced equation (8).

Problem 18. The fox and the stork

A fox one day invited a stork to dinner, and being disposed to divert himself at the expense of his guest, provided nothing for the entertainment but some thin soup in a shallow dish. This the fox lapped up very readily, while the stork, unable to gain a mouthful with her long narrow bill, was as hungry at the end of dinner as when she began. The fox meanwhile professed his regret at seeing her eat so sparingly and feared that the dish was not seasoned to her mind.

The stork said little, but begged that the fox would do her the honour of repaying her visit. Accordingly, he agreed to dine with her on the following day. He arrived true to his appointment and the dinner was ordered forthwith.

When the meal was served up, the fox found to his dismay that it was contained in a narrow-necked vessel, down which the stork readily thrust her long neck and bill, while he was obliged to content himself with licking the neck of the jar. Unable to satisfy his hunger, he retired with as good a grace as he could, observing that he could hardly find fault with his entertainer, who had only paid him back in his own coin.



An alternative end of the fable (instead of the grey sentence) could be:

However, as the fox was very clever, he took a look around and found a solution to his problem. There were many pebbles lying around. The fox did not hesitate even for a moment and started to throw them inside the jar of soup. The stork was shaking her head in confusion as the fox kept throwing the pebbles in, until the moment that the surface of the soup reached the brim of the jar. Then the fox turned to the stork with a smirk on his face and said: “Of course I will taste it,” and started to eat the soup.

A minimum volume of the soup in the jar is necessary for the fox to succeed. This volume is related to the total volume of the pebbles eventually present in the jar. This total volume is related to the number, size and way of arrangement of the pebbles.

Let us approximate the situation by a geometrical model:

- The jar is approximated as a perfect cylinder with a diameter of 10.0 cm and a height of 50.0 cm.
- A pebble is approximated as a perfect hard-sphere.
- All the spheres have the same diameter.
- The spheres are arranged as close as possible so that they touch each other.
- The soup is approximated by water.
- All pebbles are fully inside the jar (i.e. no part of any pebble is above the rim of the cylinder).

Large stones

Let us consider the radius of the sphere $r = 5$ cm.

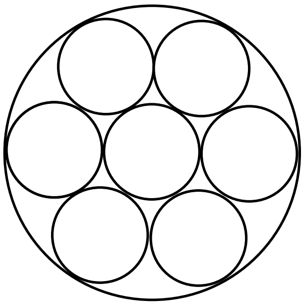
18.1 Calculate the maximum number of spheres that fit into the cylinder.

18.2 Calculate the fraction (in %) of the cylinder volume occupied by this number of spheres.

18.3 Calculate the free volume (in cm^3) among the spheres that can be filled with water.

Pebbles

Let us consider an arrangement in which 7 spheres in the first (base) layer just fit into the cylinder:



18.4 Calculate the radius of the sphere (in cm).

In the following questions, consider an arrangement in which all the higher layers copy the positions of the spheres in the base layer.

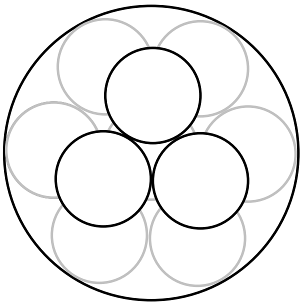
18.5 Calculate the maximum number of layers that fit in the cylinder.

18.6 Calculate the maximum number of spheres that fit in the cylinder.

18.7 Calculate the fraction (in %) of the cylinder volume occupied by this number of spheres.

18.8 Calculate the free volume (in cm^3) among the spheres that can be filled with water.

In the following questions, consider an arrangement in which each even layer consists of 3 spheres and each odd layer copies the positions of the spheres in the base layer:



18.9 Calculate the maximum number of layers that fit in the cylinder.

18.10 Calculate the maximum number of spheres that fit in the cylinder.

18.11 Calculate the fraction (in %) of the cylinder volume occupied by this number of spheres.

18.12 Calculate the free volume (in cm^3) among the spheres that can be filled with water.

Sand

Let us consider very small spheres with diameter smaller by orders of magnitude than the diameter of cylinder ($r \to 0$).

18.13 Calculate the limiting fraction (in %) of the cylinder volume occupied by the spheres.

18.14 Calculate the free volume among the spheres that can be filled with water.

Problem 19. Structures in the solid state

The structure of sodium chloride, NaCl, is one of the basic crystal structure types of ionic compounds. Its face-centred cubic unit cell is shown in Figure 1. The lattice constant of NaCl is a = 5.64 Å and the radius of the sodium(I) ion is $r(\mathrm{Na^+})$ = 1.16 Å.

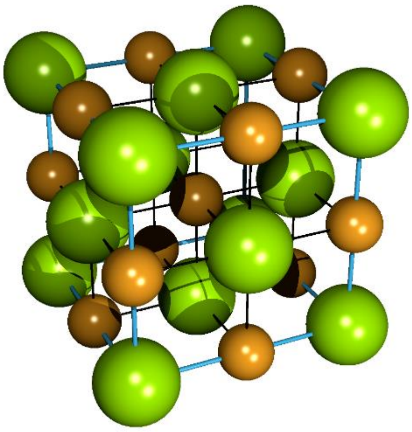


Figure 1. Unit cell of NaCl. Colour code: $\mathrm{Na^+}$ yellow, $\mathrm{Cl^-}$ green.

19.1 Calculate the ionic radius of a chloride ion, $r(\mathrm{Cl^-})$.

Potassium chloride, KCl, crystallizes in the same crystal structure type. The density of solid KCl is ρ(KCl) = 1.98 g cm^{-3}.

19.2 Calculate the ionic radius of a potassium ion, $r(\mathrm{K^+})$.

The structure of ionic compounds can be estimated using relative sizes of the cation and anion, as r_+/r_- ratio determines what kind of cavity found in the anionic lattice could be occupied by the cation.

19.3 The ionic radius of a lithium ion is $r(\mathrm{Li^+})$ = 0.90 Å. Estimate whether LiCl adopts the same crystal structure type as NaCl or not.

Some ionic compounds of divalent ions also crystallize in the crystal structure type of NaCl, for example galena, PbS. Its lattice constant is a = 5.94 Å.

19.4 Calculate the density of galena.

Since silver(I) ions can be substituted for lead(II) ions in the structure of PbS, galena is a very important silver ore. To ensure electro-neutrality of the crystal, the decrease in the overall positive charge is compensated by the vacancies of sulphide anions. The composition of such a phase can be expressed by a general formula $\mathrm{Pb}_{1-x}\mathrm{Ag}_x\mathrm{S}_y$.

19.5 Derive the value of y as a function of x.

A sample of silver-containing galena, in which a part of the lead(II) ions are substituted by silver(I) ions and the decrease in charge is compensated by the vacancies of sulphide ions, has a density of 7.21 g cm^{-3}. The lattice constant of this sample is a = 5.88 Å.

19.6 Calculate the value of the stoichiometric coefficient x.

Zinc blende (sphalerite, ZnS) crystallizes in a different crystal structure type, which is closely related to the structure of diamond. Both types of structures are shown in Figure 2.

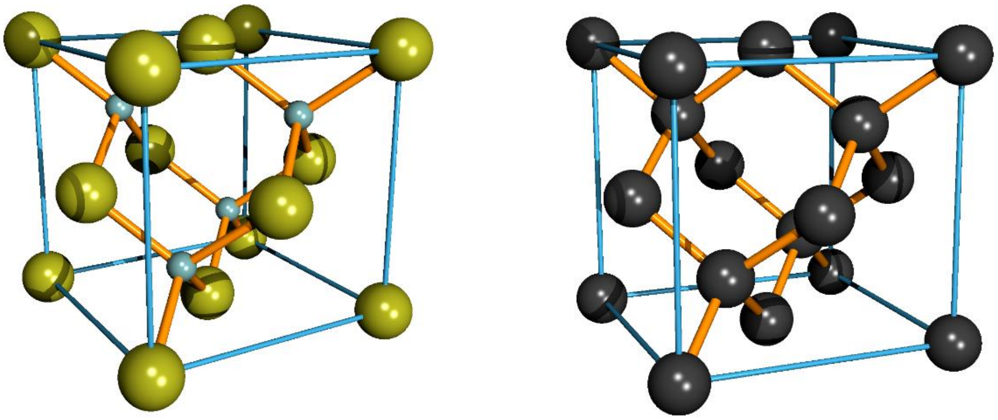


Figure 2. (a) Unit cell of sphalerite. **(b)** Unit cell of diamond.
Colour code: Zn^{2+} grey, S^{2-} yellow-green.

19.7 How many formula units (ZnS) are there in the unit cell of sphalerite?

Heavier elements of group IV (i.e. group 14), silicon and germanium, also adopt the structure of diamond. The radius of elemental germanium is r(Ge) = 1.23 Å.

19.8 Calculate the density of solid germanium.

Germanium is a semiconductor similar to silicon. It is used in electro-technology and similarly to silicon, it is also very fragile. Therefore, more flexible isoelectronic gallium arsenide, GaAs, is used in some practical applications. This compound belongs to semiconductors of III–V type (compounds of elements from groups III and V, *i.e.* groups 13 and 15, respectively) and adopts the structure of sphalerite. The lattice constants of Ge and GaAs are very similar, and a(GaAs) = 5.65 Å. An analogous compound GaP also adopts the structure of sphalerite, but has a smaller unit cell with a(GaP) = 5.45 Å.

19.9 Calculate the difference between the radii of P and As in the respective compounds with gallium (GaP versus GaAs).

Problem 20. Cyclobutanes

20.1 Draw all possible isomers of substituted cyclobutanes with the molecular formula C_7H_{14}, including enantiomers.

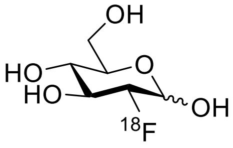
20.2 Mark all the asymmetric carbon atoms in the molecules from question 20.1 with an asterisk.

20.3 List all the compounds from question 20.1 that do **not** show optical activity.

20.4 List all pairs of enantiomers from question 20.1.

Problem 21. Fluorinated radiotracers

Fluorodeoxyglucose, namely the ^{18}F isotopomer 2-deoxy-2-[^{18}F]fluorodeoxyglucose (^{18}F-**FDG**), is a compound used in cancer diagnostics in a technique called positron emission tomography (PET). In this technique, the patient is treated with a radiotracer which is preferentially taken up by cancer cells. Upon radioactive decay, a positron is formed which rapidly annihilates with a nearby electron. A pair of γ-photons flying in opposite directions are produced and detected. This allows for the localization of the tumour with high sensitivity and spatial resolution.



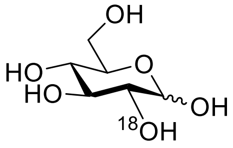
^{18}F-**FDG**

21.1 The isotope ^{18}F is produced by a proton bombardment technique. Which isotope of which element is used for the production of ^{18}F?

Since the amount of ^{18}F-**FDG** used in PET is very low, the dose is defined by units of radioactivity instead of the more commonly used molar concentration.

21.2 What is the amount of ^{18}F-**FDG** (in moles) present in one dose of 300 MBq (3×10^8 s^{-1})? The half-life of ^{18}F is 109.771 min.

Assume that all molecules of ^{18}F-**FDG** decay to ^{18}O-**glucose**, which eventually undergoes standard biochemical transformation into carbon dioxide and water.



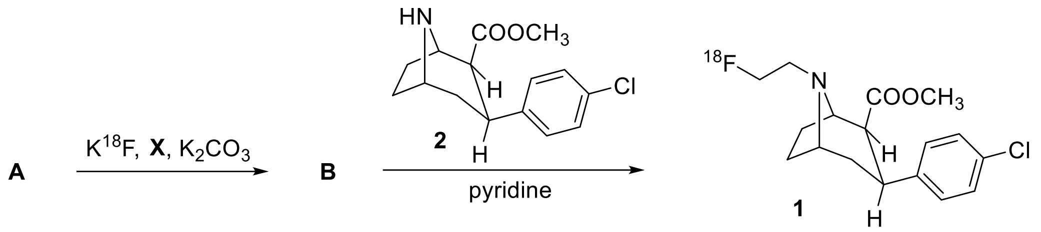
^{18}O-**glucose**

21.3 At what time point will the chemical energy of ^{18}O-**glucose**, produced by the decay of ^{18}F-**FDG**, be equal to the total energy of γ-photons not yet released from the remaining ^{18}F-**FDG**? In other words, at which time point would decomposing all obtained ^{18}O-**glucose** into CO_2 and H_2O produce the same amount of energy as the radioactive decay of all remaining ^{18}F-**FDG**? The heat of combustion of glucose is 2 800 kJ mol^{-1}.

Nevertheless, ^{18}F-**FDG** is not the only fluorinated radiotracer in use. Compound **1** is a radiotracer used in the diagnostics of Parkinson's disease (PD). Molecule **1** binds to the dopamine transporter (DAT), a membrane protein characteristic of dopaminergic neurons. Degeneration of this class of neurons is a symptom of PD. Therefore, targeted imaging of neural cells expressing DAT is advantageous in the diagnostics of the neurodegenerative disorder.

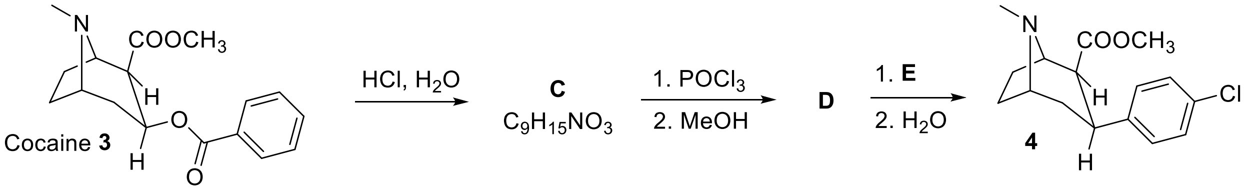
A freshly synthesized sample of K^{18}F reacts with ditosylate **A**, producing monofluorinated precursor **B**. Molecule **B** further reacts with amine **2** to give the final radiotracer **1**.

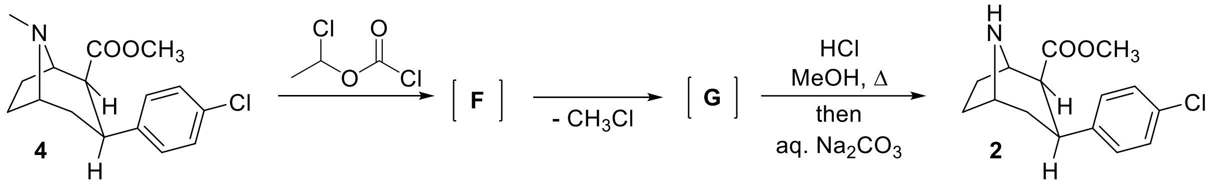
21.4 Propose the structures of tosylates **A** and **B**. What additive **X** is required to render the fluoride anion nucleophilic enough that the reaction runs to completion within minutes?



Amine **2** can be easily produced by a sequence of reactions starting from cocaine (**3**), a natural product from plants of the *Erythroxylaceae* family.

The synthesis starts with acid-catalyzed hydrolysis of cocaine (**3**) leading to compound **C** ($C_9H_{15}NO_3$). Subsequent elimination with $POCl_3$ produces, after a methanolic workup, compound **D**. Addition of magnesium-containing reagent **E** to compound **D** provides, after subsequent aqueous workup, precursor **4**. The final step in the synthesis of secondary amine **2** involves demethylation with 1-chloroethyl chloroformate followed by workup with aqueous sodium carbonate.





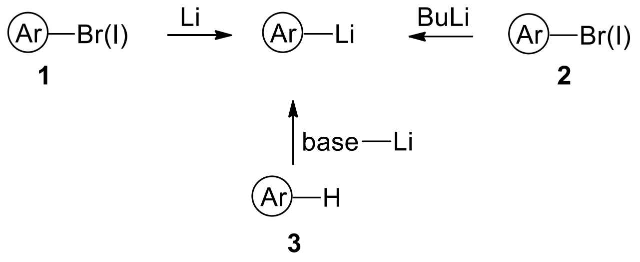
21.5 Draw the structures of compounds **C** to **E**.

21.6 Compound **4** is not the only stereoisomer which can be formed by the addition of **E** to **D**. Draw the structures of all the stereoisomers which are unwanted side-products of the transformation.

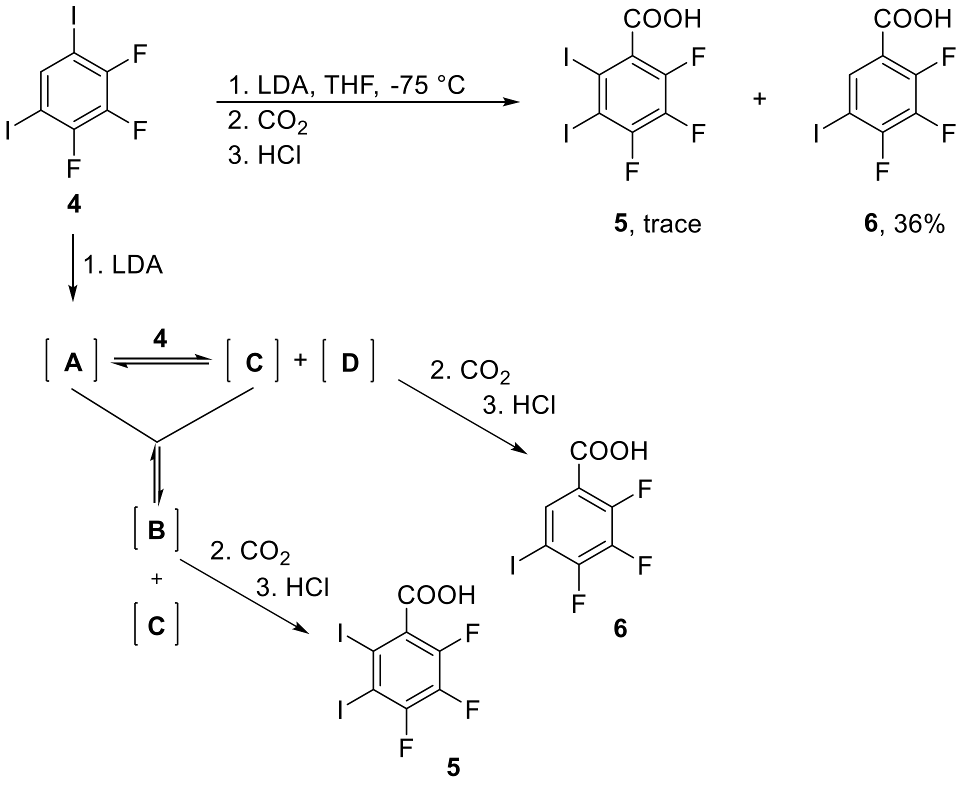
21.7 The mechanism of demethylation of **4** involves the formation of acylated intermediates **F** and **G**, and subsequent liberation of amine **2** with acidified hot methanol. Draw the structures of intermediates **F** and **G**.

Problem 22. Where is lithium?

Aryllithium reagents are key intermediates in the synthesis of a vast number of substances. The preparation of such reagents can be achieved by the reaction of aryl halides with lithium or butyllithium. Another possibility involves an acid-base reaction of aromatic/heteroaromatic compounds with a strong base.



The reaction of substituted iodobenzene **4** with lithium diisopropylamide (LDA) is an example of an aromatic carboxylic acid synthesis via an acid-base reaction known as the halogen dance reaction. In this case, the reaction affords acid **6** as the major product along with trace amount of acid **5**.



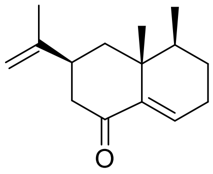
22.1 Draw the mechanism for the reaction of general aryl halide **1** with lithium.

22.2 Draw the structures of intermediates **A**, **B**, **C**, and **D** that explain the mechanism of formation of acids **5** and **6**.

22.3 Acid **5** can be prepared by the so-called haloform reaction. Suggest a synthetic route from substrate **E** ($C_8H_3F_3I_2O$) with suitable reagents.

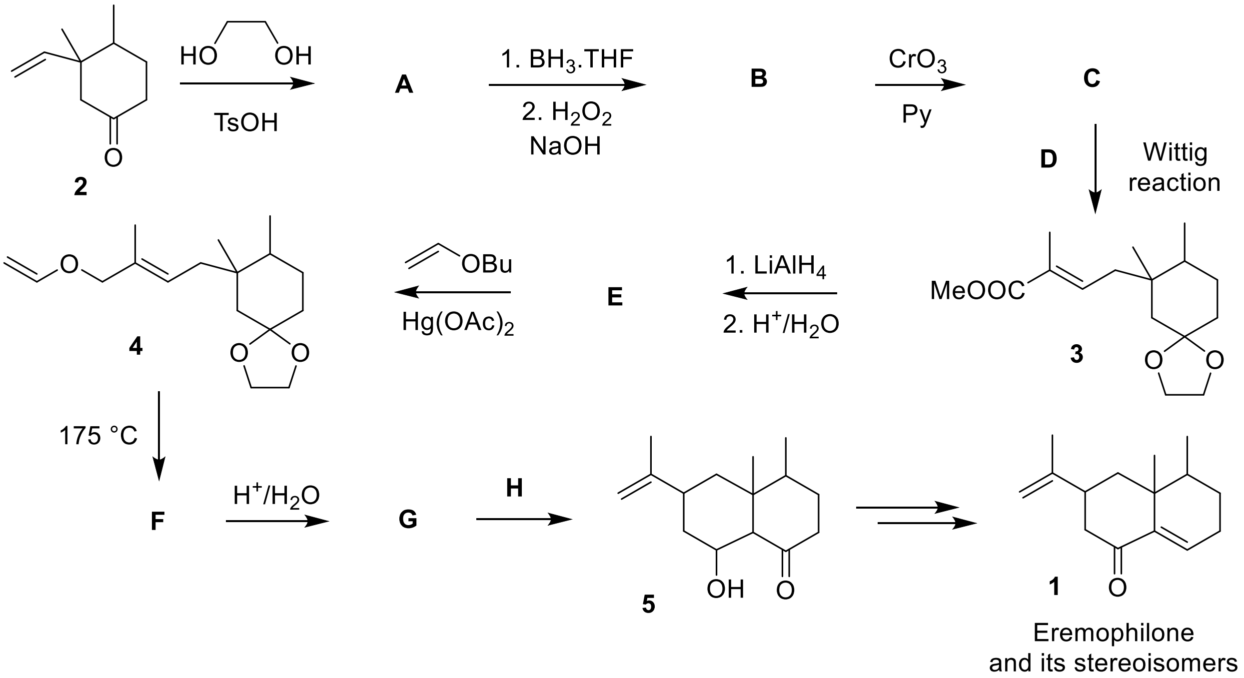
Problem 23. Synthesis of eremophilone

Eremophilone, (–)-**1a**, is a constituent of a commercially available oil with anti-inflammatory and relaxing properties, isolated from the Australian *Eremophila mitchellii* shrub (buddha wood).



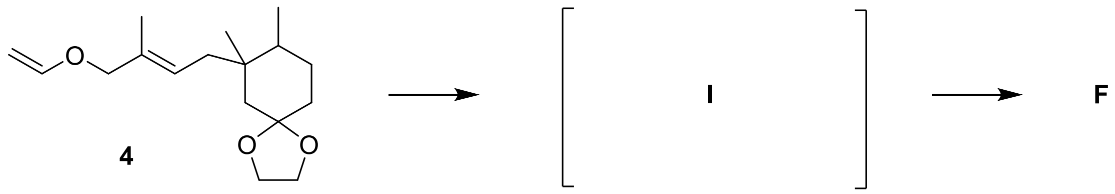
(-)-**1a**
Eremophilone

The synthesis of enantiomerically pure eremophilone is challenging due to the *cis*-configuration of the two methyl groups and the axial orientation of the isopropenyl group. The synthesis of the corresponding diastereomeric mixture **1** starts from ketone **2**, which is reacted with ethane-1,2-diol under acidic conditions to provide compound **A**, followed by regioselective reduction with a borane–THF complex. Oxidative work-up of the borane intermediate yields substance **B**. Its mild oxidation gives product **C**, which is reacted stereoselectively in the next step with an appropriate λ^5-alkylidenephosphane (ylide) **D** to furnish compound **3**. Its reduction leads to substance **E**, which reacts with butyl vinyl ether in the presence of mercury acetate to afford compound **4**. Heating of compound **4** results in its rearrangement to compound **F**, which, after deprotection, provides dioxo compound **G**. Final intramolecular aldolization using reagent **H** leads to bicyclic **5** as the key intermediate in the synthesis of eremophilone stereoisomeric mixture (**1**).



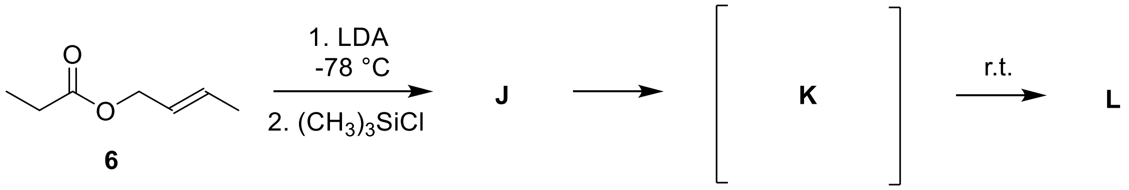
23.1 Draw the structures of the products and reagents **A–H**.

The key step in the synthesis is a thermal rearrangement of allylic vinyl ether **4**, leading to compound **F**. For the reaction to proceed, compound **4** must adopt appropriate orientation **I** to allow for the subsequent sigmatropic transformation.



23.2 Draw the required orientation of the allylic vinyl ether moiety **I** in compound **4** that enables the sigmatropic transformation. Use curved arrows to show the flow of electrons in the rearrangement step that provides compound **F**. What is the name of the rearrangement?
Note: You do not have to draw 3D structures.

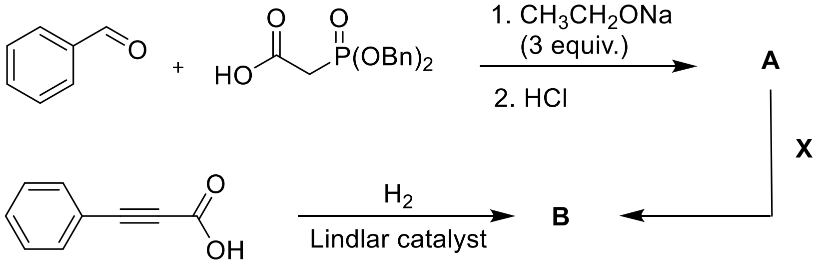
This rearrangement typically requires high temperatures, but this is not always an essential requirement. For example, allylic esters, e.g. ester **6**, can also undergo this transformation by first treatment with a strong non-nucleophilic base such as lithium diisopropylamide (LDA) at −78 °C to give the corresponding enolate. Subsequent trapping of the enolate with chlorotrimethylsilane yields silyl enol ether **J**. When allowed to warm to room temperature, substance **J** undergoes spontaneous rearrangement to substituted silyl ester **L** through conformation **K**.



23.3 Draw the structures of **J** and **L** and orientation **K** that enables the sigmatropic transformation to proceed. Use curved arrows to show the flow of electrons in the rearrangement step to compound **L**.
Note: You do not have to draw 3D structures.

Problem 24. Cinnamon all around

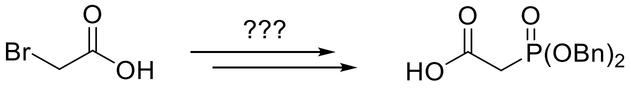
Cinnamon is an important part of many dishes and desserts, including Czech apple strudel, Swedish cinnamon rolls kanelbullar, Indian spicy rice biryani and the popular winter drink mulled wine. There are several compounds in cinnamon which are responsible for its taste and smell, mainly cinnamaldehyde and cinnamic acid and its derivatives. It is noteworthy that (*E*)-cinnamaldehyde and cinnamic acid are much more abundant in nature than their respective (*Z*)-isomers. While the former have a honey, cinnamon-like odour, the latter are completely odourless. Let us first explore the syntheses of both stereoisomers of cinnamic acid.



24.1 Draw the formulae of isomeric products **A** and **B**.

24.2 Propose reasonable reaction conditions (**X**) for the interconversion of cinnamic acid isomers (**A** → **B**).

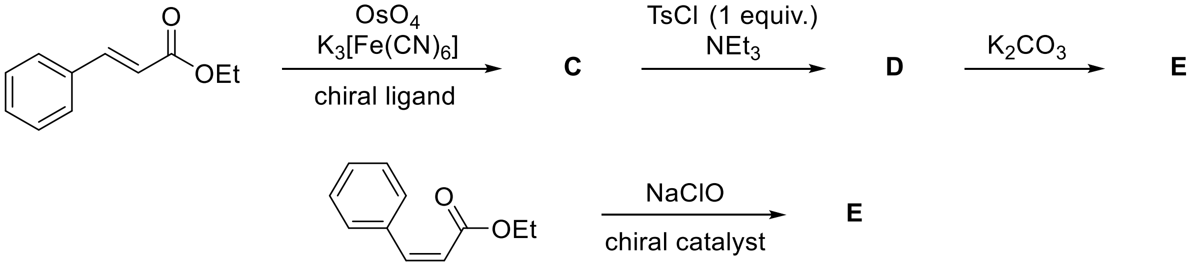
24.3 Starting from 2-bromoacetic acid, how would you prepare the phosphonate used in the above-mentioned synthesis?

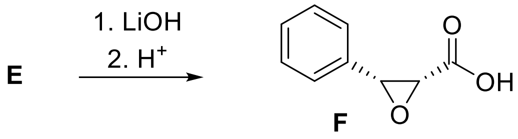


Both stereoisomers of cinnamic acid and their derivatives are often used as starting material in numerous syntheses. Let us have a look at some examples.

Docetaxel (**J**), sold under the brand name Taxotere, is a semisynthetic chemotherapy drug used to treat numerous cancer types. While the core structure, 10-deacetylbaccatin III (**G**), is extracted from yew leaves, the side chain is prepared synthetically from ethyl cinnamate.

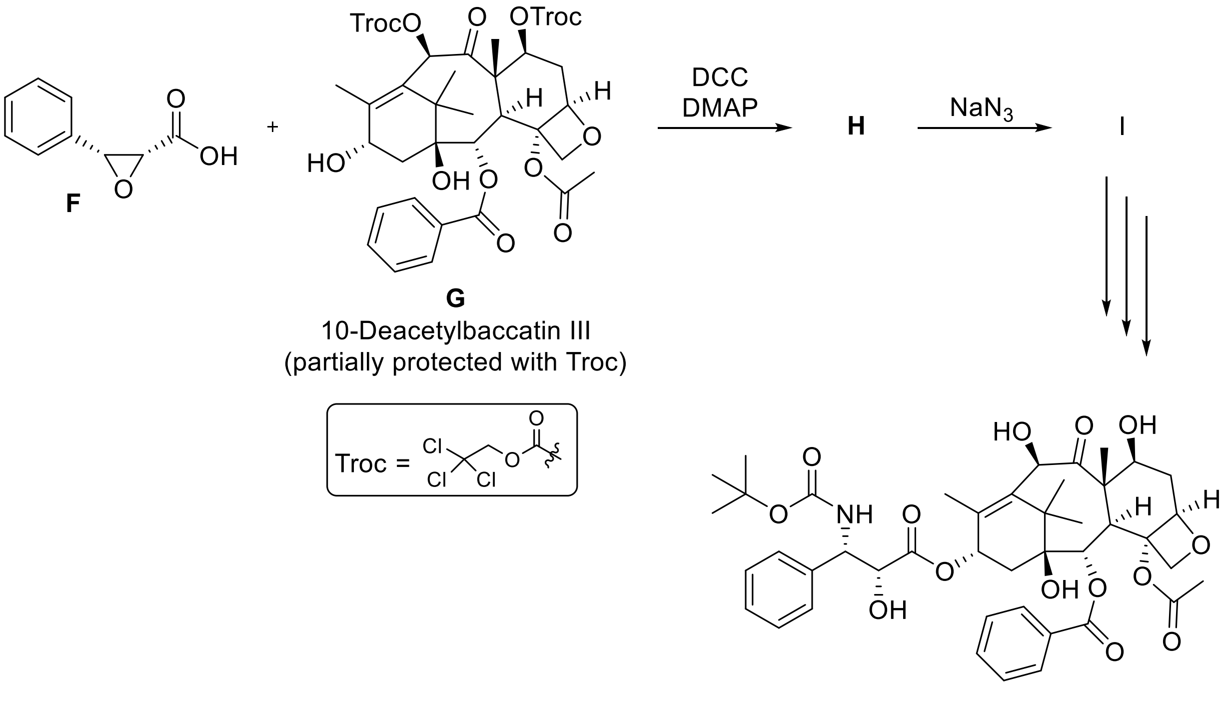
A key intermediate, epoxyacid **F**, can be prepared from both *(E)-* and *(Z)*-ethyl cinnamate. *(E)*-Ethyl cinnamate is first reacted with osmium tetroxide in the presence of a chiral ligand. Only one enantiomer of **C** is formed. The reaction of **C** with one equivalent of tosyl chloride leads to compound **D** in which the hydroxyl group at position 2 is tosylated. In a basic environment, tosylate **D** is converted to compound **E**. Alternatively, compound **E** can be prepared in one step from *(Z)*-ethyl cinnamate by hypochlorite-mediated oxidation. A chiral catalyst ensures the formation of a single enantiomer. Hydrolysis of **E** then provides acid **F**.





24.4 Draw the structures of compounds **C**, **D** and **E**, including stereochemistry. The absolute configuration of all compounds can be deduced from the known structure of acid **F**.

Epoxyacid **F** reacts with 10-deacetylbaccatin III (**G**) in the presence of *N*,*N*′-dicyclohexylcarbodiimide (DCC) to provide compound **H**. A subsequent reaction with NaN_3 leads to compound **I**, which is easily converted to docetaxel (**J**).



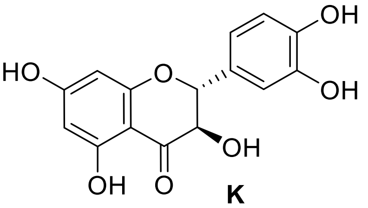
G
10-Deacetylbaccatin III
(partially protected with Troc)

J Docetaxel

24.5 Draw the structures of compounds **H** and **I**, including stereochemistry.

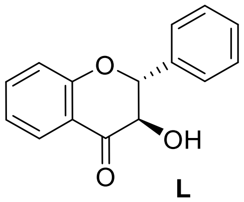
24.6 What is the role of DCC in the first step? Write the appropriate chemical equation.

Taxifolin (**K**) is an inhibitor of ovarian cancer with strong hepatoprotective properties. It belongs to 3-hydroxyflavanone (**L**) family of natural products.



K

Taxifolin

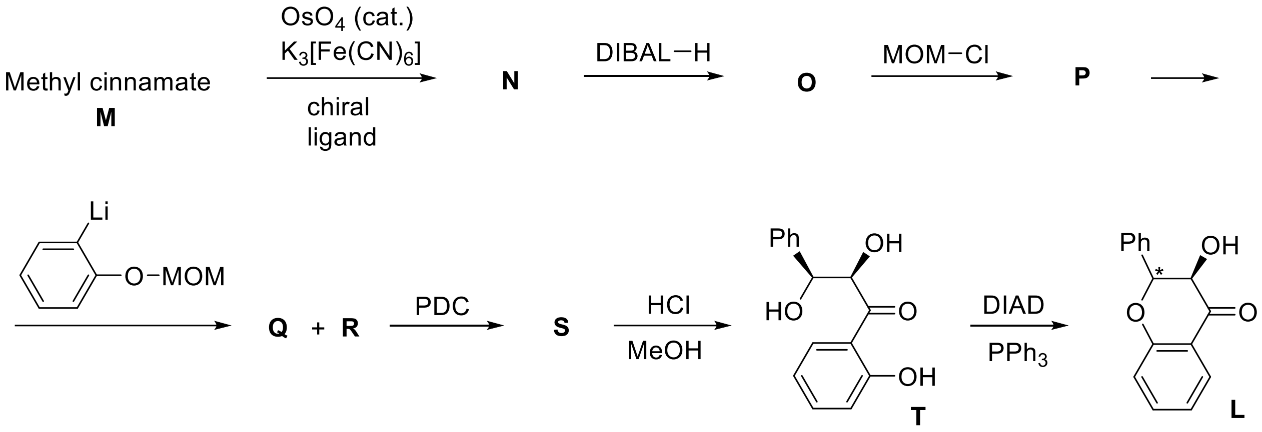


L

(2*R*,3*R*)-3-Hydroxyflavanone

The synthesis of compound **L** starts with asymmetric dihydroxylation of methyl cinnamate **M** using osmium tetroxide as catalyst, potassium ferricyanide as oxidant and a chiral ligand. The synthesis continues with the transformation of the ester group in compound **N** to compound **O** and subsequent reaction of hydroxyl groups in the presence of an excess of chloromethyl methyl ether

(MOM–Cl), yielding compound **P**. Compound **P** reacts with a protected aryllithium reagent in a non-stereoselective manner, giving a mixture of two compounds **Q** and **R**. The reaction of the mixture of compounds **Q** and **R** with PDC yields a single compound **S**, which upon acidic treatment provides compound **T**. Finally, the reaction of **T** with diisopropyl azodicarboxylate (DIAD) and triphenylphosphine proceeds by formal S_N2 substitution of one hydroxyl group with the other to furnish target compound **L**.



24.7 From the known configuration of product **T**, decide whether compound **M** is the ester of (*E*)- or (*Z*)-cinnamic acid.

24.8 Draw the structures of compounds **N**–**S** and **L**, with the correct configuration on the benzylic oxygen.

24.9 Decide whether compounds **Q** and **R** are a) constitutional isomers, b) diastereoisomers or c) enantiomers.

24.10 Why can we not react compound **O** with the aryllithium reagent directly?

24.11 Draw the structure of the PDC reagent.

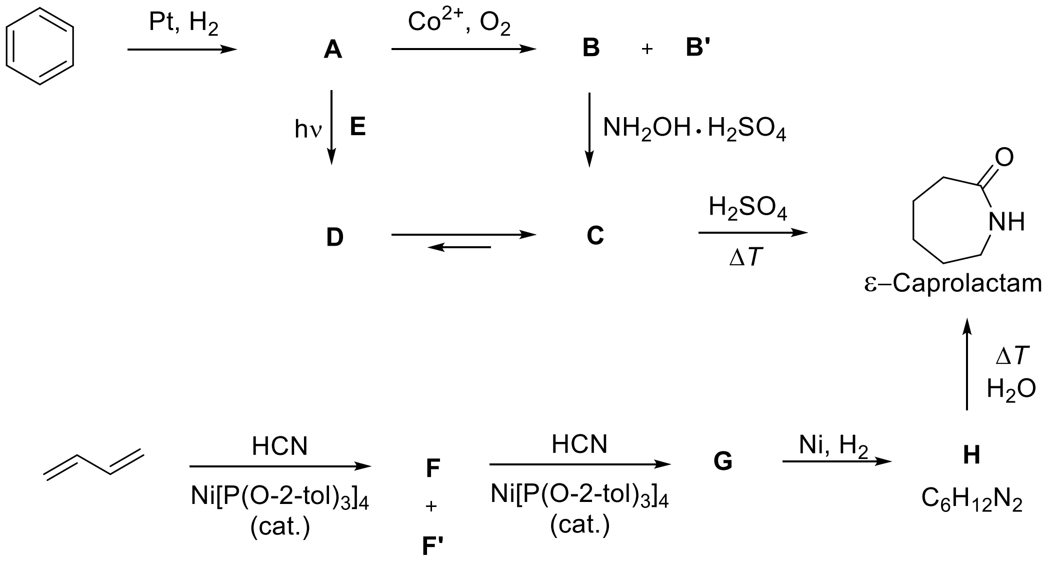
24.12 After whom is the reaction converting compound **T** to compound **L** named?

Problem 25. All roads lead to caprolactam

The synthesis of ε-caprolactam (hexano-6-lactam) starts with benzene, which is converted to compound **A** by exhaustive catalytic hydrogenation and subsequently oxidized by air in the presence of cobalt(II) salts of a fatty acid. First, the desired product **B** has to be separated from the side product **B'** by fractional distillation. Compound **C** can be obtained by heating **B** with hydroxylamine sulfate and the desired ε-caprolactam can be obtained by heating **C** with sulfuric acid.

A modern alternative to this process is the photochemical reaction of compound **A** with orange-coloured gas **E**. Compound **E** contains a chlorine atom and is also formed during the preparation of aqua regia. Compound **D** immediately rearranges to compound **C**.

Caprolactam can also be prepared from buta-1,3-diene by sequential catalytic hydrocyanation with two equivalents of hydrogen cyanide. In the first reaction, in addition to the desired compound, **F**, compound **F'** is formed and has to be separated first. Compound **G**, after partial hydrogenation, provides compound **H**, which is heated in the presence of water in order to give caprolactam.



25.1 Draw the structures of unknown compounds **A–H**.

25.2 Under which conditions will the equilibrium be most shifted from benzene to compound **A**?
- a) 300 °C, 1 atm
- b) 300 °C, 100 atm
- c) 50 °C, 1 atm
- d) 50 °C, 100 atm

25.3 Write the equation for the formation of compound **E** in the preparation of aqua regia and suggest at least one other way to prepare **E**.

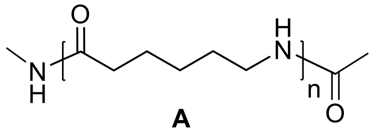
25.4 Suggest the mechanism for the photochemical reaction of **A** with compound **E**.

25.5 What is an approximate wavelength suitable to perform the mentioned photochemical reaction? *Hint:* **E** is not colourless.

25.6 Suggest a plausible mechanism for the conversion of **C** to ε-caprolactam. After whom is the reaction named?

Problem 26. Ring opening polymerization (ROP)

Prof. Otto Wichterle was a famous Czech polymer chemist and inventor of soft contact lenses. He also contributed to the production of an industrially important polymer poly(ε-caprolactam) (silon, **A**) by ring opening polymerization of ε-caprolactam (hexano-6-lactam).



A

Poly(ε-caprolactam)

The polymerization reaction is usually carried out by a special type of anionic polymerization initiated by the addition of a small amount of acetic anhydride to an excess of ε-caprolactam. Compound **B** is formed which contains an imide bond that is more susceptible to nucleophilic attack than that of the amide bond in ε-caprolactam. The molar amount of **B** is the same as the molar amount of the subsequently formed polymer chains.

26.1 Draw the structure of compound **B**.

After the initial activation, a base is added to the mixture (usually an alkali metal hydride or an alkoxide) to deprotonate another ε-caprolactam molecule (equation 1). This initiates polymerization, which proceeds almost quantitatively typically within minutes. Propagation proceeds as follows:

- nucleophilic attack of ε-caprolactam anion on compound **B** (equation 2)
- ring-opening of compound **B** (equation 3)
- protonation of the product by another ε-caprolactam molecule, resulting in a further unreactive *N*-alkyl acetamide end (equation 4).

The other end of the molecule contains the same type of activated imide as compound **B** and is susceptible to ring opening by another ε-caprolactam anion, which is formed from ε-caprolactam during the proton transfer step (equation 5).

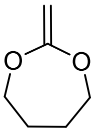
26.2 Write an arrow-pushing mechanism of the described initiation and propagation steps.

Poly(ε-caprolactone) is structurally similar to poly(ε-caprolactam), being a polyester instead of polyamide. The ring opening ε-caprolactone (hexano-6-lactone) polymerization can proceed by cationic, anionic or coordination mechanisms.

26.3 Draw the structure of poly(ε-caprolactone) prepared with sodium ethoxide as the initiator and water as the terminator.

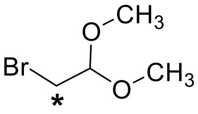
26.4 Two kilograms of ε-caprolactone were polymerized with 10 g sodium ethoxide with 83% conversion. Calculate the number-average molecular weight of the obtained polymer (use atomic masses of elements rounded to whole numbers). Neglect the weight contribution of the initiator residue to the molecular weight of the polymer.

Poly(ε-caprolactone) can also be prepared by radical ring opening polymerization of 2-methylidene-1,3-dioxepane (**C**).



C

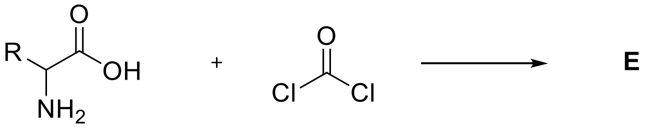
26.5 How would you synthesize precursor **C** starting from butane-1,4-diol and bromoacetaldehyde dimethyl acetal (**D**)? Write the synthetic scheme.



D

26.6 Imagine dioxepane **C** was prepared from a ^{14}C-labeled compound **D** (the labelled carbon is marked with an asterisk) and subjected to the radical polymerization reaction. Write the structure of poly(ε-caprolactone) and mark the radiolabelled carbon(s) with an asterisk.

Proteins are natural polyamides based on α-amino acids. In living organisms, they are synthesized by translation based on genetic information, but they can also be prepared synthetically by a nucleophile-initiated ring opening polymerization. In this case, the activated cyclic monomers, *N*-carboxyanhydrides **E** (also called Leuchs' anhydrides) are used. They can be prepared by the reaction of an α-amino acid with phosgene:



26.7 Draw the structure of the activated monomer **E** formed from α-alanine (2-aminopropanoic acid).

During polymerization, a gas is evolved and a polypeptide is formed.

26.8 Write the formula of the gas and the structure of the polymer formed from monomer **E** with butane-1-amine as initiator.

Natural proteins are formed exclusively from homochiral amino acids, i.e., only one enantiomer is present in the protein. This is vital for its 3D structure and function. Theoretically, if only a single amino acid in an enzyme is exchanged for its enantiomer, the chain changes its conformation, resulting in compromised catalytic efficiency.

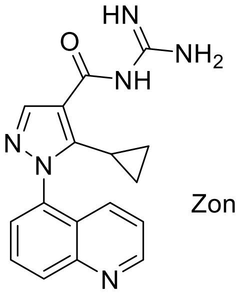
Let us investigate lysozyme, a bacterial cell wall-lysing enzyme present in egg whites and tears. It contains 129 amino acid residues, 12 of which are glycines.

26.9 What would be the % yield of functional lysozyme if the proteosynthetic apparatus of the cell did not distinguish between enantiomers of the amino acids and had both enantiomers of amino acids available in equal quantities? Consider only the chirality on the α-carbon of all amino acids as the configuration on other chiral centres (in threonine and isoleucine) has only marginal effect on overall protein 3D structure. Note that only the enzyme digesting bacterial cell walls is claimed as functional.

26.10 In one egg there is ca 120 mg of lysozyme. How much protein (in kg) would you have to synthesize under the conditions described in 26.9 to produce enough functional lysozyme for one egg? Compare your result with the mass of the planet Earth (5.972×10^{24} kg).

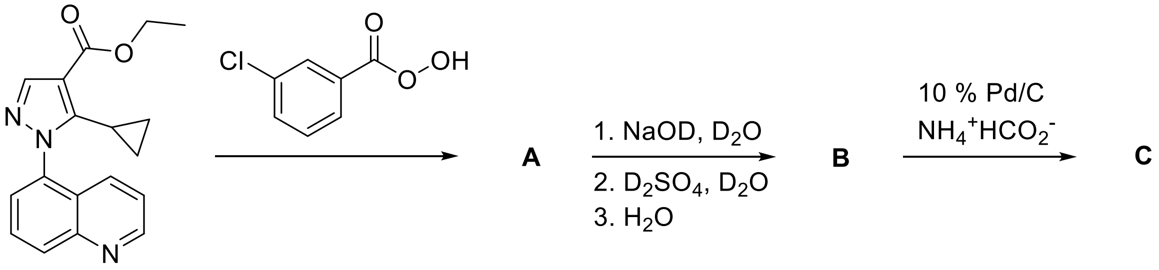
Problem 27. Zoniporide

An emerging strategy to improve the pharmacokinetics (PK) of drugs takes advantage of the kinetic isotope effect. Molecules containing non-radioactive heavy isotopes in metabolically relevant positions may be cleared more slowly from the body. Zoniporide, a cardioprotective inhibitor of the Na^+/H^+ antiporter 1 protein, was considered a candidate for improved PK upon deuteration, since the major metabolic pathway of zoniporide involves the oxidation by aldehyde oxidase in position 2 of the quinoline core.

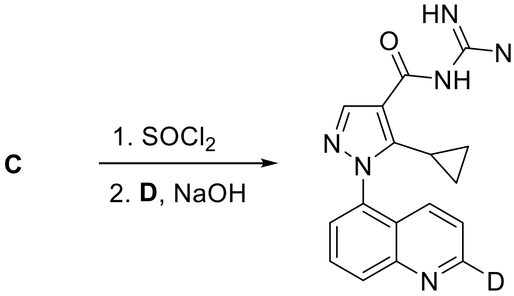


Zoniporide

^{2}H-Zoniporide, deuterated in position 2 of the quinoline core is synthesized from ester **1** by the following sequence of reactions:



1

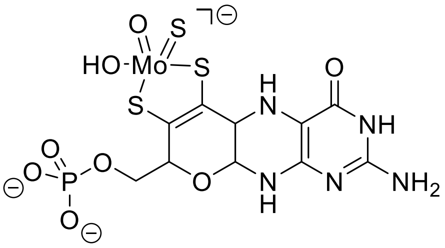


^{2}H-Zoniporide

27.1 Draw the structures of intermediates **A** through **C** and reagent **D**.

27.2 Ammonium formate decomposes upon mild heating in the presence of palladium on charcoal (transformation **B** → **C**) into three gaseous products, one of which is the reducing agent required for the aforementioned transformation. Draw the structures of these compounds.

The active site of the aldehyde oxidase enzyme contains a molybdenum(VI) cofactor chelated by pyranopterin dithiolate (PD).

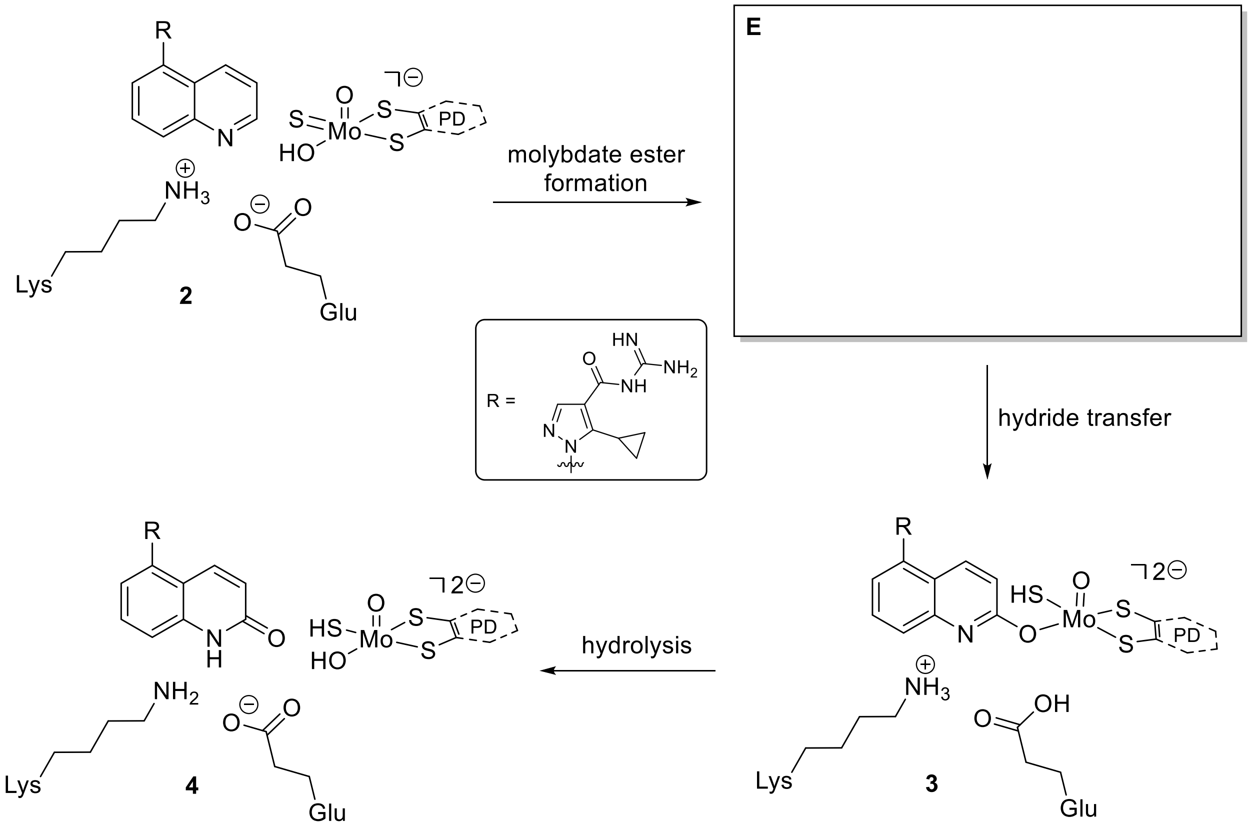


Molybdenum(VI) cofactor chelated
by pyranopterin dithiolate (PD)

Note: The negative charge next to the square bracket (⌝⊖) reflects the formal charge on Mo.

The structure of zoniporide bound in the active site of aldehyde oxidase (**2**) is shown below. Two mechanisms have been proposed for the oxidation of the drug in position 2 of the quinoline core. **Mechanism 1** involves three major individual steps: formation of a molybdate ester, a hydride transfer and a final hydrolytic step.

Mechanism 1

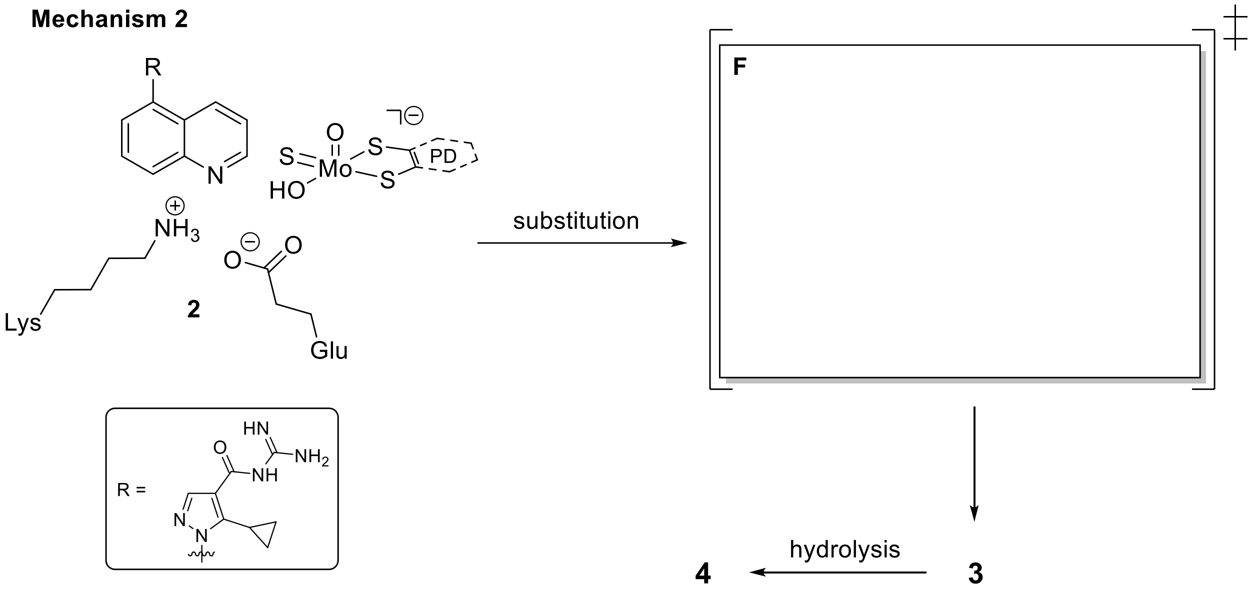


27.3 Draw the intermediate active site structure **E** involved in the proposed **Mechanism 1** of zoniporide oxidation.

27.4 Give the oxidation state of molybdenum in each of the intermediate structures **E**, **3** and **4**.

On the other hand, another proposed mechanism, **Mechanism 2**, involves a concerted substitution step yielding intermediate **3**, which is further hydrolyzed to **4** in the same fashion as in **Mechanism 1**.

Mechanism 2



27.5 Draw the transition state structure **F** for the concerted substitution step **2** → **3**. Use a dotted line for bonds which are being formed and cleaved.

The following experimental evidence was gathered to determine whether the transformation **2** → **3** in the mechanism of the oxidation of zoniporide (and related nitrogen heterocycles) by aldehyde oxidase is stepwise (**Mechanism 1**) or concerted (**Mechanism 2**):

a) The kinetic isotope effect, k_H / k_D, for zoniporide (deuterated in quinoline position 2) oxidation by aldehyde oxidase was 5.8 at 37 °C.

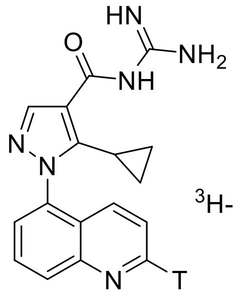
b) The introduction of electron withdrawing groups on the heterocycle core led to an increase in the reaction rate and a slight decrease in k_H / k_D.

27.6 Which of the two mechanisms (**Mechanism 1** or **Mechanism 2**) of quinoline oxidation by aldehyde oxidase is more plausible based on the aforementioned experimental evidence? Rationalize your answer.

The molybdenum cofactor further needs to be reoxidized to its original state. The reducing equivalents from one reaction are transferred, via an iron sulfide cluster cofactor and a flavin cofactor, to a single molecule of oxygen as the stoichiometric oxidant.

27.7 What small molecule byproduct is formed by the reduction of O_2 in this process?

Deuterium is not the only heavy isotope of hydrogen. In theory, an even higher kinetic isotope effect would be expected using tritium. The isotope ^3H is not used in practice to slow down the metabolism of drugs due to economic and safety reasons but let us at least theoretically look at ^3H-zoniporide.



^{3}H-Zoniporide

27.8 Calculate the theoretical tritium (k_H / k_T) kinetic isotope effect for the oxidation of zoniporide by aldehyde oxidase at 37 °C. The deuterium kinetic isotope effect for the same reaction is 5.8. Consider the following approximations:

- The harmonic oscillator approximation
- Isotope exchange does not alter the rate determining step transition state structure
- The KIE is solely affected by the ^{12}C−H/D/T stretching vibration mode
- The KIE is solely determined by zero-point vibrational energies (the role of higher vibrational levels is negligible)

$m(^1H)$ = 1.0078 amu; $m(^2H)$ = 2.0141 amu; $m(^3H)$ = 3.0160 amu; $m(^{12}C)$ = 12.0000 amu

Hint: You need to calculate 1) the relevant reduced masses; and 2) the force constant for the C–H/D bond before you get to the final KIE calculation.

Unfortunately, the k_H/k_D kinetic isotope effect of 5.8 for the oxidation of zoniporide by aldehyde oxidase does not translate into a more complex system. The degradation rate of ^{2}H-zoniporide in human liver cells is only 1.9× lower than that of ^{1}H-zoniporide. This is because aldehyde oxidase is not the only enzyme involved in zoniporide catabolism. Nonspecific cellular hydrolases, as well as cytochrome P450 enzymes compete with aldehyde oxidase for the degradation of zoniporide.

27.9 Draw the two products of zoniporide hydrolysis by nonspecific cellular hydrolases.
Hint: Non-enzymatic aqueous alkaline hydrolysis under mild conditions would result in the same products.

Problem 28. Nucleic acids

Genetic information is encoded in a sequence of nucleobases which are bonded to a sugar–phosphate backbone. Deoxyribonucleic acid (DNA) contains adenine (A), cytosine (C), guanine (G), and thymine (T), whereas ribonucleic acid (RNA) contains uracil (U) instead of thymine.

The most common structures of nucleobases are shown in Figure 1, but these are not the only possible ones. Since nucleobases contain a number of double bonds, they may occur in several different tautomeric forms. Note that even zwitterionic tautomers are possible in principle, but the tasks below deal only with uncharged molecular structures.

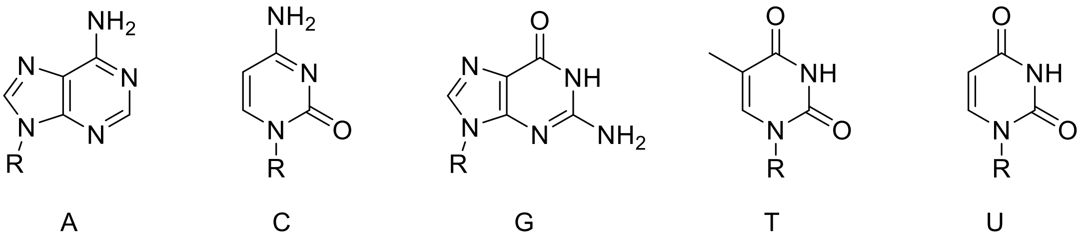


Figure 1. Structural formulae of nucleobases A, C, G, T, and U bonded to sugar-phosphate backbone (R).

28.1 Draw the structural formulae of all non-charged tautomers of cytosine. Assume the nucleobase is bonded to the sugar–phosphate backbone. Consider any pair of imino *E*/*Z* isomers as two different tautomers.

DNA undergoes so-called hybridization, in which two DNA strands form a complex in a helical shape. Hydrogen bonds between the nucleobases contribute to the correct pairing of two complementary strands of double-stranded DNA (dsDNA). Cytosine pairs with guanine, and adenine pairs with thymine (Figure 2). However, the presence of a rare tautomer in one of the DNA strands opens the possibility for non-standard pairing of nucleobases.

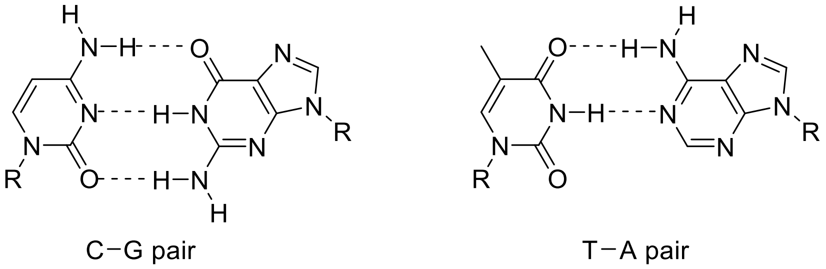


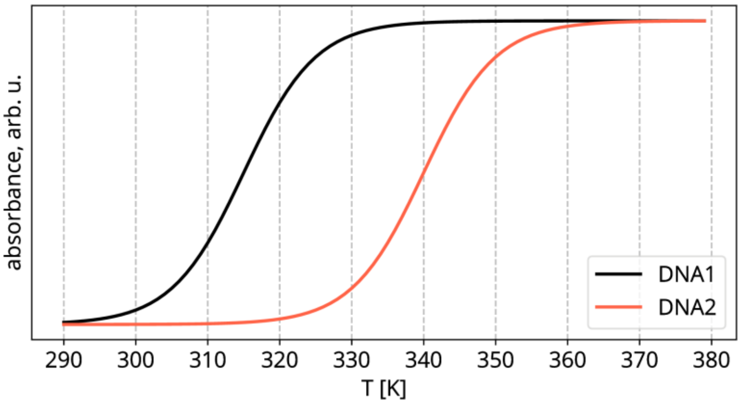
Figure 2. Standard DNA base pairs.

28.2 Draw the structural formulae of the non-standard pairs T–G*, T*–G, A–C* and A*–C, where any minor uncharged tautomer is marked with an asterisk. Keep the relative orientation of the sugar–phosphate backbone the same as in the standard pairs and maximize the number of hydrogen bonds between the nucleobases.

Spectrophotometry is an experimental technique that is particularly useful for investigating nucleic acids. Being aromatic, nucleobases absorb electromagnetic radiation in the UV range. At 260 nm, sample **1** of a nucleic acid with an unknown concentration of adenine transmits 11% UV light. A standard solution in which the concentration of adenine amounts to 27 μmol dm^{-3}, absorbs 57% UV light at the same wavelength.

28.3 Calculate the unknown concentration of adenine in sample **1**. Neglect any absorption at 260 nm by the other nucleobases and assume that both measurements were performed under identical experimental conditions (cuvette length, buffer composition, temperature, etc.).

Spectrophotometry in the near-UV region is a useful tool to monitor the hybridization of DNA as the temperature changes. Melting temperature T_m is defined as the temperature at which 50% of the original amount of DNA double helices are dissociated into separated strands. Nucleobases within dsDNA absorb less strongly than those in ssDNA, thus the dissociation of dsDNA manifests itself by an increase of absorbance. The plot below shows the absorbance at 260 nm as a function of temperature for two different DNA species (DNA1 and DNA2). Assume that both DNA species have equal molar absorption coefficients and that all the measurements were performed under otherwise identical conditions using identical equipment (initial concentrations, buffers, cuvette, etc.).



28.4 Considering the plot shown above, decide whether the following statements are true or false or whether that cannot be answered based only on the plot.

a) At 320 K, the concentration of dsDNA1 is lower than the concentration of dsDNA2.

True False Cannot be answered

b) The melting temperature T_m of DNA1 is higher than the melting temperature of DNA2.

True False Cannot be answered

c) dsDNA of the species DNA1 is more thermodynamically stable than that of the DNA2 with respect to their single-stranded forms.

True False Cannot be answered

d) dsDNA1 is composed of a larger number of nucleobase pairs than dsDNA2

True False Cannot be answered

The Rous sarcoma virus is a retrovirus. Its genetic information is stored in a single strand of RNA rather than in dsDNA; recall that RNA contains uracil instead of thymine (Figure 1). The virus uses an enzyme, reverse transcriptase, to synthesize its complementary DNA (cDNA) strand, which is then transcribed to messenger RNA (mRNA). Finally, the mRNA is translated to a polypeptide strand in the ribosome of the infected cell.

The following fragment of 8 nucleotides was identified in the RNA of the virus: 5′-CCCCAGGU-3′.

28.5 Write the sequences of cDNA and mRNA corresponding to the octanucleotide. Mind the orientation of the molecule, and identify the 5′- and 3′-termini.

28.6 How many possible single-stranded RNA octanucleotides do exist?

19th – 29th July 2018
Bratislava, SLOVAKIA
Prague, CZECH REPUBLIC

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PREPARATORY PROBLEMS: PRACTICAL

50th IChO 2018

International Chemistry Olympiad
SLOVAKIA & CZECH REPUBLIC

BACK TO WHERE IT ALL BEGAN

UPDATED 1st JUNE 2018

Table of Contents

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Fields of Advanced Difficulty

1. *Techniques in organic synthesis*: thin layer chromatography, filtration and drying of precipitates
2. *Extraction* using immiscible solvents

Notes

During the practical exam, students WILL NOT be expected to:

- Determine melting points
- Use a rotary evaporator
- Use a spectrophotometer
- Handle and work up moisture sensitive compounds (using syringes and balloons)
- Perform column chromatography

Dedication of Problems P4 and P5 to the Belousov–Zhabotinsky (BZ) oscillating reaction is entirely commemorative. Students will not be expected to have received training specifically addressing this particular reaction or other chemical oscillators.

Safety

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

The Preparatory Problems are designed to be carried out in properly equipped chemical laboratories under competent supervision **only**. 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 GHS hazard statements (H-phrases) associated with the materials used are indicated in the problems. Their meanings are as follows.

Definition of GHS hazard statements

Physical hazards

H225	Highly flammable liquid and vapour.
H226	Flammable liquid and vapour.
H228	Flammable solid.
H271	May cause fire or explosion; strong oxidizer.
H272	May intensify fire; oxidizer.
H290	May be corrosive to metals.

Health hazards

H301	Toxic if swallowed.
H302	Harmful if swallowed.
H304	May be fatal if swallowed and enters airways.
H311	Toxic in contact with skin.
H312	Harmful in contact with skin.
H314	Causes severe skin burns and eye damage.
H315	Causes skin irritation.
H317	May cause an allergic skin reaction.
H318	Causes serious eye damage.
H319	Causes serious eye irritation.
H331	Toxic if inhaled.
H332	Harmful if inhaled.
H333	May be harmful if inhaled.
H334	May cause allergy or asthma symptoms or breathing difficulties if inhaled.
H335	May cause respiratory irritation.
H336	May cause drowsiness or dizziness.
H351	Suspected of causing cancer.
H361	Suspected of damaging fertility or the unborn child.
H371	May cause damage to organs.
H372	Causes damage to organs through prolonged or repeated exposure.
H373	May cause damage to organs through prolonged or repeated exposure.

Environmental hazards

H400	Very toxic to aquatic life.
H402	Harmful to aquatic life.
H410	Very toxic to aquatic life with long lasting effects.
H411	Toxic to aquatic life with long lasting effects.
H412	Harmful to aquatic life with long lasting effects.

Problem P1. Determination of a metallic ore composition

Slovakia has a rich history in mining. Since the Middle Ages, gold, silver and copper ores have been mined in Kremnica, Banská Bystrica and especially in Banská Štiavnica, where the remnant of the extinct stratovolcano is rich in mineral raw materials. Mining in Slovakia has provided notable technological advancements. In 1763, the Academy of Mining and Forestry was founded in Banská Štiavnica. It is one of the oldest technically-oriented educational institutions in all of Europe. One particularly extraordinary division at the Academy was the Department of Chemistry, which allowed students to experiment in real laboratories.

In this task, you will determine the concentration of copper and zinc ions in a solution obtained by the decomposition and proper modification of polymetallic ore.

Figure P1. Academy of Mining and Forestry in Banská Štiavnica.

Chemicals and Reagents

- Processed aqueous sample of the ore containing Zn^{2+} and Cu^{2+}, 50 cm^3
- Strongly acidic cation exchange resin in hydrogen cycle, equivalent to Dowex 50, 15 cm^3
- 0.1 M standard sodium hydroxide solution, 200 cm^3
- 0.05 M standard Cu^{2+} solution, 50 cm^3
- 2 M hydrochloric acid solution, 200 cm^3
- 0.15 M standard EDTA disodium salt solution, 200 cm^3
- 25% aqueous ammonia solution (w/w), 50 cm^3
- 6% hydrogen peroxide solution (w/w), 1 cm^3
- 0.25 M ammonium oxalate solution, 100 cm^3
- Buffer solution (35 cm^3 of 25% ammonia (w/w) and 5.4 g of ammonium chloride diluted to 100 cm^3)
- Indicators: methyl red solution, universal pH indicator paper, murexide (solid indicator mixture), Eriochrome black T (solid indicator mixture)

Substance	Name	State	GHS Hazard Statement
NaOH	Sodium hydroxide	Aqueous solution	H314
HCl	Hydrochloric acid	Aqueous solution	H314, H318
$CuSO_4 . 5H_2O$	Copper sulfate pentahydrate	Aqueous solution	H302, H315, H410
NH_3	Ammonia	Aqueous solution	H314, H400
$C_{10}H_{14}N_2O_8Na_2 . 2H_2O$	Disodium ethylenediamine tetraacetate dihydrate	Aqueous solution	H302, H315, H319, H335
$(NH_4)_2C_2O_4$	Ammonium oxalate	Aqueous solution	H302, H312
NH_4Cl	Ammonium chloride	Solid	H302, H319
H_2O_2	Hydrogen peroxide	Aqueous solution	H271, H302, H314, H333, H402

$C_{20}H_{12}N_3O_7SNa$	Eriochrome black T	Solid	H319
$C_8H_8N_6O_6$	Murexide	Solid	Not classified
$C_{15}H_{15}N_3O_2$	Methyl red	Solution	H225, H319, H371

Equipment and Glassware

- Laboratory stand with burette clamp
- Volumetric flasks, 250 cm^3 (1) and 100 cm^3 (4)
- Titration flasks, 250 cm^3 (3)
- Burette, 25 cm^3
- Pipettes, 5, 10, 25 and 50 cm^3 with pipette filler
- Spectrophotometer with cuvettes (2, l = 1 cm)
- Ion exchange chromatography column (recommended diameter ca 1.5 cm)
- Hotplate

Procedure

I. Determination of the metal ion concentration by alkalimetry and photometry

When a solution of copper and zinc ions is passed through a column packed with a cation exchange resin, the ions are trapped on the resin, releasing an equivalent amount of H$^+$ ions into the eluate. One of these ions forms a coloured species that enables its determination in the mixture by spectrophotometry.

1. Fill the column with the strongly acidic cation exchange resin. A suitable height for the resin in the column is 12–15 cm (recommended volume of the resin is 10–15 cm^3).

2. Add 50 cm^3 of 2 M hydrochloric acid solution to the column and let the solution pass through the column with a flow rate of 2 drops per second. Allow the level of the solution to fall just above the level of the resin. Discard the eluate. Wash the column at the same flow rate with deionised water until a neutral pH of the eluate is obtained. Check the pH of the dropping eluate using the pH indicator paper. Allow the level of water to fall just above the level of the resin. The column is now ready for use in the H$^+$ cycle.

3. Add 10.00 cm^3 (V) of a sample stock solution to the column and let the level of the solution drop just above the level of the resin. Then wash the column with deionised water at a flow rate of 2 drops per second and collect the eluate into a 250 cm^3 (V_{el}) volumetric flask. After filling half of the flask, check the pH of the dropping eluate. If the pH = 7, the ion exchange is finished; if the pH < 7, continue washing the column. After a neutral pH has been reached, fill the flask up to the mark with deionised water.

4. Alkalimetric titration: Pipette 50.00 cm^3 (V_{1at}) of the eluate stock solution into the titration flask and add methyl red indicator. Titrate with the standard sodium hydroxide solution until the first visible colour change of the indicator (V_{2at}). Repeat the titration as necessary.

5. Prepare two diluted standard Cu^{2+} solutions containing ammonia solution: pipette 5.00 cm^3 of the standard Cu^{2+} solution into one 100 cm^3 volumetric flask and 10.00 cm^3 of standard Cu^{2+} solution into the second 100 cm^3 volumetric flask. Add 10 cm^3 of the ammonia solution into each flask and then fill each flask to the mark with deionised water. Label the flasks with the concentrations of the prepared solutions as c_{min} and c_{max}.

6. Pipette 25.00 cm^3 (V_{orig}) of the sample stock solution into a 100 cm^3 (V_{dil}) volumetric flask and add deionised water to the mark. From this solution, pipette 5.00 cm^3 (V_{pip}) into another 100 cm^3 (V_x) volumetric flask. Add 10 cm^3 of the ammonia solution and add water to the mark.

7. Measure the absorbance of the diluted standard solutions (A_{min} and A_{max}) and the sample solution (A_x) at proper wavelength, following the instructions given by the spectrophotometer manufacturer. Use deionized water as a blank solution.

   Note: The Cu^{2+} cation forms a coordinate covalent complex with ammonia, $[Cu(NH_3)_4]^{2+}$. This complex species absorbs light strongly in the visible region 550–650 nm. The wavelength of maximum absorption lies between 600–620 nm, nominally at 610 nm.

II. Ion exchange separation and complexometric titration

Copper and zinc ions can be trapped from the solution by the ion exchange resin as described above in Part I. When ammonium oxalate is passed through the resin, an oxalate copper complex is released. The zinc ions remain fixed to the resin under these conditions. When a strong acid solution is passed through the column, the zinc cations are released. Both cations can then be determined separately by titration using EDTA.

1. Follow steps 1, 2, and 3 from Part I.
2. Releasing the Cu^{2+} ions: wash the column with 60 cm^3 of ammonium oxalate solution (eluate No. 1).
3. Releasing the Zn^{2+} ions: wash the column with 50 cm^3 of hydrochloric acid solution (eluate No. 2).
4. Determination of copper by EDTA complexometric titration: add 6–7 drops of hydrogen peroxide solution to eluate No. 1 and boil the solution for 10 minutes. After cooling, add murexide indicator, neutralize with ammonia solution and titrate with standard EDTA from yellow to purple. The indicator colour depends on the amount of murexide, copper ion concentration and pH. The neutralization must proceed carefully to keep the solution yellow. If the solution is greenish-yellow, dilute it and wait 1–2 minutes, until it turns yellow. If the solution is not clear yellow (rusty or grey) before the endpoint has been reached, add a few drops of ammonia solution and titrate from yellow to purple. The colour change at the endpoint of the titration is sharp if the titration is performed correctly.
5. Determination of zinc by EDTA complexometric titration: neutralize acidic eluate No. 2 with ammonia solution. Titrate with standard EDTA solution using Eriochrome black T indicator from wine red to blue. If the colour turns violet before the endpoint is reached, heat it to 40–50 °C. If the colour turns to blue, the titration is finished (i.e. the endpoint has been reached), if not, continue to titrate until a blue colour is observed.

Data Analysis and Questions

I. Determination of the metal ion concentration by alkalimetry and photometry

P1.1 Write down the balanced chemical equations of the reactions which occur:
  a) In the cation exchange between the sample solution and the resin in the H^+ cycle (indicated by the symbol {R-H}(s), where (s) denotes the solid phase of the resin),
  b) At the endpoint of the titration (use HInd and Ind^- notation).

P1.2 Explain why the resin must be washed with deionised water before the ion exchange.

P1.3 Explain the role of ammonia in the spectrophotometric determination of copper.

P1.4 Explain why the selected standard concentrations of Cu^{2+} were used in the spectrophotometric experiment.

P1.5 Calculate the concentrations of both cations in the sample (in mol dm^{-3}).

II. Ion exchange separation and complexometric titration

P1.6 Write down the balanced chemical equations describing the release of the Cu^{2+} and Zn^{2+} ions from the ion exchange resin.

P1.7 Explain the role of hydrogen peroxide in step II.4.

P1.8 Calculate the number of moles of both cations in 10.00 cm^3 of the sample.

Problem P2. Determination of a carbonate rock composition

Slovakia is a landlocked Central European country with mountainous regions in the north and flat terrain in the south. The mountains are part of the Carpathian arch with a varied geological structure: ancient volcanic rock, granite in the alpine mountains and sedimentary rocks, mainly composed of calcite ($CaCO_3$), dolomite ($CaMg(CO_3)_2$) and an admixture of ankerite ($CaFe(CO_3)_2$). These carbonate minerals have a common formula of $Ca(Fe,Mg)(CO_3)_2$. Your sample comes from such a dolomite rock with dolomite as the main component, but containing also some calcite, ankerite and other inert components.

Figure P2. Krásnohorská Cave in the dolomite region of Slovak Karst is currently listed by the Guinness Book of Records as the cave containing the largest stalagmite in existence, generally accepted as being about 12 m in diameter and 32.7 m in height. There are more than 2 400 caves in Slovakia, of which to date more than 400 have been explored and 18 can be visited by tourists.

Chemicals and Reagents

- Powdered sample, ca 1 g (precise weight)
- 3 M hydrochloric acid solution, 10 cm^3
- 2 M sodium hydroxide solution, 50 cm^3
- 25% aqueous ammonia solution (w/w), 50 cm^3
- 4 M ammonium chloride solution, 50 cm^3
- 30% hydrogen peroxide solution (w/w), 5 cm^3
- 5 mM standard EDTA disodium salt solution, 200 cm^3
- Indicators: methyl red solution, sulfosalicylic acid solution (5%, w/w), Eriochrome black T (solid indicator mixture), murexide (solid indicator mixture), universal pH indicator paper

Substance	Name	State	GHS Hazard Statement
HCl	Hydrochloric acid	Aqueous solution	H314, H318
NaOH	Sodium hydroxide	Aqueous solution	H314
NH_3	Ammonia	Aqueous solution	H314, H400
NH_4Cl	Ammonium chloride	Aqueous solution	H302, H319
H_2O_2	Hydrogen peroxide	Aqueous solution	H271, H302, H314, H333, H402
$C_{10}H_{14}N_2O_8Na_2 . 2H_2O$	Disodium ethylenediamine tetraacetate dihydrate	Aqueous solution	H302, H315, H319, H335
$C_{20}H_{12}N_3O_7SNa$	Eriochrome black T	Solid	H319
$C_8H_8N_6O_6$	Murexide	Solid	Not classified

$C_7H_6O_6S$	Sulfosalicylic acid	Aqueous solution	H315, H319, H335
$C_7H_6O_3$	Salicylic acid	Aqueous solution	H302, H318
$C_{15}H_{15}N_3O_2$	Methyl red	Solution	H225, H319, H371

Equipment and Glassware

- Laboratory stand with burette clamp
- Volumetric flasks, 250 cm^3 (2)
- Burette, 25 cm^3
- Pipettes, 50 cm^3 and 2 cm^3, with pipette filler
- Graduated pipette, 1 cm^3
- Graduated cylinders, 25 cm^3 and 5 cm^3
- Titration flasks, 250 cm^3 (3)
- Beakers, 100 cm^3 (2), 150 cm^3 (1) and 250 cm^3 (1)
- Watch glass
- Plastic Pasteur pipettes
- Filtration funnel
- Filter paper
- Hotplate

Procedure

1. Calculate the volume of 3 M HCl needed to decompose the rock sample. Assume the sample is pure mineral dolomite and you need 10% excess of the acid.
2. Decompose the powdered rock sample (m_0) in a 10% excess of HCl solution. Boil the solution for two minutes. After cooling, transfer the solution quantitatively to a 250 cm^3 volumetric flask and add deionized water to the mark (V_0).
3. Pipette 50.00 cm^3 of the sample solution (V_1), add 1 cm^3 of the H_2O_2 solution and boil the resulting solution for two minutes. If necessary, adjust the pH with aqueous ammonia solution to ca 4 (indicator methyl red, red colour, pH = 4.4). Add a few drops (ca 0.5 cm^3) of sulfosalicylic acid indicator and titrate with the standard EDTA solution from purple to yellowish (V_2). Repeat the titration as necessary.
4. Pipette 50.00 cm^3 of the sample solution (V_3), add 1 cm^3 of the H_2O_2 solution, adjust the pH to the range of 6 to 7 and boil the resulting solution for two minutes. After cooling, filter the precipitate, wash it with deionized water and collect the filtrate into a 250 cm^3 volumetric flask (V_4). Then add deionized water to the mark.
5. Pipette a 20.00 cm^3 aliquot of the sample solution obtained in step 4 (V_5) into the titration flask, dilute with deionized water and adjust the pH to ca 9. Titrate with the standard EDTA solution using Eriochrome black T indicator. The endpoint of the titration (V_6) is indicated by a sharp colour change from wine red to blue.
6. Pipette 20.00 cm^3 of the sample solution obtained in step 4 (V_7) into the titration flask, dilute with water and adjust the pH to ca 12. Titrate with the standard EDTA solution using the murexide indicator until the colour changes from pink (red) to violet (V_8).

Data Analysis and Questions

P2.1 Report the calculated volume of HCl needed to decompose the rock sample.

P2.2 Estimate the pH of the solution prepared in step 2.

P2.3 Explain why it is necessary to boil the mixture in step 2.

P2.4 Explain why it is necessary to boil the mixture after the addition of the hydrogen peroxide solution in step 3.

P2.5 Explain the role of the added hydrogen peroxide solution, the pH adjustment and boiling in step 4.

P2.6 Calculate the content (%, w/w) of dolomite, ankerite and calcite minerals and inert impurities in the sample.

Problem P3. Determination and identification of organic acids

Acid concentrations can be determined by iodometry by reaction with a mixture of iodate/iodide (IO_3^-/I^-). The reaction yields a proportional amount of iodine that can be determined by titration with thiosulfate. The rate of the reaction depends on the H^+ concentration, and is decreased as the reaction proceeds. Reliable results are obtained with strong acids when the reaction mixture is left to stand for about 15 minutes. For weak acids, the completeness of the reaction can be reached in hours (or, possibly, more quickly at elevated temperatures) but risks inaccuracies due to the volatility of the produced iodine. In special cases, the strength of an acid can be modified. For example, weak oxalic acid can be converted by $CaCl_2$ to an equivalent amount of the strong acid, HCl, and calcium oxalate which precipitates out, thus driving this reaction in the forward direction. Similarly, an increased acidity is observed for hydroxy substituted carboxylic acids due to the formation of calcium complexes.

Chemicals and Reagents

- Sample solutions of unknown acids labelled **A** and **B**, 150 cm^3. Each solution contains just one acid from the following:
  - 0.1 M acetic acid solution
  - 0.1 M hydrochloric acid solution
  - Hydroxy carboxylic acid ($R(OH)_x(COOH)_y$) solution, i.e.:
    - 0.1 M lactic acid solution
    - 0.05 M tartaric acid solution or 0.05 M malic acid solution
    - 0.0333 M citric acid solution
- 0.05 M standard iodine solution in ca 0.1 M potassium iodide solution, 200 cm^3
- 0.1 M standard sodium hydroxide solution, 25 cm^3
- 0.1 M sodium thiosulfate solution, 500 cm^3
- 1 M potassium iodide solution, 50 cm^3
- 3% potassium iodate solution (w/w), 50 cm^3
- Calcium chloride, 20 g
- Starch indicator solution

Substance	Name	State	GHS Hazard Statement
HCl	Hydrochloric acid	Aqueous solution	H314, H318
CH_3COOH	Acetic acid	Aqueous solution	H226, H314
NaOH	Sodium hydroxide	Aqueous solution	H314
$Na_2S_2O_3$	Sodium thiosulfate	Aqueous solution	H315, H319, H335
I_2	Iodine	Aqueous solution	H312, H332, H400
KI	Potassium iodide	Aqueous solution	H302, H315, H317, H319, H334, H335
KIO_3	Potassium iodate	Aqueous solution	H272, H302, H315, H317, H319, H335
$CaCl_2$	Calcium chloride	Solid	H312, H319
$C_6H_8O_7$	Citric acid	Aqueous solution	H315, H319, H335
$C_3H_6O_3$	Lactic acid	Aqueous solution	H315, H318
$C_4H_6O_5$	Malic acid	Aqueous solution	H302, H315, H318, H319, H335
$C_4H_6O_6$	Tartaric acid	Aqueous solution	H315, H318, H319, H335

Equipment and Glassware

- Laboratory stand equipped with a burette clamp
- Burette, 25 cm^3
- Volumetric pipettes, 20 and 25 cm^3, with pipette filler
- Iodine flasks (Erlenmeyer flask with stopper), 250 cm^3 (2)
- Beakers, 100 cm^3 (2) and 250 cm^3 (1)
- Graduated cylinder, 25 cm^3
- Plastic transfer pipettes, 3 cm^3 (2) and 5 cm^3 (2)
- pH-Meter, accuracy ±0.01

Procedure

I. Determination of sodium thiosulfate concentration in solution

Pipette 20.00 cm^3 of the standard iodine solution (V_1) into an Erlenmeyer flask, add 25 cm^3 of distilled water and titrate with the thiosulfate solution until a colour change to a pale yellow colour is observed. Add 3 cm^3 of the starch indicator and titrate the obtained blue coloured solution until the colour disappears (V_2). Repeat the titration as necessary.

II. Identification of an unknown acid in sample solutions A and B and determination of its concentration

For the analysis of the unknown acid samples, use the following procedures **a–c**. You can conduct these titration experiments in any order. Repeat the titrations as necessary.

Procedure **a**: Pipette 20.00 cm^3 (V_{11}) of an unknown acid solution (sample **A** or **B**) into the iodine flask, add 5 cm^3 of the KI solution and 5 cm^3 of the KIO_3 solution using the plastic transfer pipettes. Stopper the flask, let it stand in the dark for 15 minutes and then titrate the produced iodine using the thiosulfate solution (V_3, V_4, respectively).

Procedure **b**: Pipette 20.00 cm^3 (V_{12}) of an unknown acid solution (sample **A** or **B**) into the iodine flask, add 5 cm^3 of the KI solution and 5 cm^3 of the KIO_3 solution. Add 4 g of $CaCl_2$. Stopper the flask, let it stand in the dark for 15 minutes and then titrate the produced iodine using the thiosulfate solution (V_5, V_6, respectively).

Procedure **c**: Pipette 20.00 cm^3 (V_{13}) of an unknown acid solution (sample **A** or **B**) into the iodine flask, add 5 cm^3 of the KI solution and 5 cm^3 of the KIO_3 solution, then 25.00 cm^3 (V_{23}) of the thiosulfate solution. Stopper the flask and let it stand in the dark for 15 minutes. Add 20.00 cm^3 (V_{33}) of the standard iodine solution and titrate the excess iodine in the flask using the thiosulfate solution (V_5, V_7, respectively).

III. Identification of an unknown hydroxy carboxylic acid in the sample

There is a possibility that the sample contains an unknown hydroxy carboxylic acid that can be determined using iodometry as described above. Differentiate the hydroxy carboxylic acids according to their acid-base properties (Table P3).

Table P3. pK_a values of selected hydroxy carboxylic acids.

Acid	**pK_{a1}**	**pK_{a2}**	**pK_{a3}**
Lactic	3.86	-	-
Malic	3.46	5.10	-
Tartaric	3.04	4.37	-
Citric	3.13	4.76	6.40

The acids can be identified by measuring the pH of the buffer prepared from the unknown acid and sodium hydroxide. The precise concentration of the hydroxy carboxylic acid is known from Part II. Calculate the volume of the NaOH standard solution needed to prepare the buffer, for example in the molar ratio 1 : 1. The pH of such solution can be determined using the available software (e.g., http://www.iq.usp.br/gutz/Curtipot_.html).

Prepare such buffers from sample **A** or **B** identified as hydroxy carboxylic acid and measure the pH.

Data Analysis and Questions

I. Determination of sodium thiosulfate concentration in solution

P3.1 Provide a balanced chemical equation for the standardization of the thiosulfate solution.

P3.2 Derive the formulae for calculating the molar concentration of the sodium thiosulfate in the solution.

P3.3 Calculate the molar concentration of the sodium thiosulfate in the solution.

II. Identification of an unknown acid in sample solutions A and B and determination of its concentration

P3.4 Based on the results obtained in Part II, fill in the table and identify the acids in the samples.

Procedure a	Volume of sample solution **A** or **B** added to the titration flask		V_{11} =
	Volumes read from the burette (perform only the necessary analyses)		
	Sample **A** *Note/observation:*	V_{3a} =	V_{3b} =
	Sample **B** *Note/observation:*	V_{4a} =	V_{4b} =
	Accepted volumes	V_3 =	V_4 =
Procedure b	Volume of sample solution **A** or **B** added to the titration flask		V_{12} =
	Volumes read from burette (perform only the necessary analyses)		
	Sample **A** *Note/observation:*	V_{5a} =	V_{5b} =
	Sample **B** *Note/observation:*	V_{6a} =	V_{6b} =

	Accepted volumes	$V_5 =$	$V_6 =$
Procedure c	Volume of sample solution **A** or **B** added to the titration flask		$V_{13} =$
	Volumes read from burette (perform only the necessary analyses)		
	Sample **A** *Note/Observation:*	$V_{7a} =$	$V_{7b} =$
	Sample **B** *Note/Observation:*	$V_{8a} =$	$V_{8b} =$
	Accepted volumes	$V_7 =$	$V_8 =$

Indicate with a ✓ the identified component in sample **A**		
HCl	CH_3COOH	$(R(OH)_x(COOH)_y)$
Indicate with a ✓ the identified component in sample **B**		
HCl	CH3COOH	(R(OH)x(COOH)y)

P3.5 Provide reasons for your conclusions about the acids identified in the samples.

P3.6 Write down the balanced chemical equations of the reactions necessary to calculate the result.

P3.7 Derive the formulae for calculating the concentration of the strong acid when Procedure **a** was used.

P3.8 Derive the formulae for calculating the concentration of the hydroxy acid when Procedure **b** was used.

P3.9 Explain the role of the excess thiosulfate in Procedure **c**.

P3.10 In an acid solution, thiosulfate undergoes an undesired side reaction. Write down the balanced chemical equation of this unwanted side reaction. Explain why it is possible to add an excess of thiosulfate to the acid sample in Procedure **c**.

P3.11 Derive the formulae for calculating the concentration of the weak acid when Procedure **c** was used.

P3.12 Calculate the molar concentration of the acid in each sample.

III. Identification of an unknown hydroxy carboxylic acid in the sample

P3.13 Identify the unknown hydroxy carboxylic acid (if present) by comparing the measured and theoretical pH values of the buffer solution.

Problem P4. A chemical oscillator and its activation energies

In 2018, we celebrate the 50th anniversary of the International Chemistry Olympiad, which was first organized in 1968 in Czechoslovakia. By coincidence, it is also the 50th anniversary of an important breakthrough that began a new era in chemical kinetics.

In July 1968, Prague hosted an international conference called "Biological and Biochemical Oscillators", one of a few rare occasions that brought together Western scientists with the scientists from the Eastern Bloc. At this conference, a young Russian chemist Anatol Zhabotinsky introduced to the crowd a new, remarkable system, an oscillator based on nothing else but chemical reactions.

The oscillations were originally discovered in the early 1950s by Boris Belousov, who was looking for an inorganic analogue of the Krebs cycle. Unfortunately, at that time, his colleagues did not accept that a homogeneous chemical oscillator could exist. For many years, Belousov’s recipe survived only as a bizarre chemical curiosity, passed on among a few Chemistry departments in Moscow.

It was the 1968 conference in Prague that marked the real turning point. Zhabotinsky’s careful verifications and extensions of Belousov’s work finally attracted the attention they deserved, and research groups studying oscillatory kinetics formed all throughout the Eastern Bloc, including Czechoslovakia, as well as in the West. The field of nonlinear chemical kinetics was born.

This famous oscillator became known as the Belousov-Zhabotinsky or, for short, the BZ reaction. In this task, your own observations of the oscillations will enable you to elucidate their core mechanism. Furthermore, you will explore a remarkable island of simplicity in the rather complex phenomenon. You will verify that the periods of the BZ oscillations still obey the Arrhenius law.

Chemicals and Reagents

- 1.50 M sulfuric acid solution, 150 cm^3
- Malonic acid, 5.203 g
- Cerium(III) sulfate tetrahydrate, 0.801 g
- 7.5 mM ferroin sulfate solution, 20 cm^3
- Sodium bromate(V), 7.545 g
- 0.05 M potassium bromide solution, 50 cm^3

Substance	**Name**	**State**	**GHS Hazard Statements**
H_2SO_4	Sulfuric acid	Aqueous solution	H290, H314
$C_3H_4O_4$	Malonic acid	Solid[a]	H319
$Ce_2(SO_4)_3 \cdot 4\ H_2O$	Cerium(III) sulfate tetrahydrate[b]	Solid[a]	H315, H319, H335
$[Fe(C_{12}H_8N_2)_3]SO_4$	Ferroin sulfate[c]	Aqueous solution	Not hazardous
$NaBrO_3$	Sodium bromate(V)	Solid[a]	H272, H315, H319, H335
KBr	Potassium bromide	Aqueous solution	Not hazardous

[a] It is recommended to start from solids if reproducible results are to be obtained. Stock solutions of these substances age quickly and results will drift as the solutions are stored, especially in the case of $Ce_2(SO_4)_3$.

[b] Other hydrates of $Ce_2(SO_4)_3$ may be used. Anhydrous $Ce_2(SO_4)_3$ can be very difficult to dissolve.

[c] The stock solution may also be prepared from $FeSO_4$ and *o*-phenanthroline, but the results may vary. Commercial ferroin sulfate indicator solution is preferred as starting material.

Equipment and Glassware

- Digital stop-watch capable of split timing
- Laboratory stand with clamps
- Jacketed beaker, 50 cm^3
- Circulating thermostat bath
- Thermometer
- Magnetic stirrer and a PTFE-coated stir bar
- Graduated pipettes, 10 cm^3, 5 cm^3 and 1 cm^3
- Volumetric flask, 50 cm^3
- Bottles for stock solutions, 50 cm^3 (3)
- Wash-bottle with deionized water
- Ultrasonic bath (if needed)

Procedure

I. Preparation of stock solutions

Note: This part may be omitted if reagents are supplied as solutions. It must be noted, however, that results will depend on storage time and conditions.

Mix solid cerium(III) sulfate with some water and transfer the suspension quantitatively into a volumetric flask charged with 1.5 cm^3 of 1.50 M sulfuric acid solution. Add enough water to dissolve and, if needed, treat with ultrasound. Then, add water to the mark, transfer the solution into the stock bottle and wash the flask well. Repeat the procedure with bromate(V) and malonic acid, except adding any sulfuric acid.

II. Setting up and getting familiar with the BZ oscillator

1. Select pipettes of appropriate volumes, one for each stock solution plus one for water.
2. To assemble the apparatus, connect the jacketed beaker to the circulating thermostat and fix it on the magnetic stirrer with a clamp. Turn on the thermostat and set the temperature to 25.0 °C.
3. Charge the jacketed beaker with 10.0 cm^3 water, 10.0 cm^3 sulfuric acid solution, 3.0 cm^3 malonic acid solution, 3.0 cm^3 cerium(III) solution, and 1.0 cm^3 ferroin solution.
4. If the stirring intensity is not set for you, you will need to find it. It should be as high as possible, but the vortex must not be so deep that bubbles of air get stirred into the solution. Once you set the right stirring intensity, maintain this setting during all your work.

   Note: The results can vary significantly with stirring intensity, just as they depend on the overall geometry of the reactor vessel, of the stir bar etc. If the results are to be compared against benchmark values, all these parameters must be preset and fixed carefully.
5. Start the reaction by adding 3.0 cm^3 of the bromate(V) solution. Initially, the solution will maintain one colour and then it will start changing gradually. At some point, there will be a sudden colour change that will restore the first colour. This colour cycle will be repeated. Note down the colour changes.

III. Determining the building blocks of the BZ chemistry

1. Prepare a BZ oscillator mixture with the same concentrations of sulfuric acid, malonic acid and bromate(V) as in Part II, but omit the metal catalysts – cerium(III) and ferroin. Instead, add 3.0 cm^3 of the bromide stock solution and increase the volume of water accordingly to keep

the total volume at 30 cm^3. Note the colour changes after you start the reaction by adding the bromate(V) solution.

2. Prepare a BZ oscillator mixture with the same concentrations of sulfuric acid, cerium(III), ferroin and bromate(V) as in Part II, but omit the malonic acid. Instead, add the same volume of the bromide stock solution. As indicated by a thermometer, wait until the solution temperature has stabilized, and record the reading. Finally, once you begin adding 3.0 cm^3 of the bromate(V) solution, immediately start the stop-watch. Note how the colour of the reaction mixture develops, and record the time when the colour changes abruptly.

IV. Timing the oscillations for various amounts of cerium(III)

1. Prepare a BZ oscillator mixture with the same concentrations of sulfuric acid, malonic acid, ferroin and bromate(V) as in Part II, but only half of the volume of cerium(III) solution. Do not add any bromide solution, but increase the volume of water accordingly to keep the total volume of the mixture at 30 cm^3. Wait until the solution temperature has stabilized and record the reading.
2. Finally, once you begin adding 3.0 cm^3 of the bromate(V) solution, immediately start the stop-watch. Every time a sudden colour transition occurs, hence indicating a new colour cycle has begun, press the SPLIT button to read the exact time while continuing to time. In this way, record the times of the first four sudden colour transitions.
3. Repeat the same timing procedure with the original volume of cerium(III) solution, 3.0 cm^3.

V. Temperature dependence

Repeat the same timing procedure with the same BZ oscillator that you observed in Part IV.3 at approximately 25 °C, with 3.0 cm^3 of the cerium(III) solution, but increase the temperature setting on the thermostat to 27.0 °C, 29.0 °C, 31.0 °C and 33.0 °C. For each temperature, record the times of the first four sudden colour changes.

Data Analysis and Questions

P4.1 Write a balanced ionic equation for the chemical reaction responsible for the colour observed when bromate(V) and bromide are mixed in an acidic solution. Write a balanced equation for the chemical reaction responsible for the disappearance of this colour in the presence of malonic acid. Sum the two equations appropriately to provide the overall reaction that has taken place in the mixture when the colour has disappeared.

P4.2 Consider your observation in the reaction in which malonic acid (MA) was replaced with Br^-. Provided that the recorded reaction time is proportional to $[Br^-]$, calculate the rate at which $[Br^-]$ is consumed. Using the average period of oscillation recorded in the BZ oscillator at 25 °C, calculate the concentration $[Br^-]$ consumed in each cycle of the BZ oscillator. How much [MA] does this consume? Where does the Br^- for each cycle come from?

P4.3 The most concise version of the BZ oscillations mechanism consist of steps that are all in the form of redox reactions with a simple 1:1:*n* stoichiometry:

oxidizing-agent species + reducing-agent species + n H^+ = products (*n* can be 0, 1, 2, …)

Usually, only a single organic step (bromomalonic acid cleavage with Ce^{4+}) is included, and the stoichiometry of its products is traditionally formulated as adjustable. In the inorganic subset, however, all steps are perfectly balanced, and stoichiometric coefficients are always integers, even for all the products. Only the following bromine-containing species are considered: Br^-, Br_2, HBrO, $HBrO_2$, BrO_2, BrO_3^-.

How many balanced equations that satisfy these criteria can you write for the step of Ce^{3+} oxidation to Ce^{4+}? Which of your experimental observations can you combine with these equations to conclude that Ce^{3+} is oxidized by BrO_2? Write down the step producing BrO_2. Which species can be eliminated in the combined equation for Ce^{3+} oxidation and BrO_2 production to show that this pair of reactions forms an autocatalytic cycle? Write down the step responsible for the inhibition of this autocatalytic cycle with Br^-.

P4.4 Compare the BZ oscillations at the two different concentrations of cerium(III) catalyst. How is increased catalyst concentration reflected in the lengths of the induction periods, i.e. in the times taken until the first sudden colour changes, and how is it reflected in the average lengths of the first three periods of oscillation? What role does this suggest for cerium(III) in the oscillations?

P4.5 Assuming that the induction periods and the average periods of oscillation directly reflect the rates of the rate-determining steps in the system, use your experimental data measured at various temperatures to plot their natural logarithms against $1/T$, and find the corresponding activation energies. Compare the results to the reference data, around 60 kJ mol^{-1} for cerium-catalyzed oscillations and around 75 kJ mol^{-1} for ferroin-catalyzed oscillations.

Problem P5. Kinetics of a chemical wave front propagation

We usually tend to think of synthesis as of making substances. In this task, however, you will use chemical reagents to synthesize *patterns*.

When a BZ oscillating reaction solution is poured onto a Petri dish, the interaction between an autocatalytic reaction and diffusion has the ability to transform the solution, initially homogeneous, into a beautifully self-ordered sea of chemical waves. This phenomenon is not only pretty, but the movement of the structures can also be used to study the kinetics of the underlying reactions.

If we have an autocatalytic reaction producing autocatalytic species **X**, the simplest form of autocatalysis is described by a simple reaction rate equation:

$$\frac{\mathrm{d}[\mathrm{X}]}{\mathrm{d}t} = k'[\mathrm{X}] \qquad (1)$$

An interesting thing happens when we have a medium capable of undergoing such an autocatalytic reaction, but **X** is initially present only in a selected region. As expected from an autocatalytic reaction, wherever **X** is available, a burst of production of even more **X** occurs. In addition, if diffusion can take place, the diffused **X** can trigger the autocatalytic production of **X** in the adjacent regions, too. This spreads like fire and we observe a chemical trigger wave. If D is the diffusion coefficient of **X**, the velocity v of the trigger wave is:

$$v = 2\sqrt{k'D} \qquad (2)$$

In the BZ oscillator, the examination of how the rate of the autocatalytic step depends on acidity and on the concentration of bromate(V) yielded the following result:

$$k' = 20\ \mathrm{M}^{-2}\ \mathrm{s}^{-1}\ [\mathrm{H}^+][\mathrm{BrO}_3^-] \qquad (3)$$

Your task is to validate this relationship experimentally, by measuring the velocity of the wave fronts at various concentrations.

Chemicals and Reagents

- 1.50 M sulfuric acid solution, 150 cm^3
- Malonic acid, 5.203 g
- Cerium(III) sulfate tetrahydrate, 0.801 g
- 25 mM ferroin sulfate solution, 25 cm^3
- Sodium bromate(V), 7.545 g

Note: The chemicals and reagents are the same as in Problem P4, except that the ferroin sulfate solution is now more concentrated, 25 mM. All safety information and all notes regarding handling and storage apply as in Problem P4.

Equipment and Glassware

- Digital stop-watch
- Petri dish, 14 cm diameter, with lid
- Millimeter graph paper
- Beaker, 100 cm^3
- Graduated pipettes, 10 cm^3 and 5 cm^3
- Wash-bottle with deionized water

Procedure

I. Preparation of stock solutions and equipment

1. The procedure for the preparation of the stock solutions is the same as in Problem P4.
2. Select pipettes of appropriate volumes, one for each stock solution plus one for water. Place the Petri dish on a sheet of millimeter graph paper.

   Note: The benchtop for this experiment must be perfectly level. Leaning against the table while a measurement is in progress must be avoided. Since the temperature of the Petri dish is not controlled, the experiment must not be performed near a source of heat or a draught.

II. General procedure for finding the chemical wave front velocity

1. Prepare a BZ oscillator by charging the beaker with water and solutions of sulfuric acid, malonic acid, cerium(III) sulfate, and ferroin sulfate, using the volumes specified in Part III. Finally, start the reaction by adding the solution of bromate(V) and swirling the beaker with your hand.
2. Pour the oscillator solution from the beaker onto the Petri dish. Swirl the dish a few times to distribute the solution evenly over its entire surface, and cover the dish with its lid. Initially, the solution will change colour uniformly, but eventually, spots of a different colour will appear. The spots will grow into rings, and when a ring becomes large enough, a new spot will appear in its center. This leads to the formation of *target patterns* (Fig. P5).

Figure P5. The patterns to be formed in a Petri dish.

3. To find the wave front velocity, measure the time that it takes for a front, preferably *inside* a target pattern, to advance by 5 mm. This will not be possible immediately, as the outmost rings in each target pattern will be regularly annihilated. At some point, however, the patterns will become large enough to allow the fronts to be followed across a 5 mm long path, at least in one direction.

   Note: Tracking the fronts along the left–right axis is preferred. To read the position of a front that is moving towards or away from the observer, it may be neccessary to close one eye, or watch the pattern from another angle. Be careful not to perturb the dish!
4. To find the mean wave front velocity in the dish, repeat the reading of the time required to cover a 5 mm distance for three different fronts, preferably in three different places on the Petri dish.

III. Dependence of the chemical wave front velocity on concentrations

Using the procedure described above, find the average wave front velocities at four different concentration sets (Table P5). All contain 3.0 cm^3 malonic acid solution, 3.0 cm^3 cerium(III) sulfate solution and 2.0 cm^3 ferroin sulfate solution. The first two sets will differ in the volumes of sulfuric acid and the other two sets will differ in the volumes of bromate(V) solution. To make sure that your data is correct, replicate each concentration set twice. If the data disagree, add more replicates for verification.

Table P5. Concentration sets for finding the dependence of the chemical wave front velocity.

Set	Water	Sulfuric acid solution	Bromate(V) solution
#1	9.0 cm^3	10.0 cm^3	3.0 cm^3
#2	12.0 cm^3	7.0 cm^3	3.0 cm^3
#3	8.1 cm^3	10.0 cm^3	3.9 cm^3
#4	9.9 cm^3	10.0 cm^3	2.1 cm^3

Data Analysis and Questions

P5.1 Assume that the total volumes of the reaction mixtures always add up to 30 cm^3. Calculate the concentrations of sulfuric acid and bromate(V) in the four concentration sets examined. Using all time readings taken in accepted replicates, calculate one mean wave front velocity, expressed in mm min^{-1}, for each concentration set. $M(NaBrO_3) = 150.89$ g mol^{-1}

P5.2 Assume that instead of equation (3), the dependence of v^2 on $[BrO_3^-]$ is described as $v^2 = p\,[BrO_3^-] + q$. What would it suggest about the kinetics of the autocatalysis, if $q > 0$, and what would it suggest if $q < 0$? Use the results from Sets #3 and #4 to evaluate p and q. Calculate the percentage of the overall reaction rate that is contributed by q. Is this significant?

P5.3 Assume that the wave front propagation velocity v is a power function of both, $[H_2SO_4]$ and $[BrO_3^-]$, i.e. $v = k\,[H_2SO_4]^a\,[BrO_3^-]^b$. Use the results from Sets #1 and #2 to calculate the exponent a, and the results from Sets #3 and #4 to calculate the exponent b. What assumption would allow us to deduce the reaction order with respect to $[H^+]$ from a? Compare the results to the values that are expected based on equation (3). Are a and b roughly as expected or does any value suggest that, for the conditions studied, the rate equation (3) should be revised?

P5.4 Assume that equation (3) applies, and that $[H^+] \approx [H_2SO_4]$. Using the reference value of the autocatalytic species diffusion coefficient $D = 2.0 \times 10^{-5}$ $cm^2\,s^{-1}$, calculate what values are suggested for the autocatalytic reaction rate constant from your experimental data. Does any of the concentration sets come close to the reference value 20 $M^{-2}\,s^{-1}$?

Problem P6. Separation of acidic, basic and neutral organic compounds

This task is designed to help you understand the chemical basis of separation of up to a four-component mixture using extraction techniques and visualizing the separation by checking the composition of the organic layer after each extraction. Extraction in an organic chemistry laboratory is most often used to isolate organic compounds from reaction mixtures after an aqueous work-up. Extraction is a particularly useful method for separating organic compounds if one compound in the mixture can be chemically converted to an ionic form. The ionic form is often more soluble in an aqueous layer and can be extracted into it. Non-ionic organic compounds in the mixture will remain dissolved in the organic layer. The separation of the two layers results in the separation of the compounds. The pK_a values of the acids provide a measure of the acidity of each compound. The extent to which an acid–base reaction proceeds to completion depends on the relative acidity of the reactants and products.

Chemicals and Reagents

- Unknown solid sample containing 3–4 of these compounds: benzoic acid, 4-nitroaniline, 2-naphthol, naphthalene; 750 mg
- Chloroform, 20 cm^3
- 20% hydrochloric acid aqueous solution (w/w), 42 cm^3
- 10% sodium bicarbonate aqueous solution (w/w), 24 cm^3
- 10% sodium hydroxide aqueous solution (w/w), 24 cm^3
- 20% potassium hydroxide aqueous solution (w/w), 30 cm^3
- Anhydrous sodium sulfate, 2 tea spoons
- Hexanes/ethyl acetate 3:1 mixture (TLC eluent), 5 cm^3

Substance	Name	State	GHS Hazard Statements
$C_7H_6O_2$	Benzoic acid	Solid	H315, H318, H372
$C_6H_6N_2O_2$	4-Nitroaniline	Solid	H301, H311, H331, H373, H412
$C_{10}H_8O$	2-Naphthol	Solid	H302, H332, H400
$C_{10}H_8$	Naphthalene	Solid	H228, H302, H351, H410
$CHCl_3$	Chloroform	Liquid	H302, H315, H319, H331, H336, H351, H361d, H372
HCl	Hydrochloric acid	Aqueous solution	H290, H314, H335
$NaHCO_3$	Sodium bicarbonate	Aqueous solution	H319
NaOH	Sodium hydroxide	Aqueous solution	H290, H314
KOH	Potassium hydroxide	Aqueous solution	H290, H302, H314, H315, H319
$C_4H_8O_2$	Ethyl acetate	Liquid	H225, H319, H336
C_6H_{14}	Hexanes (mixture of isomers)	Liquid	H225, H304, H315, H336, H411
Na_2SO_4	Sodium sulfate	Solid	Not hazardous

Equipment and Glassware

- Laboratory stand with clamps and metal ring
- Magnetic hotplate stirrer and a PTFE-coated stir bar
- Rotary evaporator
- Water aspirator (or other vacuum source for suction filtration and vacuum rotary evaporator)

- Measuring cylinders, 10 cm^3 and 20 cm^3
- Erlenmeyer flasks, 50 cm^3 (2)
- Glass rod
- TLC chamber or a Petri dish covered small beaker
- TLC plates, silica gel 60 F_{254} (4), and capillaries
- UV lamp (254 nm)
- Beakers, 50 cm^3 (1) and 100 cm^3 (3)
- Separatory funnel, 100 cm^3
- pH indicator paper
- Büchner filter funnel
- Filter paper
- Suction flask, 100 cm^3, with rubber adapter for filter funnel
- Round bottom flask, 50 cm^3
- Spatula
- Tweezers
- Marker for glass

Procedure

Warning: Chloroform and naphthalene should be handled only in a well-ventilated fumehood.

I. Sample preparation

The sample weighing 750 mg contains three to four of these compounds: benzoic acid, 4-nitroaniline, naphthalene-2-ol and naphthalene. Dissolve this sample in 20 cm^3 of chloroform in a 50 cm^3 Erlenmeyer flask.

II. TLC analysis

Check the composition of the solution before extractions (Plate 1). Spot the chloroform solution on the TLC plate using a glass capillary spotter (mark the start line at a height of 1 cm, Figure P6). Take a 50 cm^3 beaker, load it with 2 cm^3 of the TLC eluent using a measuring cylinder. Insert the TLC plate upright into the TLC developing chamber. Ensure that the eluent level is below the start line. Cover the beaker with one of the Petri dishes. Wait until the solvent system reaches the pre-drawn eluent front line. Remove the TLC plate using tweezers and let the eluent dry in air. Place the TLC plate under a UV lamp. Mark the spots of the compounds with a pencil and calculate the R_f values.

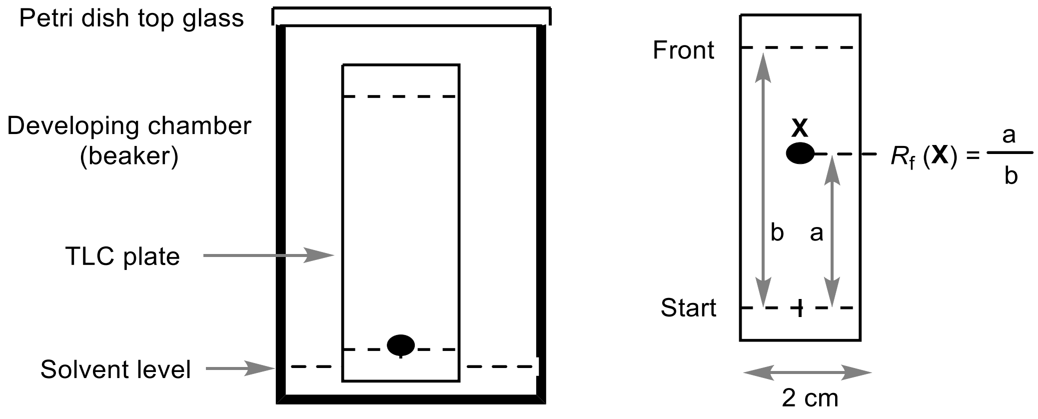


Figure P6. Developing a TLC plate (left), evaluation of R_f value (right).

III. Separation of the basic compound A

1. Place a separatory funnel with a closed stopcock into a metal ring and place a 50 cm^3 Erlenmeyer flask under it. Using a glass filter funnel, pour the chloroform solution into the separatory funnel. Measure 6 cm^3 of 20% solution of HCl using a measuring cylinder. Add it into the separatory funnel using a conic filter funnel. Hold the funnel around the top, lift it out of the supporting ring and swirl it gently (chloroform vapours may cause pressure build-up in the funnel). Return the separatory funnel to the ring and insert the stopper.
2. To perform the extraction, use both hands; hold the body of the funnel around stopcock with one and the stopper with the other. Take out the funnel from the support ring and invert it and vent it by opening the stopcock. Repeat the swirling-venting process until the pressure build-up diminishes. Then shake the funnel for 5 × 10 s. Make sure that the stopcock is closed and return the separatory funnel to the metal ring over the 50 cm^3 Erlenmeyer flask and remove the stopper.
3. Allow the layers to separate and collect the organic layer by opening the stopcock and collecting the bottom layer into the 50 cm^3 Erlenmeyer flask. Close the stopcock and pour the aqueous layer through the top neck and into the 100 cm^3 beaker, using a glass filter funnel. Keep both phases.
4. Pour the organic phase back into separatory funnel and repeat the extraction with another 6 cm^3 of the 20% solution of HCl. Combine the aqueous layers after both extractions, label the beaker as **A** and keep aside for subsequent isolation.
5. Check the composition of the organic solution after the extraction with the diluted HCl solution using TLC analysis (Plate 2).

IV. Separation of the acidic compounds B and C

1. Extract the organic layer twice with 12 cm^3 of 10% solution of $NaHCO_3$ and combine the aqueous layers after both extractions in a 100 cm^3 beaker. Label the beaker as **B** and keep aside for subsequent isolation.
2. Check the composition of your organic layer (Plate 3).
3. Then extract the organic layer twice with 12 cm^3 of 10% solution of NaOH and combine the aqueous layers after both extractions in a 100 cm^3 beaker. Label the beaker as **C** and keep aside for subsequent isolation.
4. Collect the organic phase into a 50 cm^3 Erlenmeyer flask. Check the composition of the organic layer (Plate 4).

V. Isolation of organic compounds A, B and C from the aqueous layers

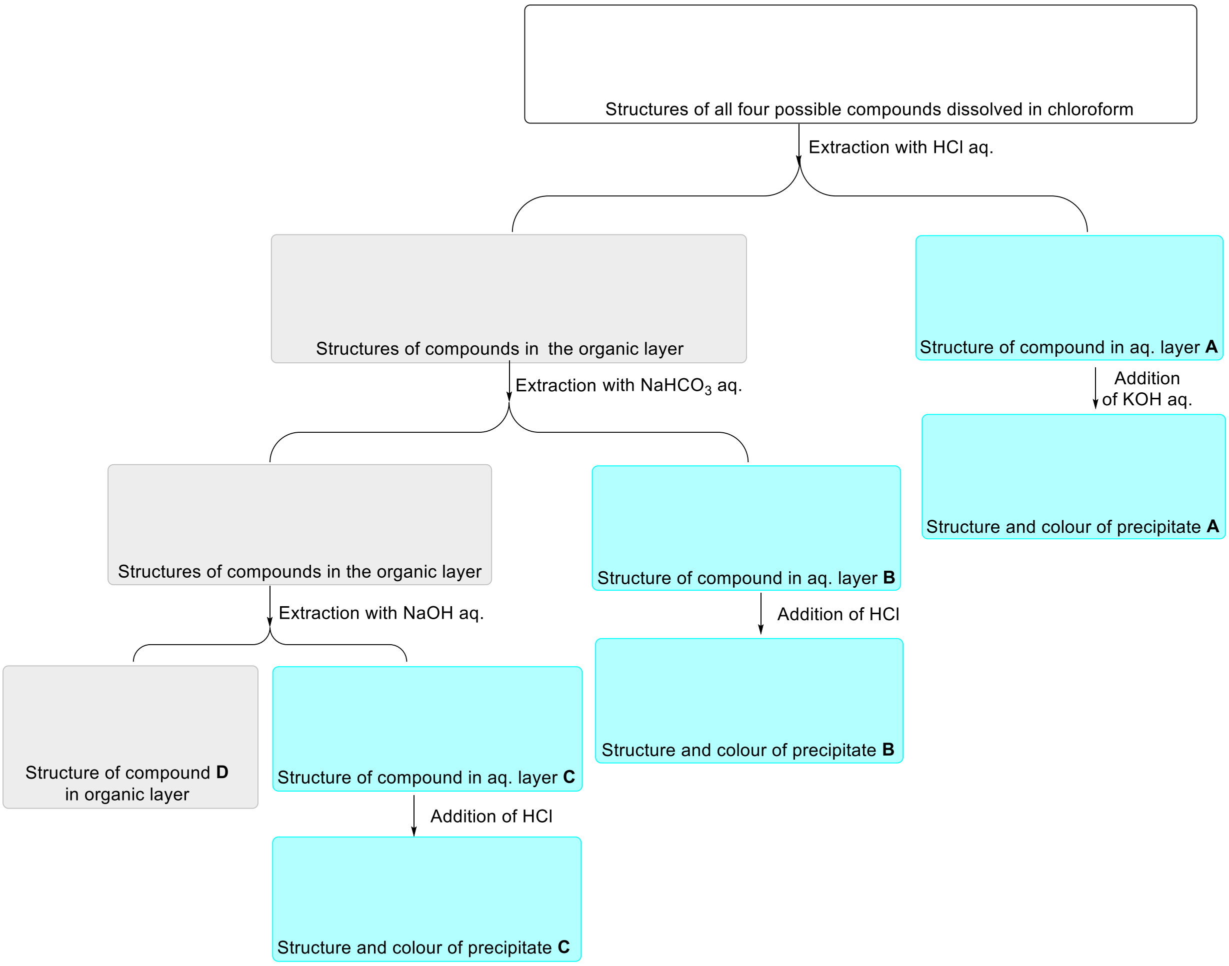
1. Basify the acidic aqueous layer in the beaker labelled **A** with a 20% solution of KOH (adjust the pH to 11, ca 12 cm^3). Yellow precipitate **A** is formed.
2. Acidify the basic aqueous extracts in beakers labelled **B** and **C** with a 20% solution of HCl (to pH 1, ca 12 cm^3). Watch out for the CO_2 evolution during the neutralization of the bicarbonate extract. White precipitate **B** and pink precipitate **C** are formed, respectively.
3. Isolate each of the precipitated compounds (**A**, **B**, **C**) by suction filtration using a Büchner funnel and filter paper. Dry all the products in air and then record the yields.

VI. Isolation of neutral organic compound D from organic layer

Dry the organic layer over anhydrous Na_2SO_4 for 10 min. Filter off the used drying agent through filter paper and collect the filtrate in a pre-weighed round bottom flask. Compound **D** can be recovered from the filtrate by evaporating the solvent on a rotary evaporator. Record the yield.

Data Analysis and Questions

P6.1 Fill in the structures of all the missing compounds and the colour of the precipitates into the flow chart:



P6.2 Compare all four TLC plates from the task and explain your observation.

P6.3 Write the equations of the acid–base reactions for the separations and isolations.

P6.4 Explain why it is important to perform the second extraction (the first extraction using the basic aqueous solution) with $NaHCO_3$ and not with the NaOH solution.

P6.5 Fill in the following table and identify compounds **A–D**.

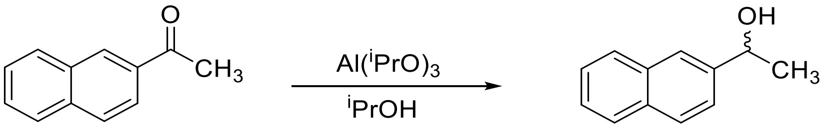
Compound	***R*$_f$**	***m* (g)**	**Compound name**
A			
B			
C			
D			

P6.6 Determine the ratio of the compounds in your sample and discuss the quantitative difference of the initial sample mass and the sum of the masses of the pure isolated compounds. Explain the difference.

Problem P7. Meerwein–Ponndorf–Verley reduction

The Meerwein–Pondorf–Verley reduction is an aluminium(III)-catalyzed hydride transfer from the α-carbon of isopropyl alcohol to the carbonyl carbon of an aldehyde or ketone. The product of this reaction is the corresponding primary or secondary alcohol, respectively, while an equimolar amount of isopropyl alcohol (which is used as a solvent and is present in large excess) is oxidized to acetone. The advantages of this reduction lie in the high degree of chemoselectivity and use of a cheap, environmentally friendly metal catalyst.

In this task, you will perform the Meerwein–Pondorf–Verley reduction on (2-naphthyl)ethanone (2-acetonaphthone).



Chemicals and Reagents

- 2-Acetonaphthone, 200 mg
- Aluminum isopropoxide, 300 mg
- Isopropyl alcohol, 4 cm^3
- Ethyl acetate, 20 cm^3
- Hexanes, 15 cm^3
- Saturated ammonium chloride aqueous solution, 8 cm^3
- Anhydrous sodium sulfate
- Inert gas (nitrogen or argon)

Substance	Name	State	GHS Hazard Statements
$C_{12}H_{10}O$	2-Acetonaphthone	Solid	H302, H315, H319, H335, H411
$Al[OCH(CH_3)_2]_3$	Aluminum isopropoxide	Solid	H228
$(CH_3)_2CHOH$	Isopropyl alcohol	Liquid	H225, H319, H336
$CH_3COOC_2H_5$	Ethyl acetate	Liquid	H225, H319, H336
C_6H_{14}	Hexanes (mixture of isomers)	Liquid	H225, H304, H315, H336, H411
NH_4Cl	Ammonium chloride	Aqueous solution	H302, H319
Na_2SO_4	Anhydrous sodium sulfate	Solid	Not hazardous

Equipment and Glassware

- Laboratory stand with clamps
- Magnetic hotplate stirrer and a PTFE-coated stir bar
- Round-bottom flask, 25 cm^3
- Reflux condenser
- Inert gas joint
- Inflatable balloon
- Water bath with paper clip
- Graduated cylinder, 10 cm^3
- Separatory funnel, 50 cm^3
- Erlenmeyer flask, 25 cm^3
- Filtration funnel
- Paper filter

- Round bottom flask, 50 cm^3
- TLC plates, silica gel 60 F_{254} (2)
- TLC chamber or a Petri dish covered small beaker
- UV lamp (254 nm)
- Petri dish
- Spatula
- Capillary
- Vial
- Ice bath
- Teflon sleeves for tapered joints or vacuum grease
- Vacuum rotary evaporator with vacuum source
- Melting point apparatus

Procedure

I. Drying of isopropyl alcohol

Place 300 mg of aluminium isopropoxide into a 25 cm^3 round-bottom flask equipped with a magnetic stir bar. Add 4 cm^3 of isopropyl alcohol and fit the reflux condenser. Fix the apparatus at the laboratory stand over the magnetic stirrer (Figure P7). Attach an inflatable balloon filled with an inert gas (N_2 or Ar). Heat the water bath with a paper clip to 90 °C. Place the flask in the water bath and stir the reaction mixture under an inert atmosphere for 1 hour. At this stage, the excess aluminium isopropoxide is used to remove the moisture present in isopropyl alcohol ($w(H_2O) \leq 0.002$). Remove the flask from the water bath and let the reaction mixture cool under the inert atmosphere.

II. Meerwein–Ponndorf–Verley reduction of 2-acetonaphthone and isolation of the product

1. Add 2-acetonaphthone to the reaction mixture, leaving a small amount (on the tip of a spatula) in the vial as a standard for TLC analysis. Then, reattach the reflux condenser with an inflatable balloon and place the flask in the water bath heated to 90 °C. Stir the reaction mixture under an inert atmosphere for 2 hours. Remove the flask from the water bath and let the reaction mixture cool down. Add 8 cm^3 of NH_4Cl saturated aqueous solution and stir the mixture at room temperature for 10 min.

2. Transfer the white suspension into the separatory funnel. Extract the aqueous phase 3 times with 5 cm^3 of ethyl acetate. Collect the organic extracts in a 25 cm^3 Erlenmeyer flask. Add one teaspoon of anhydrous Na_2SO_4, and let the organic phase stand over the drying agent for 20 min.

3. Prepare the standard solution of the starting material in a vial by dissolving a small amount of 2-acetonaphthone (set aside in step 1) in 0.5 cm^3 of ethyl acetate. Prepare the eluent mixture hexanes/ethyl acetate 6:1 and pour it into the developing chamber and cover it with a Petri dish. Spot a sample of the starting material and a sample of the extract with a capillary tube on a TLC plate. Place the TLC plate into the developing chamber, close the lid and let the eluent evolve. Mark the solvent front and the position of the starting material and the product spots under a UV light. Calculate the retention factors of the starting material and the product.

4. After 20 minutes of drying have elapsed (step 2), filter the extract through filter paper into a 50 cm^3 round-bottom flask. Remove the solvents using a vacuum rotary evaporator.

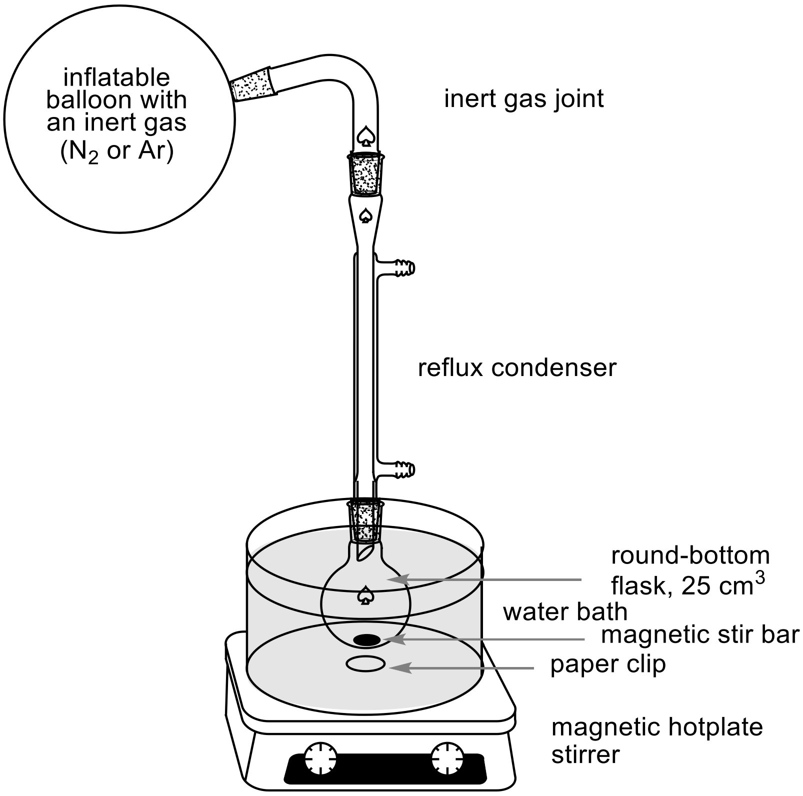


Figure P7. Apparatus for drying of isopropyl alcohol.

III. Crystallization of the product

Dilute the residue after the evaporation with 10 cm^3 of hexanes. If the crude product precipitates, attach a reflux condenser and heat the solvent to the boiling point in the water bath heated to 90 °C until the solid material dissolves. Place the flask in the ice bath and let the product crystalize. Separate the crystals by filtration on filter paper and wash them with 5 cm^3 of hexanes. Let the isolated product dry in air. Weigh the product and calculate the yield. Determine the melting point of the product. Compare the value with the reference data and draw a conclusion about the product purity.

Data Analysis and Questions

P7.1 Calculate the theoretical yield of the product in mg.

P7.2 Calculate the experimental yield of the product in %.

P7.3 Provide the melting point of the product.

P7.4 Provide the R_f values of the starting material and the product.

P7.5 Calculate the number of moles of water present in 4 cm^3 of isopropyl alcohol ($w(H_2O) = 0.002$; $d(^iPrOH) = 0.786$ g.cm^{-3}).

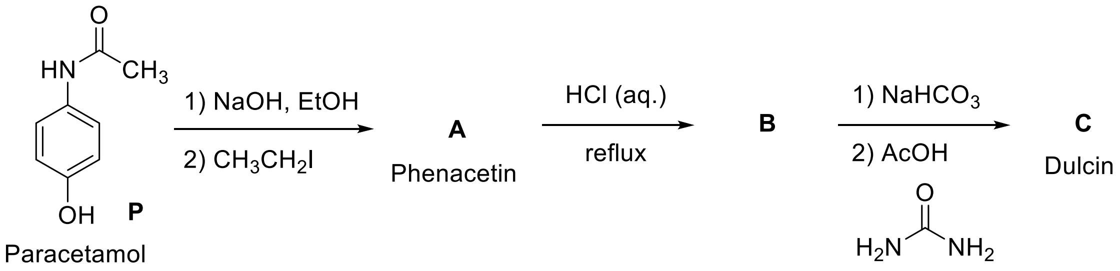
P7.6 What is the final product of the aluminium isopropoxide hydrolysis in the final step of the synthesis?

P7.7 Explain the difference in the retention factors of the starting 2-acetonaphthone and the obtained 1-(2-naphthyl)ethanol.

P7.8 Propose an alternative synthetic method for the transformation of 2-acetonaphthone to 1-(2-naphthyl)ethanol.

Problem P8. Transformation of a drug to a sweetener

In this task, you will conduct a multistep synthesis of the artificial sweetener dulcin. You will start with paracetamol (acetaminophen) tablets, which can be bought, for example, in local drug stores as the well-known drug Paralen®.



Chemicals and Reagents

- Paracetamol tablets with paracetamol content 1.00 g (or pure paracetamol)
- 1.0 M sodium hydroxide solution in 95% ethanol, 8 cm^3
- Iodoethane, 1 cm^3
- 6.0 M hydrochloric acid solution (20% w/w), 5 cm^3
- Sodium bicarbonate, 3.00 g
- Acetic acid, 2 drops
- Urea, 1.37 g
- Hexanes, 5 cm^3
- 95% ethanol (w/w), 5 cm^3
- Ethyl acetate, 5 cm^3

Substance	Name	State	GHS Hazard Statements
$C_8H_9NO_2$	Paracetamol	Tablets or pure solid	H302, H315, H317, H319
NaOH	Sodium hydroxide	Solution in 95% ethanol	H314
CH_3CH_2I	Iodoethane	Liquid (in a syringe)	H302, H315, H317, H319, H334, H335
HCl	Hydrochloric acid	Aqueous solution	H315
$NaHCO_3$	Sodium bicarbonate	Solid	Not hazardous
NH_2CONH_2	Urea	Solid	Not hazardous
CH_3COOH	Acetic acid	Liquid	H226, H314
C_6H_{14}	Hexanes (mixture of isomers)	Liquid	H225, H304, H315, H336, H411
$CH_3COOCH_2CH_3$	Ethyl acetate	Liquid	H225, H319, H336
CH_3CH_2OH	Ethanol	Liquid azeotropic mixture	H225, H319
CH_3COCH_3	Acetone	Liquid (in a wash-bottle)	H225, H319, H336

Equipment and Glassware

- Laboratory stand with clamps
- Magnetic hotplate stirrer and a PTFE-coated stir bar
- Water aspirator (or other vacuum source for suction filtration)
- Two-neck round bottom flask, 50 cm^3
- Round-bottom flask, 50 cm^3 (2)

- Round-bottom flask, 25 cm^3
- Reflux condenser with water hoses
- Suction flask, 100 cm^3 (2), with rubber adapter
- Sintered glass filter funnel, porosity S2 (2)
- Graduated cylinder, 10 cm^3 (2)
- TLC plates, silica gel 60 F$_{254}$ (2), and capillaries
- TLC chamber or a Petri dish covered small beaker
- UV lamp (254 nm)
- Erlenmeyer flask, 50 or 100 cm^3 (2)
- Filtration funnel and filter paper
- Pasteur pipettes with rubber bulb
- Syringe, 1 cm^3, with needle
- Rubber septum
- pH indicator paper
- Spatula
- Vials (3), labelled **P**, **A** and **C**
- Mortar with pestle
- Glass rod
- Wash-bottle
- Oil bath
- Ice bath
- Melting point apparatus

Procedure

I. Synthesis of phenacetine (A)

1. Grind the paracetamol tablets with the total paracetamol content of 1.0 g using a mortar and pestle. Transfer a small amount of the material (on the tip of a spatula) in vial **P** for TLC analysis. Transfer the remaining powder into a 50 cm^3 two-neck round-bottom flask, equipped with a magnetic stir bar, via plastic funnel or by using a folded weighing paper.

2. Add 8 cm^3 of 1 M NaOH solution in 95% ethanol into the flask using a Pasteur pipette. Stopper the side neck with a rubber septum and fold it over the neck. Equip the flask top neck with a reflux condenser, start running the cooling water in the condenser and immerse the flask in an oil bath. Turn the stirring on. Heat the mixture at reflux for 15 min after it has reached boiling point (the boiling point of ethanol is 78 °C).

3. Take the flask out of the oil bath (*Caution! Hot.*). Take 1.0 cm^3 of iodoethane using a 1 cm^3 syringe with a needle, pierce the septum with the needle and add the iodoethane dropwise to the hot solution (Figure P8). Remove the syringe, immerse the flask again to the oil bath and continue heating the mixture. Reflux for a further 15 min.

4. Prepare a suction filtration apparatus with a sintered glass funnel. The collector flask should contain approximately 25 cm^3 of a mixture of water and ice. Lift the flask from the oil bath, disconnect the condenser and filter the hot mixture under vacuum. You will thus filter off the insoluble starch (used as a tablet filler). Let the collector flask stand for about 2 min. A precipitate will form. Prepare another suction filtration apparatus with a sintered glass funnel and filter the contents of the collector flask under vacuum. Rinse the flask with a small amount of ice-cold water (2 × 5 cm^3). Leave a small amount of solid **A** (on the tip of a spatula) for TLC analysis in a vial labelled **A**.

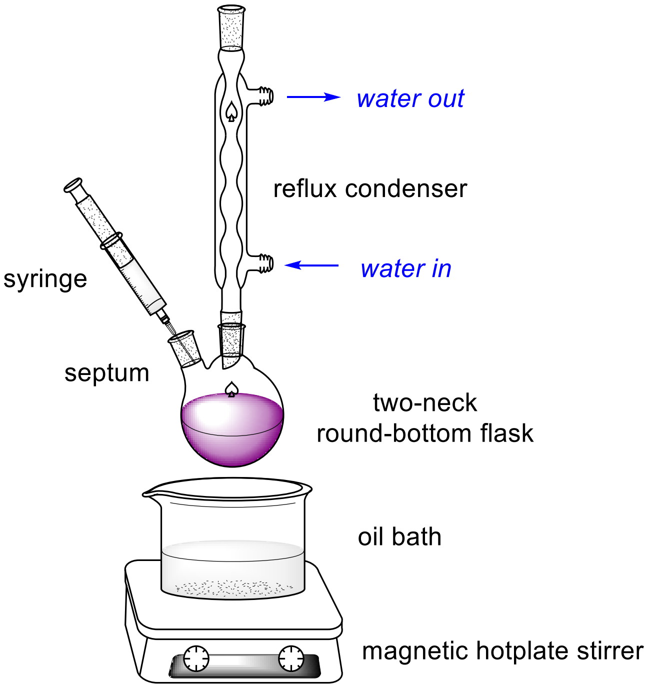


Figure P8. Adding iodoethane by syringe.

II. Synthesis of dulcin (C)

1. Transfer the filtered solid (product **A**) to a clean 50 cm^3 round-bottom flask, equipped with a magnetic stir bar. Add 5 cm^3 of 6 M HCl (aq.) by a Pasteur pipette. Equip the flask with a reflux condenser and turn on the stirring. Heat the mixture at reflux for 15 min.
2. Remove the flask from the oil bath and add solid $NaHCO_3$ to the hot mixture (3 g in 3–5 portions) for neutralization. Be careful, as CO_2 gas evolves. At the same time, stir the mixture vigorously and do not let it solidify. Check the pH of the mixture using glass rod and pH indicator paper. The final pH should be 6.0–6.5. If not, add more solid $NaHCO_3$. If the pH is higher, add diluted aq. HCl to adjust the final pH.
3. After neutralization, add 1.37 g of urea and two drops of acetic acid to the mixture using a Pasteur pipette. Immerse the flask fitted with the condenser in the oil bath. Heat the mixture under reflux for 60 min.
4. Remove the flask from the oil bath and let it cool down for 10 min. Then, immerse the flask in an ice bath. A solid will precipitate. Prepare a suction filtration apparatus with a sintered glass funnel. Filter product **C** under vacuum and wash it with ice-cold water (2 × 5 cm^3).

III. Recrystallization of dulcin (C)

1. Transfer product **C** to a clean 50 cm^3 round-bottom flask, equipped with a magnetic stir bar. Add 15 cm^3 of water, attach a reflux condenser and immerse the flask in an oil bath. Heat the mixture under reflux until all the solid dissolves. If necessary, add more water (but not more than additional 15 cm^3).
2. Remove the flask from the oil bath, filter the hot solution through filter paper into an Erlenmeyer flask and let it cool to room temperature. Then, cool the flask in an ice bath for 10 min. Crystals will start to form. Prepare a suction filtration apparatus with a sintered glass funnel. Filter the crystals of product **C** under vacuum and wash them with ice-cold water (2 × 5 cm^3). Let them air dry on the funnel.

3. If the product is not pure enough (brown colour persists), repeat the crystallization using organic solvents: Transfer the product into a 25 cm^3 round-bottom flask equipped with a magnetic stir bar and add 5 cm^3 of hexanes. Attach the reflux condenser and heat to reflux. At this point, add a few drops of ethanol by a Pasteur pipette, until all the solid dissolves. Remove the flask from the oil bath and filter the hot solution through filter paper into an Erlenmeyer flask. Let it cool for 5 min, then immerse the flask in an ice bath for 10 min. Collect the formed crystalline material using the suction filtration apparatus, as described before.
4. Transfer the product to a *pre-weighed* Petri dish.
5. Leave a small amount of the solid (**C**) for TLC analysis in a small vial labelled **C**.
6. Weigh the product and determine the melting point of product **C**.
7. Perform TLC analysis of the paracetamol standard (**P**) and your samples **A** and **C** (silica gel plate, eluent ethyl acetate).

Data Analysis and Questions

P8.1 Draw the structures of compounds **A**, **B**, and **C**.

P8.2 Calculate the theoretical yield of product **C** in mg, based on the amount of the starting material **P**.

P8.3 Calculate the experimental yield of product **C** in %.

P8.4 Provide the melting point of product **C**.

P8.5 Provide the R_f values of compounds **P**, **A**, and **C**.

P8.6 Select the correct statements, based on the observations and expected reactivity:
  a) NaOH deprotonates the OH group of paracetamol to give a coloured phenolate.
  b) NaOH deprotonates the methyl protons of the acetamide.
  c) NaOH does not react with paracetamol; it only reacts with H$^+$, which is released after the addition of iodoethane.
  d) The deprotonated, anionic substrate is much more reactive than the neutral paracetamol.
  e) Nucleophilic substitutions with iododethane are usually S$_N$1 reactions (i.e., the rate is independent of the nucleophile concentration and reactivity).
  f) Acetamide functional group is stable towards an aqueous acid (aq. HCl).
  g) Acetamide functional group is stable towards a base (NaOH in 95% EtOH).
  h) Aryl ethyl ether functional group is stable towards an aqueous acid (aq. HCl).
  i) Product **B** is a salt (it contains a cation and an anion).
  j) Product **C** is a salt.

P8.7 In the last step of the process, urea and acetic acid react to form ammonium acetate and a reactive species:
  a) Hydrogen cyanide, H–C≡N,
  b) Fulminic acid, $^{(-)}$O–N$^{(+)}$≡C–H,
  c) Hydrogen isocyanide, H–N$^{(+)}$≡C$^{(-)}$,
  d) Isocyanic acid, H–N=C=O.

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BACK TO WHERE IT ALL BEGAN

UPDATED 12TH JUNE 2018

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Problem 1. Synthesis of hydrogen cyanide

1.1 Degussa process (BMA process):

$\Delta_r H_m = -\Delta_f H_m(CH_4) - \Delta_f H_m(NH_3) + \Delta_f H_m(HCN) + 3\ \Delta_f H_m(H_2)$

$\Delta_r H_m = [-(-90.3) - (-56.3) + 129.0 + 3 \times 0]\ \text{kJ mol}^{-1} = 275.6\ \text{kJ mol}^{-1}$

Andrussow process:

$\Delta_r H_m = -\Delta_f H_m(CH_4) - \Delta_f H_m(NH_3) - 3/2\ \Delta_f H_m(O_2) + \Delta_f H_m(HCN) + 3\ \Delta_f H_m(H_2O)$

$\Delta_r H_m = [-(-90.3) - (-56.3) - 3/2 \times 0 + 129.0 + 3 \times (-250.1)]\ \text{kJ mol}^{-1} = -474.7\ \text{kJ mol}^{-1}$

1.2 An external heater has to be used in the Degussa process (BMA process) because the reaction is endothermic.

1.3 $K(1500\ \text{K}) = \exp\left(-\frac{\Delta_r G_m(1\,500\ \text{K})}{RT}\right) = \exp\left(-\frac{-112.3 \times 10^3\ \text{J mol}^{-1}}{8.314\ \text{J mol}^{-1}\ \text{K}^{-1} \times 1\,500\ \text{K}}\right) = 8\,143$

$$\ln\left(\frac{K(T_2)}{K(T_1)}\right) = -\frac{\Delta_r H_m}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \Rightarrow K(T_2) = K(T_1)\exp\left[-\frac{\Delta_r H_m}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right]$$

$$K(1\,600\text{K}) = 8\ \ 143 \times \exp\left[-\frac{275.6 \times 10^3\ \text{J mol}^{-1}}{8.314\ \text{J mol}^{-1}\ \text{K}^{-1}}\left(\frac{1}{1\,600\ \text{K}} - \frac{1}{1\,500\ \text{K}}\right)\right] = 32\,407$$

The result is in accordance with the Le Chatelier's principle because the reaction is endothermic and therefore an increase in temperature shifts the equilibrium toward products (in other words, the equilibrium constant increases).

1.4 The equilibrium constant of the reaction in the Andrussow process decreases with an increase in temperature because the reaction is exothermic.

Problem 2. Thermochemistry of rocket fuels

Notation of indexes: 0M – hydrazine, 1M – methylhydrazine, 2M – 1,1-dimethylhydrazine

Standard conditions: $T° = 298.15$ K; $p° = 101\ 325$ Pa.

All values given below are evaluated from non-rounded intermediate results.

2.1 Calculation of the number of moles corresponding to 1 g of the samples: $n_i = m_i / M_i$

$M_{0M} = 32.05$ g mol^{-1}; $M_{1M} = 46.07$ g mol^{-1}; $M_{2M} = 60.10$ g mol^{-1}.

$n_{0M} = 31.20$ mmol; $n_{1M} = 21.71$ mmol; $n_{2M} = 16.64$ mmol.

Calculation of combustion heat: $q_i = C_{cal} \times \Delta T_i$

$q_{0M} = 16.83$ kJ; $q_{1M} = 25.60$ kJ; $q_{2M} = 30.11$ kJ.

Calculation of the molar internal energies of combustion: $\Delta_c U_i = -q_i / n_i$

$\Delta_{comb}U_{0M} = -539.40$ kJ mol^{-1}; $\Delta_{comb}U_{1M} = -1\ 179.48$ kJ mol^{-1};

$\Delta_{comb}U_{2M} = -1\ 809.64$ kJ mol^{-1}.

Bomb calorimeter combustion reactions with the stoichiometric coefficients added:

Hydrazine	N_2H_4 (l) + O_2 (g) → N_2 (g) + 2 H_2O (g)
Methylhydrazine	$N_2H_3CH_3$ (l) + 2.5 O_2 (g) → N_2 (g) + CO_2 (g) + 3 H_2O (g)
1,1-Dimethylhydrazine	$N_2H_2(CH_3)_2$ (l) + 4 O_2 (g) → N_2 (g) + 2 CO_2 (g) + 4 H_2O (g)

Calculation of the molar enthalpies of combustion: $\Delta_c H_i = \Delta_c U_i + \Delta_c n(\text{gas}) RT_{std}$

$\Delta_{comb}H_{0M} = -534.44$ kJ mol^{-1}; $\Delta_{comb}H_{1M} = -1\ 173.29$ kJ mol^{-1};

$\Delta_{comb}H_{2M} = -1\ 802.20$ kJ mol^{-1}.

2.2 Calculation of the molar enthalpies of formation:

$\Delta_{form}H_{0M} = 2\ \Delta_{form}H_{H2O,g} - \Delta_{comb}H_{0M} = +50.78$ kJ mol^{-1}

$\Delta_{form}H_{1M} = 3\ \Delta_{form}H_{H2O,g} + \Delta_{form}H_{CO2} - \Delta_{comb}H_{1M} = +54.28$ kJ mol^{-1}

$\Delta_{form}H_{2M} = 4\ \Delta_{form}H_{H2O,g} + 2\ \Delta_{form}H_{CO2} - \Delta_{comb}H_{2M} = +47.84$ kJ mol^{-1}

Rocket engines combustion reactions:

Hydrazine	N_2H_4 (l) + 1/2 N_2O_4 (l) → 2 H_2O (g) + 3/2 N_2 (g)
Methylhydrazine	$N_2H_3CH_3$ (l) + 5/4 N_2O_4 (l) → CO_2 (g) + 3 H_2O (g) + 9/4 N_2 (g)
1,1-Dimethylhydrazine	$N_2H_2(CH_3)_2$ (l) + 2 N_2O_4 (l) → 3 N_2 (g) + 4 H_2O (g) + 2 CO_2 (g)

Calculation of molar reaction enthalpies, related to one mole of hydrazine derivatives:

$\Delta_{re}H_{0M} = (2\ \Delta_{form}H_{H2O,g} - 1/2\ \Delta_{form}H_{N2O4} - \Delta_{form}H_{0M}) = -538.98$ kJ mol^{-1}

$\Delta_{re}H_{1M} = (\Delta_{form}H_{CO2} + 3\ \Delta_{form}H_{H2O,g} - 5/4\ \Delta_{form}H_{N2O4} - \Delta_{form}H_{1M}) = -1\ 184.64$ kJ mol^{-1}

$\Delta_{re}H_{2M} = (2\ \Delta_{form}H_{CO2} + 4\ \Delta_{form}H_{H2O,g} - 2\ \Delta_{form}H_{N2O4} - 1\ \Delta_{form}H_{2M}) = -1\ 820.36$ kJ mol^{-1}

2.3 Calculation of the standard molar reaction enthalpies, related to one mole of hydrazine derivatives:

$\Delta_{\mathrm{re}}H^\circ_{\mathrm{0M}} = \Delta_{\mathrm{re}}H_{\mathrm{0M}} - 2\ \Delta_{\mathrm{vap}}H_{\mathrm{H2O}} = -620.28\ \mathrm{kJ\ mol^{-1}}$

$\Delta_{\mathrm{re}}H^\circ_{\mathrm{1M}} = \Delta_{\mathrm{re}}H_{\mathrm{1M}} - 3\ \Delta_{\mathrm{vap}}H_{\mathrm{H2O}} = -1\ 306.59\ \mathrm{kJ\ mol^{-1}}$

$\Delta_{\mathrm{re}}H^\circ_{\mathrm{2M}} = \Delta_{\mathrm{re}}H_{\mathrm{2M}} - 4\ \Delta_{\mathrm{vap}}H_{\mathrm{H2O}} = -1\ 982.96\ \mathrm{kJ\ mol^{-1}}$

Calculation of the standard molar reaction entropies, related to one mole of hydrazine derivatives:

$\Delta_{\mathrm{re}}S^\circ_{\mathrm{0M}} = (2\ S_{\mathrm{H2O,l}} + 3/2\ S_{\mathrm{N2}} - 1/2\ S_{\mathrm{N2O4}} - S_{\mathrm{0M}}) = 200.67\ \mathrm{J\ K^{-1}\ mol^{-1}}$

$\Delta_{\mathrm{re}}S^\circ_{\mathrm{1M}} = (S_{\mathrm{CO2}} + 3\ S_{\mathrm{H2O,l}} + 9/4\ S_{\mathrm{N2}} - 5/4\ S_{\mathrm{N2O4}} - S_{\mathrm{1M}}) = 426.59\ \mathrm{J\ K^{-1}\ mol^{-1}}$

$\Delta_{\mathrm{re}}S^\circ_{\mathrm{2M}} = (2\ S_{\mathrm{CO2}} + 4\ S_{\mathrm{H2O,l}} + 3\ S_{\mathrm{N2}} - 2\ S_{\mathrm{N2O4}} - S_{\mathrm{2M}}) = 663.69\ \mathrm{J\ K^{-1}\ mol^{-1}}$

Calculation of standard molar reaction Gibbs energies:

$\Delta_{\mathrm{re}}G^\circ_{\mathrm{0M}} = \Delta_{\mathrm{re}}H^\circ_{\mathrm{0M}} - T^\circ \times \Delta_{\mathrm{re}}S^\circ_{\mathrm{0M}} = -680.11\ \mathrm{kJ\ mol^{-1}}$

$\Delta_{\mathrm{re}}G^\circ_{\mathrm{1M}} = \Delta_{\mathrm{re}}H^\circ_{\mathrm{1M}} - T^\circ \times \Delta_{\mathrm{re}}S^\circ_{\mathrm{1M}} = -1\ 433.77\ \mathrm{kJ\ mol^{-1}}$

$\Delta_{\mathrm{re}}G^\circ_{\mathrm{2M}} = \Delta_{\mathrm{re}}H^\circ_{\mathrm{2M}} - T^\circ \times \Delta_{\mathrm{re}}S^\circ_{\mathrm{2M}} = -2\ 180.84\ \mathrm{kJ\ mol^{-1}}$

Estimation of the equilibrium constants for combustion reactions:

$K_i = \exp(-\Delta_{\mathrm{re}}G^\circ_i\ /\ (RT^\circ))$

$K_{\mathrm{0M}} = \mathrm{e}^{274.37} \approx 1 \times 10^{119}$

$K_{\mathrm{1M}} = \mathrm{e}^{578.41} \approx 1 \times 10^{251}$

$K_{\mathrm{2M}} = \mathrm{e}^{879.79} \approx 1 \times 10^{382}$

Equilibrium constants are practically equal to infinity; the equilibrium mixture of the outlet gases contains reaction products only.

2.4 All reactions increase the number of the moles of gaseous species, so increasing the pressure will suppress the extent of the reaction (though negligibly for such values of K). All reactions are strongly exothermic, so increasing the temperature will affect the equilibrium in the same direction as pressure.

2.5 Summarizing the chemical equation representing the fuel mixture combustion:

$N_2H_4\ (l) + N_2H_3CH_3\ (l) + N_2H_2(CH_3)_2\ (l) + 3.75\ N_2O_4\ (l) \rightarrow 6.75\ N_2\ (g) + 9\ H_2O\ (g) + 3\ CO_2\ (g)$

$-(\Delta_{\mathrm{re}}H_{\mathrm{0M}} + \Delta_{\mathrm{re}}H_{\mathrm{1M}} + \Delta_{\mathrm{re}}H_{\mathrm{2M}}) = \left(6.75\ C_{p(\mathrm{N_2})} + 9\ C_{p(\mathrm{H_2O})} + 3\ C_{p(\mathrm{CO_2})}\right)(T_{\mathrm{f}} - T_0)$, solve for T_{f}

$T_{\mathrm{f}} = 4\ 288.65\ \mathrm{K}$

2.6 Burning of 1,1-dimethylhydrazine with oxygen can be expressed as:

$N_2H_2(CH_3)_2\ (l) + 4\ O_2\ (g) \rightarrow N_2\ (g) + 2\ CO_2\ (g) + 4\ H_2O\ (g)$

$-\Delta_{\mathrm{comb}}H_{\mathrm{2M}} = \left(C_{p(\mathrm{N_2})} + 4\ C_{p(\mathrm{H_2O})} + 2\ C_{p(\mathrm{CO_2})}\right)(T_{\mathrm{x}} - T_0)$, solve for T_{x}

$T_{\mathrm{x}} = 5\ 248.16\ \mathrm{K}$

2.7 There is no temperature range of coexistence of both liquid oxygen and 1,1-dimethylhydrazine, either 1,1-dimethylhydrazine is liquid and O_2 is a supercritical fluid, or O_2 is liquid and 1,1-dimethylhydrazine is solid.

2.8 Very high working temperatures maximize the temperature difference term in relation to the hypothetical efficiency of the Carnot engine. Assuming the low temperature equals $T°$, we get: $\eta = (T_\mathrm{f} - T°) / T_\mathrm{f} = 93.0\%$.

Problem 3. HIV protease

3.1 Lopinavir binds most strongly, as illustrated by its smallest dissociation constant K_D.

3.2 Apply $\Delta G° = -RT \ln K_D$, and consider that the dissociation and the binding are opposite reactions. Thus, $\Delta G°(\text{bind.}) = -\Delta G°(\text{dissoc.}) = RT \ln K_D$, or in a slightly different way, $\Delta G°(\text{bind.}) = -RT \ln K_A = -RT \ln[1 / K_D] = RT \ln K_D$. See below for the numerical results.

3.3 Consider $\Delta G° = \Delta H° - T\Delta S°$. Thus, perform a linear regression of the temperature dependence of $\Delta G°$. This can be done in at least two simplified ways: (i) Plot the dependence and draw a straight line connecting the four data points in the best way visually. Then, read off the slope and intercept of the straight line, which correspond to $-\Delta S°$ and $\Delta H°$, respectively. (ii) Alternatively, choose two data points and set up and solve a set of two equations for two unknowns, which are $\Delta S°$ and $\Delta H°$. The most accurate result should be obtained if the points for the lowest and highest temperatures are used. See below for the numerical results.

Temperature		Amprenavir		Indinavir		Lopinavir	
°C	K	K_D nM	$\Delta G°$ kJ mol^{-1}	K_D nM	$\Delta G°$ kJ mol^{-1}	K_D nM	$\Delta G°$ kJ mol^{-1}
5	278.15	1.39	−47.2	3.99	−44.7	0.145	−52.4
15	288.15	1.18	−49.3	2.28	−47.7	0.113	−54.9
25	298.15	0.725	−52.2	1.68	−50.1	0.101	−57.1
35	308.15	0.759	−53.8	1.60	−51.9	0.0842	−59.4
$\Delta S°$	kJ K^{-1} mol^{-1}		0.228		0.239		0.233
$\Delta H°$	kJ mol^{-1}		16.3		21.5		12.4
coeff. of determin.			0.990		0.989		0.999

Temperature		Nelfinavir		Ritonavir		Saquinavir	
°C	K	K_D nM	$\Delta G°$ kJ mol^{-1}	K_D nM	$\Delta G°$ kJ mol^{-1}	K_D nM	$\Delta G°$ kJ mol^{-1}
5	278.15	6.83	−43.5	2.57	−45.7	0.391	−50.1
15	288.15	5.99	−45.4	1.24	−49.1	0.320	−52.4
25	298.15	3.67	−48.1	0.831	−51.8	0.297	−54.4
35	308.15	2.83	−50.4	0.720	−53.9	0.245	−56.7
$\Delta S°$	kJ K^{-1} mol^{-1}		0.236		0.273		0.218
$\Delta H°$	kJ mol^{-1}		22.4		29.8		10.5
coeff. of determin.			0.995		0.989		0.999

Note 1: $\Delta S°$ and $\Delta H°$ may also be obtained from a fit of K_D or K_A, without considering $\Delta G°$. Here, a straight line would be fitted to the dependence:

$\ln K_A = -\ln K_D = \Delta S° / R - \Delta H° / R \times 1/T$.

Note 2: It is evident that the binding is entropy-driven for all the inhibitors. The entropic gain stems from the changes in the flexibility of both the protease and the inhibitors, and also involves solvent effects. However, a molecular picture of those changes is rather complex.

3.4 The slowest dissociation is observed for the compound with the smallest dissociation rate constant, i.e. Saquinavir.

3.5 Using the relation for the dissociation constant $K_D = k_D / k_A$ and the data at 25 °C, we obtain for Amprenavir: $k_A = k_D / K_D = 4.76 \times 10^{-3}\ \mathrm{s^{-1}} / (0.725 \times 10^{-9}\ \mathrm{mol\ L^{-1}}) = 6.57 \times 10^{6}\ \mathrm{L\ mol^{-1}\ s^{-1}}$. Analogous calculations performed for the other inhibitors yield the following numerical results. The fastest association is exhibited by the compound with the largest association rate constant, i.e. Amprenavir.

	Amprenavir	Indinavir	Lopinavir	Nelfinavir	Ritonavir	Saquinavir
k_A $\mathrm{dm^3\ mol^{-1}\ s^{-1}}$	6.57×10^6	2.05×10^6	6.48×10^6	0.59×10^6	3.12×10^6	1.43×10^6

3.6 The Arrhenius equation for the rate constant reads $k = A \times \exp[-\Delta G^{\ddagger} / RT]$. For two known rate constants of dissociation k_1 and k_2 determined at temperatures T_1 and T_2, respectively, we obtain a system of two equations,

$k_1 = A \times \exp[-\Delta G^{\ddagger} / RT_1]$

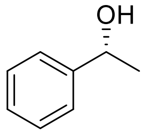
$k_2 = A \times \exp[-\Delta G^{\ddagger} / RT_2]$,

from which the activation energy of dissociation results as $\Delta G^{\ddagger} = (\ln k_1 / k_2) / (1 / RT_2 - 1 / RT_1)$. Numerically, the activation energy is 8.9 kJ mol^{-1} for Lopinavir, 32.6 kJ mol^{-1} for Amprenavir (which has the fastest association rate constant) and 36.8 kJ mol^{-1} for Saquinavir (which has the lowest dissociation rate constant).

3.7 No, these are two different compounds. The strongest protease binder is not the same inhibitor as the one with the slowest dissociation. This observation may seem counter-intuitive if the distinction between thermodynamics (here, the strength of binding expressed by the equilibrium constant) and kinetics (the rate of binding represented by the rate constant or activation energy for dissociation) is not understood properly. While the equilibrium constant of dissociation captures the thermodynamic stability of the respective protein–inhibitor complex, the rate constant describes the kinetics of the process. These are two different sets of properties and they only become related if the rates of both dissociation and association are considered, $K_D = k_D / k_A$.

Problem 4. Enantioselective hydrogenation

4.1 Structure:



(*R*)-1-phenylethan-1-ol

4.2 $90\%\ ee = \frac{R-S}{R+S}$ => $\frac{k_R}{k_S} = \frac{R}{S} = \frac{95}{5} = 19$ => $k_S = \frac{k_R}{19} = 1.3 \times 10^{-6}\ \text{s}^{-1}$

4.3 From the previous question; at −40 °C $k_R = 19 \times k_S$. Substitute from the Arrhenius equation:

$A \times e^{\frac{-E_\text{a}(R)}{R \times T}} = 19 \times A \times e^{\frac{-E_\text{a}(S)}{R \times T}}$ Therefore:

$E_\text{a}(R) = E_\text{a}(S) - R \times T \times \ln(19) = 74\ \text{kJ mol}^{-1}$

4.4 $99\%\ ee = \frac{R-S}{R+S}$ => $\frac{k_R}{k_S} = \frac{R}{S} = \frac{99.5}{0.5} = 199$

At any given temperature *T*:

$$\left(\frac{k_R}{k_S}\right)_T = \frac{A \times e^{\frac{-E_\text{a}(R)}{R \times T}}}{A \times e^{\frac{-E_\text{a}(S)}{R \times T}}} \qquad (\ddagger) \qquad \text{Therefore:}$$

$$T = \frac{E_\text{a}(S) - E_\text{a}(R)}{R \times \ln\left(\frac{k_R}{k_S}\right)_T} = 130\ \text{K}$$

At this temperature, the reaction is likely to be really slow which would prevent its actual use.

4.5 The main difference is that **(*S*)-CAT** will provide the (*S*)-product. We will do all the calculations for **(*R*)-CAT** and just invert the sign at the end. It should be noted that the amount of catalyst does not influence the enantiomeric excess; it only accelerates the reaction.

From equation (‡):

$\left(\frac{k_R}{k_S}\right)_T = e^{\frac{E_\text{a}(S) - E_\text{a}(R)}{R \times T}} = 12.35$ => *ee* = 85%

For 90% *ee*: $[\alpha]_\text{D}^{20}$ (*c* 1.00, EtOH) = +45°,

which means $[\alpha]_\text{D}^{20}$ (*c* 1.00, EtOH) = +42.5° for 85% *ee*

The same conditions are used for the measurement of the specific rotation, namely, the temperature, solvent, concentration and wavelength of the light used. Therefore, we can just invert the sign to obtain the result for the (*S*)-product:

$[\alpha]_\text{D}^{20}$ (*c* 1.00, EtOH) = −42.5° = −43°

Note: The specific rotation should be formally stated in ° $\text{dm}^{-1}\ \text{cm}^3\ \text{g}^{-1}$, but in most of the current scientific literature this is simplified to ° only.

4.6 Since the product is crystalline, the easiest method would be recrystallization. Different chiral resolution methods can also be used, for example crystallization with a chiral agent or separation by HPLC with a chiral stationary phase.

Problem 5. Ultrafast reactions

Note: In all equilibrium constants considered below, the concentrations should be in principle replaced by activities $a_i = \gamma_i \frac{c_i}{c_0}$, where we use the standard state for the solution $c_0 = 1\ \mathrm{mol\ dm^{-3}}$. In all calculations we assume that $\gamma_i = 1$ and for clarity, we also ignore the unity c_0 factor. We also skip the units of quantities in the intermediate steps of the calculations to make the solution easier to follow.

5.1 The equilibrium constant of neutralization is given as

$$K = \frac{[\mathrm{H_2O}]}{[\mathrm{H^+}][\mathrm{OH^-}]} = \frac{55.6}{10^{-7} \times 10^{-7}} = \frac{55.6}{K_\mathrm{w}} = 5.56 \times 10^{15}$$

The constant *K* is related to the free energy change of the reaction:

$$\Delta G° = -RT\ln K = -89.8\ \ \mathrm{kJ\ mol^{-1}}$$

Note that the Gibbs free energy change calculated in this way corresponds to the standard state $c_0 = 1\ \mathrm{mol\ dm^{-3}}$ for all species, including the water solvent. The Gibbs free energy change can be expressed via the enthalpy and entropy change for the reaction

$$\Delta G° = \Delta H° - T\Delta S°$$

from which

$$\Delta S° = -\frac{\Delta G° - \Delta H°}{T} = -\frac{-89.8 + 49.65}{298} = 134.8\ \mathrm{J\ K^{-1} mol^{-1}}$$

5.2 To estimate the pH of boiling water we need to evaluate K_w at 373 K using the van 't Hoff's formula (alternatively, we could recalculate the constant *K*). Note that $\Delta H°$ was defined for a reverse reaction, here we have to use $\Delta H = 49.65 \times 10^3\ \mathrm{J\ mol^{-1}}$. The temperature change is given as

$$\ln K_\mathrm{w,T2} = \ln K_\mathrm{w,T1} - \frac{\Delta H°}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

After substitution

$$\ln K_\mathrm{w,T2} = \ln 10^{-14} - \frac{49.65 \times 10^3}{R}\left(\frac{1}{373} - \frac{1}{298}\right)$$

we get

$$K_\mathrm{w,T2} = 56.23 \times 10^{-14}$$

which translates into proton concentration at the boiling point of water

$$[\mathrm{H^+}]_{T2} = \sqrt{K_{w2}} = \sqrt{56.23 \times 10^{-14}} = 7.499 \times 10^{-7} \mathrm{mol\ dm^{-3}}$$

or pH

$$\mathrm{pH} = \ -\log[\mathrm{H^+}]_{T2} = 6.125$$

5.3 pD is analogical to pH, i.e. pD = −log$[\mathrm{D^+}]$. The concentration of $[\mathrm{D^+}]$ cations at 298 K is given as

$$[\mathrm{D^+}] = \sqrt{K_w(\mathrm{D_2O})} = \sqrt{1.35 \times 10^{-15}} = 3.67 \times 10^{-8}\ \mathrm{mol\ dm^{-3}}$$

and pD is given by

$$\mathrm{pD} = -\log[\mathrm{D^+}] = 7.435$$

5.4

$$\frac{d[\mathrm{D_2O}]}{dt} = k_1[\mathrm{D^+}][\mathrm{OD^-}] - k_2[\mathrm{D_2O}]$$

5.5 We start from the rate equation derived in 5.4

$$\frac{d[\mathrm{D_2O}]}{dt} = k_1[\mathrm{D^+}][\mathrm{OD^-}] - k_2[\mathrm{D_2O}]$$

All concentrations can be expressed via the quantity *x*

$$-\frac{dx}{dt} = k_1\left(\left([\mathrm{D^+}]_{\mathrm{eq}} + x\right) \times \left([\mathrm{OD^-}]_{\mathrm{eq}} + x\right)\right) - k_2([\mathrm{D_2O}]_{\mathrm{eq}} - x)$$

Expanding the right hand side of the equation, we get

$$-\frac{dx}{dt} = k_1[\mathrm{D^+}]_{\mathrm{eq}}[\mathrm{OD^-}]_{\mathrm{eq}} + x\,k_1[\mathrm{OD^-}]_{\mathrm{eq}} + x\,k_1[\mathrm{D^+}]_{\mathrm{eq}} + k_1x^2 - k_2[\mathrm{D_2O}]_{\mathrm{eq}} + x\,k_2$$

Using the equality of the backward and forward reaction rates at equilibrium

$$k_1[\mathrm{D^+}]_{\mathrm{eq}}[\mathrm{OD^-}]_{\mathrm{eq}} = k_2[\mathrm{D_2O}]_{\mathrm{eq}}$$

and neglecting the (small) quadratic term x^2, we can rewrite the equation as

$$-\frac{dx}{dt} = x(k_1[\mathrm{D^+}]_{\mathrm{eq}} + k_1[\mathrm{OD^-}]_{\mathrm{eq}} + k_2)$$

5.6 The relaxation time is given as

$$\frac{1}{\tau} = k_1([\mathrm{D^+}]_{\mathrm{eq}} + [\mathrm{OD^-}]_{\mathrm{eq}}) + k_2$$

At equilibrium, the backward and forward reaction rates are the same. The concentration of heavy water $[\mathrm{D_2O}]_{\mathrm{eq}}$ is given as

$$[\mathrm{D_2O}]_{\mathrm{eq}} = \frac{\rho \times V \times 1\,000}{V \times M_r(\mathrm{D_2O})} = \frac{1\,107}{20.03} = 55.3\ \mathrm{mol\ dm^{-3}}$$

$$K = \frac{k_2}{k_1} = \frac{[\mathrm{D^+}]_{\mathrm{eq}}[\mathrm{OD^-}]_{\mathrm{eq}}}{[\mathrm{D_2O}]_{\mathrm{eq}}} = \frac{K_\mathrm{w}(\mathrm{D_2O})}{[\mathrm{D_2O}]_{\mathrm{eq}}} = \frac{1.35 \times 10^{-15}}{55.3} = 2.44 \times 10^{-17}$$

The relaxation time is then given as

$$\frac{1}{\tau} = k_1(K + [\mathrm{D^+}]_{\mathrm{eq}} + [\mathrm{OD^-}]_{\mathrm{eq}})$$

Substituting the values of all quantities

$$\frac{1}{0.162 \times 10^{-3}} = k_1(2.44 \times 10^{-17} + 3.67 \times 10^{-8} + 3.67 \times 10^{-8})$$

we get

$$\frac{1}{0.162 \times 10^{-3}} = 2k_1 \times 3.67 \times 10^{-8}$$

$$k_1 = 8.41 \times 10^{10}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$$

We get k_2 from the equilibrium constant *K*

$$k_2 = k_1K = 2.05 \times 10^{-6}\ \mathrm{s^{-1}}$$

5.7 The pH before irradiation is calculated from the dissociation constant of the ground state of 6-hydroxynaphthalene-2-sulfonate.

$$K_\mathrm{a} = \frac{[\mathrm{H}^+][\mathrm{A}^-]}{[\mathrm{HA}]} = 10^{-9.12} = 7.59 \times 10^{-10}$$

where $[\mathrm{A}^-]$ is the concentration of 6-oxidonaphthalene-2-sulfonate and $[\mathrm{HA}]$ is the concentration of 6-hydroxynaphthalene-2-sulfonate.

The concentration of $[\mathrm{H}^+]$ is equal to the concentration of $[\mathrm{A}^-]$ due to electroneutrality and can be denoted as y. The equilibrium concentration of the undissociated acid $[\mathrm{HA}]$ is $c - y$, where c is the analytical concentration of the acid. The equilibrium constant is then given as

$$K_\mathrm{a} = \frac{y^2}{c - y}$$

Because the amount of dissociated acid is very small, we can neglect y in the denominator

$$K_\mathrm{a} = \frac{y^2}{c}$$

From which

$$y = \sqrt{K_\mathrm{a} \times c} = \sqrt{7.59 \times 10^{-10} \times 5.0 \times 10^{-3}} = 1.9 \times 10^{-6}\ \mathrm{mol\ dm^{-3}}$$

$$\mathrm{pH} = -\log(1.9 \times 10^{-6}) = 5.72$$

During irradiation, 1 cm^3 of sample absorbs 2.228×10^{-3} J of energy. 1 dm^3 would thus absorb 2.228 J. The number of absorbed photons corresponds to the number of excited molecules of 6-hydroxynaphthalene-2-sulfonate.

One photon has energy

$$E = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} \times 3.0 \times 10^{8}}{297 \times 10^{-9}} = 6.7 \times 10^{-19}\ \mathrm{J}$$

The number of absorbed photons in 1 dm^3 is

$$N_{photons} = \frac{2.228}{6.7 \times 10^{-19}} = 3.3 \times 10^{18}$$

The number of moles of excited molecules of 6-hydroxynaphthalene-2-sulfonate is

$$n = \frac{N_{photons}}{N_\mathrm{A}} = 5.5 \times 10^{-6}\ \mathrm{mol}$$

The pH can again be calculated from the $\mathrm{p}K_\mathrm{a}^*$ in the excited state; the analytical concentration c^* of the excited acid is now $5.5 \times 10^{-6}\ \mathrm{mol\ dm^{-3}}$.

Let us denote by x the proton concentration $[\mathrm{H}^+]$ and by y^* the concentration of the 6-oxidonaphthalene-2-sulfonate in the excited state $[\mathrm{A}^-]^*$. The electroneutrality condition implies

$$x = y^* + y$$

The two equilibrium constants are expressed as

$$K_\mathrm{a}^* = \frac{x\, y^*}{c^* - y^*} = 10^{-1.66} = 0.022$$

$$K_a = \frac{x\,y}{c} = 10^{-9.12} = 7.59 \times 10^{-10}$$

where we assumed $c - c^* - y \approx c$ in the denominator of the last equation. These three equations constitute a system of equations from which we get

$$x^3 + K_a^* x^2 - (K_a c + K_a^* c^*)x - K_a K_a^* c = 0$$

or

$$x^3 + 0.022x^2 - 1.21 \times 10^{-7} x - 8.35 \times 10^{-14} = 0$$

We can solve this equation e.g. with any on-line solver of cubic equations

$$x = 6.12 \times 10^{-6}\ \mathrm{mol\ dm^{-3}}$$

Which corresponds to

$$\mathrm{pH} = -\log\,(6.12 \times 10^{-6}) = 5.21$$

It is possible to avoid solving cubic equations by an iterative solution. In the first step, we assume that $y \approx 0$. The equation for K_a^* then transforms to

$$K_a^* = \frac{x\,y^*}{c^* - y^*} \approx \frac{y^{*2}}{c^* - y^*}$$

y^* can be calculated from the quadratic equation

$$y^{*2} + K_a^*\,y^* - K_a^*\,c^* = 0$$

$$y^* = \frac{-0.022 + \sqrt{0.022^2 + 4 \times 5.5 \times 10^{-6} \times 0.022}}{2} = 5.5 \times 10^{-6}\ \mathrm{mol\ dm^{-3}}$$

Next, we update the concentration of the anion in the ground state *y* from the corresponding equilibrium constant

$$K_a = \frac{(y^* + y)\,y}{c}$$

From which *y* can be obtained by solving a quadratic equation

$$y^2 + y\,y^* - K_a\,c = 0$$

This again leads to the quadratic equation

$$y^2 + y\ \times 5.5 \times 10^{-6} - 7.59 \times 10^{-10} \times 5.0 \times 10^{-3} = 0$$

$$y = \frac{-5.5 \times 10^{-6} + \sqrt{(5.5 \times 10^{-6})^2 + 4 \times 7.59 \times 10^{-10} \times 5 \times 10^{-3}}}{2}$$

$$y = 6.2 \times 10^{-7}\ \mathrm{mol\ dm^{-3}}$$

The concentration of $[\mathrm{H}^+]$ is

$$x = y^* + y = 5.5 \times 10^{-6} + 6 \times 10^{-7} = 6.1 \times 10^{-6}\ \mathrm{mol\ dm^{-3}}$$

$$\mathrm{pH} = -\log(6.1 \times 10^{-6}) = 5.21$$

We could now repeat the whole cycle: with the first estimate of *x*, we would get a new value of y^* and continue with these new values of *y* and *x* until convergence is reached. At the level of precision in our calculations, the concentration is already converged in the first iteration. Generally, more iterative cycles would be needed.

Problem 6. Kinetic isotope effects

6.1 Reduced mass: $\mu = \frac{m_F \times m_H}{m_F + m_H} = \frac{19}{20}\ \mathrm{amu} = 1.578 \times 10^{-27}\ \mathrm{kg}$

Wavenumber: $\tilde{\nu} = \frac{\nu}{c} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}} = \frac{1}{2\pi \times 2.9979 \times 10^{8}}\sqrt{\frac{968}{1.578 \times 10^{-27}}} = 4.159 \times 10^{5}\ \mathrm{m^{-1}}$

$\tilde{\nu} = 4\,159\ \mathrm{cm^{-1}}$

Energies: $E_0 = \frac{1}{2} h \times c \times \tilde{\nu} = \frac{1}{2} \times 6.6261 \times 10^{-34} \times 2.9979 \times 10^{8} \times 4.159 \times 10^{5} =$

$= 4.13 \times 10^{-20}\ \mathrm{J}$

$E_1 = \frac{3}{2} h \times c \times \tilde{\nu} = 1.24 \times 10^{-19}\ \mathrm{J}$

6.2 We are going to determine the atomic mass *A* of the lighter isotope of the element X.

$$\left(\frac{\tilde{\nu}_1}{\tilde{\nu}_2}\right)^2 = \frac{\mu_2}{\mu_1} = \frac{\frac{2 \times (A+2)}{2 + A + 2}}{\frac{1 \times A}{A+1}} = \frac{2 \times (A+2) \times (A+1)}{A \times (A+4)}$$

$$\frac{1}{2}\left(\frac{2\,439.0}{1\,734.8}\right)^2 = \frac{A^2 + 3 \times A + 2}{A^2 + 4 \times A}$$

A = 79.4 amu

A = 79; *A* + 2 = 81; *X* = Br

The second root of the quadratic equation 2.155, which would correspond to *A* = 2 and *A* + 2 = 4, is unphysical.

6.3 The difference of the activation energies E_a(H−C) − E_a(D−C) is equal to the negatively taken difference of zero-point vibrational energies: − E_0(H−C) + E_0(D−C)

$$\frac{k(\mathrm{C{-}H})}{k(\mathrm{C{-}D})} = \exp\left(-\frac{E_a(\mathrm{C{-}H}) - E_a(\mathrm{C{-}D})}{kT}\right) = \exp\left(\frac{E_0(\mathrm{C{-}H}) - E_0(\mathrm{C{-}D})}{kT}\right)$$

$$\frac{k(\mathrm{C{-}H})}{k(\mathrm{C{-}D})} = \exp\left(\frac{hc}{2kT}(\tilde{\nu}(\mathrm{C{-}H}) - \tilde{\nu}(\mathrm{C{-}D}))\right)$$

$$\frac{k(\mathrm{C{-}H})}{k(\mathrm{C{-}D})} = \exp\left(\frac{6.6261 \times 10^{-34} \times 2.9979 \times 10^{8}}{2 \times 1.3807 \times 10^{-23} \times 300}(2.9 \times 10^{5} - 2.1 \times 10^{5})\right)$$

$$\frac{k(\mathrm{C{-}H})}{k(\mathrm{C{-}D})} = 6.81$$

6.4 E2 elimination. The value of the kinetic isotope effect of 6.5 indicates that the C−H/D bond is broken in the rate-determining step of the reaction.

6.5 For a tertiary substrate, we can expect E1 elimination, where the C−H/D bond is not broken during the rate-determining step. Therefore, we observe only a small secondary kinetic isotope effect with the k_H / k_D ratio slightly larger than 1.0.

Problem 7. Designing a photoelectrochemical cell

7.1 Reduction potentials for reactions b), c), d), f) and h) are dependent on pH.

7.2 The potential dependence on pH is a linear function with intercept equal to $E°$ and slope equal to:

$$E = E^{\circ} - \frac{RT}{zF}\ln\frac{[\mathbf{A}_{\mathrm{red}}]}{[\mathbf{A}_{\mathrm{ox}}][\mathrm{H}^{+}]^{n}} = E^{\circ} - \frac{RT}{zF}\left(\ln\frac{[\mathbf{A}_{\mathrm{red}}]}{[\mathbf{A}_{\mathrm{ox}}]} - n \times \ln[\mathrm{H}^{+}]\right) =$$

$$= E^{\circ} + \frac{nRT}{zF\log(e)} \times \log[\mathrm{H}^{+}] = E^{\circ} - \frac{nRT}{zF\log(e)} \times (-\log[\mathrm{H}^{+}]) = E^{\circ} - \frac{nRT}{zF\log(e)} \times \mathrm{pH}$$

7.3 Standard potential $E°(\mathbf{C})$ is more positive than $E°(\mathbf{B})$, hence substance **C** is a stronger oxidizer and will therefore oxidize substance **B** (a), and the standard reaction potential E_r° will be 0.288V (b):

$$\mathbf{C}_{\mathrm{ox}} + 2\mathrm{e}^{-} \rightarrow \mathbf{C}_{\mathrm{red}} \qquad E_{\mathrm{C}}^{\circ} = +0.824\ \mathrm{V}$$

$$\mathbf{B}_{\mathrm{red}} \rightarrow \mathbf{B}_{\mathrm{ox}} + 3\mathrm{e}^{-} \qquad E_{\mathrm{B}}^{*} = -0.536\ \mathrm{V}$$

$$3\mathbf{C}_{\mathrm{ox}} + 6\mathrm{e}^{-} \rightarrow 3\mathbf{C}_{\mathrm{red}}$$

$$2\mathbf{B}_{\mathrm{red}} \rightarrow 2\mathbf{B}_{\mathrm{ox}} + 6\mathrm{e}^{-}$$

$$3\mathbf{C}_{\mathrm{ox}} + 2\mathbf{B}_{\mathrm{red}} \rightarrow 3\mathbf{C}_{\mathrm{red}} + 2\mathbf{B}_{\mathrm{ox}}$$

$$E_{\mathrm{r}}^{\circ} = E_{\mathrm{C}}^{\circ} + E_{\mathrm{B}}^{*} = 0.824 - 0.536\ \mathrm{V} = +0.288\ \mathrm{V}$$

c) using formula:

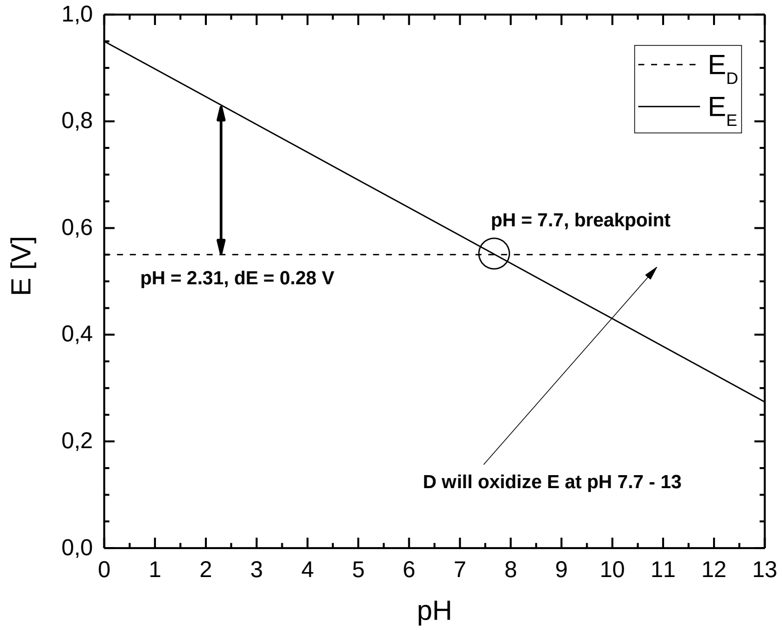
$$\Delta G^{\circ} = -RT\ln(K) = -zFE_r^{\circ}$$

$$K = \exp\left(\frac{zFE_r^{\circ}}{RT}\right) \cong \exp\left(\frac{6 \times 96\,485 \times 0.288}{8.3145 \times 298.15}\right) \cong 1.62 \times 10^{29}$$

7.4 Reaction **E** is pH-dependent and its potential drop is 52 mV per pH unit (as can be calculated from formula derived in question 7.2: $z = 1$, $n = 1$, $T = 262$ K). The reaction potential $E_r = E_E - E_D$ is calculated from the equilibrium constant:

$$RT\ln(K) = zFE_r^{\circ} \Rightarrow \frac{RT\ln(K)}{zF} = \frac{8.3145 \times 262 \times \ln(2.56 \times 10^{5})}{1 \times 96\,485} \cong 0.28\ V$$

The potential for the reduction of substance **E** is $E_E = E_D + E_r = 0.55\ \mathrm{V} + 0.28\ \mathrm{V} = 0.83\ \mathrm{V}$. This value of potential is achieved at pH = 2.31. The two lines cross at pH = 7.7 (roughly); **D** will oxidize **E** in the pH range from 7.7 to 13.



7.5 Using the formula for electrolysis:

$$Q = nzF \Longrightarrow \frac{m}{M} = \frac{Q}{zF} = \frac{It}{zF} \Longrightarrow t = \frac{mzF}{MI} = \frac{0.005 \times 3 \times 96\,485}{197 \times 0.025}\ \mathrm{s} \cong 294\ \mathrm{s}$$

7.6 Only materials **G** and **I** can be used to catalyze the given reaction, because their HOMOs lie below E_{ox} and their LUMOs are higher than E_{red}. While material **G** can be irradiated only by UV light with a wavelength lower than 388 nm, material **I** can be irradiated by either visible or UV light, because the maximal wavelength that can be used to overcome the energy difference of 2 eV is equal to 620 nm.

$$\lambda\,(\mathbf{G}) = \frac{hc}{q_e E[\mathrm{eV}]} = \frac{6.626 \times 10^{-34} \times 3 \times 10^{8}}{1.602 \times 10^{-19} \times 3.2} \cong 388 \times 10^{-9}\ \mathrm{m} = 388\ \mathrm{nm}$$

$$\lambda\,(\mathbf{I}) = \frac{hc}{q_e E[\mathrm{eV}]} = \frac{6.626 \times 10^{-34} \times 3 \times 10^{8}}{1.602 \times 10^{-19} \times 2} \cong 620 \times 10^{-9}\ \mathrm{m} = 620\ \mathrm{nm}$$

Problem 8. Fuel cells

8.1 First, find the driving force, i.e., the Gibbs energy of the reaction $H_2 + ½\, O_2 \rightarrow H_2O$ under standard conditions (298 K and 1 bar). Then, convert it to the EMF (voltage).

The standard reaction enthalpy and entropy are

$$\Delta_r H° = \Delta_f H°\big(\mathrm{H_2O(l)}\big) = -286\ \mathrm{kJ\ mol^{-1}}$$

$$\Delta_r S° = S°\big(\mathrm{H_2O(l)}\big) - \left(S°\big(\mathrm{H_2(g)}\big) + \frac{1}{2}S°\big(\mathrm{O_2(g)}\big)\right) = 70 - \left(131 + \frac{205}{2}\right) =$$
$$= \ -163.5\ \mathrm{J\ K^{-1}mol^{-1}}$$

The standard change of Gibbs energy is

$$\Delta_r G° = \Delta_r H° - T\Delta_r S° = -286 - 298 \times (-163.5 \times 10^{-3}) = -237.3\ \mathrm{kJ\ mol^{-1}}$$

The standard EMF is then

$$E° = -\frac{\Delta_r G°}{|z|F} = \frac{-237.3 \times 10^3}{2 \times 96\,485} = 1.23\ \mathrm{V}$$

8.2 The solution is similar to the previous one with the difference of water state.

$$\Delta_r H° = \Delta_f H°\big(\mathrm{H_2O(g)}\big) = -242\ \mathrm{kJ\ mol^{-1}}$$

$$\Delta_r S° = S°\big(\mathrm{H_2O(g)}\big) - \left(S°\big(\mathrm{H_2(g)}\big) + \frac{1}{2}S°\big(\mathrm{O_2(g)}\big)\right) = 189 - \left(131 + \frac{205}{2}\right) =$$
$$= \ -44.5\ \mathrm{J\ K^{-1}mol^{-1}}$$

The standard change of Gibbs energy is

$$\Delta_r G° = \Delta_r H° - T\Delta_r S° = -242\ - 298 \times (-44.5 \times 10^{-3}) = -228.7\ \mathrm{kJ\ mol^{-1}}$$

The standard EMF is then

$$E° = -\frac{\Delta_r G°}{|z|F} = \frac{-228.7 \times 10^3}{2 \times 96\,485} = 1.19\ \mathrm{V}$$

8.3 The ideal thermodynamic efficiency is:

$$\eta_t = \frac{\Delta_r G°}{\Delta_r H°} = \frac{\Delta_r H° - T\Delta_r S°}{\Delta_r H°} = 1 - T \times \frac{\Delta_r S°}{\Delta_r H°}$$

For both cells and for various temperatures, we get:

$$\eta_t(\mathrm{H_2O(l), 298\ K}) = 1 - 298 \times \left(\frac{-163.5}{-286 \times 10^3}\right) = 0.830$$

$$\eta_t(\mathrm{H_2O(l), 373\ K}) = 1 - 373 \times \left(\frac{-163.5}{-286 \times 10^3}\right) = 0.787$$

$$\eta_t(\mathrm{H_2O(g), 298\ K}) = 1 - 298 \times \left(\frac{-44.5}{-242 \times 10^3}\right) = 0.945$$

$$\eta_t(\mathrm{H_2O(g), 373\ K}) = 1 - 373 \times \left(\frac{-44.5}{-242 \times 10^3}\right) = 0.931$$

8.4 Cathode: $O_2 + 4\,e^- + 4\,H^+ \rightarrow 2\,H_2O$

Anode: $C_4H_{10} + 8\,H_2O \rightarrow 4\,CO_2 + 26\,H^+ + 26\,e^-$

8.5 The overall reaction is:

$2\,C_4H_{10} + 13\,O_2 \rightarrow 8\,CO_2 + 10\,H_2O$

The reaction as accompanied by the transfer of 52 electrons. Hence, at standard temperature:

$$\Delta_f G^\circ\big(\mathrm{H_2O(l)}\big) = -237.3\ \mathrm{kJ\ mol^{-1}}$$

$$\Delta_f G^\circ\big(\mathrm{CO_2(g)}\big) = -393 - 298 \times \Big(\big(214 - (6 + 205)\big) \times 10^{-3}\Big) = -393.9\ \mathrm{kJ\ mol^{-1}}$$

$$\Delta_f G^\circ\big(\mathrm{C_4H_{10}(g)}\big) = -17\ \mathrm{kJ\ mol^{-1}}$$

$$\Delta_f G^\circ\big(\mathrm{O_2(g)}\big) = 0$$

$$\Delta_r G^\circ = \Big(8\Delta_f G^\circ\big(\mathrm{CO_2(g)}\big) + 10\Delta_f G^\circ\big(\mathrm{H_2O(l)}\big)\Big) - \Big(2\Delta_f G^\circ\big(\mathrm{C_4H_{10}(g)}\big) + 13\Delta_f G^\circ\big(\mathrm{O_2(g)}\big)\Big) =$$
$$= \big(8 \times (-393.9) + 10 \times (-237.3)\big) - (2 \times (-17) + 13 \times 0) = -5\,490\ \mathrm{kJ\ mol^{-1}}$$

$$E^\circ = -\frac{\Delta_r G^\circ}{|z|F} = -\frac{-5\,490 \times 10^3}{52 \times 96\,485} = 1.09\ \mathrm{V}$$

8.6 The ideal thermodynamic efficiency is determined as:

$$\eta_t = \frac{\Delta_r G^\circ}{\Delta_r H^\circ} = \frac{-5\,490.2}{\big(8 \times (-393) + 10 \times (-286)\big) - \big(2 \times (-126) + 13 \times 0\big)} = 0.954$$

8.7 It is the same as in the previous answer. The overall reaction is the same.

8.8 Anode: $CH_3OH + H_2O \rightarrow 6\,H^+ + 6\,e^- + CO_2$

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

Overall: $2\,CH_3OH + 3\,O_2 \rightarrow 2\,CO_2 + 4\,H_2O$

8.9 Nernst equation

$$E = E^\circ - \frac{RT}{12F}\ln\frac{\left(\frac{c_{\mathrm{H_2O}}}{c^\circ}\right)^4\left(\frac{p_{\mathrm{CO_2}}}{p^\circ}\right)^2}{\left(\frac{c_{\mathrm{CH_3OH}}}{c^\circ}\right)^2\left(\frac{p_{\mathrm{O_2}}}{p^\circ}\right)^3}$$

Any answer with correctly expressed activities (e.g. using molar fractions) is assumed to be correct.

8.10 We use van ’t Hoff equation, in which we substitute EMFs for equilibrium constants. We obtain reaction enthalpy and Gibbs free energy changes, which we use to calculate the entropy change:

$$\ln\frac{K(T_2)}{K(T_1)} = \frac{\Delta_r H^\circ}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right);\ \ \ln K(T) = \frac{|z|FE^\circ}{RT} \quad \rightarrow \quad \frac{|z|FE^\circ(T_2)}{RT_2} - \frac{|z|FE^\circ(T_1)}{RT_1} = \frac{\Delta_r H^\circ}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\Delta_r H^\circ = \frac{R \times \left(\frac{|z|FE^\circ(T_2)}{RT_2} - \frac{|z|FE^\circ(T_1)}{RT_1}\right)}{\frac{1}{T_1} - \frac{1}{T_2}} = \frac{|z|F \times \left(\frac{E^\circ(T_2)}{T_2} - \frac{E^\circ(T_1)}{T_1}\right)}{\frac{1}{T_1} - \frac{1}{T_2}} = \frac{12 \times 96\,485 \times \left(\frac{1.20}{373} - \frac{1.21}{298}\right)}{\frac{1}{298} - \frac{1}{373}} = -1\,447\ \mathrm{kJ\ mol^{-1}}$$

$$\Delta_r G^\circ = -|z|FE^\circ(T_1) = -12 \times 96\,485 \times 1.21 = -1\,401\ \mathrm{kJ\ mol^{-1}}$$

$$\Delta_r S^\circ = \frac{\Delta_r H^\circ - \Delta_r G^\circ}{T_1} = \frac{-1\,447 \times 10^3 - (-1\,401 \times 10^3)}{298} = -154.4\ \mathrm{J\ K^{-1}mol^{-1}}$$

Problem 9. Acid-base equilibria in blood

9.1 CO_2 concentration:

$$[\mathrm{CO_2}] = H^{cp} \times p(\mathrm{CO_2})$$

$$[\mathrm{CO_2}] = 2.3 \times 10^{-7} \times 5\,300 \ \ \mathrm{mol\,dm^{-3}}$$

$$[\mathrm{CO_2}] = 1.219 \times 10^{-3}\ \mathrm{mol\,dm^{-3}}$$

The initial concentration of bicarbonate in blood with no acid added, *c*(HCO_3^-, 37 °C):

$$\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log\frac{[\mathrm{HCO_3^-}]}{[\mathrm{CO_2}]}$$

$$\log[\mathrm{HCO_3^-}] = \mathrm{pH} - \mathrm{p}K_\mathrm{a} + \log[\mathrm{CO_2}]$$

$$\log[\mathrm{HCO_3^-}] = 7.4 - 6.1 + \log(1.219 \times 10^{-3})$$

$$\log[\mathrm{HCO_3^-}] = 7.4 - 6.1 - 2.9$$

$$\log[\mathrm{HCO_3^-}] = -1.6$$

$$[\mathrm{HCO_3^-}] = 24\ \mathrm{mmol\,dm^{-3}}$$

pH after 10 mmol of acids were added to 1 dm^3 of the buffer solution:

$$\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log\frac{[\mathrm{HCO_3^-}] - [\mathrm{H^+}]}{[\mathrm{CO_2}] + [\mathrm{H^+}]}$$

$$\mathrm{pH} = 6.1 + \log\frac{0.024 - 0.010}{0.001219 + 0.010}$$

$$\mathrm{pH} = 6.21$$

9.2

$$\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log\frac{[\mathrm{HCO_3^-}] - [\mathrm{H^+}]}{[\mathrm{CO_2}]}$$

$$\mathrm{pH} = 6.1 + \log\frac{0.024 - 0.010}{0.001219}$$

$$\mathrm{pH} = 7.17$$

The buffering capacity of the bicarbonate buffer is higher when the system is open. However, pH is still outside the physiologic range (pH = 7.36–7.44). Non-bicarbonate buffers (e.g. albumin, phosphate, haemoglobin) that are present in blood additionally increase the overall buffering capacity of blood and help to keep pH within the physiologic range.

9.3 The van ’t Hoff’s equation will be used:

$$-\frac{d\ln K}{dT} = -\frac{\Delta_r H}{T^2}$$

First, the integrated form is applied to calculate the reaction enthalpy from the pK_a values at 37 °C and 25 °C.

$$\ln K_2 - \ln K_1 = -\frac{\Delta_r H}{\mathrm{R}}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln K_{310.15\ \mathrm{K}} - \ln K_{298.15\ \mathrm{K}} = -\frac{\Delta_r H}{\mathrm{R}}\left(\frac{1}{310.15} - \frac{1}{298.15}\right)$$

$$-14.05 + 14.62 = 1.30 \times 10^{-4} \times \frac{\Delta_r H}{8.314}$$

$$\Delta_r H = 36.88\ \mathrm{kJ\ mol^{-1}}$$

Then, that same equation is used to calculate the pK_a at 20 °C:

$$\ln K_2 - \ln K_1 = -\frac{\Delta_r H}{\mathrm{R}}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln K_{293.15} + 14.62 = -\frac{36\,520}{8.314}\left(\frac{1}{293.15} - \frac{1}{298.15}\right)$$

$$\ln K_{293.15} = -14.87$$

$$K_{293.15} = 3.48 \times 10^{-7}$$

$$\mathrm{p}K_\mathrm{a}(293.15\ \mathrm{K}) = 6.46$$

Henry's solubility of CO_2 is recalculated in an analogous way:

$$H^{\mathrm{cp}}_{\mathrm{T}_2} = H^{\mathrm{cp}}_{\mathrm{T}_1} \times e^{\frac{-\Delta H_{\mathrm{vap}}}{\mathrm{R}}\left(\frac{1}{\mathrm{T}_2} - \frac{1}{\mathrm{T}_1}\right)}$$

$$H^{\mathrm{cp}}_{293.15\ \mathrm{K}} = 2.3 \times 10^{-4} \times e^{2\,400 \times \left(\frac{1}{293.15} - \frac{1}{310.15}\right)}$$

$$H^{\mathrm{cp}}_{293.15\ \mathrm{K}} = 3.6 \times 10^{-4}\ \mathrm{mol\ m^{-3}\ Pa^{-1}}$$

Finally, the pH of blood at 20 °C is obtained using these recalculated values:

$$\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log \frac{[\mathrm{HCO_3^-}]}{\mathrm{H^{cp}} \times p(\mathrm{CO_2})}$$

$$\mathrm{pH} = 6.46 + \log \frac{0.024}{3.6 \times 10^{-7} \times 5\ 300}$$

$$\mathrm{pH} = 7.57$$

9.4 In a working muscle, high oxygen supply is ensured by lowering the affinity towards oxygen in an acidic environment. In lungs, by contrast, CO_2 is liberated from haemoglobin in red blood cells, which, in turn, binds oxygen with a greater affinity.

Problem 10. Ion exchange capacity of a cation exchange resin

10.1 The molecular formula of one unit of the catex polymer is $C_{17}H_{16}O_5S_1$, which corresponds to the molecular weight of 332.369 g mol^{-1}. Mass percentage of an atom w_x is

$$w_x = \frac{a_x A_x}{M}$$

where a_x and A_x are the number of atoms and the atomic weight of an atom X, respectively. M is the molecular weight of one unit of the catex polymer. For sulfur (a_S = 1, A_S = 32.06 g mol^{-1}) and carbon (a_C = 17, A_C = 12.011 g mol^{-1}), the mass percentage is w_S = 9.65% and w_C = 61.43%, respectively.

10.2 The theoretical ion exchange capacity is the amount of exchange groups in one unit of the catex polymer per mass of the unit, i.e.

$$Q_{\mathrm{m,x}} = \frac{a_x}{M}$$

For -SO_3H (one ion exchange group, a_{SO3H} = 1) and -COOH (one ion exchange group a_{COOH} = 1) we get $Q_{m,SO3H} = Q_{m,COOH}$ = 3.01 mmol g^{-1}.

10.3 The total ion exchange capacity is a sum of individual strong and weak exchange capacities. For $Q_{m,SO3H} = Q_{m,COOH}$ = 3.01 mmol g^{-1} we get $Q_{m,total}$ = 6.02 mmol g^{-1}.

10.4 The total ion exchange capacity in mmol cm^{-3} of a swollen resin $Q_{V,total}$ is

$$Q_{\mathrm{V,total}} = Q_{\mathrm{m,total}}(1-\varepsilon)\,\rho\,(1-w)$$

where ε and ρ are porosity and density, respectively, of a swollen resin and w is the mass ratio of water bound to the resin. For $Q_{m,total}$ = 6.02 mmol g^{-1}, ε = 0.48, ρ = 1.28 g cm^{-3}, and w = 0.45 we get $Q_{V,total}$ = 6.02 × (1 − 0.48) × 1.28 × (1 − 0.45) = 2.20 mmol cm^{-3}.

Problem 11. Weak and strong cation exchange resin

11.1 At the beginning, all cation exchange sites are occupied with Na^+ ions. Weak acetic acid exchanges all the weakly bound Na^+ ions (weak cation exchange sites) and some of the strongly bound Na^+ ions (strong cation exchange sites). The amount of Na^+ in solution A is n_1. When the resin is rinsed with a neutral solution of Mg^{2+} ions, all ions at the strong cation exchange sites are exchanged for Mg^{2+}. Thus, solution B contains n_2 moles of Na^+ and n_3 moles of H^+.

The electrode potential is linearly proportional to the logarithm of concentration; i.e. for sodium ion selective electrode $E = k + S \log_{10}[Na^+]$. Based on a two-point calibration, we get the following equations

$-0.2283 = k + S \log(0.0100)$ and $-0.3466 = k + S \log(0.00010)$

Solving the system of equations, we get $k = -0.1100$ V and $S = 0.05915$ V.

The amounts of Na^+ ions in solutions A (V_A = 1 000 cm^3) and B (V_B = 500 cm^3) are

$$n_1 = V_A c_{Na,A} = V_A 10^{\frac{E_1-k}{S}} = 1 \times 10^{\frac{-0.2313-(-0.1100)}{0.05915}} = 8.90 \text{ mmol}$$

$$n_2 = V_B c_{Na,B} = V_B 10^{\frac{E_4-k}{S}} = 0.5 \times 10^{\frac{-0.2534-(-0.1100)}{0.05915}} = 1.88 \text{ mmol}$$

The alkalimetric titration is based on 1:1 stoichiometry of the reaction of OH^- (titration agent) and H^+ (titrant). Then amount of H^+ ions in solution B (V_a is an aliquot of 100 cm^3) is

$$n_3 = V_{NaOH} \times c_{NaOH} \times \frac{V_B}{V_a} = 0.0125 \times 0.1000 \times \frac{0.500}{0.100} = 6.25 \text{ mmol}$$

Ion exchange capacities of the strong and weak ion exchange resins (V_0 = 4 cm^3)

$$Q_{V,SO3H} = Q_{V,strong} = \frac{n_2 + n_3}{V_0} = \frac{1.88 + 6.25}{4} = 2.033 \text{ mmol cm}^{-3}$$

$$Q_{V,COOH} = Q_{V,weak} = \frac{n_1 - n_3}{V_0} = \frac{8.90 - 6.25}{4} = 0.662 \text{ mmol cm}^{-3}$$

11.2 The total ion exchange capacity is

$$Q_{V,total} = Q_{V,SO3H} + Q_{V,COOH} = 2.033 + 0.662 = 2.695 \text{ mmol cm}^{-3}$$

Problem 12. Uranyl extraction

12.1 First, $[\mathrm{HA}]_{\mathrm{org}}$ is calculated:

$$c_{\mathrm{HA,org,0}} = 2[(\mathrm{HA})_2]_{\mathrm{org}} + [\mathrm{HA}]_{\mathrm{org}} + [\mathrm{HA}]_{\mathrm{aq}} \ + \ [\mathrm{A}^-]_{\mathrm{aq}}$$

The concentration of UO_2A_2 is omitted as recommended in the introductory text.

From the definition of $K_{\mathrm{p,HA}}$, $K_{\mathrm{D,HA}}$ and $K_{\mathrm{a,HA}}$, $[\mathrm{HA}]_{\mathrm{org}}$ can be obtained by solving the quadratic equation

$$2K_{\mathrm{p}} \times [\mathrm{HA}]_{\mathrm{org}}^2 + [\mathrm{HA}]_{\mathrm{org}} \times \left(1 + \frac{1}{K_{\mathrm{D,HA}}} + \frac{K_{\mathrm{a,HA}}}{K_{\mathrm{D,HA}} \times [\mathrm{H}^+]_{\mathrm{aq}}}\right) - c_{\mathrm{HA,org,0}} = 0$$

i.e.

$$[\mathrm{HA}]_{\mathrm{org}} = \frac{-\left(1 + \frac{1}{K_{\mathrm{D,HA}}} + \frac{K_{\mathrm{a,HA}}}{K_{\mathrm{D,HA}} \times [\mathrm{H}^+]_{\mathrm{aq}}}\right) + \sqrt{\left(1 + \frac{1}{K_{\mathrm{D,HA}}} + \frac{K_{\mathrm{a,HA}}}{K_{\mathrm{D,HA}} \times [\mathrm{H}^+]_{\mathrm{aq}}}\right)^2 + 8K_{\mathrm{p}} \times c_{\mathrm{HA,org,0}}}}{4K_{\mathrm{p}}}$$

Considering that the proton concentration corresponds to the analytic concentration of HNO_3, $[\mathrm{H}^+]_{\mathrm{aq}} = 10^{-\mathrm{pH}} = 2.00 \times 10^{-2}$ mol dm^{-3}, we get $[\mathrm{HA}]_{\mathrm{org}} = 3.41 \times 10^{-3}$ mol dm^{-3}. Next, the uranyl ion distribution ratio, $D_{\mathrm{c,UO_2^{2+}}}$ is expressed as:

$$D_{\mathrm{c,UO_2^{2+}}} = \frac{c_{\mathrm{UO_2^{2+},org}}}{c_{\mathrm{UO_2^{2+},aq}}} = \frac{[\mathrm{UO_2A_2}]_{\mathrm{org}}}{[\mathrm{UO_2^{2+}}]_{\mathrm{aq}} + [\mathrm{UO_2A_2}]_{\mathrm{aq}} + \sum_{i=1}^{4}[\mathrm{UO_2(OH)}_i^{2-i}]_{\mathrm{aq}}}$$

Using $\beta_{2,\mathrm{UO_2A_2}}$, $K_{\mathrm{D,UO_2A_2}}$, $K_{\mathrm{a,HA}}$ and β_i for $[\mathrm{UO_2(OH)}_i]^{2-i}$ complexes, $D_{\mathrm{c,UO_2^{2+}}}$ can be expressed as

$$D_{\mathrm{c,UO_2^{2+}}} = \frac{K_{\mathrm{D,UO_2A_2}}}{1 + \frac{K_{\mathrm{D,HA}}^2}{\beta_{2,\mathrm{UO_2A_2}} \times K_{\mathrm{a,HA}}^2} \times \frac{[\mathrm{H}^+]_{\mathrm{aq}}^2}{[\mathrm{HA}]_{\mathrm{org}}^2} \times \left(1 + \sum_{i=1}^{4}\beta_i \times [\mathrm{OH}^-]_{\mathrm{aq}}^i\right)}$$

The concentration of hydroxyl ions is obtained from the concentration of protons,

$$[\mathrm{OH}^-]_{\mathrm{aq}} = \frac{K_{\mathrm{w}}}{[\mathrm{H}^+]_{\mathrm{aq}}}$$

For $[\mathrm{H}^+]_{\mathrm{aq}} = 2.00 \times 10^{-2}$ mol dm^{-3}, we get

$$[\mathrm{OH}^-]_{\mathrm{aq}} = \frac{10^{14}}{2\times10^{-2}} = 5 \times 10^{-13} \ \text{mol dm}^{-3}$$

Casting this value, $[\mathrm{HA}]_{\mathrm{org}} = 3.41 \times 10^{-3}$ mol dm^{-3} and all the necessary constants into the expression for the distribution ratio, we obtain

$$D_{\mathrm{c,UO_2^{2+}}} = 5.61$$

Then, the yield R defined as

$$R = \frac{n_{\mathrm{,org}}}{n_{\mathrm{,org}} + n_{\mathrm{,aq}}} = \frac{D_{\mathrm{c,UO_2^{2+}}}}{D_{\mathrm{c,UO_2^{2+}}} + \frac{V_{\mathrm{aq}}}{V_{\mathrm{org}}}}$$

can be calculated, providing the final result of

$$R = \frac{5.61}{5.61 + 1} = 84.9\%$$

12.2 For the conditions of $[H^+] = 10^{-\mathrm{pH}} = 5.01 \times 10^{-11}$ mol dm^{-3}, using the same calculation procedure, we get

$[HA]_{org} = 1.50 \times 10^{-5}$ mol dm^{-3}

$D_{\mathrm{c,UO_2^{2+}}} = 1.22 \times 10^{-4}$

and the yield R = 0.0122%.

Problem 13. Determination of active chlorine in commercial products

13.1 (i) $Cl_2 + H_2O \rightarrow HClO$ (**A**) + HCl (**B**)

(ii) $NaClO + H_2O \rightarrow HClO$ (**A**) + NaOH (**C**)

In alkaline aqueous solution, hypochlorite ion (ClO^-) will dominate.

13.2

$$c(\mathrm{NaClO}) = \frac{\rho(\mathrm{Cl_2})}{M(\mathrm{Cl_2})}$$

$$c(\mathrm{NaClO}) = \frac{22.4}{70.906} = 0.3159\ \mathrm{mol\ dm^{-3}}$$

13.3 $ClO^- + 2\ I^- + 2\ H^+ \rightarrow I_2 + H_2O + Cl^-$

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

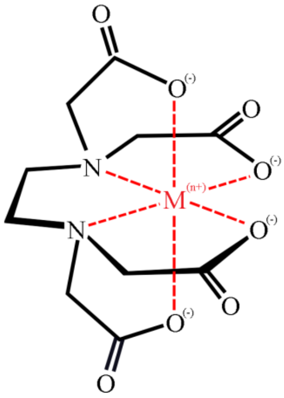
$$w(\mathrm{NaClO}) = c(\mathrm{S_2O_3}^{2-}) \times V(\mathrm{S_2O_3}^{2-}) \times \frac{1}{2} \times M(\mathrm{NaClO}) \times \frac{V_\mathrm{flask}}{\rho_\mathrm{SAVO} \times V_\mathrm{SAVO} \times V_\mathrm{a}}$$

$$w(\mathrm{NaClO}) = 0.0503 \times 0.01015 \times \frac{1}{2} \times 74.44 \times \frac{0.250}{1.070\ \times\ 0.010\ \times\ 0.010} \times 100\% = 4.44\%$$

Problem 14. Chemical elements in fireworks

14.1 An aqueous sample is introduced to a hot, non-luminous flame, where the tested compound is partially evaporated, atomized and free atoms are excited. During de-excitation, the energy difference between the atomic energy levels is emitted as a photon of an appropriate wavelength, characteristic of the particular chemical element. In this case, all three wavelengths are in the visible region of the spectrum and the corresponding colours for sodium, barium and lithium are yellow, lime green and red, respectively.

14.2 The structure of a metal–EDTA complex is



$\delta(HY^{3-}) = [HY^{3-}] / c(EDTA) = \beta_1 [H^+] / (1 + \beta_1 [H^+] + \beta_2 [H^+]^2 + \beta_3 [H^+]^3 + \beta_4 [H^+]^4)$

$\delta(Y^{4-}) = [Y^{4-}] / c(EDTA) = 1 / (1 + \beta_1 [H^+] + \beta_2 [H^+]^2 + \beta_3 [H^+]^3 + \beta_4 [H^+]^4)$,

where $\beta_1 = 1 / K_{a4}$, $\beta_2 = 1 / (K_{a4} K_{a3})$, $\beta_3 = 1 / (K_{a4} K_{a3} K_{a2})$, $\beta_4 = 1 / (K_{a4} K_{a3} K_{a2} K_{a1})$

$\delta(HY^{3-}) = 1.82 \times 10^{10} \times 10^{-10} / (1 + 1.82 \times 10^{10} \times 10^{-10} + 2.63 \times 10^{16} \times 10^{-20} + 1.23 \times 10^{19} \times 10^{-30} + {} + 1.23 \times 10^{21} \times 10^{-40}) = 0.6453$, i.e. 64.53%

$\delta(Y^{4-}) = 1 / (1 + 1.82 \times 10^{10} \times 10^{-10} + 2.63 \times 10^{16} \times 10^{-20} + 1.23 \times 10^{19} \times 10^{-30} + 1.23 \times 10^{21} \times 10^{-40}) = {} = 0.3546$, i.e. 35.46%

$\delta(HY^{3-}) + \delta(Y^{4-}) = 99.99\%$, hence other forms are present at molar ratios lower than 0.5%.

14.3 Ammonium buffer is a mixture of ammonia and ammonium chloride. Ions of alkaline earth metals form weak complexes with EDTA (log K_{MY} between 7.7 and 10.7) and are present only in alkaline media (pH > 9).

14.4 $Zn^{2+} + 4\ CN^- \rightarrow [Zn(CN)_4]^{2-}$
$[Zn(CN)_4]^{2-} + 4\ HCHO + 4\ H_2O \rightarrow Zn^{2+} + 4\ HOCH_2CN + 4\ OH^-$

14.5 2,3-Disulfanylpropan-1-ol is used for masking lead ions.

14.6 Step i: Zinc is masked in the cyanide complex, lead and magnesium react with EDTA

$n(Pb) + n(Mg) = n_1(EDTA)$

Step ii: EDTA released from its complex with lead ions reacts with magnesium standard solution

$n(Pb) = n_{std}(Mg)$

Step iii: Zinc released from cyanide complex reacts with EDTA

$n(Zn) = n_2(EDTA)$

Masses of the elements in the sample (m_1 = 1 g)

$$m(\mathrm{Pb}) = c_{\mathrm{std}}(\mathrm{Mg}) \times V_{\mathrm{std}}(\mathrm{Mg}) \times \frac{A(\mathrm{Pb})}{m(\mathrm{sample})} \times m_1$$

$$m(\mathrm{Pb}) = 0.01087 \times 0.0128 \times \frac{207.20}{0.8472} \times 1 = 34.03\ \mathrm{mg}$$

$$n(\mathrm{Mg}) = n_1(EDTA) - n_{\mathrm{std}}(\mathrm{Mg})$$

$$m(\mathrm{Mg}) = \left(c(\mathrm{EDTA}) \times V_1(\mathrm{EDTA}) - c_{\mathrm{std}}(\mathrm{Mg}) \times V_{\mathrm{std}}(\mathrm{Mg})\right) \times \frac{A(\mathrm{Mg})}{m(\mathrm{sample})} \times m_1$$

$$m(\mathrm{Mg}) = (0.01983 \times 0.0359 - 0.01087 \times 0.0128) \times \frac{24.305}{0.8472} \times 1 = 16.43\ \mathrm{mg}$$

$$m(\mathrm{Zn}) = c(\mathrm{EDTA}) \times V_2(\mathrm{EDTA}) \times \frac{A(\mathrm{Zn})}{m(\mathrm{sample})} \times m_1$$

$$m(\mathrm{Zn}) = 0.01983 \times 0.0241 \times \frac{65.38}{0.8472} \times 1 = 36.88\ \mathrm{mg}$$

14.7 Complexation equation: $\mathrm{Ca^{2+} + Y^{4-} \rightarrow CaY^{2-}}$

Final analytical concentrations after dilution are:

$$c(\mathrm{Ca^{2+}}) = \frac{10}{100} \times 0.05 = 5.0 \times 10^{-3}\ \mathrm{mol\ dm^{-3}} \qquad c(\mathrm{Y^{4-}}) = \frac{50}{100} \times 0.04 = 2.0 \times 10^{-2}\ \mathrm{mol\ dm^{-3}}$$

The coefficient for EDTA side reactions

$\alpha(\mathrm{EDTA}) = (1 + \beta_1\,[\mathrm{H^+}] + \beta_2\,[\mathrm{H^+}]^2 + \beta_3\,[\mathrm{H^+}]^3 + \beta_4\,[\mathrm{H^+}]^4)$

(definitions of β_i are in 14.2); for pH = 6

$\alpha(\mathrm{EDTA}) = (1 + 1.82 \times 10^{10} \times 10^{-6} + 2.63 \times 10^{16} \times 10^{-12} + 1.23 \times 10^{19} \times 10^{-18} + 1.23 \times 10^{21} \times 10^{-24}) =$
$= 4.45 \times 10^4$

The final concentration of free $\mathrm{Ca^{2+}}$ ions in the solution is:

$$\beta^I = \frac{\beta(\mathrm{Ca{-}EDTA})}{\alpha(\mathrm{EDTA})} = \frac{10^{10.61}}{4.45 \times 10^4} = 10^{5.96}$$

Based on the mass balances

$$[\mathrm{Ca^{2+}}] = \frac{c(\mathrm{Ca^{2+}})}{1 + \beta^I[\mathrm{Y^{4-}}]}$$

$$[\mathrm{Y^{4-}}] = c(\mathrm{Y^{4-}}) - [\mathrm{CaY^{2-}}] = c(\mathrm{Y^{4-}}) - (c(\mathrm{Ca^{2+}}) - [\mathrm{Ca^{2+}}])$$

we get a quadratic equation with the following solution

$$\beta^I[\mathrm{Ca^{2+}}]^2 + (1 + \beta^I c(\mathrm{Y^{4-}}) - \beta^I c(\mathrm{Ca^{2+}}))[\mathrm{Ca^{2+}}] - c(\mathrm{Ca^{2+}}) = 0$$

$$[\mathrm{Ca^{2+}}] = 3.642 \times 10^{-7}\ \mathrm{mol\ dm^{-3}}$$

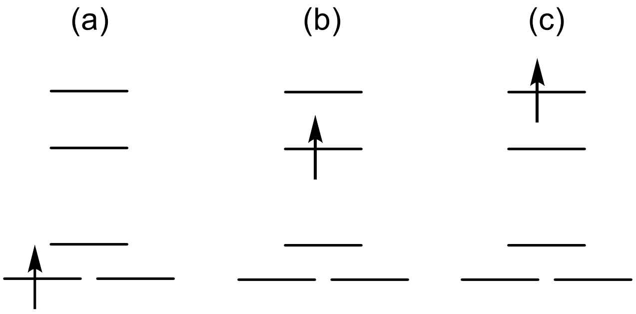
Problem 15. Colours of complexes

15.1 Ground state: Excited state:

15.2 The wavenumber of 20 300 cm^{-1} corresponds to the wavelength of 493 nm which means the absorption of the blue-green light. The colour of the complex is the complementary one, i.e. orange-red.

15.3 The complex absorbs visible light in the range from 493 to 575 nm, i.e. blue-green to yellow-green. The complex is purple.

15.4 Electron configurations:



15.5 Equations:

(1) $2\ CoCl_2 + 3\ F_2 \rightarrow 2\ CoF_3 + 2\ Cl_2$

(2) $CoF_3 + 3\ KF \rightarrow K_3[CoF_6]$

(3) $4\ CoF_3 + 2\ H_2O \rightarrow 4\ HF + 4\ CoF_2 + O_2$

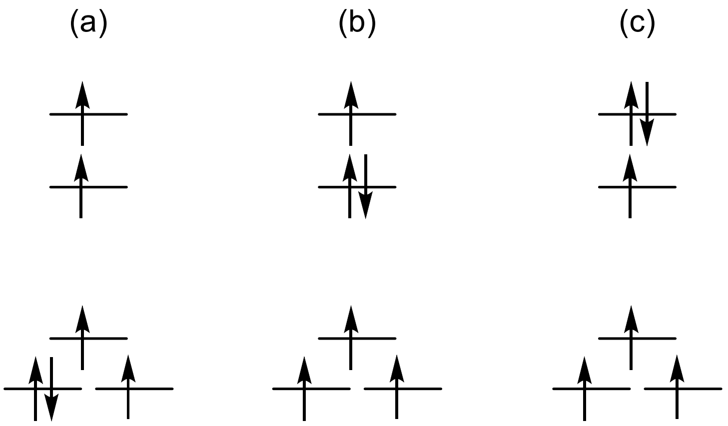
15.6 Equation:

(4) $4\ CoCl_2 + 4\ NH_4Cl + 20\ NH_3 + O_2 \rightarrow 4\ [Co(NH_3)_6]Cl_3 + 2\ H_2O$

15.7 The wavenumbers correspond to the wavelengths of 475 nm (blue light) and 340 nm (UV region). The second band has no effect on the observed colour and the complex is orange. Luteus means yellow in Latin (it refers to the yellow-orange colour of the complex).

15.8 Due to their position in the spectrochemical series, fluoride ions (F^-) cause only small splitting, which leads to a high-spin configuration with four unpaired electrons. Ammonia molecules (NH_3) cause greater splitting, which means that all the electrons in the t_{2g} orbitals pair up and a low-spin configuration is formed

15.9 Electron configurations:



15.10 The wavenumbers correspond to the wavelengths of 877 nm (IR region) and 690 nm (red light). The first band has no effect on the observed colour and the complex is blue-green.

Problem 16. Iron chemistry

16.1 The requested potentials are calculated as follows, (1)–(3):

$E°(FeO_4^{2-},H^+/Fe^{2+}) = (3 × 1.90 + 1 × 0.77) / 4\ V = 1.62\ V$ (1)

$E°(FeO_4^{2-},H^+/Fe) = (3 × 1.90 + 1 × 0.77 + 2 × (−0.44)) / 6\ V = 0.93\ V$ (2)

$E°(Fe^{3+}/Fe) = (1 × 0.77 + 2 × (−0.44)) / 3\ V = −0.04\ V$ (3)

The corresponding Latimer diagram is depicted in Figure 1.

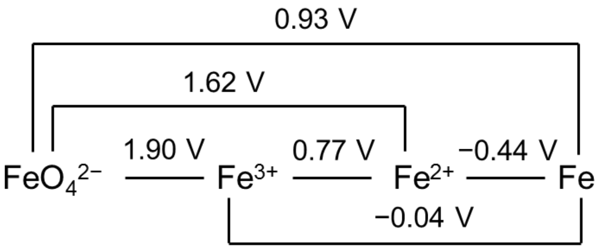


Figure 1. Latimer diagram for iron species in water (pH 0).

16.2 The voltage equivalent is defined as a product of the formal oxidation state *N* and the standard redox potential *E*° (4) for the reduction of the particular species to the elemental state. The Frost diagram (Figure 2) then plots voltage equivalents versus oxidation state.

Voltage equivalent = $N × E°$(species/element) (4)

The individual voltage equivalents are calculated from the data above (5)–(8).

Voltage equivalent (Fe) = 0 × 0 V (def.) = 0 V (5)

Voltage equivalent (Fe^{2+}) = 2 × (−0.44) V = −0.88 V (6)

Voltage equivalent (Fe^{3+}) = 3 × (−0.04) V = −0.12 V (7)

Voltage equivalent (FeO_4^{2-}) = 6 × 0.93 V = 5.58 V (8)

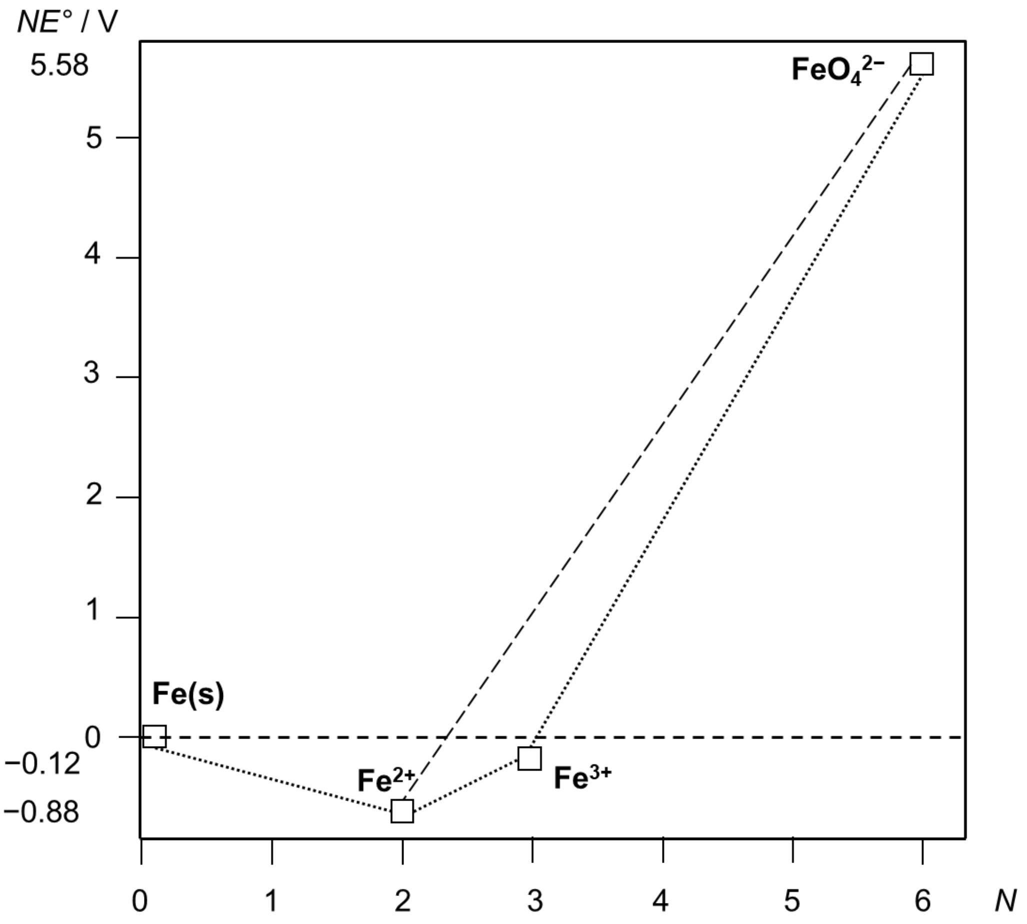


Figure 2. Frost diagram for iron species (pH 0).

Since the imaginary line connecting both the requested oxidation states (FeO_4^{2-} and Fe^{2+}, dashed line in Figure 2) lies above the Fe^{3+} point in the diagram, a synproportionation will be favoured, (9):

$$FeO_4^{2-} + 3\ Fe^{2+} + 8\ H^+ \rightarrow 4\ Fe^{3+} + 4\ H_2O \qquad (9)$$

16.3

(a) The individual zone labels follow the successive uptake of electrons (from up to down) and hydroxide anions as ligands (from left to right). The identity of any zone can be checked by comparing the appropriate borderline definitions. The answers are displayed in Figure 3.

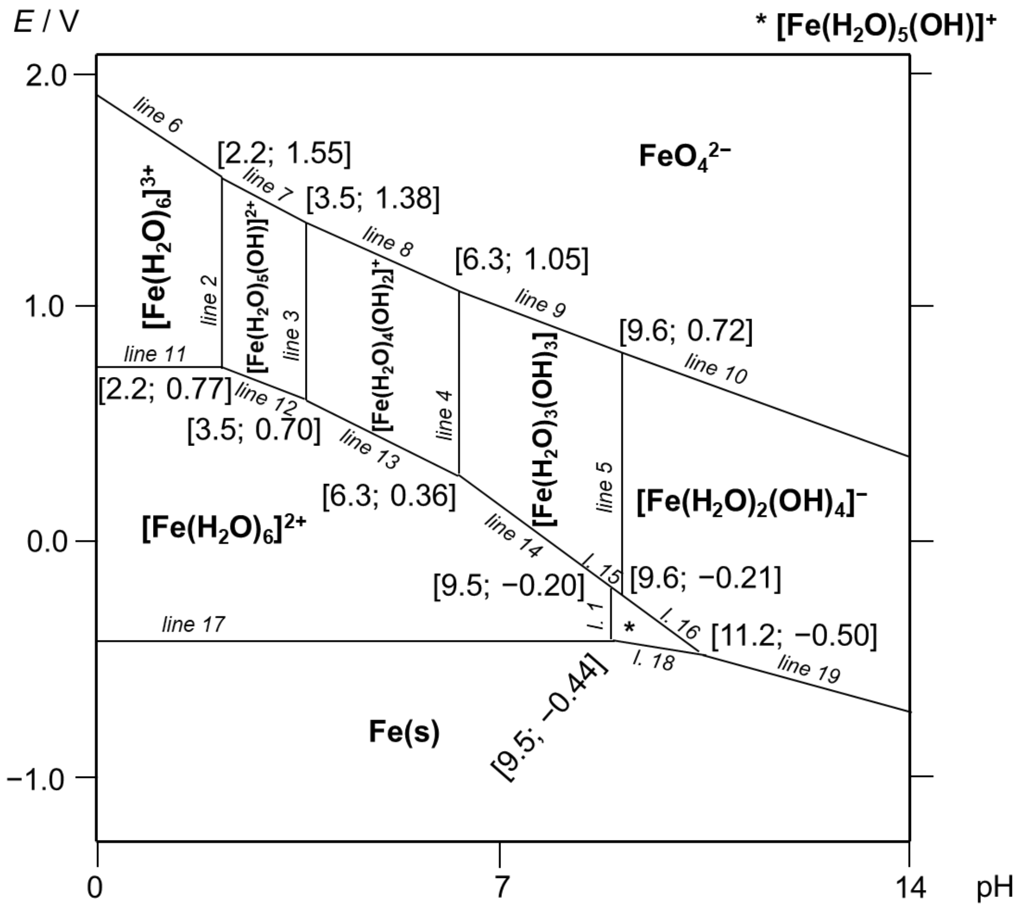


Figure 3. Pourbaix diagram for dissolved iron species and metallic iron.

It should be noted that this type of Pourbaix diagram would be valid only in highly diluted solutions of iron species. The increase in concentration will lead to the precipitation of insoluble (first ferric, then ferrous) oxides/hydroxides as well as the formation of polynuclear hydroxido complexes.

(b) Each borderline is drawn with the assumption that the activities of both participating species are equal. The equations which refer to *lines 11* and *17*, respectively, can be derived from the corresponding forms of the Nernst–Peterson equation (10) and (11) assuming the equilibrium conditions $[Fe^{3+}] = [Fe^{2+}]$ and $[Fe^{2+}] = a(Fe,s)$. Because there is no term which depends on pH, the results are horizontal constant lines numerically equal to the standard redox potentials, see Figure 3.

line 11 (Fe^{3+}/Fe^{2+}): $E = E° - 0.059 \times \log([Fe^{2+}] / [Fe^{3+}])$, thus $E = 0.77$ (10)

line 17 (Fe^{2+}/Fe): $E = E° - (0.059 / 2) \times \log(a(Fe,s) / [Fe^{2+}])$, thus $E = -0.44$ (11)

The conditions for *lines 2* and *5* are $[Fe^{3+}] = [Fe(OH)^{2+}]$ and $[Fe(OH)_3] = [Fe(OH)_4^-]$, respectively, i.e. the expressions imply constant lines again, but in this case vertical ones, since there is no connection with the redox potential. The analytical expressions are represented by equations (12) and (13).

line 2 ($Fe^{3+}/[Fe(OH)]^{2+}$): $pH = pK_w - \log\beta_1$, thus pH = 2.2 (12)

line 5 ($[Fe(OH)_3]/[Fe(OH)_4]^-$): $pH = pK_w + \log\beta_3 - \log\beta_4$, thus pH = 9.6 (13)

(c) The analytic expression of *line 6* (14) is also derived from the Nernst–Peterson equation under the assumption $[FeO_4^{2-}] = [Fe^{3+}]$.

line 6 (FeO_4^{2-}/Fe^{3+}): $E = E° - (0.059 / 3) \times \log\{[Fe^{3+}] / ([FeO_4^{2-}] \times [H^+]^8)\}$,

thus $E = 1.90 - 0.157 \times pH$ (14)

The first coordinate of the intersection of *lines 2*, *6* and *7* is obviously pH = 2.2. The second coordinate can be calculated by substituting for pH = 2.2 in equation (14), i.e. $E = 1.55$.

Although it was not required to derive the expressions for all the lines, they are given in the following list for completeness, (15)–(28), and shown in Figure 3.

line 1 ($Fe^{2+}/[Fe(OH)]^+$): pH = 9.5 (15)

line 3 ($[Fe(OH)]^{2+}/[Fe(OH)_2]^+$): pH = 3.5 (16)

line 4 ($[Fe(OH)_2]^+/[Fe(OH)_3]$): pH = 6.3 (17)

line 7 ($FeO_4^{2-}/[Fe(OH)]^{2+}$): $E = 1.86 - 0.138 \times pH$ (18)

line 8 ($FeO_4^{2-}/[Fe(OH)_2]^+$): $E = 1.79 - 0.118 \times pH$ (19)

line 9 ($FeO_4^{2-}/[Fe(OH)_3]$): $E = 1.66 - 0.098 \times pH$ (20)

line 10 ($FeO_4^{2-}/[Fe(OH)_4]^-$): $E = 1.48 - 0.079 \times pH$ (21)

line 12 ($[Fe(OH)]^{2+}/Fe^{2+}$): $E = 0.90 - 0.059 \times pH$ (22)

line 13 ($[Fe(OH)_2]^+/Fe^{2+}$): $E = 1.11 - 0.118 \times pH$ (23)

line 14 ($[Fe(OH)_3]/Fe^{2+}$): $E = 1.48 - 0.177 \times pH$ (24)

line 15 ($[Fe(OH)_3]/[Fe(OH)]^+$): $E = 0.92 - 0.118 \times pH$ (25)

line 16 ($[Fe(OH)_4]^-/[Fe(OH)]^+$): $E = 1.48 - 0.177 \times pH$ (26)

line 18 ($[Fe(OH)]^+/Fe$): $E = -0.16 - 0.030 \times pH$ (27)

line 19 ($[Fe(OH)_4]^-/Fe$): $E = 0.38 - 0.079 \times pH$ (28)

(d) Ferrate ion can only be produced in a very basic solution by strong oxidizing agents (stronger than elemental oxygen under these conditions), e.g. hypochlorite (32). This will overcome *line 10* and produce some ferrate ions.

$$2\,[Fe(OH)_4]^- + 3\,ClO^- + 2\,OH^- \rightarrow 2\,FeO_4^{2-} + 3\,Cl^- + 5\,H_2O \qquad (32)$$

Other possibilities are for example oxidation in a mixture of melted sodium nitrate with sodium hydroxide or analogous reactions in melts.

16.4 From the viewpoint of "Hard and Soft Acid-Base" (HSAB) theory, Fe^{2+} is an intermediary hard, Fe^{3+} hard and imaginary "Fe^{6+}" would be an extremely hard acid (the hardness correlates with the ionic radii and the surface charge density). Hard acids prefer hard bases and soft acids prefer soft bases. In aqueous solutions, H_2O, OH^- and O^{2-} are available (although the oxide ion is not present in water at all, it can be at least formally "extracted" by e.g. a precipitation process). Therefore, the tendency to attract harder OH^- ions is higher for Fe^{3+} than for Fe^{2+} which leads to a higher proton acidity of the hexaaquaferric ion and easier hydrolysis to the corresponding hydroxido species. For the Fe^{6+} centre, only a similarly extremely hard base is acceptable, i.e. O^{2-} ion (although only formally, since there are covalent bonds between Fe(VI) and O atoms). Therefore, iron in the oxidation state +6 exists only in an anionic form.

16.5 The answers are summarized in Table 1.

Table 1: Electronic and magnetic properties of selected iron species.

Species	Conf.	Spin state		Magn.	LFSE
$[Fe(H_2O)_6]^{2+}$	d^6	high-	$t_{2g}^4e_g^2$	para-	$-0.4\Delta_o$ **
$[Fe(CN)_6]^{4-}$	d^6	low-	$t_{2g}^6e_g^0$	dia-	$-2.4\Delta_o + 2P$ **
$[Fe(H_2O)_6]^{3+}$	d^5	high-	$t_{2g}^3e_g^2$	para-	0
$[Fe(H_2O)_5OH]^{2+}$	d^5	high-	$(t_{2g}^3e_g^2)$*	para-	0
$[Fe(CN)_6]^{3-}$	d^5	low-	$t_{2g}^5e_g^0$	para-	$-2.0\Delta_o + 2P$

Remark: * not O_h symmetry

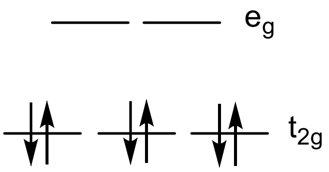
** with respect to free ion configuration

16.6 a) $FeCl_3$, b) $Fe_4[Fe(CN)_6]_3$.

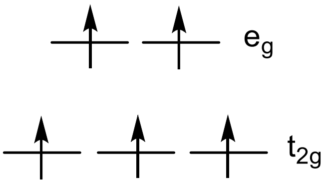
Problem 17. Cyanido- and fluorido-complexes of manganese

17.1 (1) $2\ Mn + 12\ NaCN + 2\ H_2O \rightarrow 2\ Na_5[Mn(CN)_6] + H_2 + 2\ NaOH$

17.2 Diagram – low-spin configuration d^6:

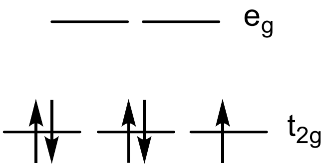


17.3 Diagram – high-spin configuration d^5:



The complex has five unpaired electrons.

17.4 Diagram – low-spin configuration d^5:



17.5 Equations:

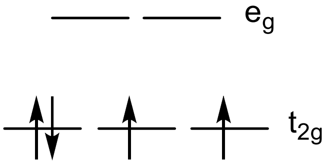
(2) $4\ Mn^{2+} + O_2 + 24\ CN^- + 2\ H_2O \rightarrow 4\ [Mn(CN)_6]^{3-} + 4\ OH^-$

(3) $2\ [Mn(CN)_6]^{4-} + H_2O_2 \rightarrow 2\ [Mn(CN)_6]^{3-} + 2\ OH^-$

(4) $3\ MnCl_2 + HNO_3 + 3\ H_3PO_4 \rightarrow 3\ MnPO_4\downarrow + NO + 6\ HCl + 2\ H_2O$

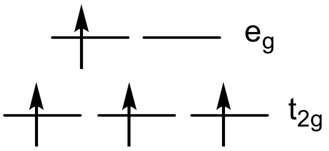
(5) $MnPO_4 + 6\ KCN \rightarrow K_3[Mn(CN)_6] + K_3PO_4$

17.6 Diagram – low-spin configuration d^4:

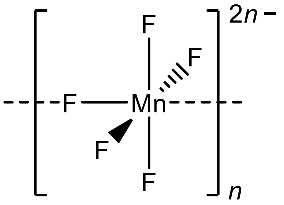


17.7 (6) $4\ MnO_2 + 12\ KHF_2 \rightarrow 4\ K_3[MnF_6] + O_2 + 6\ H_2O$

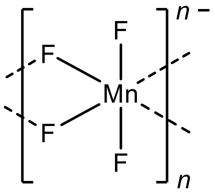
17.8 Diagram – high-spin configuration d^4:



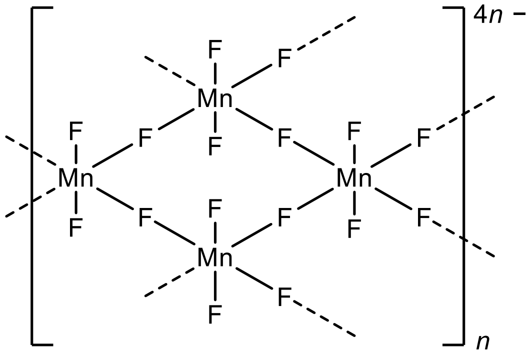
17.9 Sharing 1 bridging F atom between 2 neighbouring octahedral units corresponds to the stoichiometry $[MnF_5]^{2-}$:



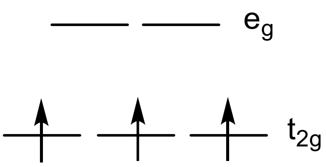
17.10 The stoichiometry $[MnF_4]^-$ could be achieved in a chain structure having 2 bridging F atoms between 2 neighbouring octahedral units:



However, the structure is a 2D-anionic layer, so it is necessary to extend the structure to 2 dimensions – to have 4 bridging F atoms for each octahedral unit:

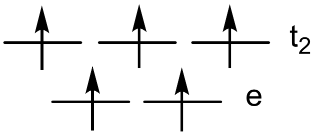


17.11 Diagram – configuration d^3:



17.12 Since the magnitude of splitting in tetrahedral crystal field is about a half of octahedral (exactly $\Delta_{tet} = -\frac{4}{9}\Delta_{oct}$; the negative sign refers to the inverse order of split d-orbitals with respect to the octahedral crystal field), it is always lower than electron pairing energy ($\Delta_{tet} < P$) which leads to high-spin configurations in tetrahedral complexes.

Diagram – high-spin configuration d^5:



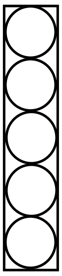
17.13 (7) $2\ KMnO_4 + 3\ H_2O_2 + 2\ KHF_2 + 8\ HF \rightarrow 2\ K_2[MnF_6] + 3\ O_2 + 8\ H_2O$

17.14 Manganese(IV) complexes have a configuration of d^3. Since these three electrons occupy the t_{2g} level only, low- and high-spin configurations cannot form regardless of the magnitude of the crystal field splitting.

17.15 (8) $K_2[MnF_6] + 2\ SbF_5 \rightarrow 2\ K[SbF_6] + MnF_2 + F_2$

Problem 18. The fox and the stork

Large stones



18.1 Each layer consists of one sphere only: $n = 50 / (2 \times 5) = 5$

18.2 The volume of 5 spheres: $V = 5 \times \frac{4}{3}\pi r^3 = 5 \times \frac{4}{3}\pi \times 5^3 = 2\,618\ \mathrm{cm}^3$

The volume of cylinder: $V = \pi r^2 \times v = \pi \times 5^2 \times 50 = 3\,927\ \mathrm{cm}^3$

The fraction of volume: $f = 2\,618 / 3\,927 = 0.667$, i.e. 66.7 %

18.3 The free volume: $V_{\text{free}} = 3\,927 - 2\,618 = 1\,309\ \mathrm{cm}^3$

Pebbles

18.4 Radius: $r = 10 / 6 = 1.667$ cm

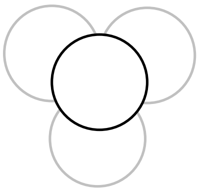
18.5 Number of layers: $N = 50 / (2 \times 1.667) = 15$

18.6 Number of spheres: $n = 15 \times 7 = 105$

18.7 The volume of 105 spheres: $V = 105 \times \frac{4}{3}\pi r^3 = 105 \times \frac{4}{3}\pi \times (1.667)^3 = 2\,036\ \mathrm{cm}^3$

The fraction of volume: $f = 2\,036 / 3\,927 = 0.518$, i.e. 51.8 %

18.8 The free volume: $V_{\text{free}} = 3\,927 - 2\,036 = 1\,891\ \mathrm{cm}^3$



18.9 The interlayer distance can be calculated as a height of a regular tetrahedron formed by 4 spheres with edge $a = 2 \times r$ (the formula can be simply derived from the Pythagorean theorem):

$$h = a \times \sqrt{\frac{2}{3}} = 2 \times 1.667 \times \sqrt{\frac{2}{3}} = 2.722\ \mathrm{cm}$$

The distance of the first and the last layer from the bases of the cylinder will be at minimum equal to r. Thus the maximum number of layers:

$N = (50 - 2 \times r) / h + 1 = (50 - 2 \times 1.667) / 2.722 + 1 = 18.14 \Rightarrow 18$ layers

18.10 The total number of spheres: each of the 9 odd layers contains 7 spheres, each of the 9 even layers contains 3 spheres, the total number is:

$n = 9 \times 7 + 9 \times 3 = 90$

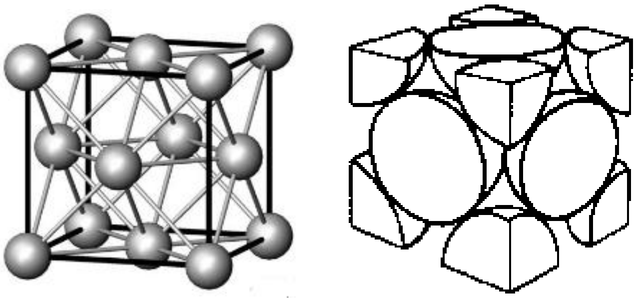
18.11 The volume of 90 spheres: $V = 90 \times \frac{4}{3}\pi r^3 = 90 \times \frac{4}{3}\pi \times (1.667)^3 = 1\,745\ \mathrm{cm}^3$

The fraction of volume: $f = 1\,745 / 3\,927 = 0.444$, i.e. 44.4 %

18.12 The free volume: $V_{\text{free}} = 3\,927 - 1\,745 = 2\,182\ \mathrm{cm}^3$

Sand

18.13 The situation corresponds to the theoretical maximum possible space filling by spheres known as "close-packing of equal spheres". The limiting fraction is $\frac{\pi}{3\sqrt{2}} = 0.7405$, i.e. 74.05 %. There are many ways to derive this ratio. The derivation from a face centered cubic (fcc) elementary cell is shown.



The lattice constant a is $2 \times r \times \sqrt{2}$. Then the volume of the elementary cell is:

$$V_{\mathrm{cell}} = a^3 = 16\sqrt{2} \times r^3$$

The number of spheres belonging to the elementary cell is:

$$n = 8 \times \frac{1}{8}\ (\text{spheres in vertices}) + 6 \times \frac{1}{2}\ (\text{speheres in the centers of faces}) = 4$$

Thus the fraction volume occupied by the spheres is:

$$V = 4 \times \frac{4}{3}\pi r^3 = \frac{16}{3}\pi r^3$$

$$f = \frac{(4 \times \frac{4}{3}\pi r^3)}{16\sqrt{2} \times r^3} = \frac{\pi}{3\sqrt{2}} = 0.7405,\ \text{i.e. } 74.05\%$$

18.14 The free volume: $V_{\mathrm{free}} = 3\,927 \times (1 - 0.7405) = 1\,019\ \mathrm{cm}^3$

Problem 19. Structures in the solid state

19.1 It is obvious from the picture that:

$a(\text{NaCl}) = 2 \times r(\text{Na}^+) + 2 \times r(\text{Cl}^-)$, and therefore:

$r(\text{Cl}^-) = \frac{1}{2} \times (5.64 - 2 \times 1.16)\ \text{Å} = 1.66\ \text{Å}$.

19.2 The density of KCl is:

$\rho(\text{KCl}) = m / V = [4 \times M(\text{KCl})] / [N_\text{A} \times a(\text{KCl})^3]$, and therefore:

$a(\text{KCl}) = \{[4 \times M(\text{KCl})] / [N_\text{A} \times \rho(\text{KCl})]\}^{1/3} = [(4 \times 74.55) / (6.022 \times 10^{23} \times 1.98)]^{1/3}\ \text{cm} =$

$= 6.30 \times 10^{-8}\ \text{cm} = 6.30\ \text{Å}$

$r(\text{K}^+) = \frac{1}{2} \times [a(\text{KCl}) - 2 \times r(\text{Cl}^-)]\ \text{Å} = \frac{1}{2} \times (6.30 - 2 \times 1.66)\ \text{Å} = 1.49\ \text{Å}$.

19.3 The ratio of ionic radii of Li^+ to Cl^- is:
$r(\text{Li}^+) / r(\text{Cl}^-) = 0.90 / 1.66 = 0.54$. It is higher than the relative size of the octahedral cavity (0.41), which is a critical value for an ion to occupy this cavity. Thus, occupying this cavity by Li^+ ion will result in a stable arrangement and LiCl should crystallize in the NaCl type of structure.

(Taking into account the smaller size of Li^+ compared to Na^+, it is not necessary to consider the upper limit of an ion size for a stable arrangement. However, for completeness, one can assume that the relative size of a cation with respect to an anion higher than 0.73 should lead to the change of the coordination sphere and enforce a cubic coordination environment and the structure type of CsCl. In fact, the ratio for KCl is somewhat above this limiting value, but KCl still adopts the structural type of NaCl as stated above.)

19.4 $\rho(\text{PbS}) = m / V = [4 \times M(\text{PbS})] / [N_\text{A} \times a(\text{PbS})^3] = (4 \times 239.3) / (6.022 \times 10^{23} \times 5.94^3)\ \text{g Å}^{-3} =$
$= 7.58\ \text{g cm}^{-3}$

19.5 Due to total electro-neutrality, one can derive:

$2(1 - x) + 1x = 2y$, and thus:

$y = 1 - \frac{1}{2}x$

A general formula of silver-containing galena is thus $\text{Pb}_{1-x}\text{Ag}_x\text{S}_{1-\frac{1}{2}x}$.

19.6 $\rho(\text{Pb}_{1-x}\text{Ag}_x\text{S}_{1-\frac{1}{2}x}) = m / V = [4 \times M(\text{Pb}_{1-x}\text{Ag}_x\text{S}_{1-\frac{1}{2}x})] / [N_\text{A} \times a(\text{Pb}_{1-x}\text{Ag}_x\text{S}_{1-\frac{1}{2}x})^3]$, and therefore:

$M(\text{Pb}_{1-x}\text{Ag}_x\text{S}_{1-\frac{1}{2}x}) = \rho(\text{Pb}_{1-x}\text{Ag}_x\text{S}_{1-\frac{1}{2}x}) \times N_\text{A} \times a(\text{Pb}_{1-x}\text{Ag}_x\text{S}_{1-\frac{1}{2}x})^3 / 4 =$

$= [7.21 \times 6.022 \times 10^{23} \times (5.88 \times 10^{-8})^3] / 4\ \text{g mol}^{-1} = 220.7\ \text{g mol}^{-1}$, and thus:

$207.2(1 - x) + 107.9x + 32.1(1 - \frac{1}{2}x) = 220.7$, and $x = 0.16$

19.7 Four.

19.8 According to the crystal structure type, the bond distance of Ge–Ge corresponds to one fourth of the body diagonal of the unit cell and, thus, atomic radius is equal to one eighth of the body diagonal. Thus, the lattice parameter $a(\text{Ge})$ is:

$a(\text{Ge}) = 8 \times r(\text{Ge}) / \sqrt{3} = 8 \times 1.23 / \sqrt{3}\ \text{Å} = 5.68\ \text{Å}$, giving the density:

$\rho(\text{Ge}) = m / V = [8 \times M(\text{Ge})] / [N_A \times a(\text{Ge})^3] = (8 \times 72.6) / (6.022 \times 10^{23} \times 5.68^3)$ g Å^{-3} = 5.26 g cm^{-3}

(Alternatively, substituting the a(Ge) by the term 8 × r(Ge) / √3 in the latter equation gives the following formula:

$\rho(\text{Ge}) = m / V = [3\sqrt{3} \times M(\text{Ge})] / [64 \times N_A \times r(\text{Ge})^3]$ = 5.26 g cm^{-3}

without the need to calculate the lattice parameter. However, the similarity of the lattice constant of Ge with that of the isoelectronic GaAs [a(GaAs) = 5.65 Å] is emphasized by the previous approach.)

19.9 According to the crystal structure type, the bond distance of Ga–As (and Ga–P) corresponds to one fourth of the body diagonal of the unit cell. Thus:

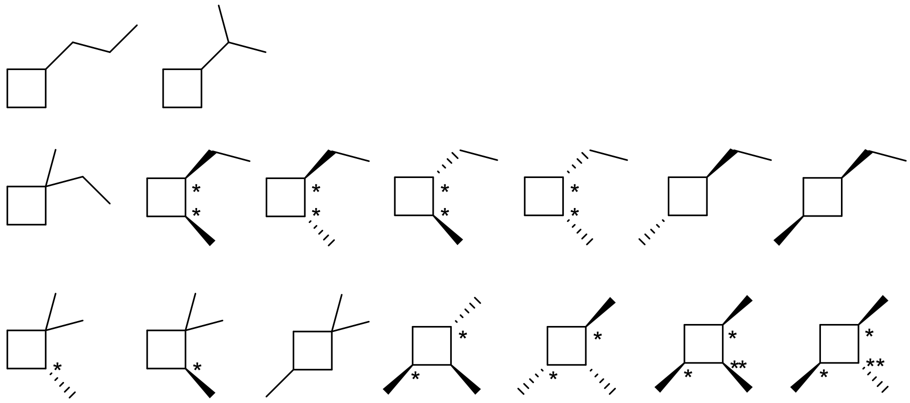
d(Ga–As) = (5.65 × √3) / 4 Å = 2.45 Å

d(Ga–P) = (5.45 × √3) / 4 Å = 2.36 Å

The radius of phosphorus in these types of compounds is 0.09 Å smaller than the radius of arsenic.

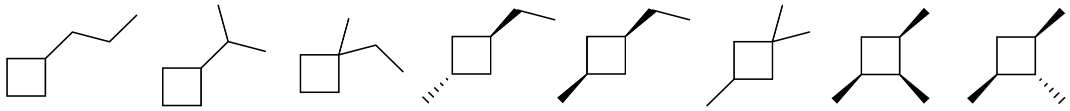
Problem 20. Cyclobutanes

20.1 and 20.2



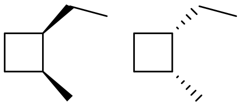
Note that the two carbon atoms marked with a double asterisk (**) are pseudo-asymmetric. They have two constitutionally identical ligands which differ in configuration.

20.3

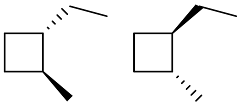


20.4

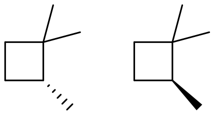
A)



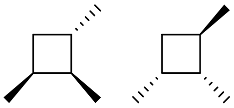
B)



C)



D)



Problem 21. Fluorinated radiotracers

21.1 ^{18}O (18-fluorine is synthesized by the following reaction: $^{18}O + p \rightarrow {}^{18}F + n$)

21.2 $\tau_{1/2}$ (^{18}F) = 6 586 s

$k = \ln 2 / (6\,586\ \mathrm{s}) = 1.052 \times 10^{-4}\ \mathrm{s}^{-1}$

$n = N / N_A = 300\ \mathrm{MBq} / (1.052 \times 10^{-4}\ \mathrm{s}^{-1} \times 6.022 \times 10^{23}\ \mathrm{mol}^{-1}) = 4.73 \times 10^{-12}\ \mathrm{mol}$

21.3 Heat of combustion of glucose = 2 800 kJ mol^{-1}

Chemical energy of one glucose molecule: $E_c = 2\,800\ \mathrm{kJ} / N_A = 4.650 \times 10^{-18}\ \mathrm{J}$

Energy of γ-photons per one glucose molecule: $E_p = 2 \times m_e \times c^2 = 1.637 \times 10^{-13}\ \mathrm{J}$

Calculation of time:

Total chemical energy of ^{18}O-glucose = Total energy of not yet released γ-photons

$E_c \times N(\mathrm{glucose}) = E_p \times N(^{18}F)$

$E_c \times [N_0(^{18}F) - N(^{18}F)] = E_p \times N(^{18}F)$

$E_c \times N_0(^{18}F) \times (1 - e^{-kt}) = E_p \times N_0(^{18}F) \times e^{-kt}$

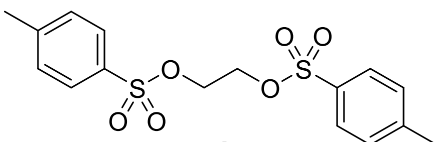
$E_c = E_p \times e^{-kt} + E_c \times e^{-kt}$

$E_c / (E_c + E_p) = e^{-kt}$

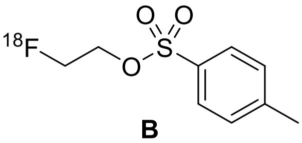
$\ln [E_c / (E_c + E_p)] = - k \times t$

$t = \ln [(E_c + E_p) / E_c] \times (1 / k) = \ln (35\,213) / (1.052 \times 10^{-4}\ \mathrm{s}^{-1}) = 9.95 \times 10^{4}\ \mathrm{s} = 27\ \mathrm{h}\ 38\ \mathrm{min}$

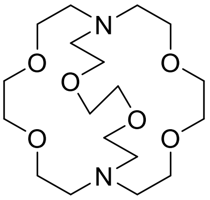
21.4 See structures below. **X** can be any K$^+$ chelator (e.g. 18-crown-6 ether), not only [2.2.2]cryptand shown below.



A

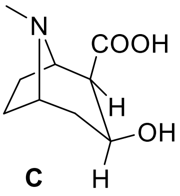


B

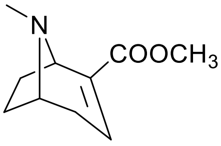


X = [2.2.2]cryptand

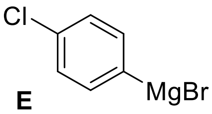
21.5



C

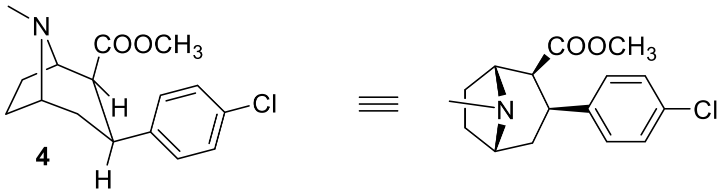


D

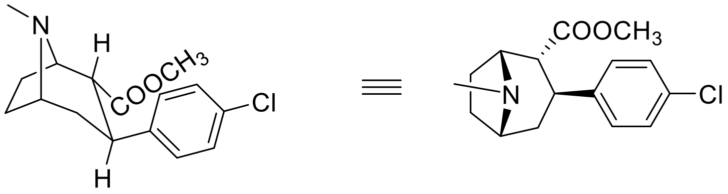


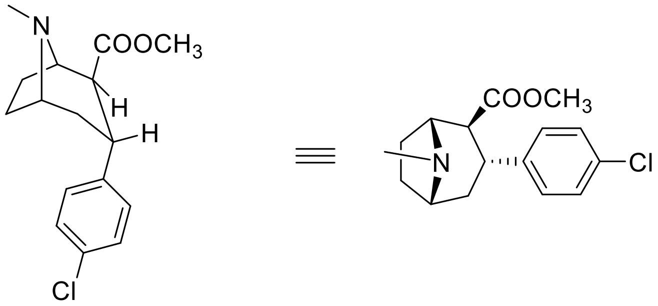
E

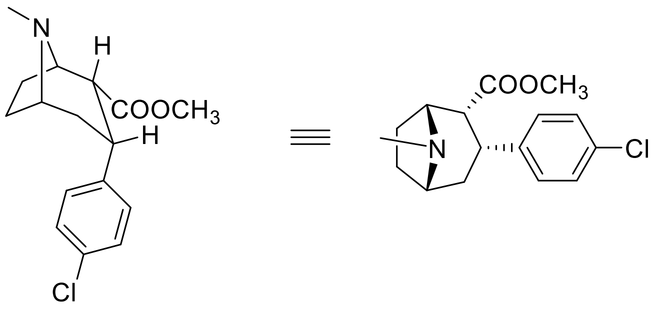
21.6


4

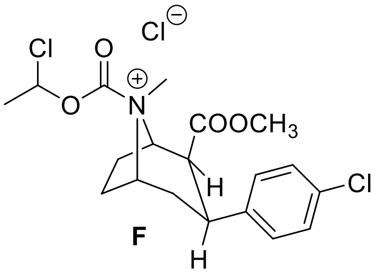
The other possible isomers are:

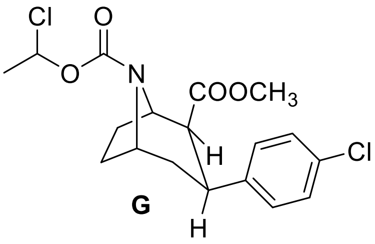






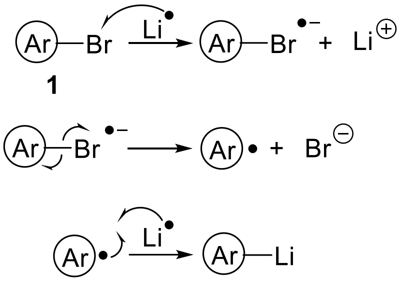
21.7


F

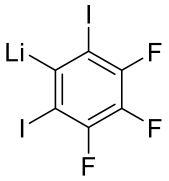

G

Problem 22. Where is lithium?

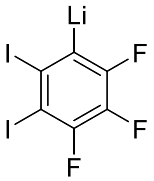
22.1 The formation of organolithium reagents involves a radical pathway.



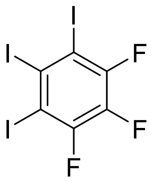
22.2 The structures of intermediates **A**, **B**, **C**, and **D**:



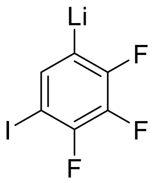
A



B

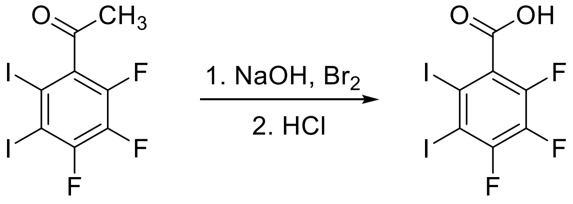


C



D

22.3 Reaction scheme for the haloform reaction:

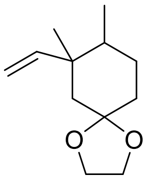


E **5**

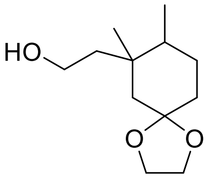
Other reagents, such as NaOH + I_2 or NaClO can also be used.

Problem 23. Synthesis of eremophilone

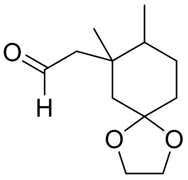
23.1



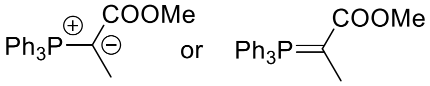
A



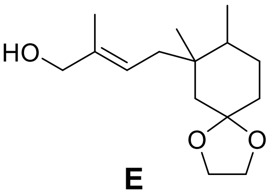
B



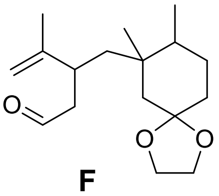
C



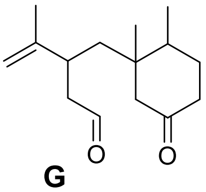
D



E



F

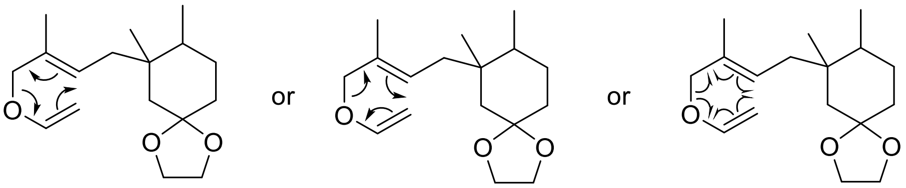


G

NaOH or NaOMe;
other bases used
for aldolization are
also acceptable

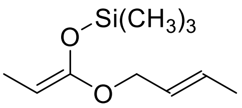
H

23.2 This reaction is called the Claisen rearrangement.

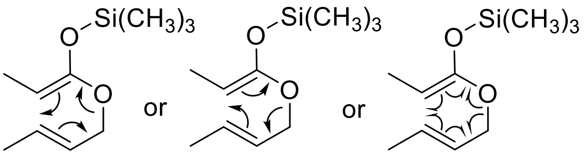


I

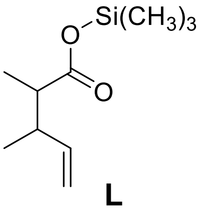
23.3



J



K

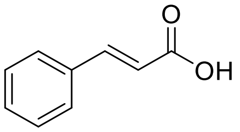


L

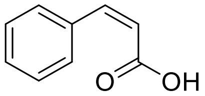
Problem 24. Cinnamon all around

24.1

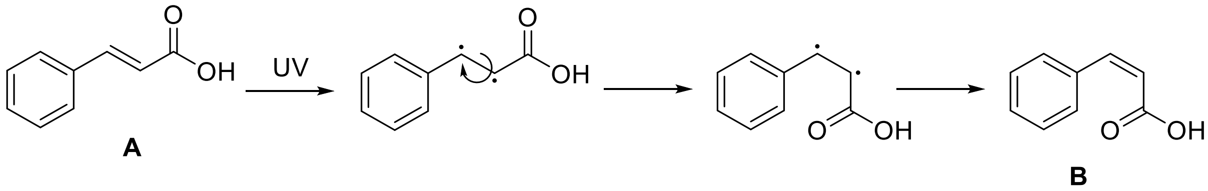
A



B

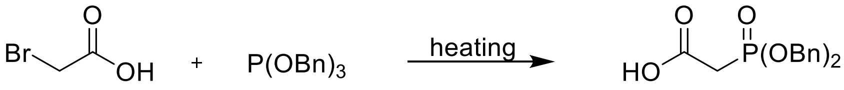


24.2 Direct UV irradiation (313 nm, acetonitrile). A conformationally mobile biradical is formed. Under these conditions, **B** and **A** are obtained in a 79 : 21 ratio.



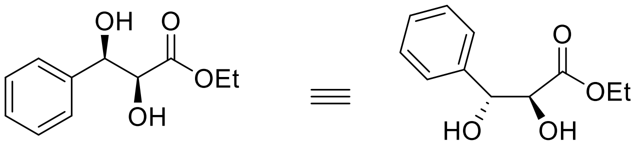
Alternatively, UV irradiation with sensitizers (e.g. riboflavin), or reagents such as diphenyldiselenide, hydrogen peroxide etc. can be used.

24.3 Arbuzov reaction with 2-bromoacetic acid and tribenzyl phosphite:

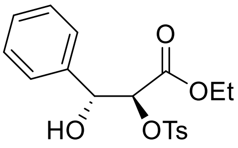


24.4

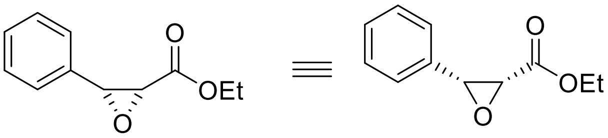
C



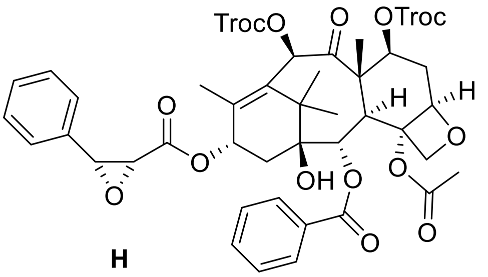
D



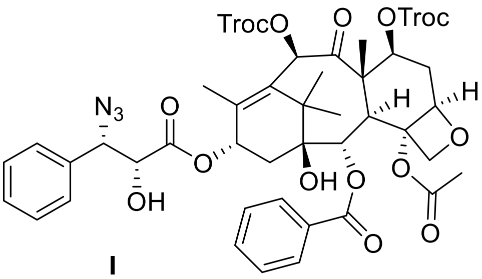
E



24.5

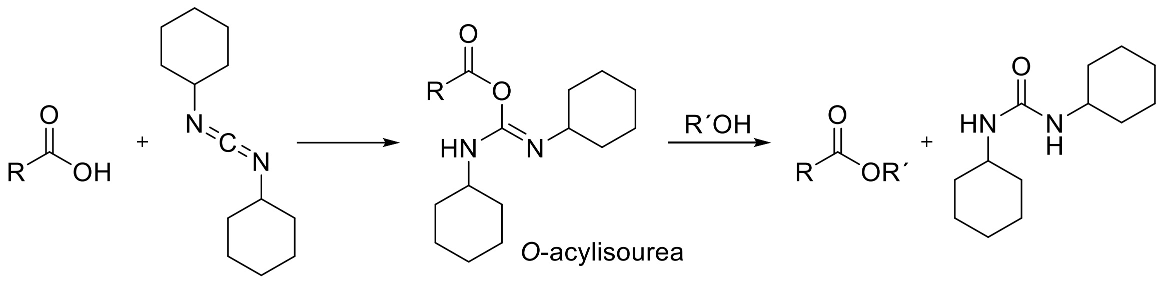


H



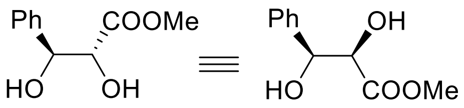
I

24.6 The carboxylic acid functional group reacts with DCC to form an *O*-acylisourea, which serves as the reactive intermediate in reactions with nucleophiles (e.g. alcohols or amines) in acyl nucleophilic substitutions.



24.7 The starting compound is (*E*)-cinnamic acid methyl ester.

24.8



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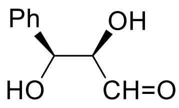

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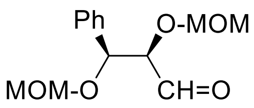
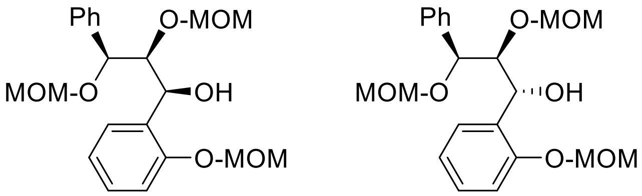
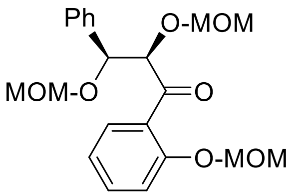


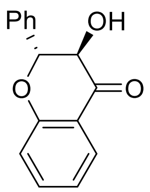
P



Q + **R**



S

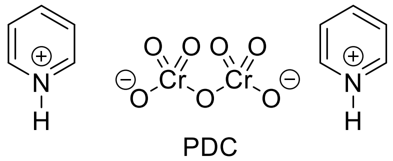


L

24.9 The two isomers **Q** and **R** are diastereoisomers (diastereomers).

24.10 The acidic hydrogens of the OH groups would decompose the organolithium compound.

24.11

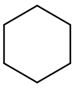


PDC
pyridinium dichromate

24.12 The reaction is named after Prof. Mitsunobu.

Problem 25. All roads lead to caprolactam

25.1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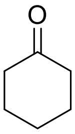
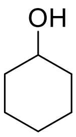
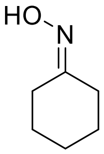
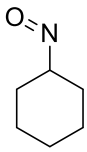
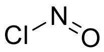
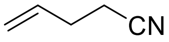

B

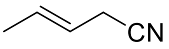

B'

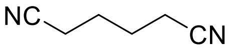

C

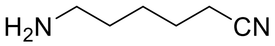

D


E


F


F'


G


H

25.2 d)

25.3

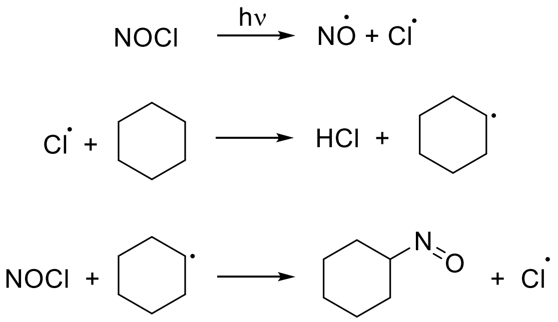
$$HNO_3 + 3\ HCl \longrightarrow NOCl + 2\ H_2O + Cl_2$$

$$HNO_2 + HCl \longrightarrow H_2O + NOCl$$

$$NO_2^- + 2\ HCl \longrightarrow H_2O + NOCl + Cl^-$$

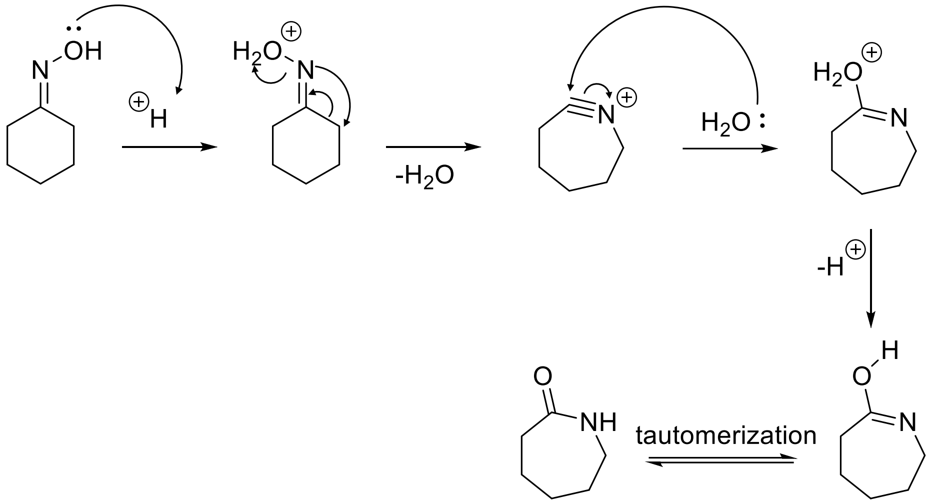
$$2\ NO + Cl_2 \longrightarrow 2\ NOCl$$

25.4



25.5 Gas **E** (NOCl) is orange. Therefore, the optimal wavelength would be below 530 nm (green and blue light).

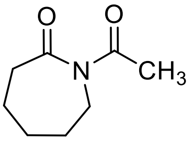
25.6 Beckmann rearrangement.



-H2O
H2O
-H⊕
tautomerization

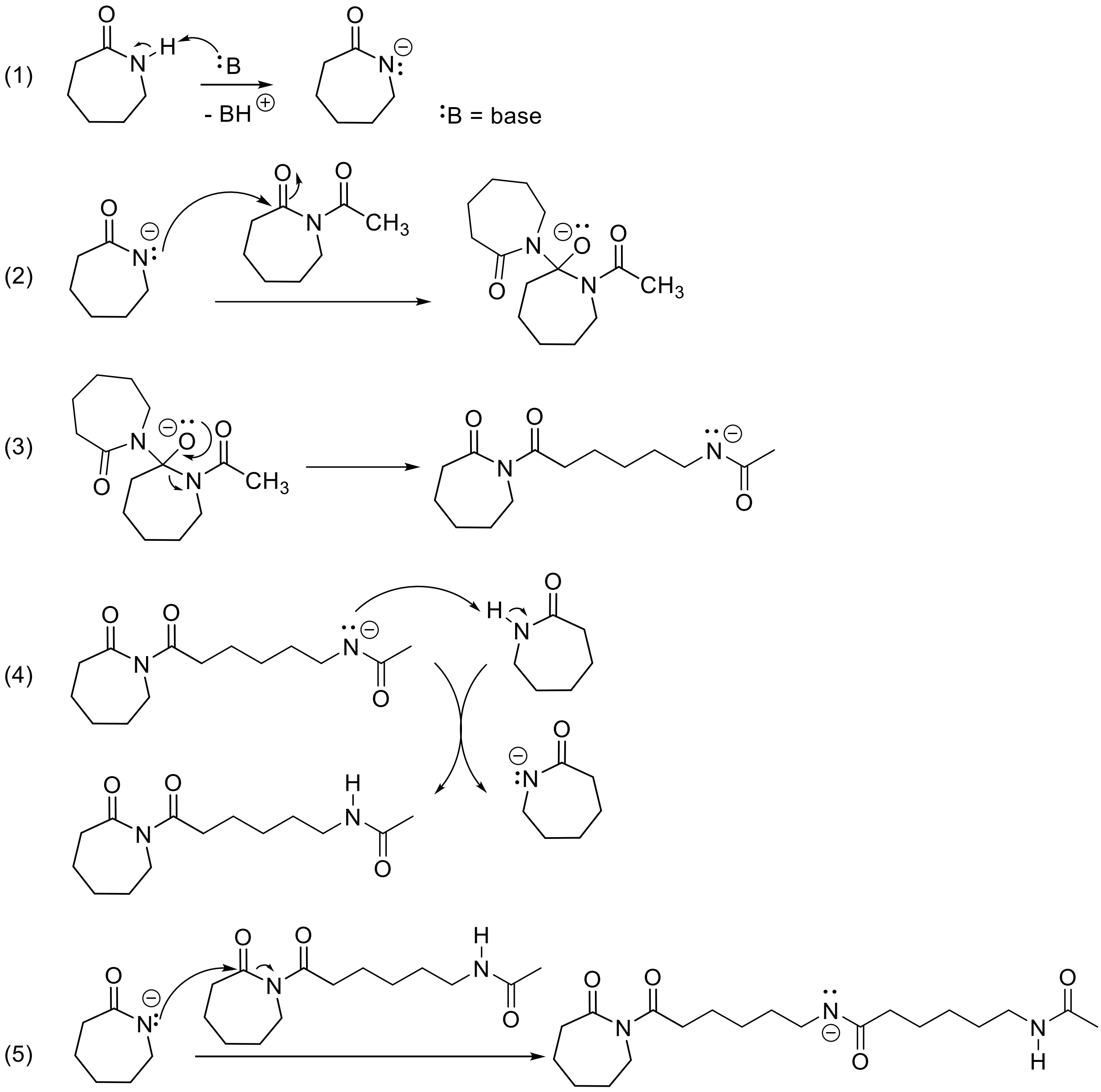
Problem 26. Ring opening polymerizations (ROP)

26.1

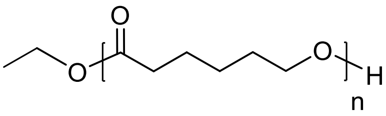


B

26.2

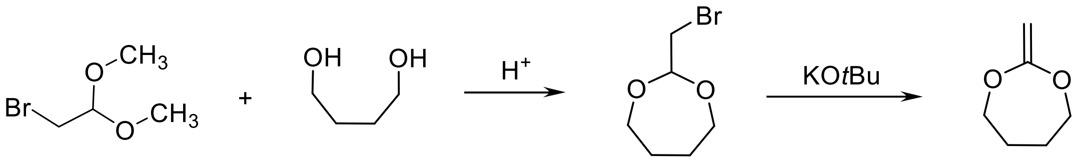


26.3

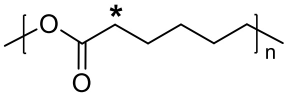


26.4 Ten grams of sodium ethoxide correspond to 10 / (2 × 12 + 5 × 1 + 1 × 16 + 1 × 23) = 0.1471 mol. Two kilograms consumed with 83% conversion means 2 000 × 0.83 = 1 660 g embedded into polymer. Each molecule of the initiator initiates one chain, so the number-average molecular weight is 1 660 / 0.1471 = 11 288 g mol^{-1}. After rounding to two digits, we get the number-average molecular weight of 11 000 g mol^{-1}.

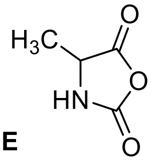
26.5



26.6



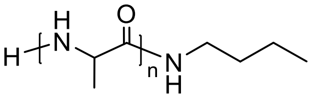
26.7



E

26.8

CO_2 (g)



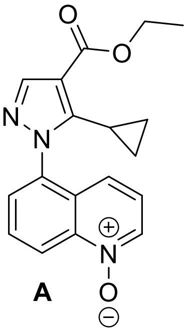
26.9 A single wrong enantiomer of an amino acid in the protein structure causes loss of activity. Glycine is not chiral, so there are 129 − 12 = 117 chiral amino acids in lysozyme. The overall yield is $(1/2)^{117} \times 100\% = 6.02 \times 10^{-34}$ %.

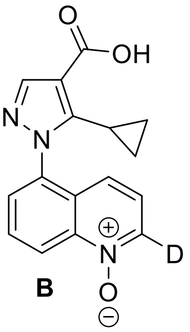
Theoretically, in the "world behind the mirror" the all-D-protein would be active against the all-chiral reversed proteoglycan. However, this does not meet the condition that only the enzyme digesting native peptidoglycan is considered functional.

26.10 The amount of enzyme (120 mg = 0.000 12 kg) obtained with 6.02×10^{-34} % yield (see the the answer in 26.9) would require the production of $0.00012 / ((1/2)^{117}) = 1.99 \times 10^{31}$ kg of material. As the Earth weighs 5.972×10^{24} kg, this corresponds to $1.99 \times 10^{31} / 5.972 \times 10^{24} =$ $= 3.34 \times 10^{6}$ times the mass of the Earth.

Problem 27. Zoniporide

27.1


A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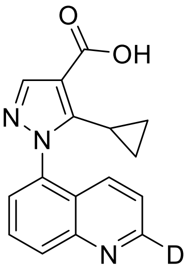
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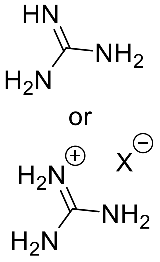
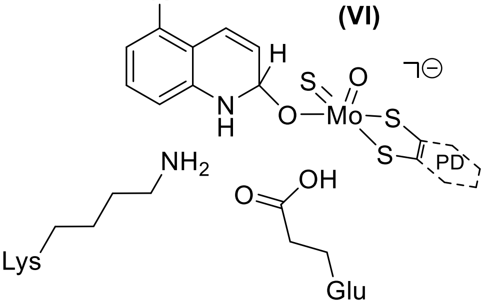

D

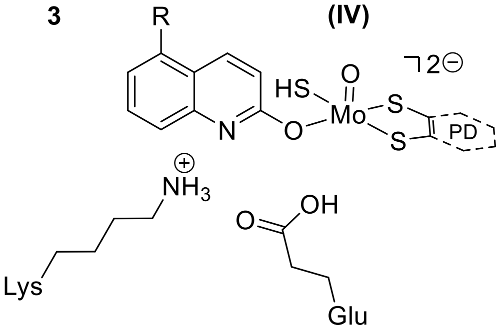
27.2 Ammonia (NH_3), carbon dioxide (CO_2) and hydrogen (H_2)

27.3 and 27.4

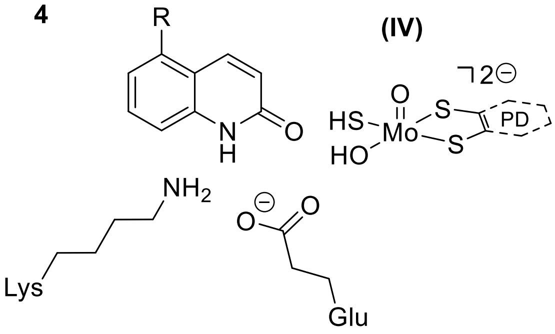
E



3

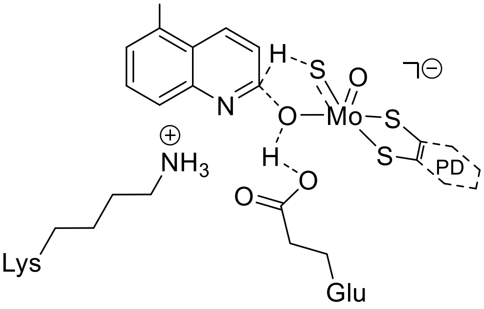


4

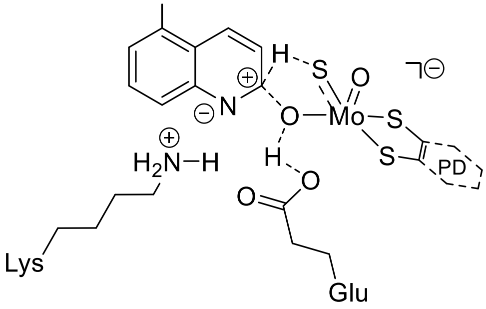


27.5

F



or



27.6 **Mechanism 2**

From a) the KIE is >> 1 which indicates that the C^2–H bond is being cleaved during the rate determining step (RDS). For **Mechanism 1** the RDS would have to be **E** → **3**, for **Mechanism 2** the RDS would be the concerted **2** → **3** transformation.

From b) we know that electron withdrawing groups (EWGs) on the heterocyclic core speed up the reaction. This indicates that the RDS involves either buildup of negative charge on the quinoline ring (e.g. by a nucleophilic attack) or loss of positive charge from the ring (e.g. by deprotonation). In **Mechanism 1**, this is true for the **2** → **E** step (an electron rich nucleophile adds to the quinoline core) but not for the **E** → **3** step (expulsion of a hydride nucleophuge is disfavoured in the presence of EWGs). This contradiction disproves **Mechanism 1**; therefore, the correct answer is **Mechanism 2**.

27.7 Hydrogen peroxide (H_2O_2)

27.8

$$\frac{k_\mathrm{H}}{k_\mathrm{D}} = \exp\left(\frac{E_{0,\mathrm{H}} - E_{0,\mathrm{D}}}{k_B T}\right)$$

$$E_{0,\mathrm{H}} - E_{0,\mathrm{D}} = \frac{1}{2}\hbar(\omega_\mathrm{H} - \omega_\mathrm{D})$$

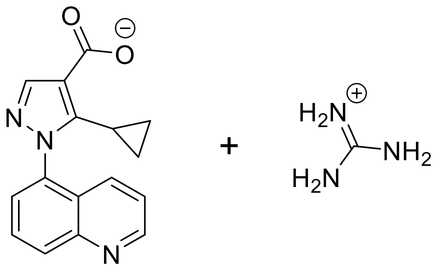
$$\omega_{\mathrm{H/D}} = \sqrt{\frac{k}{\mu_{\mathrm{H/D}}}}$$

$$\mu_{\mathrm{H/D/T}} = \frac{m_{\mathrm{H/D/T}}\, m_{^{12}\mathrm{C}}}{m_{\mathrm{H/D/T}} + m_{^{12}\mathrm{C}}}$$

$$\sqrt{k} = \frac{2k_B T\, \ln\left(\frac{k_\mathrm{H}}{k_\mathrm{D}}\right)}{\hbar\left(\frac{1}{\sqrt{\mu_\mathrm{H}}} - \frac{1}{\sqrt{\mu_\mathrm{D}}}\right)} = 21.105\ \mathrm{kg}^{\frac{1}{2}}\,\mathrm{s}^{-1} \Rightarrow k = 445.4\ \mathrm{kg\,s}^{-2}$$

$$\frac{k_\mathrm{H}}{k_\mathrm{T}} = \exp\left(\frac{\hbar\sqrt{k}}{2k_B T}\left(\frac{1}{\sqrt{\mu_\mathrm{H}}} - \frac{1}{\sqrt{\mu_\mathrm{T}}}\right)\right) = 12.2(59)$$

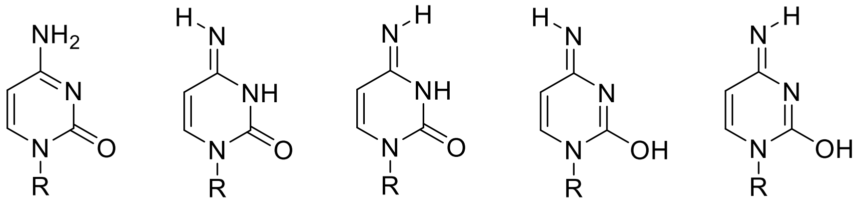
27.9



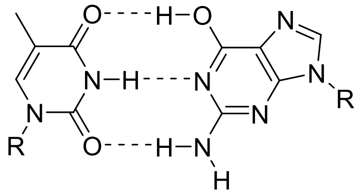
(or their conjugate base/acid)

Problem 28. Nucleic acids

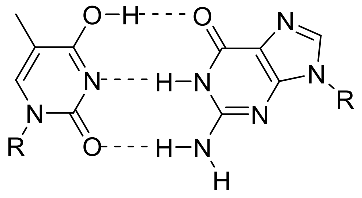
28.1



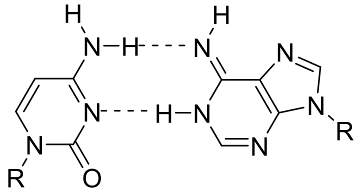
28.2



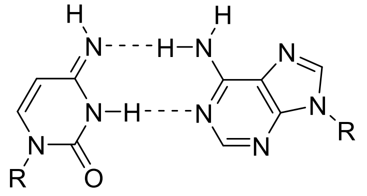
T−G* pair



T*−G pair



C−A* pair



C*−A pair

28.3

Unknown sample (**1**) transmittance: $T_1 = 0.11$

Known sample (**2**) transmittance: $T_2 = 1 - 0.57 = 0.43$

Using Lambert–Beer law: $-\log_{10} T = \varepsilon\, l\, c$

$(-\log_{10} T_2) / c_2 = (-\log_{10} T_1) / c_1$

$c_1 = c_2 \times (-\log_{10} T_1) / (-\log_{10} T_2) = 27\ [\mu\text{mol dm}^{-3}]\ (-\log_{10} 0.11) / (-\log_{10} 0.43) = 70.6\ \mu\text{mol dm}^{-3}$

28.4

a) **True.** According to the Lambert–Beer law, absorbance is directly proportional to concentration (as long as the cuvette length and the molar absorption coefficients are assumed equal). The higher absorbance of DNA1 actually means that the concentration of dsDNA1, which absorbs less radiation than ssDNA1, is lower.

b) **False.** Thermodynamic stability is described in terms of T_m, which can be read as the inflexion point of the sigmoidal curve; here T_m(DNA1) ~ 315 K and T_m(DNA2) ~ 340 K.

c) **False.** Since T_m(DNA1) ~ 315 K and T_m(DNA2) ~ 340 K, dsDNA2 is more stable than dsDNA1 with respect to their single-stranded forms.

d) **Cannot be answered.** The thermodynamic stability of a DNA double helix depends on both its length (i.e. the number of nucleobase pairs) and its sequence (roughly, the content of G–C nucleobase pairs). Since no information about the G–C pairs content is given, no conclusions about the DNA lengths can be drawn.

28.5 cDNA: 5′-ACCTGGGG-3′, mRNA: 5′-CCCCAGGU-3′

28.6 Each position of the 8-nucleobase sequence can be occupied by one of the four nucleobases (A, C, G, U). Hence, there are $4^8 = 65\,536$ theoretically possible single-stranded octanucleotides.

19th – 29th July 2018
Bratislava, SLOVAKIA
Prague, CZECH REPUBLIC

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SOLUTIONS AND SUPPLEMENTARY INFORMATION

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International Chemistry Olympiad
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BACK TO WHERE IT ALL BEGAN

UPDATED 1ST JUNE 2018

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Problem P1. Determination of a metallic ore composition

Provide an aqueous sample containing only Zn^{2+} and Cu^{2+} nitrates in a mass ratio of about 1:1; the total concentration of the metals in the solution should be about 35 g dm^{-3}.

I. Determination of the metal ion concentration by alkalimetry and photometry

P1.1 a) Cation exchange between the sample solution and the resin:

$$M^{2+} + 2\,\{R\text{-}H\}(s) \rightarrow \{M(R)_2\}(s) + 2\,H^+$$

b) Indication of the titration endpoint:

$$HInd\ (red) + OH^- \rightarrow Ind^-\ (yellow) + H_2O$$

P1.2 The column must be washed to neutral pH due to the possible presence of acidic solution in the internal space of the resin. The solution with $pH < 7$ which remains in the gel, microporous or porous resin, increases the amount of the “released” H^+ ions after the sample ion exchange.

P1.3 A tetraammine complex of Cu^{2+} is formed after adding ammonia. Copper ammine complexes are intensively blue coloured and thus are suitable for the spectrophotometric determination of copper.

P1.4 The concentrations of Cu^{2+} were selected to obtain the absorbance in the range <0.1; 1.0>, optimal for the accuracy of the spectrophotometric experiment. Additionally, linear range of Lambert–Beer law is used for the spectrophotometric determination.

P1.5 ***Acid–base titration***

Total amount of cations bound to the resin:
$n = n(Cu^{2+}) + n(Zn^{2+})$

Total amount of released H^+ ions:
$n(H^+) = 2 \times n$

Total amount of OH^- ions determined by alkalimetric titration (abbreviation “at”):
$n(OH^-) = c(NaOH) \times V_{2at} = n_{at}(H^+)$

Total amount of M^{2+} cations determined by the alkalimetric titration:
$n_{at} = n_{at}(H^+) / 2 = n(OH^-) / 2 = c(NaOH) \times V(NaOH) / 2$

Total amount of determined cations bound to the resin, volume V, step I.3:
$n = n_{at} \times V_{el} / V_{1at}$

Spectrophotometric analysis

Concentration of Cu^{2+} ions, c_x:
$c_x = A_x \times (c_{max} - c_{min}) / (A_{max} - A_{min})$

Concentration of Cu^{2+} ions in the original sample:
$c(Cu^{2+}) = c_x \times (V_{sp} / V_{pip}) \times (V_{dil} / V_{orig})$

Concentration of Zn^{2+} ions in the original sample:
$c(Zn^{2+}) = n / V - c(Cu^{2+})$

II. Ion exchange separation and complexometric titration

P1.6 Reactions which occur in the ion exchange (release of the Cu^{2+} and Zn^{2+} ions):

$$\{(R)_2Cu\}(s) + 2\ C_2O_4^{2-} + 2\ H_2O \rightarrow 2\ \{R\text{-}H\}(s) + [Cu(C_2O_4)_2]^{2-} + 2\ OH^-$$

$$\{(R)_2Zn\}(s) + 2\ H^+ \rightarrow 2\ \{R\text{-}H\}(s) + Zn^{2+}$$

P1.7 Copper oxalate is decomposed by hydrogen peroxide and the released Cu^{2+} ions are determined by complexometric titration with the standard EDTA solution.

P1.8 For both eluates, it is a simple direct titration (reaction stoichiometry ratio for titrant and titrand 1 : 1).

Problem P2. Determination of a carbonate rock composition

Provide a powdered sample prepared by mixing carbonates, so that the sample composition corresponds to the typical values for a dolomite rock. The typical values are (in %, w/w): dolomite 65–75%, calcite 6–10%, ankerite 5–8%, other compounds 10–20% (use sodium bicarbonate).

P2.1 The following calculation is performed for a pure dolomite sample weighing $m_0 = 0.7654$ g. Dolomite (abbreviation "dol"), $CaMg(CO_3)_2$

$n_0 = m_0 / M(\text{dol}) = 0.7654 \text{ g} / 184.41 \text{ g mol}^{-1} = 4.151 \times 10^{-3} \text{ mol}$

$$CaMg(CO_3)_2 + 4\ HCl \rightarrow CaCl_2 + MgCl_2 + 2\ H_2O + 2\ CO_2$$

$n(HCl) = 4 \times n_0 = 1.660 \times 10^{-2} \text{ mol}$

$V(HCl) = n(HCl) / c(HCl) = 0.01660 \text{ mol} / 3 \text{ mol dm}^{-3} = 5.53 \times 10^{-3} \text{ dm}^3$

10% excess of the calculated volume of the HCl solution used for the quantitative decomposition of the sample: $1.1 \times 5.53 \times 10^{-3} \text{ dm}^3 = 6.08 \times 10^{-3} \text{ dm}^3$

P2.2 The pH will be estimated from the content of a strong acid. The rest of the compounds are weak acids, the influence of which is suppressed by the presence of the strong acid. The excess volume of 3 M HCl is $(6.08 - 5.53) \text{ cm}^3 = 0.55 \text{ cm}^3$, which is diluted to 250 cm^3:

$[H^+] = c(HCl) \times V(HCl) / V_0 = 3 \text{ mol dm}^{-3} \times 0.55 \text{ cm}^3 / 250 \text{ cm}^3 = 0.007 \text{ mol dm}^{-3}$

$pH = -\log[H^+] = 2.2$

P2.3 Boiling the reaction mixture in step 1 removes dissolved carbon dioxide.

P2.4 In step 2, iron is oxidized to Fe^{3+} and the excess of peroxide is removed as it would oxidize the indicators.

P2.5 Iron oxidized to Fe^{3+} is separated by precipitation as a hydroxide.

P2.6 The reaction of EDTA with metal ions has the stoichiometry 1 : 1 in each case. (Abbreviations: "ank" = ankerite; "dol" = dolomite; "cal" = calcite, "admix" = inert impurities)

Content of ankerite in % (w/w), from step 3

$n(Fe) / n(EDTA) = 1/1$

Ankerite is the only source of iron and contains one iron atom per molecule.

$n(\text{ank}) = n(Fe) = V_2 \times c(EDTA) \times V_0 / V_1$

$m(\text{ank}) = n(\text{ank}) \times M(\text{ank});\ \ M(\text{ank}) = 215.95 \text{ g mol}^{-1}$

$w(\text{ank}) = m(\text{ank}) / m_0$

Content of dolomite in % (w/w), from steps 5 and 6

$n(Me^{2+}) / n(EDTA) = 1/1$

$n(Ca+Mg)$ is determined in step 5, $n(Ca)$ is determined in step 6

$n(Mg)$ is determined as the difference from steps 5 and step 6

Dolomite is the only source of magnesium and contains one magnesium atom per molecule.

$n(\text{dol}) = n(Mg) = n(Ca+Mg) - n(Ca)$

$n(\text{dol}) = V_6 \times c(\text{EDTA}) \times (V_0 / V_3) \times (V_4 / V_5) - V_8 \times c(\text{EDTA}) \times (V_0 / V_3) \times (V_4 / V_7)$

$m(\text{dol}) = n(\text{dol}) \times M(\text{dol})$; $M(\text{dol}) = 184.41\ \text{g mol}^{-1}$

$w(\text{dol}) = m(\text{dol}) / m_0$

Content of calcite in % (w/w), from step 6

Calcium is present in all three compounds. All the compounds contain one calcium atom per molecule.

The total amount of calcium is determined in step 6:

$n(\text{Ca}) = n(\text{dol}) + n(\text{ank}) + n(\text{cal}) = V_8 \times c(\text{EDTA}) \times (V_0 / V_3) \times (V_4 / V_7)$

$n(\text{cal}) = V_8 \times c(\text{EDTA}) \times (V_0 / V_3) \times (V_4 / V_7) - n(\text{dol}) - n(\text{ank})$

$m(\text{cal}) = n(\text{cal}) \times M(\text{cal})$; $M(\text{cal}) = 100.09\ \text{g mol}^{-1}$

$w(\text{cal}) = m(\text{cal}) / m_0$

Content of inert impurities in % (w/w)

$w(\text{total}) = w(\text{ank}) + w(\text{dol}) + w(\text{cal})$

$w(\text{admix}) = 1 - w(\text{total})$

Problem P3. Determination and identification of organic acids

I. Determination of sodium thiosulfate concentration in solution

P3.1 $I_2 + 2\ S_2O_3^{2-} \rightarrow 2\ I^- + S_4O_6^{2-}$

P3.2 $c(S_2O_3^{2-}) = n(S_2O_3^{2-}) / V_2$

$n(S_2O_3^{2-}) / n(I_2) = 2/1$

$n(S_2O_3^{2-}) = 2 \times n(I_2) = 2 \times c(I_2) \times V_1$

$c(S_2O_3^{2-}) = 2 \times c(I_2) \times V_1 / V_2$

II. Identification of an unknown acid in sample solutions A and B and determination of its concentration

P3.4 Table of the titration results (the data serve as an example only).

Procedure a	Volume of sample solution **A** or **B** added to the titration flask	V_{11} = 20.00 cm^3
	Volumes read from burette (perform only the necessary analyses)	
	Sample **A**	V_{3a} = 21.00 cm^3 V_{3b} = 21.00 cm^3 *Note/Observation: fast reaction = sharp and stable end point of titration*
	Sample **B**	V_{4a} = 18.00 cm^3 V_{4b} = 20.00 cm^3 *Note/observation: slow reaction = after the first colour change, the solution resumes its original colour*
	Accepted volumes	V_3 = 21.00 cm^3 V_4 = –
Procedure b	Volume of sample solution **A** or **B** added to the titration flask	V_{12} = 20.00 cm^3
	Volumes read from burette (perform only the necessary analyses)	
	Sample **A**	V_{5a} = – V_{5b} = *Note/Observation: the experiment was omitted based on the results in procedure **a***
	Sample **B**	V_{6a} = 22.00 cm^3 V_{6b} = 22.00 cm^3 *Note/Observation: fast reaction = sharp and stable end point of titration*
	Accepted volumes	V_5 = 21.00 cm^3 *(from procedure **a**)* V_6 = 22.00 cm^3
Procedure c	Volume of sample solution **A** or **B** added to the titration flask	V_{13} = 20.00 cm^3
	Volumes read from burette (perform only the necessary analyses)	
	Sample **A**	V_{7a} = – V_{7b} = – *Note/Observation: Not measured, it is a strong acid, as proved in procedure **a***
	Sample **B**	V_{8a} = 17.00 cm^3 V_{8b} = 17.00 cm^3 *Note/Observation: This measurement is necessary as according to the results in procedures **a** and **b** the acid is neither strong nor a hydroxy derivative*

<table>
<tr><td></td><td>Accepted volumes</td><td colspan="2">V_7 = –</td><td>V_8 = 17.00 cm^3</td></tr>
<tr><td colspan="5">Indicate with a ✓ the identified component in sample A</td></tr>
<tr><td colspan="2">HCl✓</td><td colspan="2">CH_3COOH</td><td>$(R(OH)_x(COOH)_y)$</td></tr>
<tr><td colspan="5">Indicate with a ✓ the identified component in sample B</td></tr>
<tr><td colspan="2">HCl</td><td colspan="2">CH_3COOH ✓</td><td>$(R(OH)_x(COOH)_y)$</td></tr>
</table>

P3.5 - Strong hydrochloric acid will give the same result in all the procedures.

- Weak acids react slowly in Procedure **a**, the equivalence point is not indicated properly.
- In Procedure **b**, hydroxy derivative acts as a strong acid and the equivalence point can be indicated as for the strong acid in Procedure **a**.

P3.6

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

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

P3.7 Calculation in Procedure **a** (for a strong acid)

$n(S_2O_3^{2-})\ /\ n(I_2) = 2/1$

$n(I_2) = (1/2) \times n(S_2O_3^{2-}) = (1/2) \times c(S_2O_3^{2-}) \times V(S_2O_3^{2-})$

$n(H^+)\ /\ n(I_2) = 6/3 = 2$

$n(H^+) = 2 \times n(I_2) = 2 \times (1/2) \times n(S_2O_3^{2-}) = n(S_2O_3^{2-}) = c(S_2O_3^{2-}) \times V(S_2O_3^{2-})$

$c(HCl) = c(S_2O_3^{2-}) \times V(S_2O_3^{2-})\ /\ V(HCl)$

$c(HCl) = c(S_2O_3^{2-}) \times V_3\ /\ V_{11}$

Justification: A strong acid can be determined using the simplest procedure (although all three procedures are possible) – direct titration and minimized number of added compounds minimize the possible error sources.

P3.8 Calculation in the case of Procedure **b** (shown for citric acid H_3A)

$n(S_2O_3^{2-})\ /\ n(I_2) = 2/1$

$n(I_2) = 1/2 \times n(S_2O_3^{2-}) = 1/2 \times c(S_2O_3^{2-}) \times V(S_2O_3^{2-})$

$n(H^+)\ /\ n(I_2) = 6/3 = 2$

$n(H^+) = 2 \times n(I_2) = 2 \times 1/2 \times n(S_2O_3^{2-}) = n(S_2O_3^{2-}) = c(S_2O_3^{2-}) \times V(S_2O_3^{2-})$

$n(H^+)\ /\ n(H_3A) = 3/1$

$n(H_3A) = 1/3\ n(H^+)$

$c(H_3A) = 1/3 \times c(S_2O_3^{2-}) \times V(S_2O_3^{2-})\ /\ V(H_3A)$

$c(H_3A) = 1/3 \times c(S_2O_3^{2-}) \times V_6\ /\ V_{12}$

Justification: The addition of Ca^{2+} increases the strength of hydroxy acid species. The direct titration then works well.

P3.9 As there is excess of thiosulfate in Procedure **c**, the equilibrium of the reaction iodate/iodide is shifted to the reaction products due to the consumption of iodine by the reaction with thiosulfate present in the mixture.

P3.10 In an acidic solution, thiosulfate undergoes an undesired side reaction (elemental sulfur can be observed):

$$H^+ + S_2O_3^{2-} \rightarrow S^0 + HSO_3^-$$

Thiosulfate must be added as last, when the concentration of H^+ is decreased due to the reaction with the mixture iodate/iodide

P3.11 Calculation when weak acid (for example acetic acid) is determined – Procedure **c**.

There are two sources of iodine in the titration flask: the added I_2 solution ($n_1(I_2)$) and I_2 formed in reaction of H^+ with the mixture iodate/iodide ($n_2(I_2)$).

Total amount of iodine in the titration flask:

$n(I_2) = n_1(I_2) + n_2(I_2)$

The iodine reacts with the thiosulfate added by the pipette $n_1(S_2O_3^{2-})$ and by the burette $n_2(S_2O_3^{2-})$.

$n(S_2O_3^{2-}) = n_1(S_2O_3^{2-}) + n_2(S_2O_3^{2-}) = (V_{23} + V_8) \times c(S_2O_3^{2-})$

The corresponding amount of iodine: $n(S_2O_3^{2-}) / n(I_2) = 2/1$

$n(I_2) = (1/2) \times n(S_2O_3^{2-}) = (1/2) \times (V_{23} + V_8) \times c(S_2O_3^{2-})$

Iodine originated from the reaction of the acid sample

$n_2(I_2) = n(I_2) - n1(I_2) = 1/2 \times (V_{23} + V_8) \times c_1 - c(I_2) \times V_{33}$

The corresponding acid:

$n(H^+) / n_2(I_2) = 6/3 = 2$

$n(H^+) = 2 \times n_2(I_2)$

$c(HAc) = n(H^+) / V_{13}$

Justification: Weak acid must be determined by back titration, when equilibrium is shifted due to the iodine consumption by the reaction with added thiosulfate.

III. Identification of an unknown hydroxy carboxylic acid in the sample

P3.13 For example, when the acids are neutralized to 50%, the values of pH are 3.71 for tartaric acid, 3.86 for lactic acid, 4.28 for malic acid, and 4.78 for citric acid.

Other points of titration curves can be used for this purpose from the region of partially neutralized acid with NaOH solution.

Problem P4. A chemical oscillator and its activation energies

P4.1 The yellow colour observed is due to Br_2 formation and its disappearance due to malonic acid bromination:

$$BrO_3^- + 5\ Br^- + 6\ H^+ \rightarrow 3\ Br_2 + 3\ H_2O$$

$$HOOC–CH_2–COOH + Br_2 \rightarrow HOOC–CHBr–COOH + Br^- + H^+ \qquad / \times 3$$

Overall:

$$3\ HOOC–CH_2–COOH + BrO_3^- + 2\ Br^- + 3\ H^+ \rightarrow 3\ HOOC–CHBr–COOH + 3\ H_2O$$

P4.2 A typical t = 114.25 s (may depend significantly on the reactor geometry, stirring rate etc.)

$$[Br^-] = 5.0\ \text{mM, thus } d[Br^-]/dt = 5.0 / 114.25\ \text{mM s}^{-1} = 4.38 \times 10^{-2}\ \text{mM s}^{-1}.$$

The average period of oscillation in the BZ oscillator with the same temperature and the same [Ce(III)] was 96.19 s, consuming 96.19 × 4.38 × 10^{-2} mM s^{-1} = 4.21 mM Br^-. According to the stoichiometry shown above, this corresponds to 6.32 mM malonic acid. The bromide for each cycle comes from the oxidative degradation of bromomalonic acid.

P4.3 In the list of the bromine-containing species, we need to look at the bromine oxidation states and at the numbers of bromine atoms. Only two of the species can be combined with the one-electron oxidation of Ce^{3+} to Ce^{4+} to give the desired 1:1:n stoichiometry for the reactants and an integer stoichiometric coefficient for the reduced bromine-containing product. The two species are BrO_3^- and BrO_2, capable of undergoing one-electron reduction to BrO_2 and $HBrO_2$, respectively:

$$Ce^{3+} + BrO_3^- + 2\ H^+ \rightarrow Ce^{4+} + BrO_2 + H_2O$$

$$Ce^{3+} + BrO_2 + H^+ \rightarrow Ce^{4+} + HBrO_2$$

However, the oxidation must proceed with BrO_2, because plenty of BrO_3^- was observed to be present side by side with the reduced Ce^{3+} during the Br-inhibited reaction in part I.1. BrO_2 is produced from BrO_3^- and $HBrO_2$:

$$BrO_3^- + HBrO_2 + H^+ \rightarrow 2\ BrO_2 + H_2O$$

The equations for Ce^{3+} oxidation and BrO_2 production can be combined in two ways, eliminating either BrO_2 or $HBrO_2$. Nevertheless, both results are autocatalytic:

$$BrO_3^- + HBrO_2 + 2\ Ce^{3+} + 3\ H^+ \rightarrow 2\ HBrO_2 + 2\ Ce^{4+} + H_2O$$

$$BrO_3^- + BrO_2 + Ce^{3+} + 2\ H^+ \rightarrow 2\ BrO_2 + Ce^{4+} + H_2O$$

Bromide ions inhibit the autocatalytic cycle by consuming $HBrO_2$:

$$Br^- + HBrO_2 + H^+ \rightarrow 2\ HBrO$$

P4.4 A typical set of results is as follows:

[Ce] / mM	**Induction period / s**	**Periods of oscillation / s**			
		1st	**2nd**	**3rd**	**Average**
2.5	152.18	88.43	86.55	86.23	87.07
5.0	149.78	96.97	94.92	96.69	96.19

As the concentration of cerium was doubled, the induction period was practically not affected, it decreased only negligibly. On the contrary, the average period of oscillations increased slightly. The increase was, however, only by about 10%. These results suggest that the reactions of cerium are the fast ones, and not rate-determining.

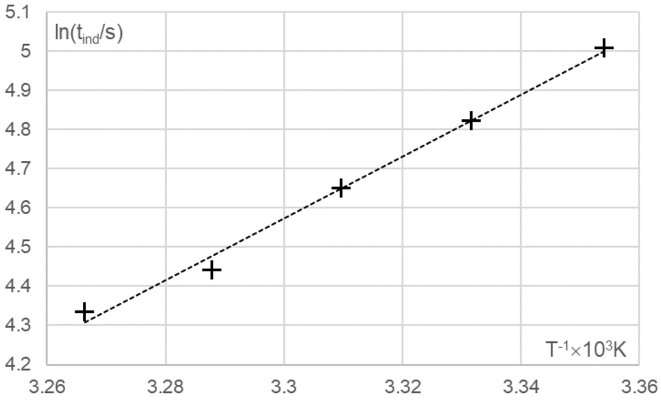
P4.5 A typical set of results is as follows:

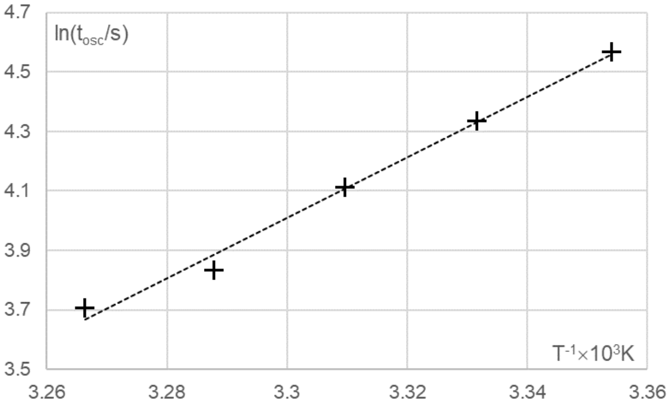
Temperature / °C	**Induction period / s**	**Periods of oscillation / s**			
		1st	**2nd**	**3rd**	**Average**
25.0	149.78	96.97	94.92	96.69	96.19
27.0	124.26	76.92	75.23	77.12	76.42
29.0	104.56	61.09	61.18	60.81	61.03
31.0	84.92	46.90	45.90	45.78	46.19
33.0	76.36	41.30	40.26	40.70	40.75

This yields the following values of 1/*T* and natural logarithms:

T^{-1} / 10^{-3} K^{-1}	**ln (induction period / s)**	**ln (period of oscillations / s)**
3.354	5.00917	4.5664
3.332	4.82238	4.3363
3.310	4.64976	4.1113
3.288	4.4417	3.8328
3.267	4.3355	3.7075

We obtain two graphs that look very similar, but they yield different values of E_a:





The slope of the graph with the induction periods is 7 890 K, therefore the corresponding activation energy is 7 890 K × *R* = 65.6 kJ mol^{-1}. The slope of the graph made for the periods of oscillation is 10 140 K, thus the activation energy is 10 140 K × *R* = 84.3 kJ mol^{-1}. The activation energy determined from the induction periods is closer to the reference value for cerium, whereas the activation energy determined for the periods of oscillation is closer to the reference value for ferroin, despite the fact that cerium is in large excess.

Problem P5. Kinetics of a chemical wave front propagation

P5.1 Typical experimental results look like this:

Set	$[H_2SO_4]$	$[BrO_3^-]$	Times from accepted replicates / s			v / mm min^{-1}
#1	0.50 M	0.10 M	61.58	63.41	60.18	4.81
			63.14	62.00	63.57	
#2	0.35 M	0.10 M	108.10	106.75	109.26	2.80
			107.22	106.93	104.78	
#3	0.50 M	0.13 M	56.32	53.45	55.42	5.41
			56.48	56.12	54.71	
#4	0.50 M	0.070 M	78.22	75.60	76.25	3.89
			77.99	78.37	76.32	

P5.2 Non-zero values of q would suggest that alternative parallel reaction pathways capable of affecting the autocatalysis may exist side by side with the production of **X** dependent on bromate(V). If q is positive, there may be additional autocatalytic pathways capable of making **X** without bromate(V). If q is negative, there may be reactions inhibiting the autocatalysis, as if not all bromate(V) was effectively contributing to the reaction.

The usual calculation of slope and intercept applies:

$$p = \frac{v_{\#3}^2 - v_{\#4}^2}{[BrO_3^-]_{\#3} - [BrO_3^-]_{\#4}} = \frac{5.41^2 - 3.89^2}{0.13 - 0.07}\ \mathrm{mm^2\ min^{-1}\ M^{-1}} = 235.6\ \mathrm{mm^2\ min^{-2}\ M^{-1}}$$

$$q = v_{\#3}^2 - p\,[BrO_3^-]_{\#3} = (29.27 - 235.6 \times 0.13)\ \mathrm{mm^2\ min^{-2}} = -1.4\ \mathrm{mm^2\ min^{-2}}$$

The calculation above also demonstrates how the individual terms contribute: while $p\,[BrO_3^-]$ represents 30.6 mm^2 min^{-2}, the value of q is much smaller, making up around 5% of the total at 0.13 M and around 9% at 0.070 M bromate(V). Such contributions could easily come from other factors of measurement, and they cannot be regarded as significant.

P5.3 This is a usual calculation of partial reaction orders:

$$a = \frac{\log\,(v_{\#1}/v_{\#2})}{\log\,([H_2SO_4]_{\#1}/[H_2SO_4]_{\#2})} = \frac{\log\,(4.81/2.80)}{\log\,(0.50/0.35)} = 1.517$$

$$b = \frac{\log\,(v_{\#3}/v_{\#4})}{\log\,([BrO_3^-]_{\#3}/[BrO_3^-]_{\#4})} = \frac{\log\,(5.41/3.89)}{\log\,(0.13/0.070)} = 0.533$$

The value of b is in a good agreement with the expected value of 0.5, corresponding to the first order kinetics with respect to bromate.

On the other hand, the value of a does not agree. In fact, $a \approx 1.5$ suggests a third-order dependence of the reaction rate on $[H_2SO_4]$. This can be interpreted as the partial reaction order with respect to $[H^+]$, if the same dissociation degree of H_2SO_4 is assumed in 0.50 M and 0.35 M solutions. In this concentration range, rate equation (3) needs to be reconsidered.

Note: Reaction conditions were chosen deliberately in this range with increased sensitivity to the acid concentration. Above 0.50 M H_2SO_4, the expected value of a ≈ 0.5 would be obtained.

P5.4 Based on (2) and (3), we can calculate the rate constant in the following way:

$$k = \frac{v^2}{4D[\mathrm{BrO_3^-}][\mathrm{H^+}]} \approx \frac{v^2}{4D[\mathrm{BrO_3^-}][\mathrm{H_2SO_4}]}$$

Converting the values of v to cm s^{-1} and evaluating the formula above, we find:

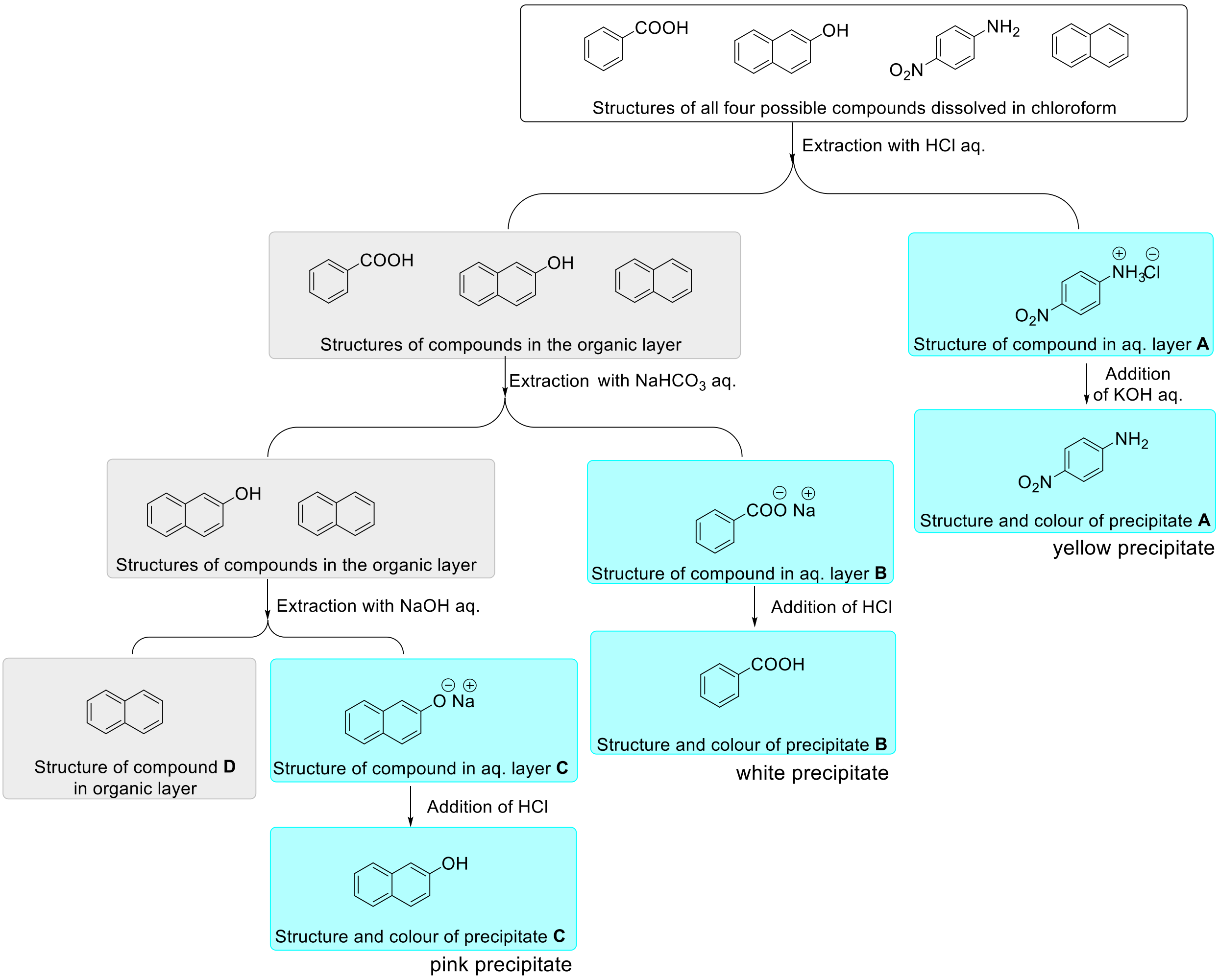
	Set #1	**Set #2**	**Set #3**	**Set #4**
v / 10^{-2} cm s^{-1}	8.02	4.67	9.02	6.48
k / M^{-2} s^{-1}	16.1	7.78	15.6	15.0

The values of k found from concentration sets #1, #3 and #4 are in relatively good agreement with the reference value of 20 M^{-2} s^{-1}. The value from concentration set #2 is considerably smaller and confirms a different mode in the kinetics of the reaction under these conditions.

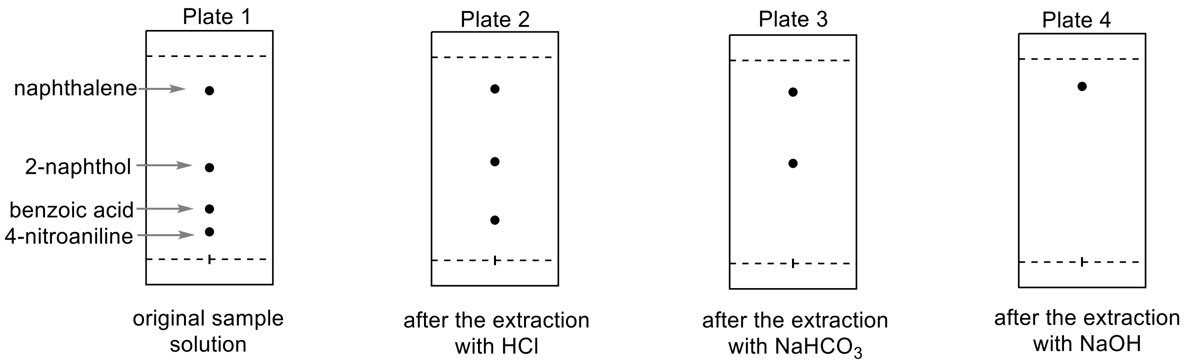
Problem P6. Separation of acidic, basic and neutral organic compounds

Prepare samples which may contain 3–4 of the following compounds: benzoic acid, 4-nitroaniline, naphthalene-2-ol and naphthalene, mixed in ratio w/w 1:1:1:1 for a four-component mixture, or 0:1:1:1, 1:1:1:0 or 1:1:0:1 for three-component mixtures. Note that 4-nitroaniline has to be present in any sample. The following solution is given for a 4-component mixture.

P6.1



P6.2 Comparison of the TLC plates shows that after each extraction one of the compounds “disappears” from the organic phase as it is extracted into the aqueous phase of an appropriate pH (one component would be missing in three-component mixtures).



original sample solution

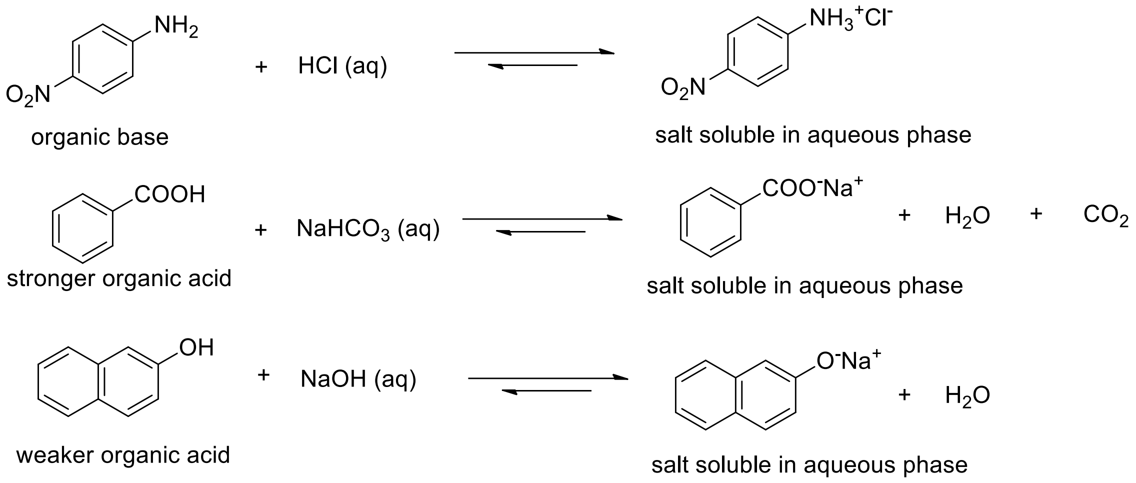
after the extraction with HCl

after the extraction with $NaHCO_3$

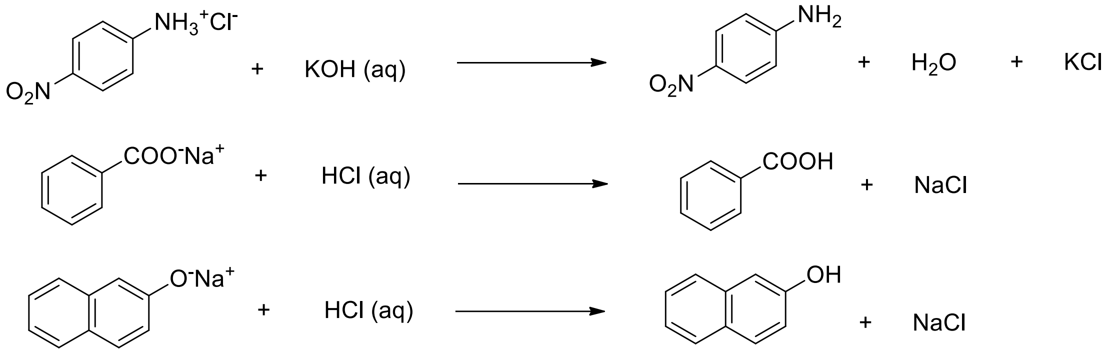
after the extraction with NaOH

P6.3

SEPARATION EQUATIONS



ISOLATION EQUATIONS



P6.4 The use of $NaHCO_3$ for the second extraction is necessary to separate compound **B** (benzoic acid) from compound **C** (2-naphthol). A stronger organic acid (benzoic acid) is extracted into the bicarbonate solution as its conjugate base. A weaker organic acid (2-naphthol) remains in the organic phase. If the first extraction were performed with hydroxide solution, both organic acids (benzoic acid and 2-naphthol) would be extracted into the basic aqueous phase as conjugate bases and they would not get separated.

P6.5

Compound	***R*$_f$**	***m* (g)[a]**	**Compound name**
A	0.21–0.22	0.112–0.141 (60–75%)	4-nitroaniline
B	0.33–0.34	0.109–0.131 (58–70%)	benzoic acid
C	0.53–0.54	0.151–0.166 (59–83%)	2-naphthol
D	0.85–0.86	0.110–0.155 (59–83%)	naphthalene

[a] isolated yields of dried compound obtained from 1:1:1:1 mixture

P6.6 Students should find out that the ratio of the compounds in the sample was 1:1:1:1 and that the sum of the masses of the isolated compounds is smaller than the original sample weight. Some of the material is lost in each step: transfers of material, imperfect layer separation during extractions, loss occurring during the precipitation, filtration, etc.

Problem P7. Meerwein–Ponndorf–Verley reduction

P7.1–P7.4 Characteristics and yield of the product:

TLC analysis (silica gel, hexanes/ethyl acetate 6:1): R_f(ketone) = 0.37; R_f(alcohol) = 0.13

Product: white crystals, yield after crystallization from hexanes 145 mg (72%), melting point 72.0–73.0 °C (hexanes).

P7.5 $m(^i\text{PrOH}) = V(^i\text{PrOH}) \times d(^i\text{PrOH})$

$m(^i\text{PrOH}) = 4\ \text{cm}^3 \times 0.786\ \text{g cm}^{-3} = 3.144\ \text{g}$

$m(H_2O) = m(^i\text{PrOH}) \times w(H_2O)$

$m(H_2O) = 3.144\ \text{g} \times 0.002 = 6.3 \times 10^{-3}\ \text{g}$

$n(H_2O) = m(H_2O) / M(H_2O)$

$n(H_2O) = 6.3 \times 10^{-3}\ \text{g} / 18.01\ \text{g mol}^{-1} = 3.5 \times 10^{-4}\ \text{mol} = 0.35\ \text{mmol}$

The number of moles of water present in 4 cm^3 of isopropyl alcohol is 0.35 mmol.

P7.6 The products of aluminium isopropoxide hydrolysis are aluminium hydroxide and isopropyl alcohol.

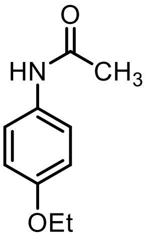
$$\text{Al}(^i\text{PrO})_3 + 3\ H_2O \rightarrow \text{Al(OH)}_3 + 3\ ^i\text{PrOH}$$

P7.7 The spot of the alcohol product has a lower retention factor (shorter distance of the spot from the start) compared to the starting ketone. This is caused by the higher polarity of the alcohol product and the ability of alcohol to act as a H-bonding donor, resulting in a higher affinity to the stationary phase.

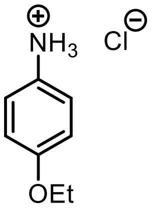
P7.8 2-Acetonaphthone can be converted to 1-(2-naphthyl)ethanol by the treatment with hydrides such as LiAlH_4, NaBH_4 or DIBAL-H. Another method for the reduction of ketones is a transition metal catalyzed hydrogenation. Platinum or ruthenium are common catalysts. Complexes of transition metals (e.g. Wilkinson catalyst) can be used in homogeneous catalysis. Complexes with chiral ligands allow stereoselective reduction of ketones.

Problem P8. Transformation of a drug to a sweetener

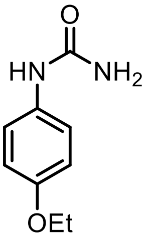
P8.1 Structures:



A:Phenacetin



B



C: Dulcin

P8.2 $n(\mathbf{P}) = m(\mathbf{P}) / M(\mathbf{P}) = 1.00\ \text{g} / 151.17\ \text{g mol}^{-1} = 6.615 \times 10^{-3}\ \text{mol}$

$n(\mathbf{C}) = n(\mathbf{P})$

$m(\text{theor. }\mathbf{C}) = n(\mathbf{C}) \times M(\mathbf{C}) = 6.615 \times 10^{-3}\ \text{mol} \times 180.21\ \text{g mol}^{-1} = 1.19\ \text{g}$

P8.3 *Exp. yield*(**C**) = *m*(actual yield **C**) / *m*(theor. **C**); expressed in %, rounded to integers

The yield of the isolated phenacetin (**A**) is 85–90% (not marked). A typical yield of the isolated dulcin (**C**) after thorough drying is 0.50 g (42% yield from paracetamol). If recrystallization from organic solvents is required, the yield drops to ca 0.20 g (17% yield from paracetamol), but essentially pure white crystalline material is obtained.

P8.4 M.p.(**C**) = 173.0–174.0 °C; impurities lower the m.p. dramatically.

P8.5 $R_f(\mathbf{P}) = 0.37$

$R_f(\mathbf{A}) = 0.46$

$R_f(\mathbf{C}) = 0.19$

P8.6 a) NaOH deprotonates the OH group of paracetamol to give a coloured phenolate.
d) The deprotonated, anionic substrate is much more reactive than the neutral paracetamol.
g) Acetamide functional group is stable towards a base (NaOH in 95% EtOH).
h) Aryl ethyl ether functional group is stable towards an aqueous acid (aq. HCl).
i) Product **B** is a salt (it contains a cation and an anion).

P8.7 d) Isocyanic acid, H–N=C=O