PREPARATORY PROBLEMS: THEORETICAL

SOLUTIONS

50th IChO 2018

International Chemistry Olympiad
SLOVAKIA & CZECH REPUBLIC

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):

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

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

Andrussow process:

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

$\Delta_r H_m = [- (-90.3) - (-56.3) - 3/2 \times 0 + 129.0 + 3 \times (-250.1)]$ kJ mol^{-1} = −474.7 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: $q_i = C_{cal} \times \Delta T_i$
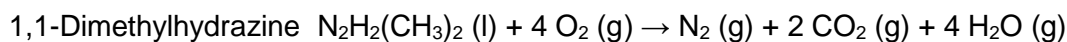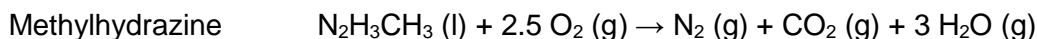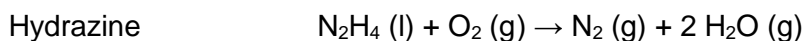
$q_{0M} = 16.83$ kJ; $q_{1M} = 25.60$ kJ; $q_{2M} = 30.11$ kJ.

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: $\Delta_c H_i = \Delta_c U_i + \Delta_c n(gas) R T_{std}$

$\Delta_{comb} H_{0M} = -534.44$ 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)
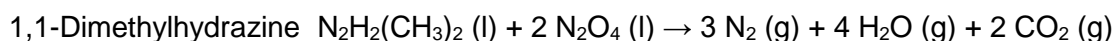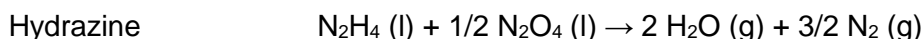
Calculation of molar reaction enthalpies, related to one mole of hydrazine derivatives:

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

$\Delta_{re}H°_{0M} = \Delta_{re}H_{0M} − 2 \Delta_{vap}H_{H2O} = −620.28$ kJ mol$^{−1}$

$\Delta_{re}H°_{1M} = \Delta_{re}H_{1M} − 3 \Delta_{vap}H_{H2O} = −1\ 306.59$ kJ mol$^{−1}$

$\Delta_{re}H°_{2M} = \Delta_{re}H_{2M} − 4 \Delta_{vap}H_{H2O} = −1\ 982.96$ kJ mol$^{−1}$

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

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

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

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

Calculation of standard molar reaction Gibbs energies:

$\Delta_{re}G°_{0M} = \Delta_{re}H°_{0M} − T° \times \Delta_{re}S°_{0M} = −680.11$ kJ mol$^{−1}$

$\Delta_{re}G°_{1M} = \Delta_{re}H°_{1M} − T° \times \Delta_{re}S°_{1M} = −1\ 433.77$ kJ mol$^{−1}$

$\Delta_{re}G°_{2M} = \Delta_{re}H°_{2M} − T° \times \Delta_{re}S°_{2M} = −2\ 180.84$ kJ mol$^{−1}$

Estimation of the equilibrium constants for combustion reactions:

$K_i = \exp(−\Delta_{re}G°_i / (RT°))$

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

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

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

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) → 6.75 N_2 (g) + 9 H_2O (g) + 3 CO_2 (g)

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

$T_f = 4\ 288.65$ 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) → N_2 (g) + 2 CO_2 (g) + 4 H_2O (g)
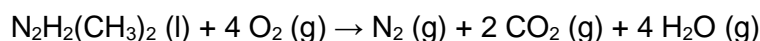
$-\Delta_{comb}H_{2M} = \left(C_{p(N_2)} + 4\ C_{p(H_2O)} + 2\ C_{p(CO_2)}\right)(T_x − T_0)$, solve for T_x

$T_x = 5\ 248.16$ 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: $\eta = (T_f - T°) / T_f = 93.0\%$.

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	$\Delta G°$	K_D	$\Delta G°$	K_D	$\Delta G°$
		nM	kJ mol^{-1}	nM	kJ mol^{-1}	nM	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	$\Delta G°$	K_D	$\Delta G°$	K_D	$\Delta G°$
		nM	kJ mol^{-1}	nM	kJ mol^{-1}	nM	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: $k_A = k_D / K_D = 4.76 \times 10^{-3} \text{ s}^{-1} / (0.725 \times 10^{-9} \text{ mol L}^{-1}) = 6.57 \times 10^6 \text{ L mol}^{-1} \text{ s}^{-1}$. 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 $\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	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 $k = A \times \exp[-\Delta G^‡ / RT]$. 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,
$k_1 = A \times \exp[-\Delta G^‡ / RT_1]$
$k_2 = A \times \exp[-\Delta G^‡ / RT_2]$,
from which the activation energy of dissociation results as $\Delta G^‡ = (\ln k_1 / k_2) / (1 / RT_2 - 1 / RT_1)$. 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:
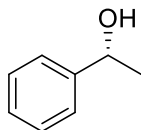
(R)-1-phenylethan-1-ol

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

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

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

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

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

At any given temperature T:

$\left(\dfrac{k_R}{k_S}\right)_T = \dfrac{A \times e^{\frac{-E_a(R)}{R \times T}}}{A \times e^{\frac{-E_a(S)}{R \times T}}}$ (‡)   Therefore:

$T = \dfrac{E_a(S) - E_a(R)}{R \times \ln\left(\dfrac{k_R}{k_S}\right)_T} = 130 \; \text{K}$

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 (‡):

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

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

which means $[\alpha]_D^{20}$ (*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:

$[\alpha]_D^{20}$ (*c* 1.00, EtOH) $= -42.5° = -43°$

Note: The specific rotation should be formally stated in ° dm^{-1} cm^3 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 $c_0 = 1 \text{ mol dm}^{-3}$.

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

$$K = \frac{[\text{H}_2\text{O}]}{[\text{H}^+][\text{OH}^-]} = \frac{55.6}{10^{-7} \times 10^{-7}} = \frac{55.6}{K_{\text{w}}} = 5.56 \times 10^{15}$$

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

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

Note that the Gibbs free energy change calculated in this way corresponds to the standard state $c_0 = 1 \text{ mol dm}^{-3}$ 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

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

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 $\Delta H = 49.65 \times 10^3 \text{ J mol}^{-1}$. The temperature change is given as

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

After substitution

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

we get

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

which translates into proton concentration at the boiling point of water

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

or pH

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

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

$$[\text{D}^+] = \sqrt{K_w(\text{D}_2\text{O})} = \sqrt{1.35 \times 10^{-15}} = 3.67 \times 10^{-8} \text{ mol dm}^{-3}$$

and pD is given by

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

5.4

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

5.5   We start from the rate equation derived in 5.4

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

All concentrations can be expressed via the quantity x

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

Expanding the right hand side of the equation, we get

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

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

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

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

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

5.6   The relaxation time is given as

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

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

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

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

The relaxation time is then given as

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

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

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

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

We get k_2 from the equilibrium constant K

$$k_2 = k_1 K = 2.05 \times 10^{-6} \text{ s}^{-1}$$

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

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

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

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

$$K_a = \frac{y^2}{c - y}$$

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

$$K_a = \frac{y^2}{c}$$

From which

$$y = \sqrt{K_a \times c} = \sqrt{7.59 \times 10^{-10} \times 5.0 \times 10^{-3}} = 1.9 \times 10^{-6} \text{ mol dm}^{-3}$$

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

During irradiation, 1 cm³ of sample absorbs 2.228 × 10⁻³ J of energy. 1 dm³ 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

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

The number of absorbed photons in 1 dm³ 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

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

The pH can again be calculated from the pK_a^* in the excited state; the analytical concentration c^* of the excited acid is now 5.5×10^{-6} mol dm⁻³.

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

$$x = y^* + y$$

The two equilibrium constants are expressed as

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

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

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

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

We can solve this equation e.g. with any on-line solver of cubic equations

$$x = 6.12 \times 10^{-6} \text{ mol dm}^{-3}$$

Which corresponds to

$$\text{pH} = -\log\left(6.12 \times 10^{-6}\right) = 5.21$$

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

$$y^{*2} + K_a^* y^* - K_a^* c^* = 0$$

$$y^* = \frac{-0.022 + \sqrt{0.022^2 + 4 \times 5.5 \times 10^{-6} \times 0.022}}{2} = 5.5 \times 10^{-6} \text{ mol dm}^{-3}$$

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

$$y^2 + y \times 5.5 \times 10^{-6} - 7.59 \times 10^{-10} \times 5.0 \times 10^{-3} = 0$$

$$y = \frac{-5.5 \times 10^{-6} + \sqrt{(5.5 \times 10^{-6})^2 + 4 \times 7.59 \times 10^{-10} \times 5 \times 10^{-3}}}{2}$$

$$y = 6.2 \times 10^{-7} \text{ mol dm}^{-3}$$

The concentration of $[H^+]$ is

$$x = y^* + y = 5.5 \times 10^{-6} + 6 \times 10^{-7} = 6.1 \times 10^{-6} \text{ mol dm}^{-3}$$

$$\text{pH} = -\log(6.1 \times 10^{-6}) = 5.21$$

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: $\mu = \frac{m_{\mathrm{F}} \times m_{\mathrm{H}}}{m_{\mathrm{F}} + m_{\mathrm{H}}} = \frac{19}{20}$ amu $= 1.578 \times 10^{-27}$ kg

Wavenumber: $\tilde{v} = \frac{v}{c} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}} = \frac{1}{2\pi \times 2.9979 \times 10^8}\sqrt{\frac{968}{1.578 \times 10^{-27}}} = 4.159 \times 10^5$ m^{-1}

$\tilde{v} = 4\,159$ cm^{-1}

Energies: $E_0 = \frac{1}{2}h \times c \times \tilde{v} = \frac{1}{2} \times 6.6261 \times 10^{-34} \times 2.9979 \times 10^8 \times 4.159 \times 10^5 =$

$= 4.13 \times 10^{-20}$ J

$E_1 = \frac{3}{2}h \times c \times \tilde{v} = 1.24 \times 10^{-19}$ J

6.2 We are going to determine the atomic mass A of the lighter isotope of the element X.

$$\left(\frac{\tilde{v}_1}{\tilde{v}_2}\right)^2 = \frac{\mu_2}{\mu_1} = \frac{\frac{2 \times (A+2)}{2 + A + 2}}{\frac{1 \times A}{A+1}} = \frac{2 \times (A+2) \times (A+1)}{A \times (A+4)}$$

$$\frac{1}{2}\left(\frac{2\,439.0}{1\,734.8}\right)^2 = \frac{A^2 + 3 \times A + 2}{A^2 + 4 \times A}$$

$A = 79.4$ 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 $E_a(\mathrm{H{-}C}) - E_a(\mathrm{D{-}C})$ is equal to the negatively taken difference of zero-point vibrational energies: $- E_0(\mathrm{H{-}C}) + E_0(\mathrm{D{-}C})$

$$\frac{k(\mathrm{C{-}H})}{k(\mathrm{C{-}D})} = \exp\left(-\frac{E_a(\mathrm{C{-}H}) - E_a(\mathrm{C{-}D})}{kT}\right) = \exp\left(\frac{E_0(\mathrm{C{-}H}) - E_0(\mathrm{C{-}D})}{kT}\right)$$

$$\frac{k(\mathrm{C{-}H})}{k(\mathrm{C{-}D})} = \exp\left(\frac{hc}{2kT}\left(\tilde{v}(\mathrm{C{-}H}) - \tilde{v}(\mathrm{C{-}D})\right)\right)$$

$$\frac{k(\mathrm{C{-}H})}{k(\mathrm{C{-}D})} = \exp\left(\frac{6.6261 \times 10^{-34} \times 2.9979 \times 10^8}{2 \times 1.3807 \times 10^{-23} \times 300}(2.9 \times 10^5 - 2.1 \times 10^5)\right)$$

$$\frac{k(\mathrm{C{-}H})}{k(\mathrm{C{-}D})} = 6.81$$

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 $k_\mathrm{H} / k_\mathrm{D}$ 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:

$$E = E° - \frac{RT}{zF}\ln\frac{[\mathbf{A}_{\text{red}}]}{[\mathbf{A}_{\text{ox}}][\text{H}^+]^n} = E° - \frac{RT}{zF}\left(\ln\frac{[\mathbf{A}_{\text{red}}]}{[\mathbf{A}_{\text{ox}}]} - n \times \ln[\text{H}^+]\right) =$$

$$= E° + \frac{nRT}{zF\log(e)} \times \log[\text{H}^+] = E° - \frac{nRT}{zF\log(e)} \times (-\log[\text{H}^+]) = E° - \frac{nRT}{zF\log(e)} \times \text{pH}$$

7.3   Standard potential $E°(\mathbf{C})$ is more positive than $E°(\mathbf{B})$, hence substance $\mathbf{C}$ is a stronger oxidizer and will therefore oxidize substance $\mathbf{B}$ (a), and the standard reaction potential $E_r°$ will be 0.288V (b):

$$\mathbf{C}_{\text{ox}} + 2e^- \rightarrow \mathbf{C}_{\text{red}} \qquad E_{\mathbf{C}}° = +0.824\,\text{V}$$

$$\mathbf{B}_{\text{red}} \rightarrow \mathbf{B}_{\text{ox}} + 3e^- \qquad E_{\mathbf{B}}^* = -0.536\,\text{V}$$

$$3\mathbf{C}_{\text{ox}} + 6e^- \rightarrow 3\mathbf{C}_{\text{red}}$$

$$2\mathbf{B}_{\text{red}} \rightarrow 2\mathbf{B}_{\text{ox}} + 6e^-$$

$$3\mathbf{C}_{\text{ox}} + 2\mathbf{B}_{\text{red}} \rightarrow 3\mathbf{C}_{\text{red}} + 2\mathbf{B}_{\text{ox}}$$

$$E_r° = E_{\mathbf{C}}° + E_{\mathbf{B}}^* = 0.824 - 0.536\,\text{V} = +0.288\,\text{V}$$
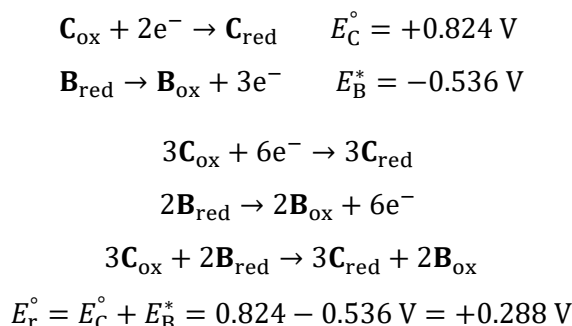
c) using formula:

$$\Delta G° = -RT\ln(K) = -zFE_r°$$

$$K = \exp\left(\frac{zFE_r°}{RT}\right) \cong \exp\left(\frac{6 \times 96\,485 \times 0.288}{8.3145 \times 298.15}\right) \cong 1.62 \times 10^{29}$$

7.4   Reaction $\mathbf{E}$ 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 $E_r = E_{\mathbf{E}} - E_{\mathbf{D}}$ is calculated from the equilibrium constant:

$$RT\ln(K) = zFE_r° \Rightarrow \frac{RT\ln(K)}{zF} = \frac{8.3145 \times 262 \times \ln(2.56 \times 10^5)}{1 \times 96\,485} \cong 0.28\,V$$

The potential for the reduction of substance $\mathbf{E}$ is $E_{\mathbf{E}} = E_{\mathbf{D}} + E_r = 0.55$ V + 0.28 V = 0.83 V. This value of potential is achieved at pH = 2.31. The two lines cross at pH = 7.7 (roughly); $\mathbf{D}$ will oxidize $\mathbf{E}$ in the pH range from 7.7 to 13.
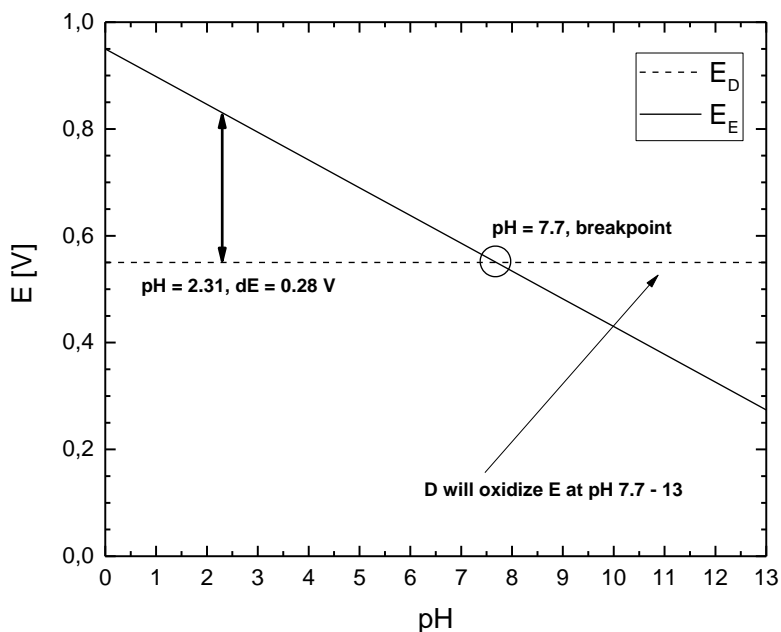
7.5 Using the formula for electrolysis:

$$Q = nzF \Longrightarrow \frac{m}{M} = \frac{Q}{zF} = \frac{It}{zF} \Longrightarrow t = \frac{mzF}{MI} = \frac{0.005 \times 3 \times 96\,485}{197 \times 0.025}\ s \cong 294\ s$$

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 $H_2 + \frac{1}{2} O_2 \rightarrow H_2O$ under standard conditions (298 K and 1 bar). Then, convert it to the EMF (voltage).

The standard reaction enthalpy and entropy are

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

$$\Delta_r S° = S°\big(H_2O(l)\big) - \left(S°\big(H_2(g)\big) + \frac{1}{2} S°\big(O_2(g)\big)\right) = 70 - \left(131 + \frac{205}{2}\right) =$$
$$= -163.5 \text{ J K}^{-1}\text{mol}^{-1}$$

The standard change of Gibbs energy is

$$\Delta_r G° = \Delta_r H° - T\Delta_r S° = -286 - 298 \times (-163.5 \times 10^{-3}) = -237.3 \text{ kJ mol}^{-1}$$

The standard EMF is then

$$E° = -\frac{\Delta_r G°}{|z|F} = \frac{-237.3 \times 10^3}{2 \times 96\,485} = 1.23 \text{ V}$$

8.2 The solution is similar to the previous one with the difference of water state.

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

$$\Delta_r S° = S°\big(H_2O(g)\big) - \left(S°\big(H_2(g)\big) + \frac{1}{2} S°\big(O_2(g)\big)\right) = 189 - \left(131 + \frac{205}{2}\right) =$$
$$= -44.5 \text{ J K}^{-1}\text{mol}^{-1}$$

The standard change of Gibbs energy is

$$\Delta_r G° = \Delta_r H° - T\Delta_r S° = -242 - 298 \times (-44.5 \times 10^{-3}) = -228.7 \text{ kJ mol}^{-1}$$

The standard EMF is then

$$E° = -\frac{\Delta_r G°}{|z|F} = \frac{-228.7 \times 10^3}{2 \times 96\,485} = 1.19 \text{ V}$$

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:

$$\eta_t(H_2O(l), 298 \text{ K}) = 1 - 298 \times \left(\frac{-163.5}{-286 \times 10^3}\right) = 0.830$$

$$\eta_t(H_2O(l), 373 \text{ K}) = 1 - 373 \times \left(\frac{-163.5}{-286 \times 10^3}\right) = 0.787$$

$$\eta_t(H_2O(g), 298 \text{ K}) = 1 - 298 \times \left(\frac{-44.5}{-242 \times 10^3}\right) = 0.945$$

$$\eta_t(H_2O(g), 373 \text{ K}) = 1 - 373 \times \left(\frac{-44.5}{-242 \times 10^3}\right) = 0.931$$

8.4   Cathode: $O_2 + 4\,e^- + 4\,H^+ \rightarrow 2\,H_2O$

Anode: $C_4H_{10} + 8\,H_2O \rightarrow 4\,CO_2 + 26\,H^+ + 26\,e^-$
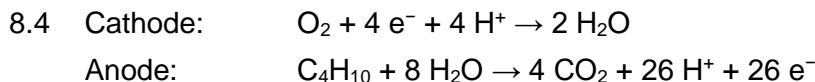
8.5   The overall reaction is:

$2\,C_4H_{10} + 13\,O_2 \rightarrow 8\,CO_2 + 10\,H_2O$
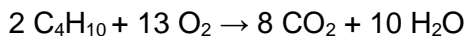
The reaction as accompanied by the transfer of 52 electrons. Hence, at standard temperature:

$$\Delta_f G^\circ\big(H_2O(l)\big) = -237.3 \text{ kJ mol}^{-1}$$

$$\Delta_f G^\circ\big(CO_2(g)\big) = -393 - 298 \times \big((214 - (6 + 205)) \times 10^{-3}\big) = -393.9 \text{ kJ mol}^{-1}$$

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

$$\Delta_f G^\circ\big(O_2(g)\big) = 0$$

$$\Delta_r G^\circ = \big(8\Delta_f G^\circ(CO_2(g)) + 10\Delta_f G^\circ(H_2O(l))\big) - \big(2\Delta_f G^\circ(C_4H_{10}(g)) + 13\Delta_f G^\circ(O_2(g))\big) =$$
$$= \big(8 \times (-393.9) + 10 \times (-237.3)\big) - (2 \times (-17) + 13 \times 0) = -5\,490 \text{ kJ mol}^{-1}$$

$$E^\circ = -\frac{\Delta_r G^\circ}{|z|F} = -\frac{-5\,490 \times 10^3}{52 \times 96\,485} = 1.09 \text{ V}$$

8.6   The ideal thermodynamic efficiency is determined as:

$$\eta_t = \frac{\Delta_r G^\circ}{\Delta_r H^\circ} = \frac{-5\,490.2}{\big(8 \times (-393) + 10 \times (-286)\big) - (2 \times (-126) + 13 \times 0)} = 0.954$$

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: $2\,CH_3OH + 3\,O_2 \rightarrow 2\,CO_2 + 4\,H_2O$
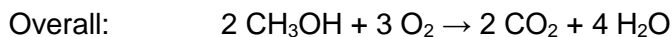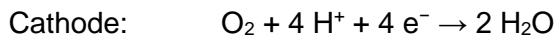
8.9   Nernst equation

$$E = E^\circ - \frac{RT}{12F}\ln\frac{\left(\frac{c_{H_2O}}{c^\circ}\right)^4 \left(\frac{p_{CO_2}}{p^\circ}\right)^2}{\left(\frac{c_{CH_3OH}}{c^\circ}\right)^2 \left(\frac{p_{O_2}}{p^\circ}\right)^3}$$

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:

$$\ln\frac{K(T_2)}{K(T_1)} = \frac{\Delta_r H^\circ}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right); \quad \ln K(T) = \frac{|z|FE^\circ}{RT} \quad \rightarrow \quad \frac{|z|FE^\circ(T_2)}{RT_2} - \frac{|z|FE^\circ(T_1)}{RT_1} = \frac{\Delta_r H^\circ}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\Delta_r H^\circ = \frac{R \times \left(\frac{|z|FE^\circ(T_2)}{RT_2} - \frac{|z|FE^\circ(T_1)}{RT_1}\right)}{\frac{1}{T_1} - \frac{1}{T_2}} = \frac{|z|F \times \left(\frac{E^\circ(T_2)}{T_2} - \frac{E^\circ(T_1)}{T_1}\right)}{\frac{1}{T_1} - \frac{1}{T_2}} = \frac{12 \times 96\,485 \times \left(\frac{1.20}{373} - \frac{1.21}{298}\right)}{\frac{1}{298} - \frac{1}{373}} = -1\,447 \text{ kJ mol}^{-1}$$

$$\Delta_r G^\circ = -|z|FE^\circ(T_1) = -12 \times 96\,485 \times 1.21 = -1\,401 \text{ kJ mol}^{-1}$$

$$\Delta_r S^\circ = \frac{\Delta_r H^\circ - \Delta_r G^\circ}{T_1} = \frac{-1\,447 \times 10^3 - (-1\,401 \times 10^3)}{298} = -154.4 \text{ J K}^{-1}\text{mol}^{-1}$$

Problem 9. Acid-base equilibria in blood

9.1 CO_2 concentration:

$$[CO_2] = H^{cp} \times p(CO_2)$$

$$[CO_2] = 2.3 \times 10^{-7} \times 5\,300 \ \text{mol dm}^{-3}$$

$$[CO_2] = 1.219 \times 10^{-3} \ \text{mol dm}^{-3}$$

The initial concentration of bicarbonate in blood with no acid added, $c(HCO_3^-, 37 \degree C)$:

$$pH = pK_a + \log \frac{[HCO_3^-]}{[CO_2]}$$

$$\log[HCO_3^-] = pH - pK_a + \log[CO_2]$$

$$\log[HCO_3^-] = 7.4 - 6.1 + \log(1.219 \times 10^{-3})$$

$$\log[HCO_3^-] = 7.4 - 6.1 - 2.9$$

$$\log[HCO_3^-] = -1.6$$

$$[HCO_3^-] = 24 \ \text{mmol dm}^{-3}$$

pH after 10 mmol of acids were added to 1 dm^3 of the buffer solution:

$$pH = pK_a + \log \frac{[HCO_3^-] - [H^+]}{[CO_2] + [H^+]}$$

$$pH = 6.1 + \log \frac{0.024 - 0.010}{0.001219 + 0.010}$$

$$pH = 6.21$$

9.2

$$pH = pK_a + \log \frac{[HCO_3^-] - [H^+]}{[CO_2]}$$

$$pH = 6.1 + \log \frac{0.024 - 0.010}{0.001219}$$

$$pH = 7.17$$

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.

$$\ln K_2 - \ln K_1 = -\frac{\Delta_r H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln K_{310.15\,K} - \ln K_{298.15\,K} = -\frac{\Delta_r H}{R}\left(\frac{1}{310.15} - \frac{1}{298.15}\right)$$

$$-14.05 + 14.62 = 1.30 \times 10^{-4} \times \frac{\Delta_r H}{8.314}$$

$$\Delta_r H = 36.88 \text{ kJ mol}^{-1}$$

Then, that same equation is used to calculate the pK_a at 20 °C:

$$\ln K_2 - \ln K_1 = -\frac{\Delta_r H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln K_{293.15} + 14.62 = -\frac{36\,520}{8.314}\left(\frac{1}{293.15} - \frac{1}{298.15}\right)$$

$$\ln K_{293.15} = -14.87$$

$$K_{293.15} = 3.48 \times 10^{-7}$$

$$pK_a(293.15\text{ K}) = 6.46$$

Henry's solubility of CO_2 is recalculated in an analogous way:

$$H_{T_2}^{cp} = H_{T_1}^{cp} \times e^{\frac{-\Delta H_{vap}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)}$$

$$H_{293.15\,K}^{cp} = 2.3 \times 10^{-4} \times e^{2\,400 \times \left(\frac{1}{293.15} - \frac{1}{310.15}\right)}$$

$$H_{293.15\,K}^{cp} = 3.6 \times 10^{-4} \text{ mol m}^{-3}\text{ Pa}^{-1}$$

Finally, the pH of blood at 20 °C is obtained using these recalculated values:

$$pH = pK_a + \log\frac{[HCO_3^-]}{H^{cp} \times p(CO_2)}$$

$$pH = 6.46 + \log\frac{0.024}{3.6 \times 10^{-7} \times 5\,300}$$

$$pH = 7.57$$

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.

$$Q_{m,x} = \frac{a_x}{M}$$

For -SO$_3$H (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

$$Q_{V,total} = Q_{m,total}(1 - \varepsilon)\,\rho\,(1 - w)$$

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}, $\varepsilon = 0.48$, $\rho = 1.28$ g cm^{-3}, and $w = 0.45$ we get $Q_{V,total} = 6.02 \times (1 - 0.48) \times 1.28 \times (1 - 0.45) = 2.20$ 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

$$-0.2283 = k + S \log(0.0100) \quad \text{and} \quad -0.3466 = k + S \log(0.00010)$$

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, $[HA]_{org}$ is calculated:

$$c_{HA,org,0} = 2[(HA)_2]_{org} + [HA]_{org} + [HA]_{aq} + [A^-]_{aq}$$

The concentration of UO_2A_2 is omitted as recommended in the introductory text.

From the definition of $K_{p,HA}$, $K_{D,HA}$ and $K_{a,HA}$, $[HA]_{org}$ can be obtained by solving the quadratic equation

$$2K_p \times [HA]_{org}^2 + [HA]_{org} \times \left(1 + \frac{1}{K_{D,HA}} + \frac{K_{a,HA}}{K_{D,HA} \times [H^+]_{aq}}\right) - c_{HA,org,0} = 0$$

i.e.

$$[HA]_{org} = \frac{-\left(1 + \frac{1}{K_{D,HA}} + \frac{K_{a,HA}}{K_{D,HA} \times [H^+]_{aq}}\right) + \sqrt{\left(1 + \frac{1}{K_{D,HA}} + \frac{K_{a,HA}}{K_{D,HA} \times [H^+]_{aq}}\right)^2 + 8K_p \times c_{HA,org,0}}}{4K_p}$$

Considering that the proton concentration corresponds to the analytic concentration of HNO_3, $[H^+]_{aq} = 10^{-pH} = 2.00 \times 10^{-2}$ mol dm^{-3}, we get $[HA]_{org} = 3.41 \times 10^{-3}$ mol dm^{-3}. Next, the uranyl ion distribution ratio, $D_{c,UO_2^{2+}}$ is expressed as:

$$D_{c,UO_2^{2+}} = \frac{c_{UO_2^{2+},org}}{c_{UO_2^{2+},aq}} = \frac{[UO_2A_2]_{org}}{[UO_2^{2+}]_{aq} + [UO_2A_2]_{aq} + \sum_{i=1}^{4}[UO_2(OH)_i^{2-i}]_{aq}}$$

Using β_{2,UO_2A_2}, K_{D,UO_2A_2}, $K_{a,HA}$ and β_i for $[UO_2(OH)_i]^{2-i}$ complexes, $D_{c,UO_2^{2+}}$ can be expressed as

$$D_{c,UO_2^{2+}} = \frac{K_{D,UO_2A_2}}{1 + \frac{K_{D,HA}^2}{\beta_{2,UO_2A_2} \times K_{a,HA}^2} \times \frac{[H^+]_{aq}^2}{[HA]_{org}^2} \times (1 + \sum_{i=1}^{4} \beta_i \times [OH^-]_{aq}^i)}$$

The concentration of hydroxyl ions is obtained from the concentration of protons,

$$[OH^-]_{aq} = \frac{K_w}{[H^+]_{aq}}$$

For $[H^+]_{aq} = 2.00 \times 10^{-2}$ mol dm^{-3}, we get

$$[OH^-]_{aq} = \frac{10^{14}}{2 \times 10^{-2}} = 5 \times 10^{-13} \text{ mol dm}^{-3}$$

Casting this value, $[HA]_{org} = 3.41 \times 10^{-3}$ mol dm^{-3} and all the necessary constants into the expression for the distribution ratio, we obtain

$$D_{c,UO_2^{2+}} = 5.61$$

Then, the yield R defined as

$$R = \frac{n_{,org}}{n_{,org} + n_{,aq}} = \frac{D_{c,UO_2^{2+}}}{D_{c,UO_2^{2+}} + \frac{V_{aq}}{V_{org}}}$$

can be calculated, providing the final result of

$$R = \frac{5.61}{5.61 + 1} = 84.9\%$$

12.2 For the conditions of $[H^+] = 10^{-pH} = 5.01 \times 10^{-11}$ mol dm^{-3}, using the same calculation procedure, we get

$[HA]_{org} = 1.50 \times 10^{-5}$ mol dm^{-3}

$D_{c,UO_2^{2+}} = 1.22 \times 10^{-4}$

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**)
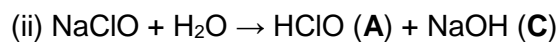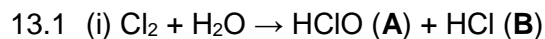
In alkaline aqueous solution, hypochlorite ion (ClO^-) will dominate.

13.2

$$c(\text{NaClO}) = \frac{\rho(\text{Cl}_2)}{M(\text{Cl}_2)}$$

$$c(\text{NaClO}) = \frac{22.4}{70.906} = 0.3159 \text{ mol dm}^{-3}$$

13.3 $ClO^- + 2\,I^- + 2\,H^+ \rightarrow I_2 + H_2O + Cl^-$

$I_2 + 2\,S_2O_3^{2-} \rightarrow 2\,I^- + S_4O_6^{2-}$
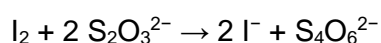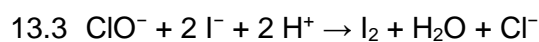
$$w(\text{NaClO}) = c\left(S_2O_3{}^{2-}\right) \times V\left(S_2O_3{}^{2-}\right) \times \frac{1}{2} \times M(\text{NaClO}) \times \frac{V_{\text{flask}}}{\rho_{\text{SAVO}} \times V_{\text{SAVO}} \times V_a}$$

$$w(\text{NaClO}) = 0.0503 \times 0.01015 \times \frac{1}{2} \times 74.44 \times \frac{0.250}{1.070 \,\times\, 0.010 \,\times\, 0.010} \times 100\% = 4.44\%$$

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
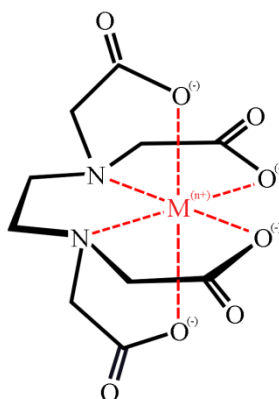
$\delta(HY^{3-}) = [HY^{3-}] / c(EDTA) = \beta_1 [H^+] / (1 + \beta_1 [H^+] + \beta_2 [H^+]^2 + \beta_3 [H^+]^3 + \beta_4 [H^+]^4)$

$\delta(Y^{4-}) = [Y^{4-}] / c(EDTA) = 1 / (1 + \beta_1 [H^+] + \beta_2 [H^+]^2 + \beta_3 [H^+]^3 + \beta_4 [H^+]^4)$,

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 $Zn^{2+} + 4 CN^- \rightarrow [Zn(CN)_4]^{2-}$
$[Zn(CN)_4]^{2-} + 4 HCHO + 4 H_2O \rightarrow Zn^{2+} + 4 HOCH_2CN + 4 OH^-$
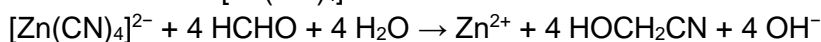
14.5 2,3-Disulfanylpropan-1-ol is used for masking lead ions.

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)

$$m(\text{Pb}) = c_{\text{std}}(\text{Mg}) \times V_{\text{std}}(\text{Mg}) \times \frac{A(\text{Pb})}{m(\text{sample})} \times m_1$$

$$m(\text{Pb}) = 0.01087 \times 0.0128 \times \frac{207.20}{0.8472} \times 1 = 34.03 \text{ mg}$$

$$n(\text{Mg}) = n_1(EDTA) - n_{\text{std}}(\text{Mg})$$

$$m(\text{Mg}) = \left(c(\text{EDTA}) \times V_1(\text{EDTA}) - c_{\text{std}}(\text{Mg}) \times V_{\text{std}}(\text{Mg})\right) \times \frac{A(\text{Mg})}{m(\text{sample})} \times m_1$$

$$m(\text{Mg}) = (0.01983 \times 0.0359 - 0.01087 \times 0.0128) \times \frac{24.305}{0.8472} \times 1 = 16.43 \text{ mg}$$

$$m(\text{Zn}) = c(\text{EDTA}) \times V_2(\text{EDTA}) \times \frac{A(\text{Zn})}{m(\text{sample})} \times m_1$$

$$m(\text{Zn}) = 0.01983 \times 0.0241 \times \frac{65.38}{0.8472} \times 1 = 36.88 \text{ mg}$$

14.7 Complexation equation: $Ca^{2+} + Y^{4-} \rightarrow CaY^{2-}$

Final analytical concentrations after dilution are:

$$c(Ca^{2+}) = \frac{10}{100} \times 0.05 = 5.0 \times 10^{-3} \text{ mol dm}^{-3} \quad c(Y^{4-}) = \frac{50}{100} \times 0.04 = 2.0 \times 10^{-2} \text{ mol dm}^{-3}$$

The coefficient for EDTA side reactions

$\alpha(\text{EDTA}) = (1 + \beta_1 [H^+] + \beta_2 [H^+]^2 + \beta_3 [H^+]^3 + \beta_4 [H^+]^4)$

(definitions of β_i are in 14.2); for pH = 6

$\alpha(\text{EDTA}) = (1 + 1.82 \times 10^{10} \times 10^{-6} + 2.63 \times 10^{16} \times 10^{-12} + 1.23 \times 10^{19} \times 10^{-18} + 1.23 \times 10^{21} \times 10^{-24}) =$
$= 4.45 \times 10^4$

The final concentration of free Ca^{2+} ions in the solution is:

$$\beta^I = \frac{\beta(Ca-EDTA)}{\alpha(\text{EDTA})} = \frac{10^{10.61}}{4.45 \times 10^4} = 10^{5.96}$$

Based on the mass balances

$$[Ca^{2+}] = \frac{c(Ca^{2+})}{1 + \beta^I[Y^{4-}]}$$

$$[Y^{4-}] = c(Y^{4-}) - [CaY^{2-}] = c(Y^{4-}) - (c(Ca^{2+}) - [Ca^{2+}])$$

we get a quadratic equation with the following solution

$$\beta^I[Ca^{2+}]^2 + (1 + \beta^I c(Y^{4-}) - \beta^I c(Ca^{2+}))[Ca^{2+}] - c(Ca^{2+}) = 0$$

$$[Ca^{2+}] = 3.642 \times 10^{-7} \text{ mol dm}^{-3}$$

Problem 15. Colours of complexes
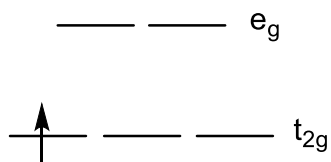
15.1   Ground state: Excited state:
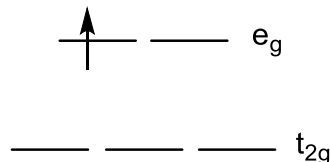
15.2   The wavenumber of 20 300 cm^{-1} corresponds to the wavelength of 493 nm which means the absorption of the blue-green light. The colour of the complex is the complementary one, i.e. orange-red.

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) $4\ CoCl_2 + 4\ NH_4Cl + 20\ NH_3 + O_2 \rightarrow 4\ [Co(NH_3)_6]Cl_3 + 2\ H_2O$
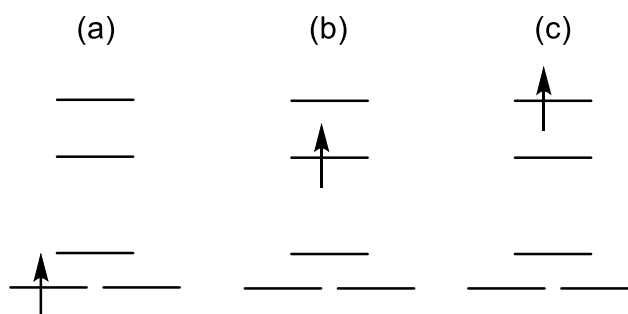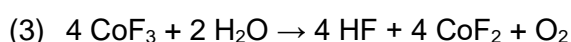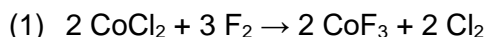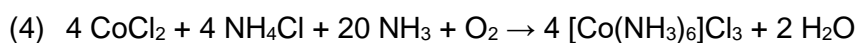
15.7   The wavenumbers correspond to the wavelengths of 475 nm (blue light) and 340 nm (UV region). The second band has no effect on the observed colour and the complex is orange. Luteus means yellow in Latin (it refers to the yellow-orange colour of the complex).

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:
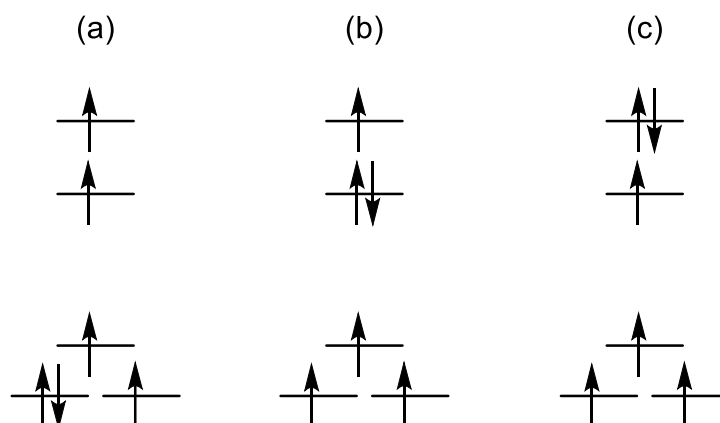
15.10 The wavenumbers correspond to the wavelengths of 877 nm (IR region) and 690 nm (red light). The first band has no effect on the observed colour and the complex is blue-green.

Problem 16. Iron chemistry

16.1 The requested potentials are calculated as follows, (1)–(3):

$$E°(FeO_4^{2-},H^+/Fe^{2+}) = (3 × 1.90 + 1 × 0.77) / 4 \text{ V} = 1.62 \text{ V} \qquad (1)$$

$$E°(FeO_4^{2-},H^+/Fe) = (3 × 1.90 + 1 × 0.77 + 2 × (−0.44)) / 6 \text{ V} = 0.93 \text{ V} \qquad (2)$$

$$E°(Fe^{3+}/Fe) = (1 × 0.77 + 2 × (−0.44)) / 3 \text{ V} = −0.04 \text{ V} \qquad (3)$$

The corresponding Latimer diagram is depicted in Figure 1.
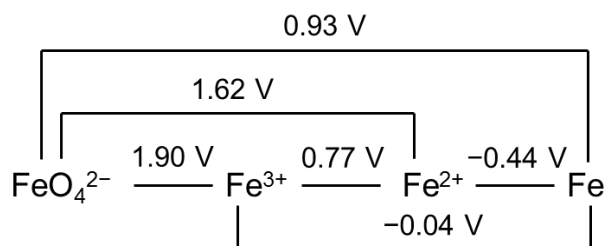
Figure 1. Latimer diagram for iron species in water (pH 0).

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.

$$\text{Voltage equivalent} = N × E°(\text{species/element}) \qquad (4)$$

The individual voltage equivalents are calculated from the data above (5)–(8).

$$\text{Voltage equivalent (Fe)} = 0 × 0 \text{ V (def.)} = 0 \text{ V} \qquad (5)$$

$$\text{Voltage equivalent (Fe}^{2+}) = 2 × (−0.44) \text{ V} = −0.88 \text{ V} \qquad (6)$$

$$\text{Voltage equivalent (Fe}^{3+}) = 3 × (−0.04) \text{ V} = −0.12 \text{ V} \qquad (7)$$

$$\text{Voltage equivalent (FeO}_4^{2-}) = 6 × 0.93 \text{ V} = 5.58 \text{ V} \qquad (8)$$
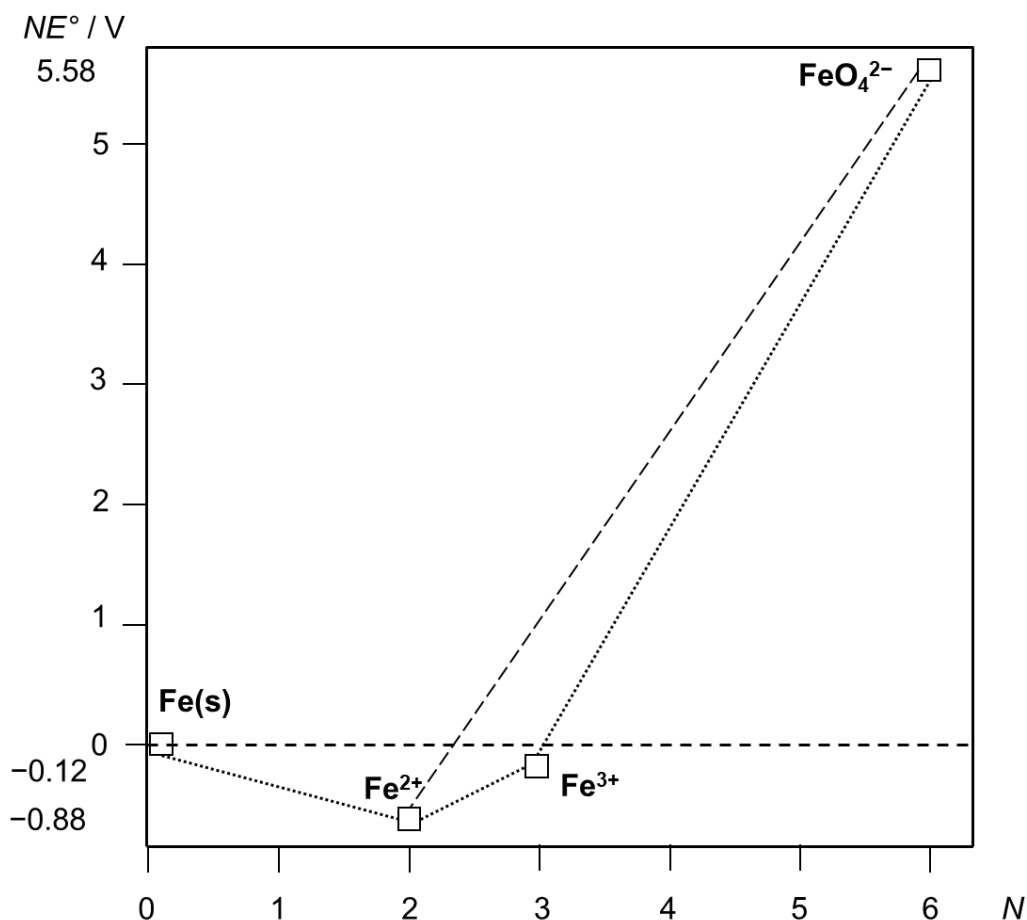
Figure 2. Frost diagram for iron species (pH 0).

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):

$$FeO_4^{2-} + 3\,Fe^{2+} + 8\,H^+ \rightarrow 4\,Fe^{3+} + 4\,H_2O \tag{9}$$
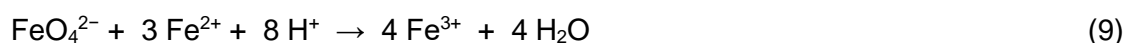
16.3

(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.
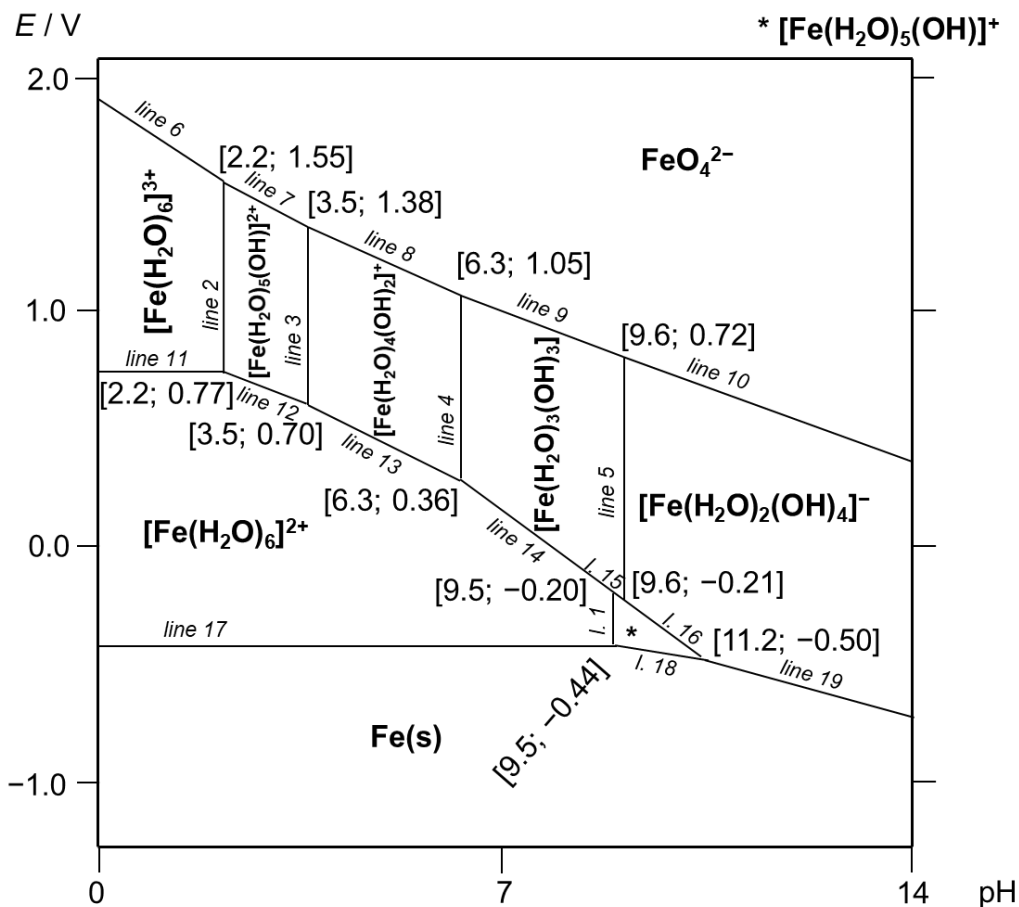
Figure 3. Pourbaix diagram for dissolved iron species and metallic iron.

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+}): $E = E° − 0.059 × \log([Fe^{2+}] / [Fe^{3+}])$, thus $E = 0.77$ (10)

line 17 (Fe^{2+}/Fe): $E = E° − (0.059 / 2) × \log(a(Fe,s) / [Fe^{2+}])$, 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.

$2 [Fe(OH)_4]^- + 3 ClO^- + 2 OH^- \rightarrow 2 FeO_4^{2-} + 3 Cl^- + 5 H_2O$ (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-	$t_{2g}^4 e_g^2$	para-	$-0.4\Delta_o$ **
$[Fe(CN)_6]^{4-}$	d^6	low-	$t_{2g}^6 e_g^0$	dia-	$-2.4\Delta_o + 2P$ **
$[Fe(H_2O)_6]^{3+}$	d^5	high-	$t_{2g}^3 e_g^2$	para-	0
$[Fe(H_2O)_5OH]^{2+}$	d^5	high-	$(t_{2g}^3 e_g^2)$*	para-	0
$[Fe(CN)_6]^{3-}$	d^5	low-	$t_{2g}^5 e_g^0$	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) $2\ Mn + 12\ NaCN + 2\ H_2O \rightarrow 2\ Na_5[Mn(CN)_6] + H_2 + 2\ NaOH$
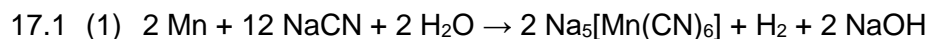
17.2 Diagram – low-spin configuration d^6:

$$\underline{\quad\quad}\ \underline{\quad\quad}\quad e_g$$

$$\underline{\uparrow\downarrow}\ \ \underline{\uparrow\downarrow}\ \ \underline{\uparrow\downarrow}\quad t_{2g}$$
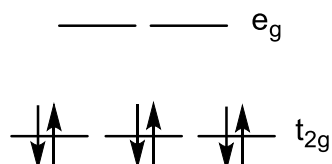
17.3 Diagram – high-spin configuration d^5:

$$\underline{\ \uparrow\ }\ \ \underline{\ \uparrow\ }\quad e_g$$

$$\underline{\ \uparrow\ }\ \ \underline{\ \uparrow\ }\ \ \underline{\ \uparrow\ }\quad t_{2g}$$
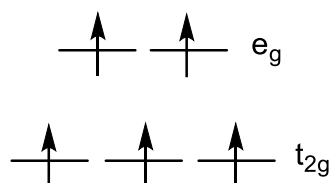
The complex has five unpaired electrons.

17.4 Diagram – low-spin configuration d^5:

$$\underline{\quad\quad}\ \underline{\quad\quad}\quad e_g$$

$$\underline{\uparrow\downarrow}\ \ \underline{\uparrow\downarrow}\ \ \underline{\ \uparrow\ }\quad t_{2g}$$

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:

$$\underline{\quad\quad}\ \underline{\quad\quad}\quad e_g$$

$$\underline{\uparrow\downarrow}\ \ \underline{\ \uparrow\ }\ \ \underline{\ \uparrow\ }\quad t_{2g}$$

17.7 (6) $4\ MnO_2 + 12\ KHF_2 \rightarrow 4\ K_3[MnF_6] + O_2 + 6\ H_2O$
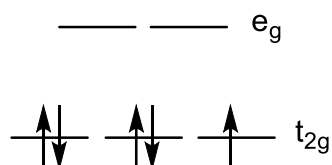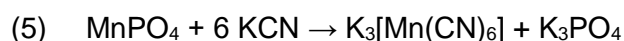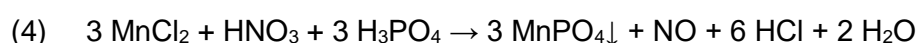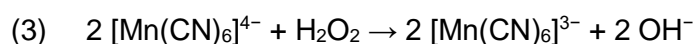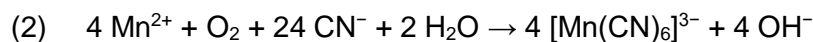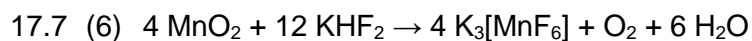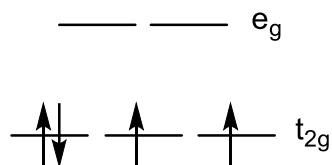
17.8 Diagram – high-spin configuration d^4:

$$\underline{\ \uparrow\ }\ \ \underline{\quad\quad}\quad e_g$$

$$\underline{\ \uparrow\ }\ \ \underline{\ \uparrow\ }\ \ \underline{\ \uparrow\ }\quad t_{2g}$$
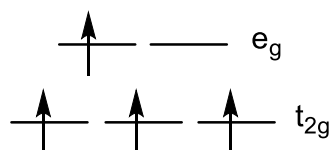
17.9 Sharing 1 bridging F atom between 2 neighbouring octahedral units corresponds to the stoichiometry $[MnF_5]^{2-}$:
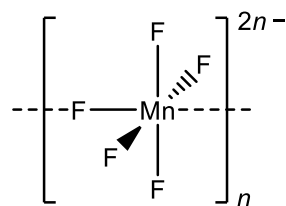
17.10 The stoichiometry $[MnF_4]^-$ could be achieved in a chain structure having 2 bridging F atoms between 2 neighbouring octahedral units:
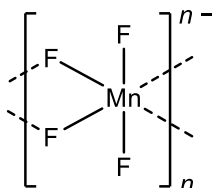
However, the structure is a 2D-anionic layer, so it is necessary to extend the structure to 2 dimensions – to have 4 bridging F atoms for each octahedral unit:
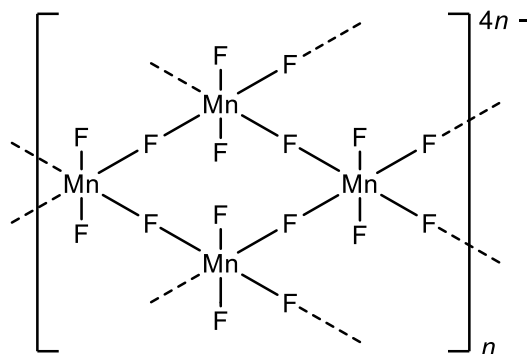
17.11 Diagram – configuration d^3:
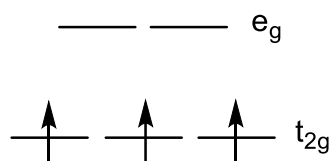
17.12 Since the magnitude of splitting in tetrahedral crystal field is about a half of octahedral (exactly $\Delta_{tet} = -\frac{4}{9}\Delta_{oct}$; the negative sign refers to the inverse order of split d-orbitals with respect to the octahedral crystal field), it is always lower than electron pairing energy ($\Delta_{tet} < P$) which leads to high-spin configurations in tetrahedral complexes.

Diagram – high-spin configuration d^5:

17.13 (7) $2\ KMnO_4 + 3\ H_2O_2 + 2\ KHF_2 + 8\ HF \rightarrow 2\ K_2[MnF_6] + 3\ O_2 + 8\ H_2O$
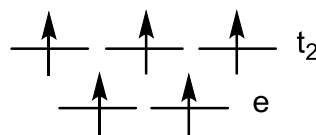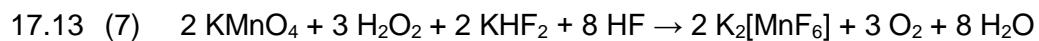
17.14 Manganese(IV) complexes have a configuration of d^3. Since these three electrons occupy the t_{2g} level only, low- and high-spin configurations cannot form regardless of the magnitude of the crystal field splitting.

17.15 (8) $K_2[MnF_6] + 2\ SbF_5 \rightarrow 2\ K[SbF_6] + MnF_2 + F_2$
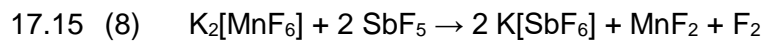
Problem 18. The fox and the stork

Large stones

18.1 Each layer consists of one sphere only: $n = 50 / (2 \times 5) = 5$

18.2 The volume of 5 spheres: $V = 5 \times \frac{4}{3}\pi r^3 = 5 \times \frac{4}{3}\pi \times 5^3 = 2\,618\text{ cm}^3$

The volume of cylinder: $V = \pi r^2 \times v = \pi \times 5^2 \times 50 = 3\,927\text{ cm}^3$

The fraction of volume: $f = 2\,618 / 3\,927 = 0.667$, i.e. 66.7 %

18.3 The free volume: $V_{\text{free}} = 3\,927 - 2\,618 = 1\,309\text{ cm}^3$

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: $V = 105 \times \frac{4}{3}\pi r^3 = 105 \times \frac{4}{3}\pi \times (1.667)^3 = 2\,036\text{ cm}^3$

The fraction of volume: $f = 2\,036 / 3\,927 = 0.518$, i.e. 51.8 %

18.8 The free volume: $V_{\text{free}} = 3\,927 - 2\,036 = 1\,891\text{ cm}^3$

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):

$$h = a \times \sqrt{\frac{2}{3}} = 2 \times 1.667 \times \sqrt{\frac{2}{3}} = 2.722\text{ cm}$$

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: $V = 90 \times \frac{4}{3}\pi r^3 = 90 \times \frac{4}{3}\pi \times (1.667)^3 = 1\,745\text{ cm}^3$

The fraction of volume: $f = 1\,745 / 3\,927 = 0.444$, i.e. 44.4 %

18.12 The free volume: $V_{\text{free}} = 3\,927 - 1\,745 = 2\,182\text{ cm}^3$
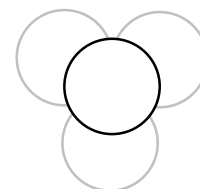
Sand

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.
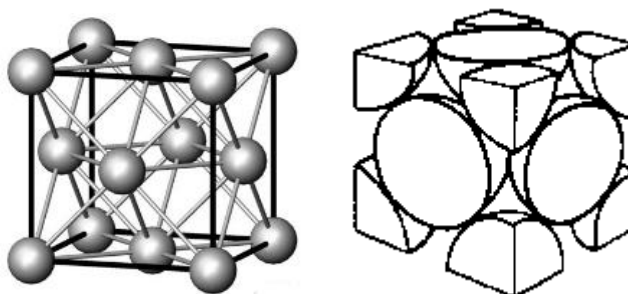
The lattice constant a is $2 \times r \times \sqrt{2}$. Then the volume of the elementary cell is:

$$V_{\text{cell}} = a^3 = 16\sqrt{2} \times r^3$$

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_{free} = 3 927 × (1 − 0.7405) = 1 019 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:

$r(\text{Cl}^-) = \frac{1}{2} \times (5.64 - 2 \times 1.16)$ Å = 1.66 Å.

19.2 The density of KCl is:

$\rho(\text{KCl}) = m / V = [4 \times M(\text{KCl})] / [N_A \times a(\text{KCl})^3]$, and therefore:

$a(\text{KCl}) = \{[4 \times M(\text{KCl})] / [N_A \times \rho(\text{KCl})]\}^{1/3} = [(4 \times 74.55) / (6.022 \times 10^{23} \times 1.98)]^{1/3}$ cm =

$= 6.30 \times 10^{-8}$ cm = 6.30 Å

$r(\text{K}^+) = \frac{1}{2} \times [a(\text{KCl}) - 2 \times r(\text{Cl}^-)]$ Å $= \frac{1}{2} \times (6.30 - 2 \times 1.66)$ Å = 1.49 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 $\rho(\text{PbS}) = m / V = [4 \times M(\text{PbS})] / [N_A \times a(\text{PbS})^3] = (4 \times 239.3) / (6.022 \times 10^{23} \times 5.94^3)$ g Å^{-3} =
$= 7.58$ 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 Pb$_{1-x}$Ag$_x$S$_{1-\frac{1}{2}x}$.

19.6 $\rho(\text{Pb}_{1-x}\text{Ag}_x\text{S}_{1-\frac{1}{2}x}) = m / V = [4 \times M(\text{Pb}_{1-x}\text{Ag}_x\text{S}_{1-\frac{1}{2}x})] / [N_A \times a(\text{Pb}_{1-x}\text{Ag}_x\text{S}_{1-\frac{1}{2}x})^3]$, and therefore:

$M(\text{Pb}_{1-x}\text{Ag}_x\text{S}_{1-\frac{1}{2}x}) = \rho(\text{Pb}_{1-x}\text{Ag}_x\text{S}_{1-\frac{1}{2}x}) \times N_A \times a(\text{Pb}_{1-x}\text{Ag}_x\text{S}_{1-\frac{1}{2}x})^3 / 4 =$

$= [7.21 \times 6.022 \times 10^{23} \times (5.88 \times 10^{-8})^3] / 4$ g mol$^{-1} = 220.7$ 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:

$a(\text{Ge}) = 8 \times r(\text{Ge}) / \sqrt{3} = 8 \times 1.23 / \sqrt{3}$ Å = 5.68 Å,

giving the density:

ρ(Ge) = m / V = [8 × M(Ge)] / [N_A × a(Ge)^3] = (8 × 72.6) / (6.022 × 10^{23} × 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:

ρ(Ge) = m / V = [3√3 × M(Ge)] / [64 × N_A × r(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
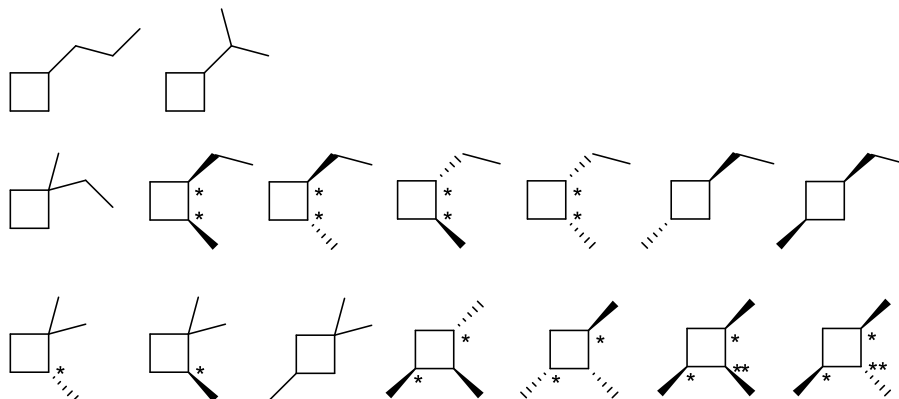
Note that the two carbon atoms marked with a double asterisk (**) are pseudo-asymmetric. They have two constitutionally identical ligands which differ in configuration.

20.3

20.4

A)

B)

C)

D)
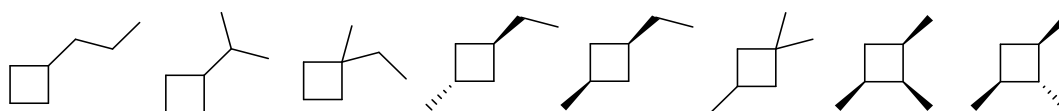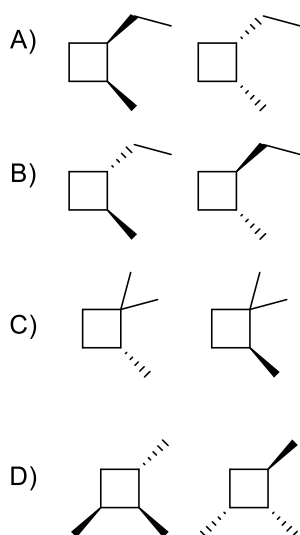
Problem 21. Fluorinated radiotracers

21.1 ^{18}O (18-fluorine is synthesized by the following reaction: ^{18}O + p → ^{18}F + n)

21.2 $\tau_{1/2}$ (^{18}F) = 6 586 s

k = ln 2 / (6 586 s) = 1.052 × 10^{-4} s^{-1}

$n = N / N_A$ = 300 MBq / (1.052 × 10^{-4} s^{-1} × 6.022 × 10^{23} mol^{-1}) = 4.73 × 10^{-12} mol

21.3 Heat of combustion of glucose = 2 800 kJ mol^{-1}

Chemical energy of one glucose molecule: E_c = 2 800 kJ / N_A = 4.650 × 10^{-18} J

Energy of γ-photons per one glucose molecule: E_p = 2 × m_e × c^2 = 1.637 × 10^{-13} J

Calculation of time:

Total chemical energy of ^{18}O-glucose = Total energy of not yet released γ-photons

E_c × N(glucose) = E_p × N(^{18}F)

E_c × [N_0(^{18}F) − N(^{18}F)] = E_p × N(^{18}F)

E_c × N_0(^{18}F) × (1 − e^{-kt}) = E_p × N_0(^{18}F) × e^{-kt}

E_c = E_p × e^{-kt} + E_c × e^{-kt}

E_c / (E_c + E_p) = e^{-kt}

ln [E_c / (E_c + E_p)] = − k × t

t = ln [(E_c + E_p) / E_c] × (1 / k) = ln (35 213) / (1.052 × 10^{-4} s^{-1}) = 9.95 × 10^4 s = 27 h 38 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.
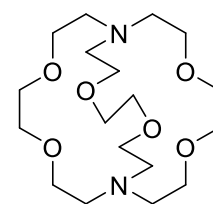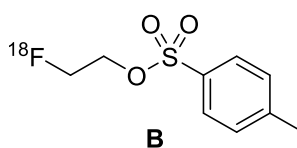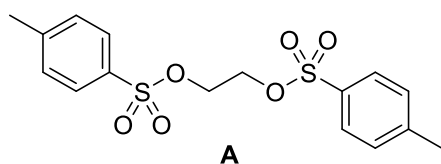
X = [2.2.2]cryptand

21.5
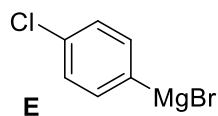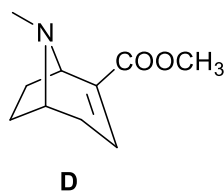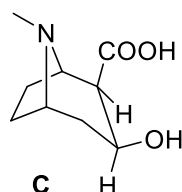
21.6
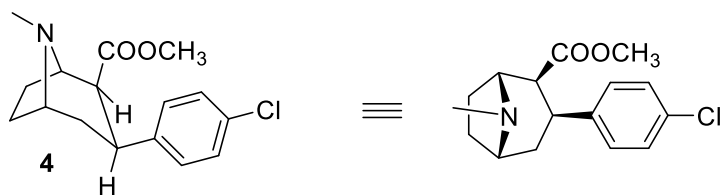
The other possible isomers are:
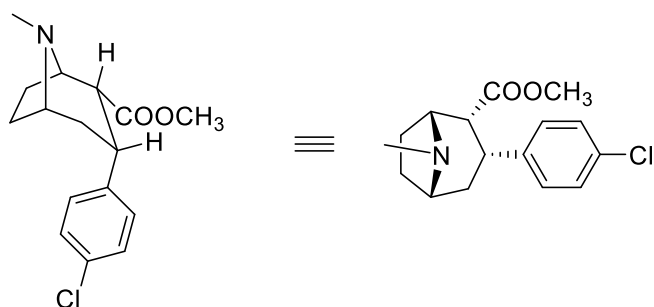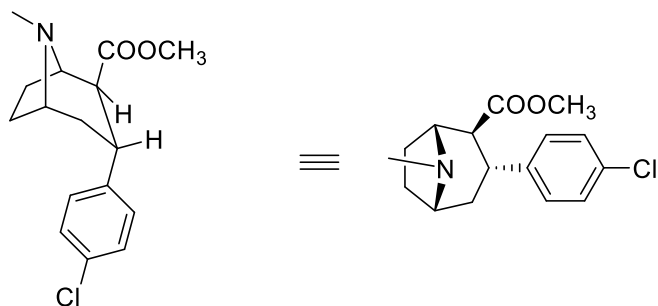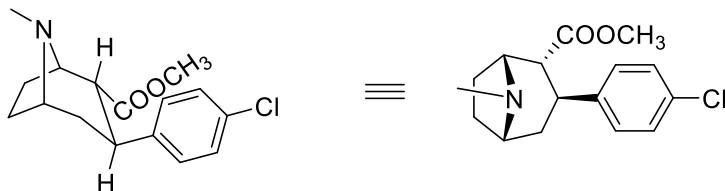
21.7
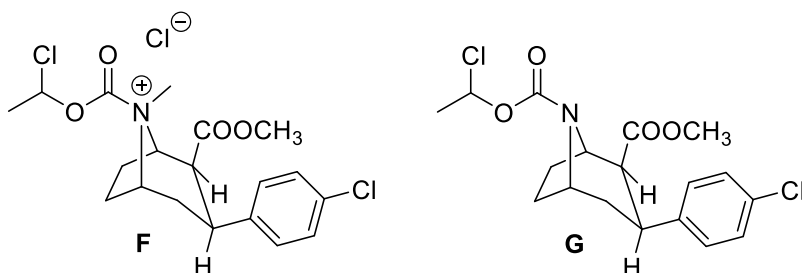
Problem 22. Where is lithium?

22.1 The formation of organolithium reagents involves a radical pathway.
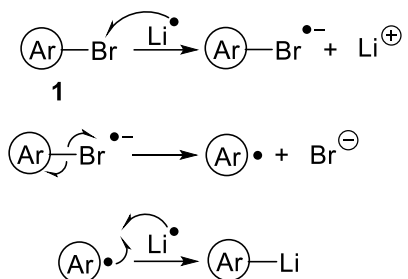
22.2 The structures of intermediates **A**, **B**, **C**, and **D**:
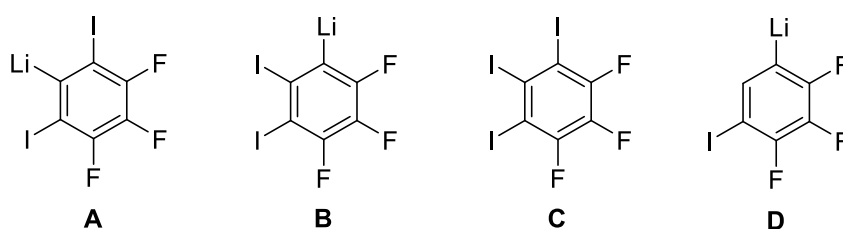
22.3 Reaction scheme for the haloform reaction:
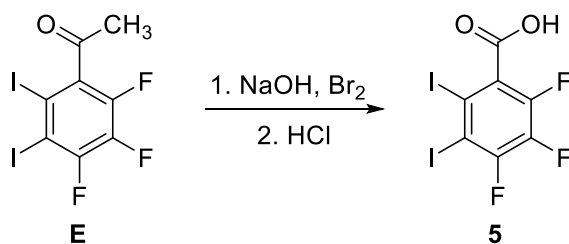
Other reagents, such as NaOH + I_2 or NaClO can also be used.

Problem 23. Synthesis of eremophilone

23.1

A   B   C   D

E   F   G   H

NaOH or NaOMe; other bases used for aldolization are also acceptable
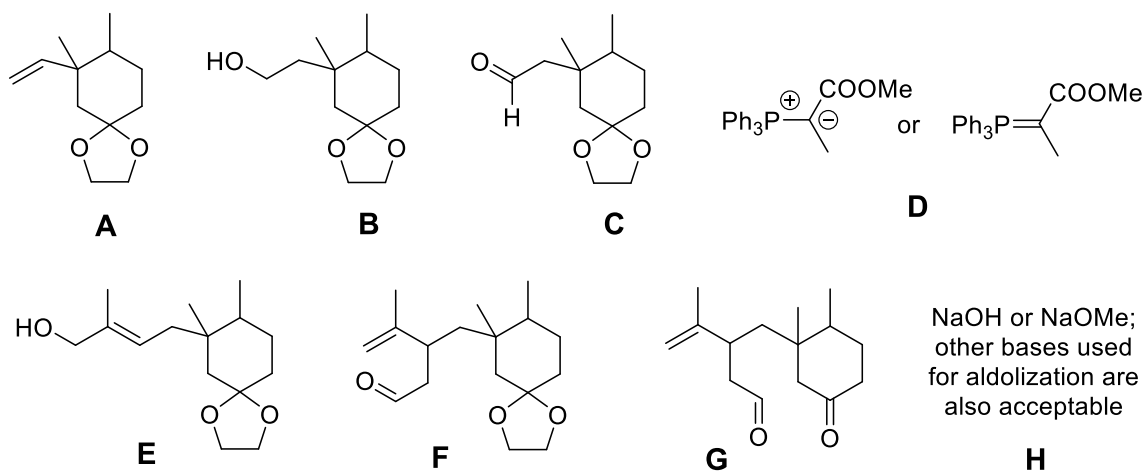
23.2 This reaction is called the Claisen rearrangement.

or   or

I

23.3

J   or   K   or   L
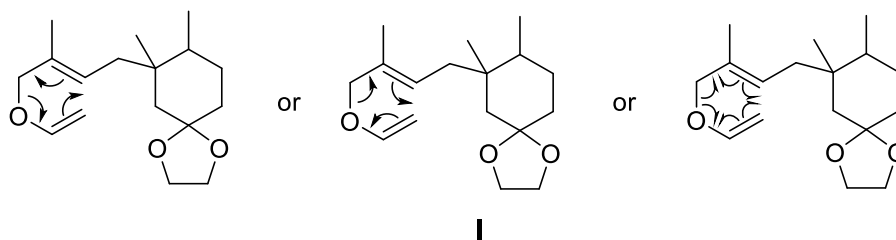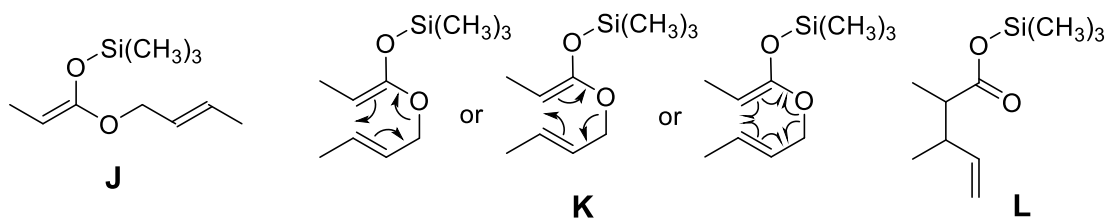
Problem 24. Cinnamon all around

24.1

A (trans-cinnamic acid) **B** (cis-cinnamic acid)
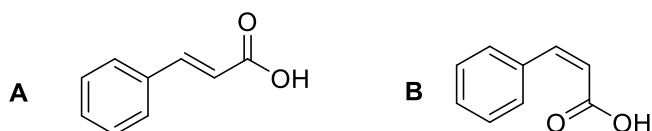
24.2 Direct UV irradiation (313 nm, acetonitrile). A conformationally mobile biradical is formed. Under these conditions, **B** and **A** are obtained in a 79 : 21 ratio.
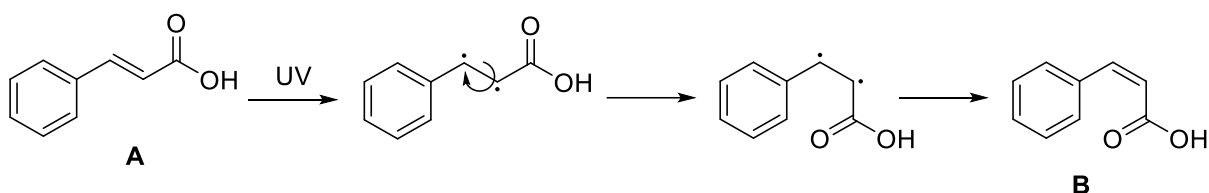
Alternatively, UV irradiation with sensitizers (e.g. riboflavin), or reagents such as diphenyldiselenide, hydrogen peroxide etc. can be used.

24.3 Arbuzov reaction with 2-bromoacetic acid and tribenzyl phosphite:
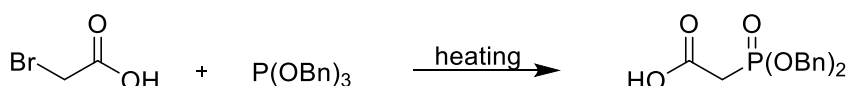
24.4
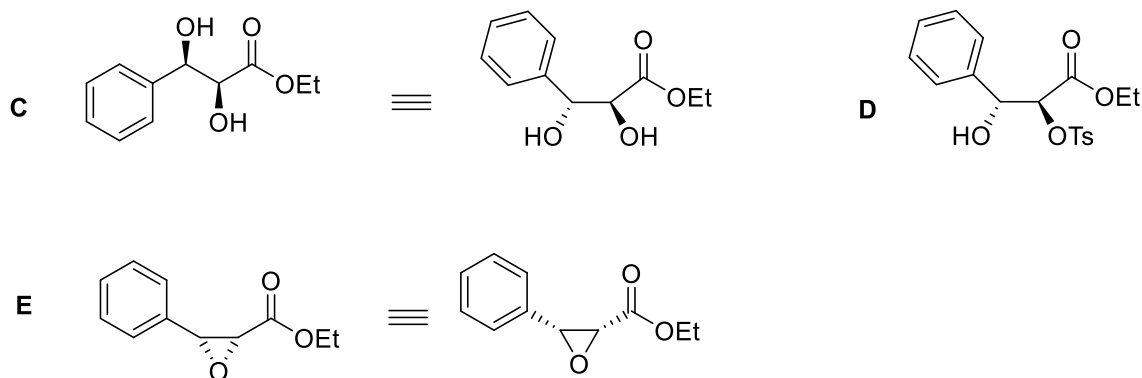
24.5
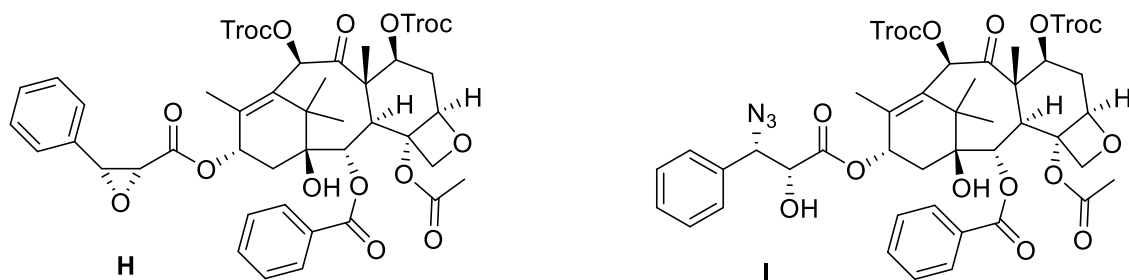
24.6 The carboxylic acid functional group reacts with DCC to form an *O*-acylisourea, which serves as the reactive intermediate in reactions with nucleophiles (e.g. alcohols or amines) in acyl nucleophilic substitutions.
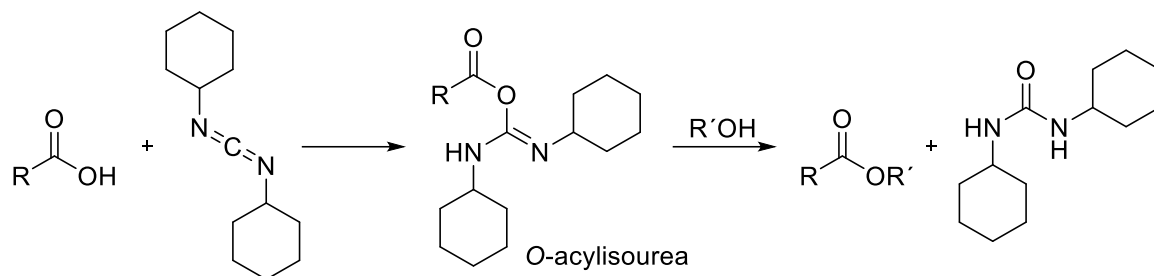
24.7 The starting compound is (*E*)-cinnamic acid methyl ester.

24.8
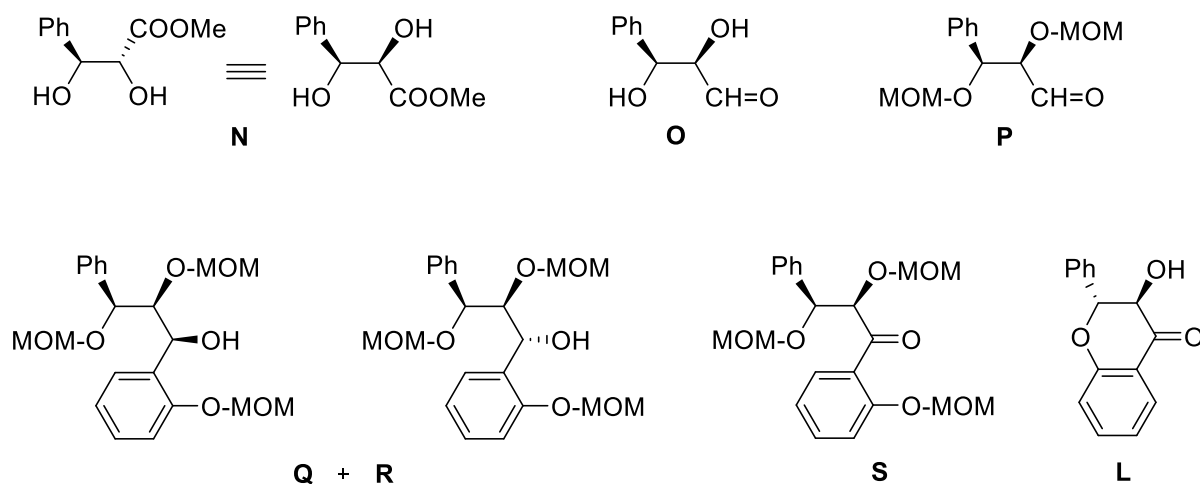
24.9 The two isomers **Q** and **R** are diastereoisomers (diastereomers).

24.10 The acidic hydrogens of the OH groups would decompose the organolithium compound.

24.11

PDC
pyridinium dichromate
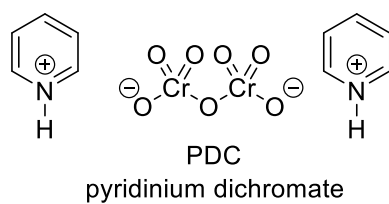
24.12 The reaction is named after Prof. Mitsunobu.

Problem 25. All roads lead to caprolactam

25.1

25.2 d)

25.3

$$HNO_3 + 3\ HCl \longrightarrow NOCl + 2\ H_2O + Cl_2$$

$$HNO_2 + HCl \longrightarrow H_2O + NOCl$$

$$NO_2^- + 2\ HCl \longrightarrow H_2O + NOCl + Cl^-$$

$$2\ NO + Cl_2 \longrightarrow 2\ NOCl$$
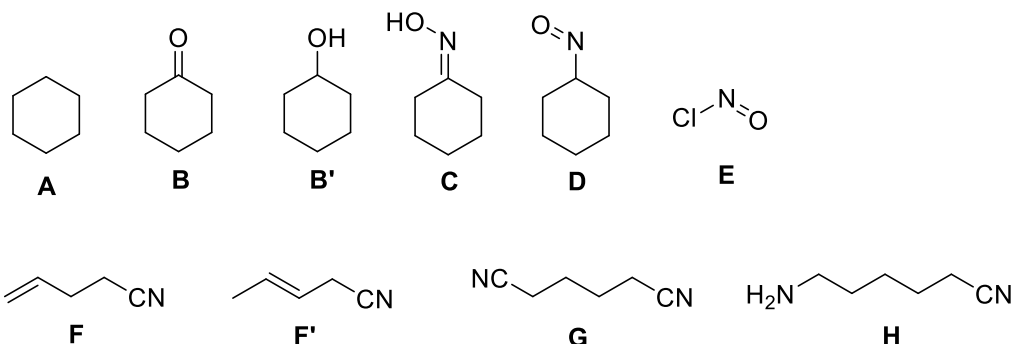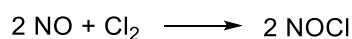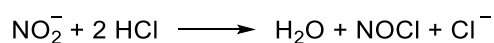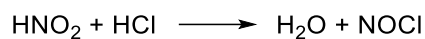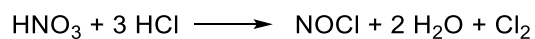
25.4
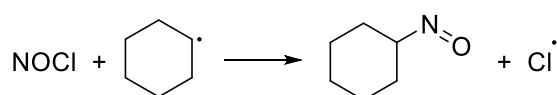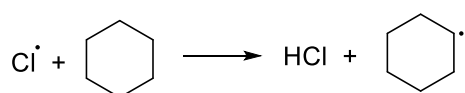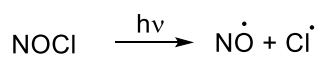
25.5 Gas **E** (NOCl) is orange. Therefore, the optimal wavelength would be below 530 nm (green and blue light).

**25.6** Beckmann rearrangement.
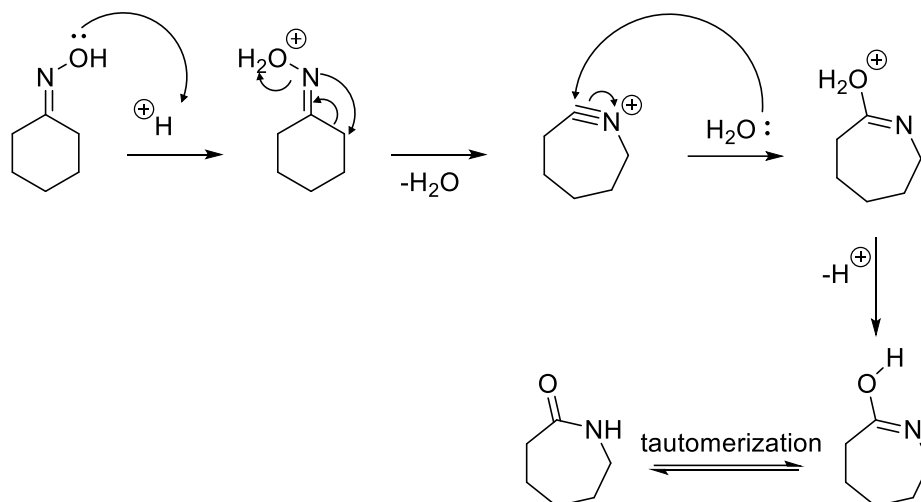
Problem 26. Ring opening polymerizations (ROP)

**26.1**

B

26.2

(1)

:B = base

(2)

(3)

(4)

(5)
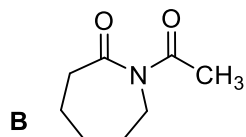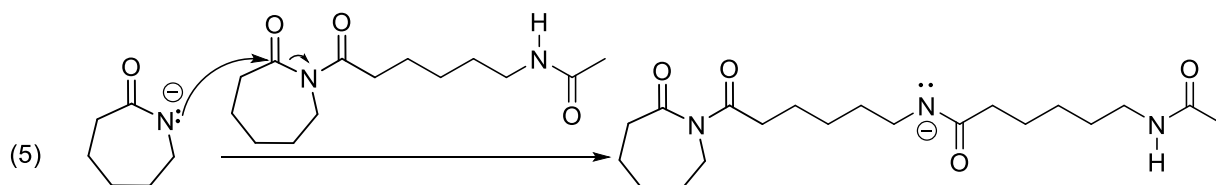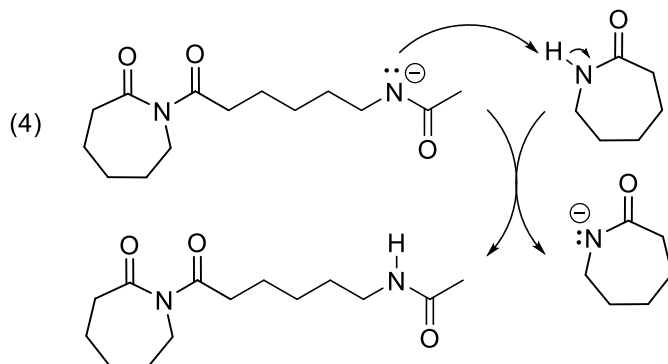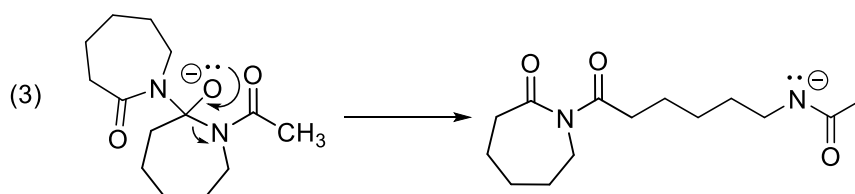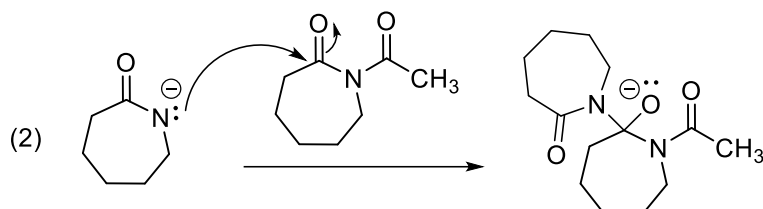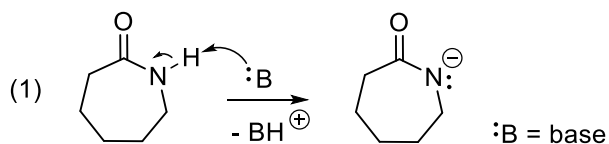
26.3
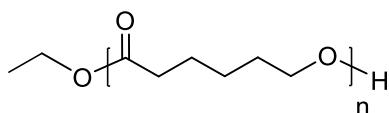
26.4 Ten grams of sodium ethoxide correspond to 10 / (2 × 12 + 5 × 1 + 1 × 16 + 1 × 23) = 0.1471 mol. Two kilograms consumed with 83% conversion means 2 000 × 0.83 = 1 660 g embedded into polymer. Each molecule of the initiator initiates one chain, so the number-average molecular weight is 1 660 / 0.1471 = 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)
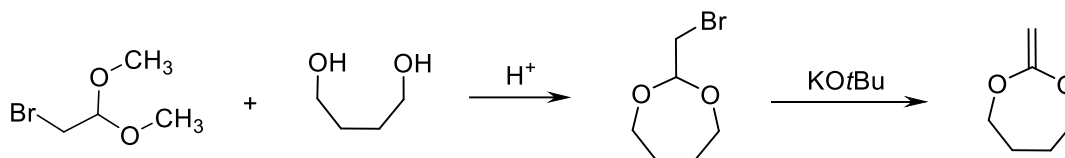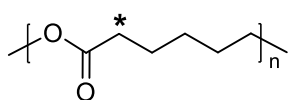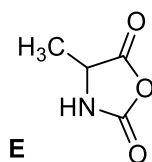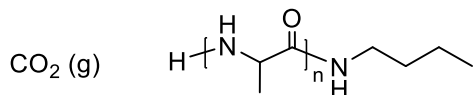
26.9 A single wrong enantiomer of an amino acid in the protein structure causes loss of activity. Glycine is not chiral, so there are 129 − 12 = 117 chiral amino acids in lysozyme. The overall yield is $(1/2)^{117}$ × 100% = 6.02 × 10^{-34} %.

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 × 10^{31} kg of material. As the Earth weighs 5.972 × 10^{24} kg, this corresponds to 1.99 × 10^{31} / 5.972 × 10^{24} = = 3.34 × 10^6 times the mass of the Earth.
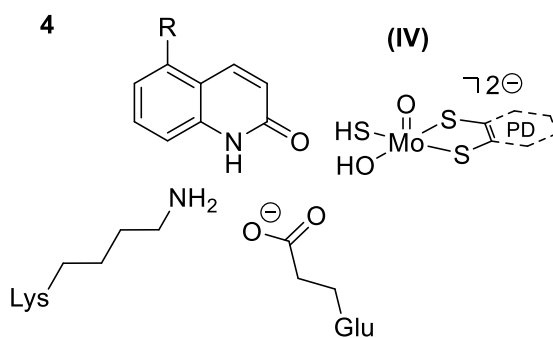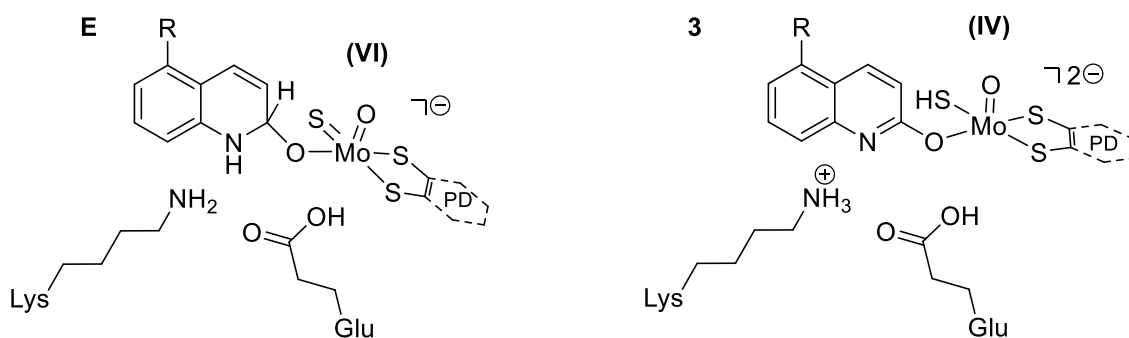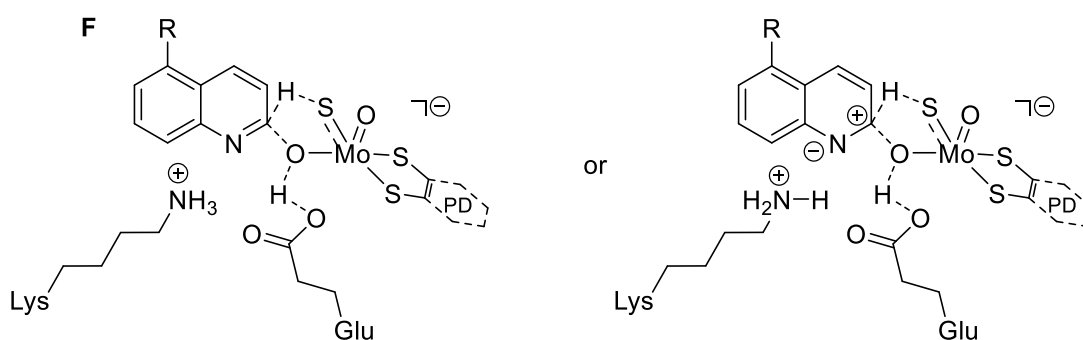
Problem 27. Zoniporide

27.1
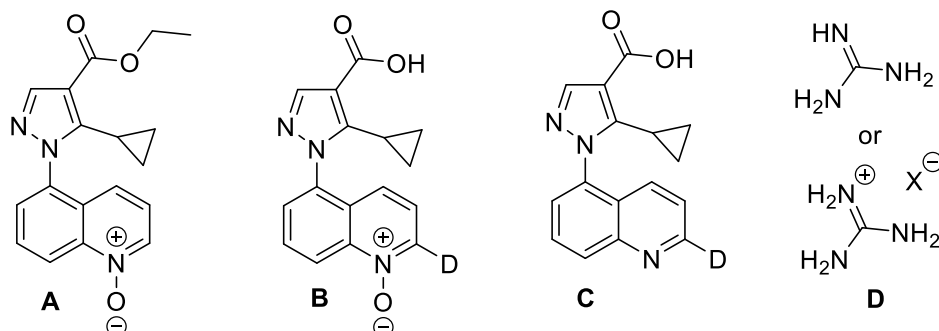
27.2 Ammonia (NH_3), carbon dioxide (CO_2) and hydrogen (H_2)

27.3 and 27.4

27.5

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

$$\frac{k_H}{k_D} = \exp\left(\frac{E_{0,H} - E_{0,D}}{k_B T}\right)$$

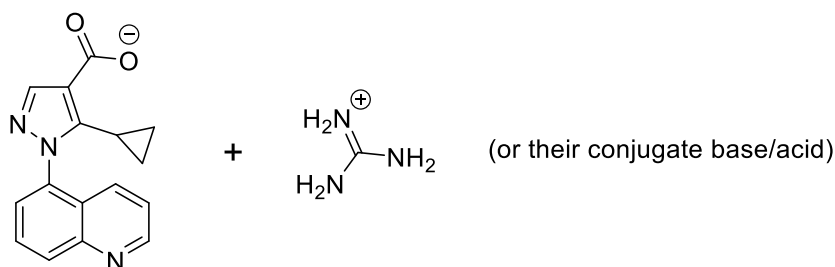$$E_{0,H} - E_{0,D} = \frac{1}{2}\hbar(\omega_H - \omega_D)$$

$$\omega_{H/D} = \sqrt{\frac{k}{\mu_{H/D}}}$$

$$\mu_{H/D/T} = \frac{m_{H/D/T}\, m_{^{12}C}}{m_{H/D/T} + m_{^{12}C}}$$

$$\sqrt{k} = \frac{2 k_B T \, \ln\left(\frac{k_H}{k_D}\right)}{\hbar\left(\frac{1}{\sqrt{\mu_H}} - \frac{1}{\sqrt{\mu_D}}\right)} = 21.105 \text{ kg}^{\frac{1}{2}}\,\text{s}^{-1} \implies k = 445.4 \text{ kg s}^{-2}$$

$$\frac{k_H}{k_T} = \exp\left(\frac{\hbar\sqrt{k}}{2 k_B T}\left(\frac{1}{\sqrt{\mu_H}} - \frac{1}{\sqrt{\mu_T}}\right)\right) = 12.2(59)$$
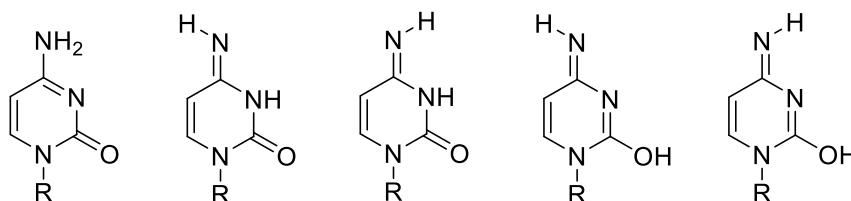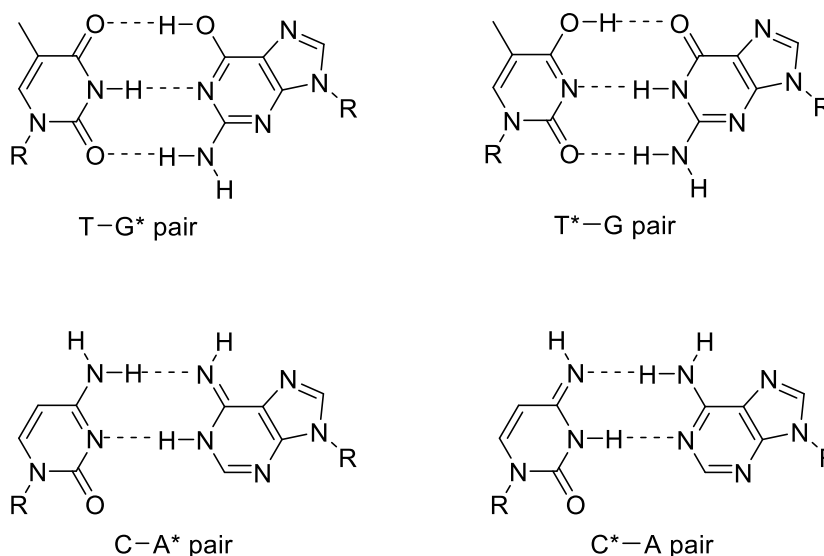
27.9

(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 $T_m(\text{DNA1}) \sim 315$ K and $T_m(\text{DNA2}) \sim 340$ K.

c) **False.** Since $T_m(\text{DNA1}) \sim 315$ K and $T_m(\text{DNA2}) \sim 340$ 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.