Baltic Chemistry Olympiad

2013

Problem 1. Photosynthesis

Photosynthesis consists of light and dark phase reactions. Light reactions produce NADPH and ATP, which is followed by dark reactions where the carbon dioxide is being fixed. Chlorophyll becomes excited when a light photon hits it.

(a) Which one is preferably absorbed by the active chlorophyll, green (532 nm) or red (680 nm) photon?

> Chlorophyll itself is green, which means it has to absorb photons whose color is opposite to green on the color wheel. Because of this, red (680 nm) photon is preferably absorbed.

Standard reduction for chlorophyll equals 0.78 V.

(b) Calculate the standard reduction potential for chlorophyll for the photochemical process:
$\text{Chlorophyll}^+ + e^- \longrightarrow \text{Chlorophyll}^*$, where an asterisk denotes the excited state.

> The whole process can be split into two:
>
> 1. $\text{Chlorophyll}^+ + e^- \longrightarrow \text{Chlorophyll} \quad \Delta G = -nFE = -1 \cdot 96485\,\text{C}\,\text{mol}^{-1} \cdot 0.78\,\text{V} \approx -75258\,\text{J}\,\text{mol}^{-1}$
> 2. $\text{Chlorophyll}^+ \longrightarrow \text{Chlorophyll}^*$
>
> Assuming a red photon is absorbed, $\lambda = 680\,\text{nm}$.
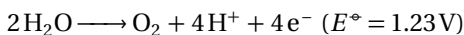>
> $$E_{photon} = \frac{hc}{\lambda}$$
>
> $$\Delta G \approx E_{photon} N_A = \frac{hc}{\lambda} N_A = \frac{6.62 \times 10^{-34}\,\text{J}\,\text{s} \cdot 3.00 \times 10^8\,\text{m}\,\text{s}^{-1}}{6.8 \times 10^{-7}\,\text{m}} \cdot 6.022 \times 10^{23}\,\text{mol}^{-1} \approx 175878\,\text{J}\,\text{mol}^{-1}$$
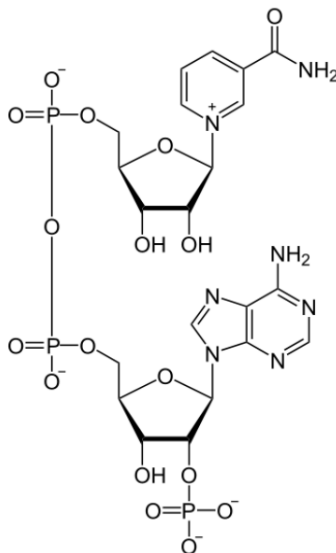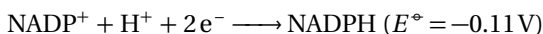>
> For full reaction:
>
> $$\Delta G = 175878\,\text{J}\,\text{mol}^{-1} - 75258\,\text{J}\,\text{mol}^{-1} = 100620\,\text{J}\,\text{mol}^{-1}$$
>
> $$E_r = -\frac{\Delta G}{nF} = -\frac{100620\,\text{J}\,\text{mol}^{-1}}{1 \cdot 96485\,\text{C}\,\text{mol}^{-1}} \approx -1.04\,\text{V}$$

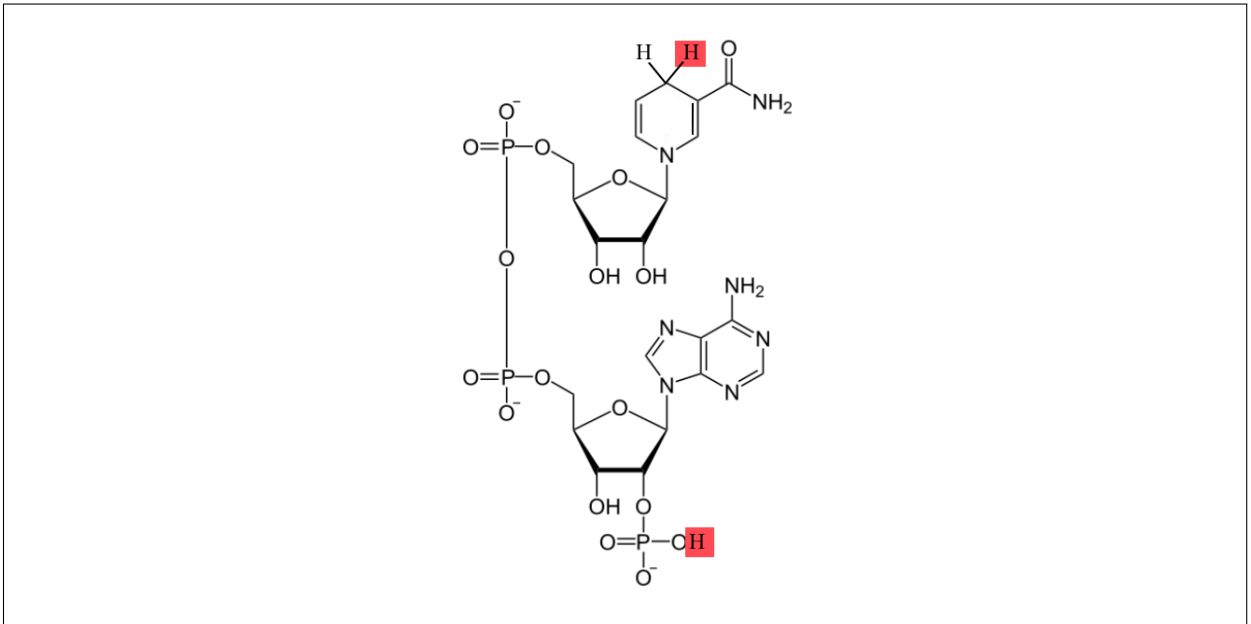The splitting of water produces protons and dioxygen, when the electrons are carried to the redox systems:
$2\,\text{H}_2\text{O} \longrightarrow \text{O}_2 + 4\,\text{H}^+ + 4\,e^- \; (E^\ominus = 1.23\,\text{V})$

The electrons from the reaction are used to form NADPH:
$\text{NADP}^+ + \text{H}^+ + 2\,e^- \longrightarrow \text{NADPH} \; (E^\ominus = -0.11\,\text{V})$

Actually, NADP^+ (shown in figure) binds two protons.

(c) Mark the two new hydrogens in the NADPH structure.

(d) Calculate the potential for cell conditions (pH $= 7$).

$$E° = (-0.11 - 0.414/2)\,V = -0.32\,V$$

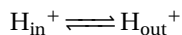**(e)** Calculate the ΔG for the NADPH formation reaction.

$$\Delta G° = -2 \cdot 96485 \cdot (-0.32) = 62\ kJ/mol$$

The accumulation of protons inside the chloroplast thylakoid creates a concentration cell.

(f) Calculate the voltage of such a concentration cell if the pH outside the membrane is 7.8, but inside the membrane, the pH is 5.4.

The overall process is

$$H_{in}{}^+ \rightleftharpoons H_{out}{}^+$$

At the equilibrium $K = 1$ and $\Delta G° = 0$. That means

$$\Delta G = RT \ln Q = -zFE,$$

where $Q = \frac{[H_{out}{}^+]}{[H_{in}{}^+]}$ and z is the charge of the ion (in this case, $z = 1$).

$$E = -\frac{RT}{zF} \ln \frac{[H_{out}{}^+]}{[H_{in}{}^+]} = -\frac{RT}{zF} \ln \frac{10^{-pH_{out}}}{10^{-pH_{in}}} = -\frac{RT}{zF} \ln 10^{pH_{in}-pH_{out}} =$$

$$= -\ln 10 \frac{RT}{zF} \left(pH_{in} - pH_{out}\right) = -\ln 10 \frac{8.314\,J\,K^{-1}\,mol^{-1} \cdot 298\,K}{1 \cdot 96485\,C\,mol^{-1}} (5.4 - 7.8) \approx 0.14\,V$$

However, nature has used a different approach – the protons are used for the preparation of ATP. The protons synthesized in the inner side of the membrane pass out through the spinning enzyme ATP synthase, producing ATP from phosphate and ADP:

$$ADP + P_i \longrightarrow ATP + H_2O \ (\Delta G° = +30.5\,kJ\,mol^{-1})$$
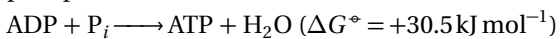
(g) Draw the ATP structure.
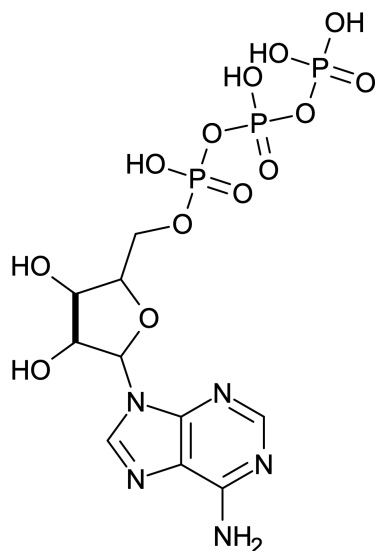
(h) Calculate ΔG for ATP hydrolysis in real cell conditions if the ATP concentration is twice larger than the ADP concentration and the phosphate concentration is 5 mM.

$$\Delta G = \Delta G^{\circ} + RT \ln Q$$

$$Q = \frac{[\text{ATP}]}{[\text{ADP}][\text{P}_i]} = \frac{2[\text{ADP}]}{[\text{ADP}][\text{P}_i]} = \frac{2}{[\text{P}_i]} = \frac{2}{5 \times 10^{-3}} = 400$$

This is for synthesis. For hydrolysis, $Q = 2.5 \times 10^{-3}$.

$$\Delta G = -30\,500\,\text{J}\,\text{mol}^{-1} + 8.314\,\text{J}\,\text{mol}^{-1}\,\text{K}^{-1} \cdot 298\,\text{K} \cdot \ln(2.5 \times 10^{-3}) \approx -45\,344\,\text{J}\,\text{mol}^{-1} \approx -45.3\,\text{kJ}\,\text{mol}^{-1}$$

**(i)** Calculate the approximate number of protons needed for the preparation of one ATP molecule.

$$\Delta G(\text{proton}) = -1 \cdot 0.142 \cdot 96485 = -13.7\,\text{kJ/mol}$$

$$n(\text{proton}) = -45.3 / -13.7 = 3.3$$

The following are the dark reactions, which do not need light to function, just a supply of energetic compounds and CO_2. Carbon dioxide is bound in a cascade of reactions called the Calvin cycle. Some of the intermediates in the Calvin cycle are used to make glucose as well as other bioorganic compounds.

The NADH-reducing properties are used in the third reaction of the cycle, where 1,3-bisphosphoglycerate is converted to glyceraldehyde-3-phosphate.

(j) Write the equation with the correct chemical structures.
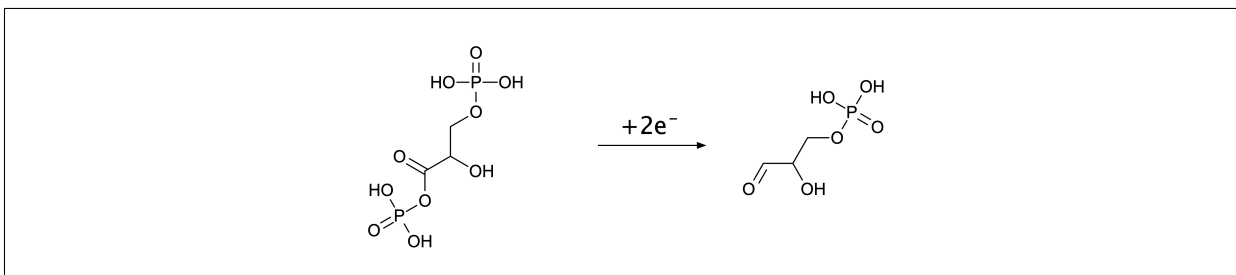
It also takes 18 ATP molecules to prepare one glucose molecule.

(k) Write the summary reaction for the dark phase of photosynthesis if one molecule of glucose is formed.

$$6\,CO_2 + 12\,NADPH + 12\,H^+ + 18\,ATP + 12\,H_2O \longrightarrow C_6H_{12}O_6 + 12\,NADP^+ + 18\,ADP + 18\,P_i$$
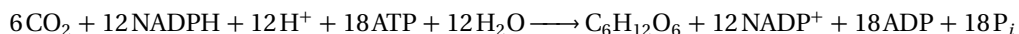
(l) Calculate Gibbs energy for this reaction in cell conditions.

$$\Delta G = 2880\,\text{kJ}\,\text{mol}^{-1} - 12 \cdot 62\,\text{kJ}\,\text{mol}^{-1} - 18 \cdot 45.3\,\text{kJ}\,\text{mol}^{-1} - 6 \cdot 4 \cdot 96485 \cdot 0.82/1000 = -578\,\text{kJ}\,\text{mol}^{-1}$$

In summary, green plants utilize sunlight to convert CO_2 and H_2O to organic compounds (glucose $C_6H_{12}O_6$) and O_2. The reaction $\Delta G = 2880\,\text{kJ}\,\text{mol}^{-1}$ and $\Delta S = -257\,\text{J}\,\text{mol}^{-1}\,\text{K}^{-1}$.

(m) Calculate the minimum number of photons ($\lambda = 680\,\text{nm}$) required to make one molecule of glucose from CO_2 and H_2O.

$$\Delta G \cdot \frac{1\,(\text{glucose molecule})}{N_A} \approx N \cdot \frac{hc}{\lambda}$$

where N is the number of photons.

$$N = \frac{\Delta G \lambda}{hc N_A} = \frac{2\,880\,000\,\text{J}\,\text{mol}^{-1} \cdot 6.8 \times 10^{-7}\,\text{m}}{6.62 \times 10^{-34}\,\text{J s} \cdot 3.00 \times 10^{8}\,\text{m s}^{-1} \cdot 6.022 \times 10^{23}\,\text{mol}^{-1}} \approx 16.4 \approx 17$$

(n) Comment on the spontaneity of this reaction at 25 °C and other temperatures.

As $\Delta G > 0$, it is not spontaneous at 25 °C and because $\Delta S < 0$ and $\Delta H > 0$, it is not spontaneous at any temperature.

Problem 2. Phenolsulfonphthalein

Two main methods are used to determine the endpoint in acid-base titration: either indicator or potentiometric titration. One possible indicator is phenolsulfonphthalein.
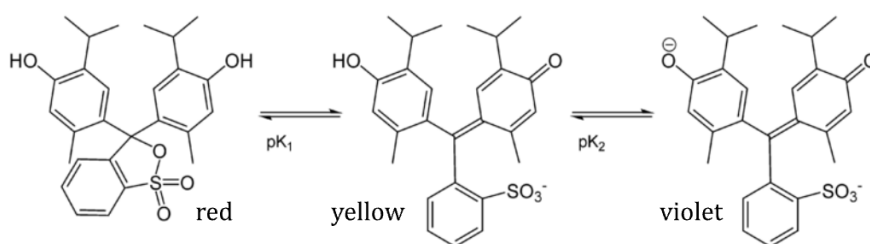
pH	A
5,02	0,0043
7,42	0,0350
8,32	0,2116
9,23	0,6828
10,26	0,9631
12,61	1,0076

Unfortunately not all indicators are applicable for all acid-base titrations. A suitable indicator needs to have its' transition range (the pH range where the indicator changes color) near the equivalent point of the titration curve. The transition range is mostly the pH range where the ratio of protonated and deprotonated form of the indicator changes from 1:10 to 10:1 or *vice versa*.

In order to validate if phenolsulfonphthalein is a suitable indicator its pK_{a2} value was determined with spectrophotometric method. In order to do this, the absorbance of phenolsulfonphthalein was measured ($\lambda = 590\,\text{nm}$) at different pH values (the concentration of phenolsulfonphthalein and optical length were kept constant). The obtained results are indicated in the table. It is known that at the lowest measured pH, only HA^- occurs in the solution, and at the highest measured pH, only A^{2-} occurs. It is also known that Beer's law is additive:

$$A = A_{HA^-} + A_{A^{2-}} = \varepsilon_{HA^-} l [HA^-] + \varepsilon_{A^{2-}} l [A^{2-}]$$

where ε is the molecular absorbance coefficient, and l is the optical length in the cuvette.

(a) Derive a formula to evaluate the pK_{a2} values according to the previously described information.

> Let c_0 be the concentration of phenolsulfonphthalein, A_n absorbance of n-th measurement, pH_n pH of n-th measurement.
>
> $$A_1 = \varepsilon_{HA^-} l\, c_0$$
>
> $$A_6 = \varepsilon_{A^{2-}} l\, c_0$$
>
> $$[HA^-] + [A^{2-}] = c_0$$
>
> $$A_n = \varepsilon_{HA^-} l [HA^-] + \varepsilon_{A^{2-}} l [A^{2-}]$$
>
> $$A_n = \frac{A_1}{c_0}[HA^-] + \frac{A_6}{c_0}[A^{2-}]$$
>
> $$c_0 A_n = A_1 [HA^-] + A_6 \left(c_0 - [HA^-] \right)$$
>
> $$c_0 (A_n - A_6) = [HA^-](A_1 - A_6)$$
>
> $$[HA^-] = c_0 \frac{A_n - A_6}{A_1 - A_6}$$
>
> $$c_0 \frac{A_n - A_6}{A_1 - A_6} + [A^{2-}] = c_0$$
>
> $$[A^{2-}] = c_0 \frac{A_1 - A_n}{A_1 - A_6}$$
>
> $$pH_n = pK_{a2} + \log \frac{A_1 - A_n}{A_n - A_6}$$

(b) Calculate the estimated pK_{a2} values (4 values) and the average pK_{a2} value according to the data given in the table.

n	pH	pK_{a2}
2	7.42	8.92
3	8.32	8.90
4	9.23	8.91
5	10.26	8.93
Avg	-	8.92

$50.00\,\text{cm}^3$ of $0.010\,00\,\text{M}$ ammonia ($pK_b = 4.75$) is titrated with HCl ($0.1000\,\text{M}$).

(c) Calculate the pH of the titration solution if **i)** 4.90, **ii)** 5.00, and **iii)** $5.10\,\text{cm}^3$ of the titrant is added to the solution.

$$NH_3 + HCl \longrightarrow NH_4^+ + Cl^-$$

i)
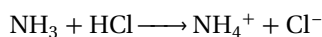
$$n_{NH_3} = 0.010\,00\,\text{M} \cdot 0.050\,00\,\text{dm}^3 - 0.1000\,\text{M} \cdot 4.90 \times 10^{-3}\,\text{dm}^3 = 1.000 \times 10^{-5}\,\text{mol}$$

$$n_{NH_4^+} = 0.1000\,\text{M} \cdot 4.90 \times 10^{-3}\,\text{dm}^3 = 4.9000 \times 10^{-4}\,\text{mol}$$

$$[NH_3] = \frac{1.000 \times 10^{-5}\,\text{mol}}{0.050\,00\,\text{dm}^3 + 4.90 \times 10^{-3}\,\text{dm}^3} \approx 1.821\,49 \times 10^{-4}\,\text{M}$$

$$[NH_4^+] = \frac{4.9000 \times 10^{-4}\,\text{mol}}{0.050\,00\,\text{dm}^3 + 4.90 \times 10^{-3}\,\text{dm}^3} \approx 8.9253 \times 10^{-3}\,\text{M}$$
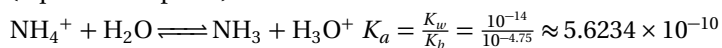
$$pOH = pK_b + \log \frac{[NH_4^+]}{[NH_3]} = 4.75 \log \frac{8.9253 \times 10^{-3}\,\text{M}}{1.821\,49 \times 10^{-4}\,\text{M}} \approx 6.440$$

$$pH = 14 - pOH = 14 - 6.440 = 7.56$$

ii)

$$n_{NH_3} = 0.010\,00\,\text{M} \cdot 0.050\,00\,\text{dm}^3 - 0.1000\,\text{M} \cdot 5.00 \times 10^{-3}\,\text{dm}^3 = 1.000 \times 10^{-5}\,\text{mol} = 0$$

(equivalence point)

$$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+ \quad K_a = \frac{K_w}{K_b} = \frac{10^{-14}}{10^{-4.75}} \approx 5.6234 \times 10^{-10}$$

$$[NH_4^+] = \frac{0.1000\,\text{M} \cdot 5.00 \times 10^{-3}\,\text{dm}^3}{0.050\,00\,\text{dm}^3 + 5.00 \times 10^{-3}\,\text{dm}^3} \approx 9.0909 \times 10^{-3}\,\text{M}$$

$$K_a = \frac{x^2}{9.0909 \times 10^{-3} - x} = 5.6234 \times 10^{-10}$$

$$\frac{x^2}{9.0909 \times 10^{-3}} \approx 5.6234 \times 10^{-10}$$

$$x \approx 2.261\,01 \times 10^{-6}$$

$$[H^+] \approx 2.261\,01 \times 10^{-6}\,\text{M}$$

$$pH = -\log 2.261\,01 \times 10^{-6} \approx 5.65$$

iii)
(past equivalence point)

$$n_{H^+\text{excess}} = 0.1000\,\text{M} \cdot 5.10 \times 10^{-3}\,\text{dm}^3 - 0.010\,00\,\text{M} \cdot 0.050\,00\,\text{dm}^3 = 1.000 \times 10^{-5}\,\text{mol}$$

$$[H^+\text{excess}] = \frac{1.000 \times 10^{-5}\,\text{mol}}{5.10 \times 10^{-3}\,\text{dm}^3 + 0.050\,00\,\text{dm}^3} \approx 1.8149 \times 10^{-4}\,\text{M}$$

$$pH = -\log 1.8149 \times 10^{-4} \approx 3.74$$

**(d)** Can phenolsulfonphthalein be used as an indicator for this titration?

According to formula

$$pH = pK_a + \log\frac{[A^-]}{[HA]},$$

transition range for phenolsulfonphthalein is 7.92-9.92. At the equivalence point, pH of this titration is 5.65, which means phenolsulfonphthalein cannot be used.

$50.00\,cm^3$ of $0.010\,00\,M$ acetic acid ($pK_a = 4.76$) is titrated with NaOH ($0.1000\,M$).

(e) Calculate the pH of the titration solution if **i)** 4.90, **ii)** 5.00, and **iii)** $5.10\,cm^3$ of the titrant is added to the solution.

$$CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$$
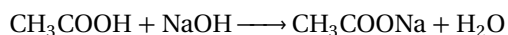
i)

$$[CH_3COOH] = \frac{0.010\,00\,M \cdot 0.050\,00\,dm^3 - 0.1000\,M \cdot 4.90 \times 10^{-3}\,dm^3}{4.90 \times 10^{-3}\,dm^3 + 0.050\,00\,dm^3} \approx 1.821\,49 \times 10^{-4}\,M$$

$$[CH_3COO^-] = \frac{0.1000\,M \cdot 4.90 \times 10^{-3}\,dm^3}{4.90 \times 10^{-3}\,dm^3 + 0.050\,00\,dm^3} \approx 8.9253 \times 10^{-3}\,M$$

$$pH = pK_a + \log\frac{[CH_3COO^-]}{[CH_3COOH]} = 4.76 + \log\frac{8.9253 \times 10^{-3}\,M}{1.821\,49 \times 10^{-4}\,M} \approx 6.45$$

ii)

$$n_{CH_3COOH} = 0.010\,00\,M \cdot 0.050\,00\,dm^3 - 0.1000\,M \cdot 5.00 \times 10^{-3}\,dm^3 = 0$$

(equivalence point)

$$[CH_3COO^-] = \frac{0.1000\,M \cdot 5.00 \times 10^{-3}\,dm^3}{0.050\,00\,dm^3 + 5.00 \times 10^{-3}\,dm^3} \approx 9.0909 \times 10^{-3}\,M$$

$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^- \quad K_b = \frac{K_w}{K_a} = \frac{10^{-14}}{10^{-4.76}} \approx 5.754\,40 \times 10^{-10}$$
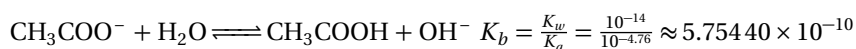
$$K_b = \frac{x^2}{9.0909 \times 10^{-3} - x} = 5.754\,40 \times 10^{-10}$$

$$\frac{x^2}{9.0909 \times 10^{-3}} \approx 5.754\,40 \times 10^{-10}$$

$$x \approx 2.2872 \times 10^{-6}$$

$$[OH^-] = 2.2872 \times 10^{-6}\,M$$

$$[H^+] = \frac{K_w}{[OH^-]} = \frac{10^{-14}}{2.2872 \times 10^{-6}} \approx 4.372 \times 10^{-9}\,M$$

$$pH = -\log 4.372 \times 10^{-9} \approx 8.36$$

iii)
(past equivalence point)

$$n_{OH^-excess} = 0.1000\,M \cdot 5.10 \times 10^{-3}\,dm^3 - 0.010\,00\,M \cdot 0.050\,00\,dm^3 = 1.000 \times 10^{-5}\,mol$$

$$[OH^-excess] = \frac{1.000 \times 10^{-5}\,mol}{5.10 \times 10^{-3}\,dm^3 + 0.050\,00\,dm^3} \approx 1.8149 \times 10^{-4}\,M$$

$$[H^+] = \frac{K_w}{[OH^-excess]} = \frac{10^{-14}}{1.8149 \times 10^{-4}} = 5.5099 \times 10^{-11}\,M$$

$$pH = -\log 5.5099 \times 10^{-11} \approx 10.26$$

(f) Can phenolsulfonphthalein be used as an indicator for this titration?

Yes, because $7.92 < 8.36 < 9.92$.

Problem 3. Hydrides

Hydrogen is a versatile element. It forms a wide range of binary compounds with metallic and nonmetallic elements. With transition metals, hydrogen forms so-called metallic or interstitial hydrides. When chromium is electrodeposited at low temperatures, a face-centered cubic chromium hydride CrH_x can be produced. The unit cell of this hydride may be described as consisting of chromium atoms in a face-centered cubic arrangement and hydrogen atoms located in tetrahedral holes of this cell.

(a) Write a theoretically possible chemical formula of chromium hydride assuming that all tetrahedral holes were filled with hydrogen atoms.

> Each unit cell has 8 tetrahedral holes, which means 8 H atoms. The number of Cr atoms in the FCC unit cell is
> $$\frac{1}{8} \cdot 8 + \frac{1}{2} \cdot 6 = 4$$
> $$Cr : H = 4 : 8 = 1 : 2$$
>
> **Formula:** CrH_2

In reality, metallic hydrides are nonstoichiometric compounds, e.g. palladium forms hydride $PdH_{0.7}$ instead of theoretically possible PdH. This hydride forms upon passing hydrogen gas over palladium. On the other hand, when heating palladium hydride, hydrogen gas is readily released. This fact has an important commercial application – palladium is used for the purification of hydrogen gas and could be used as a fuel tank for hydrogen-powered cars.

The hydrogen storage capacity of a palladium-based fuel tank may be characterized by the ratio $\frac{V(\text{liquid} H_2)}{V(\text{solid hydride})}$ when both volumes contain the same amount of hydrogen atoms. The density of liquid H_2 is $0.0710\,g\,cm^{-3}$. The density of $PdH_{0.7}$ is $12.1\,g\,cm^{-3}$.

(b) Calculate ratio $\frac{V(\text{liquid} H_2)}{V(\text{solid hydride})}$ for $PdH_{0.7}$.

> n is the amount of H atoms (mol).
> $$V(\text{liquid} H_2) = \frac{\frac{n}{2} \cdot M_{H_2}}{\rho_{H_2}} = \frac{n M_{H_2}}{2\rho_{H_2}}$$
> $$V(\text{solid hydride}) = \frac{\frac{n}{0.7} \cdot M_{PdH_{0.7}}}{\rho_{PdH_{0.7}}} = \frac{n M_{PdH_{0.7}}}{0.7\rho_{PdH_{0.7}}}$$
> $$\frac{V(\text{liquid} H_2)}{V(\text{solid hydride})} = \frac{n M_{H_2}}{2\rho_{H_2}} \cdot \frac{0.7\rho_{PdH_{0.7}}}{n M_{PdH_{0.7}}} = \frac{0.7}{2} \cdot \frac{\rho_{PdH_{0.7}}}{\rho_{H_2}} \cdot \frac{M_{H_2}}{M_{PdH_{0.7}}} =$$
> $$= \frac{0.7}{2} \cdot \frac{12.1\,g\,cm^{-3}}{0.0710\,g\,cm^{-3}} \cdot \frac{2.016\,g\,mol^{-1}}{107.1256\,g\,mol^{-1}} \approx 1.12$$

Another type of hydride are ionic or salt-like hydride. These compounds contain H^- ions. Unknown metal **M** forms hydride $\mathbf{M}H_x$, where x is an integer number. When $1.000\,g$ of $\mathbf{M}H_x$ reacted with excess of water, $3.216\,dm^3$ of gas was collected over water at $25\,°C$ and $100.00\,kPa$ pressure. The vapor pressure of water at a given temperature is $23.0\,mm$ Hg.

(c) Determine the unknown metal **M**.

> General equation is $\mathbf{M}H_x + x H_2O \longrightarrow \mathbf{M}(OH)_x + x H_2$. Collected gas was H_2O and H_2. The amount of H_2 can be found using partial pressures.
> $$p = p_{H_2O} + p_{H_2}$$
> $$p_{H_2} = p - p_{H_2O} = 1.00000 \times 10^5\,Pa - 23.0\,mmHg \cdot \frac{133.322\,Pa}{1\,mmHg} = 96\,933.594\,Pa$$
> $$n_{H_2} = \frac{p_{H_2} V}{RT} = \frac{96\,933.594\,Pa \cdot 3.216 \times 10^{-3}\,m^3}{8.314\,J\,K^{-1}\,mol^{-1} \cdot 298.15\,°C} \approx 0.125\,76\,mol$$
> Moles of $\mathbf{M}H_x$ can be expressed as
> $$n_{\mathbf{M}H_x} = \frac{m}{M_M + x M_H}$$

Using general equation

$$\frac{m x}{M_M + x M_H} = n_{H_2}$$

$$\frac{m}{n_{H_2}} x = M_M + x M_H$$

$$M_M = x \left(\frac{m}{n_{H_2}} - M_H \right)$$

$$M_M = x \left(\frac{1.000\,g}{0.125\,76\,mol} - 1.008\,g\,mol^{-1} \right) \approx 6.94 x$$

If $x = 1$, then $M_M = M_{Li}$ and **M** is Li.

The crystalline structure of MH_x could be described as follows: H^- ions are arranged in a face-centered cubic lattice and metal ions occupy some holes in this lattice. The lattice constant is a. Let us assume that we have a sample of MH_x that consists of very small cubic crystals having exactly the same size. For a short time, this sample was exposed to open air. Due to the reaction with water vapor, all surface H^- ions were transformed into OH^- ions. However, the ions inside of the crystals remained unchanged. After that the sample was investigated by ^{1}H-NMR-spectroscopy. There are two peaks (for H^- and OH^-) in the ratio, accordingly 150:1 in the resulting spectrum.

(d) Determine the edge length (expressed as a multiple of a) of the crystals in the sample.

Let there be $n \cdot n \cdot n$ unit cells in one crystal. Count of H^- ions is then:

- $4n^3$ - all unit cell atoms
- $8 \cdot \frac{7}{8}$ - missing parts of corner ions
- $12 \cdot (n-1) \cdot \frac{3}{4}$ - missing parts of edge ions
- $6 \cdot \frac{1}{2} \cdot \left[n^2 + (n-1)^2 \right]$ - missing parts of face ions

$$N_{H^-} = 4n^3 + 7 + 9 \cdot (n-1) + 3 \left[n^2 + (n-1)^2 \right] = 4n^3 + 7 + 9 \cdot (n-1) + 3 \left(2n^2 - 2n + 1 \right) =$$
$$= 4n^3 + 6n^2 + 3n + 1$$

Count of surface H^- ions is:

- 8 - corner ions
- $12 \cdot (n-1)$ - edge ions
- $6 \cdot \left[n^2 + (n-1)^2 \right]$ - face ions

$$N_{surface} = 8 + 12 \cdot (n-1) + 6 \cdot \left[n^2 + (n-1)^2 \right] = 8 + 12n - 12 + 6 \left(2n^2 - 2n + 1 \right) = 12n^2 + 2$$

$$N_{OH^-} = N_{surface}$$

$$N_{H^- \text{after}} = N_{H^-} - N_{surface} = 4n^3 + 6n^2 + 3n + 1 - \left(12n^2 + 2 \right) =$$
$$= 4n^3 - 6n^2 + 3n - 1$$

$$\frac{N_{H^- \text{after}}}{N_{OH^-}} = 150$$

$$\frac{4n^3 - 6n^2 + 3n - 1}{12n^2 + 2} = 150$$

Approximating $4n^3 - 6n^2 + 3n - 1 \approx 4n^3 - 6n^2 + 3n$ and $12n^2 + 2 \approx 12n^2$.

$$\frac{4n^3 - 6n^2 + 3n}{12n^2} = 150$$

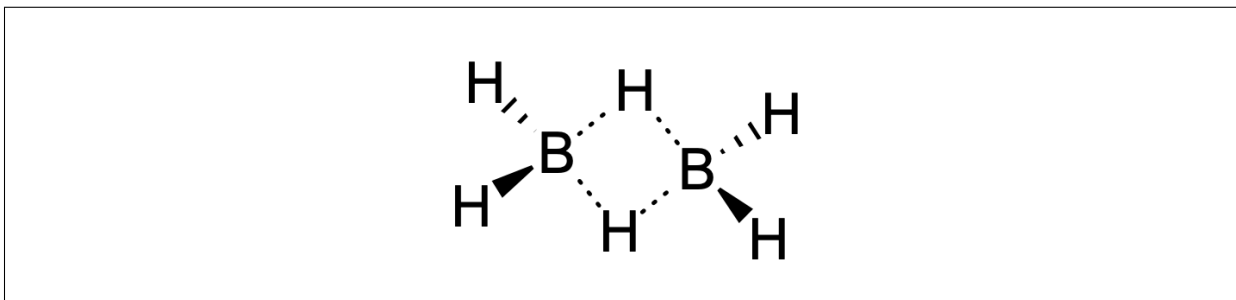$$\frac{4n^2 - 6n + 3}{12n} = 150$$

$$4n^2 - 1806n + 3 = 0$$

$$n \approx 450$$

The edge length is $l = a n \approx 450a$.

With non-metals hydrogen forms covalent hydrides. Some of these compounds consist of small molecules, some are polymeric substances.

Boron forms a wide range of binary compounds with hydrogen. The simplest of these compounds is diborane B_2H_6.

(e) Draw a spatial structure of a B_2H_6 molecule.

Problem 4. Physostigmine

Physostigmine is a reversible acetylcholinesterase inhibitor that can be extracted from Physostigma venenosum beans. This compound can be used to treat myasthenia gravis, glaucoma, and Alzheimer's disease. In addition, physostigmine enhances short-term memory. Physostigmine is easily obtained from compound **X**.
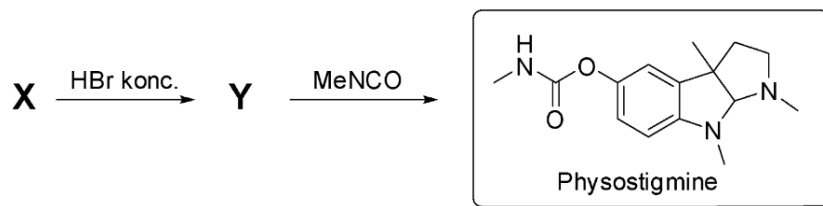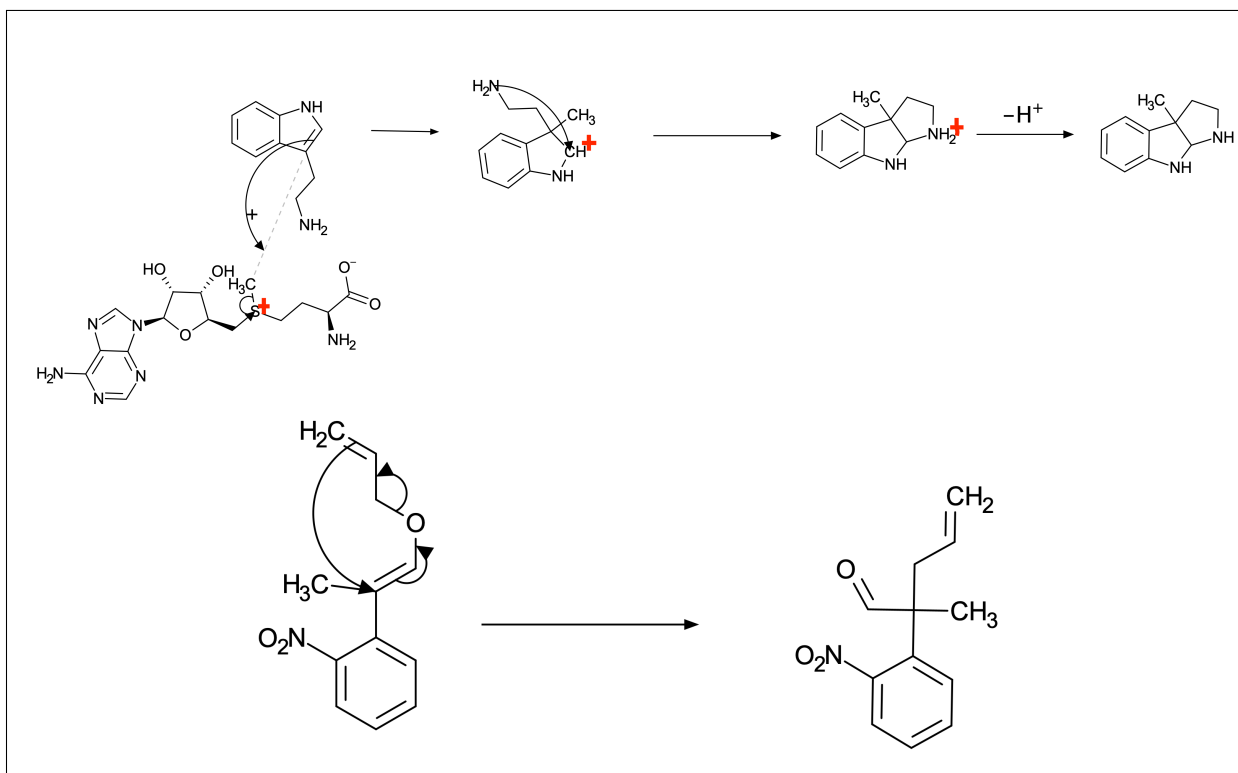

Compound **X** can be produced using two different methods:
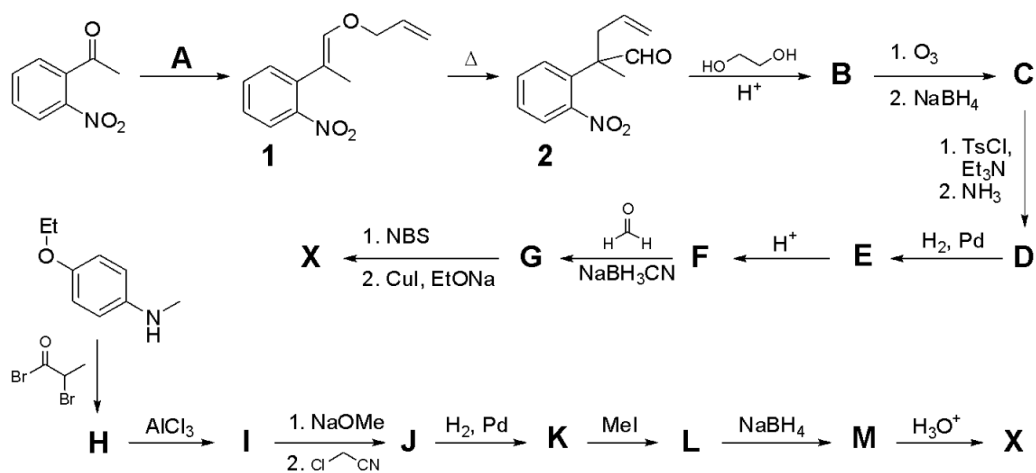
(a) Provide skeletal formulas for the compounds A-M, X and Y.

A	B	C
D	**E**	**F**
G	**H**	**I**
J	**K**	**L**
M	**X**	**Y**
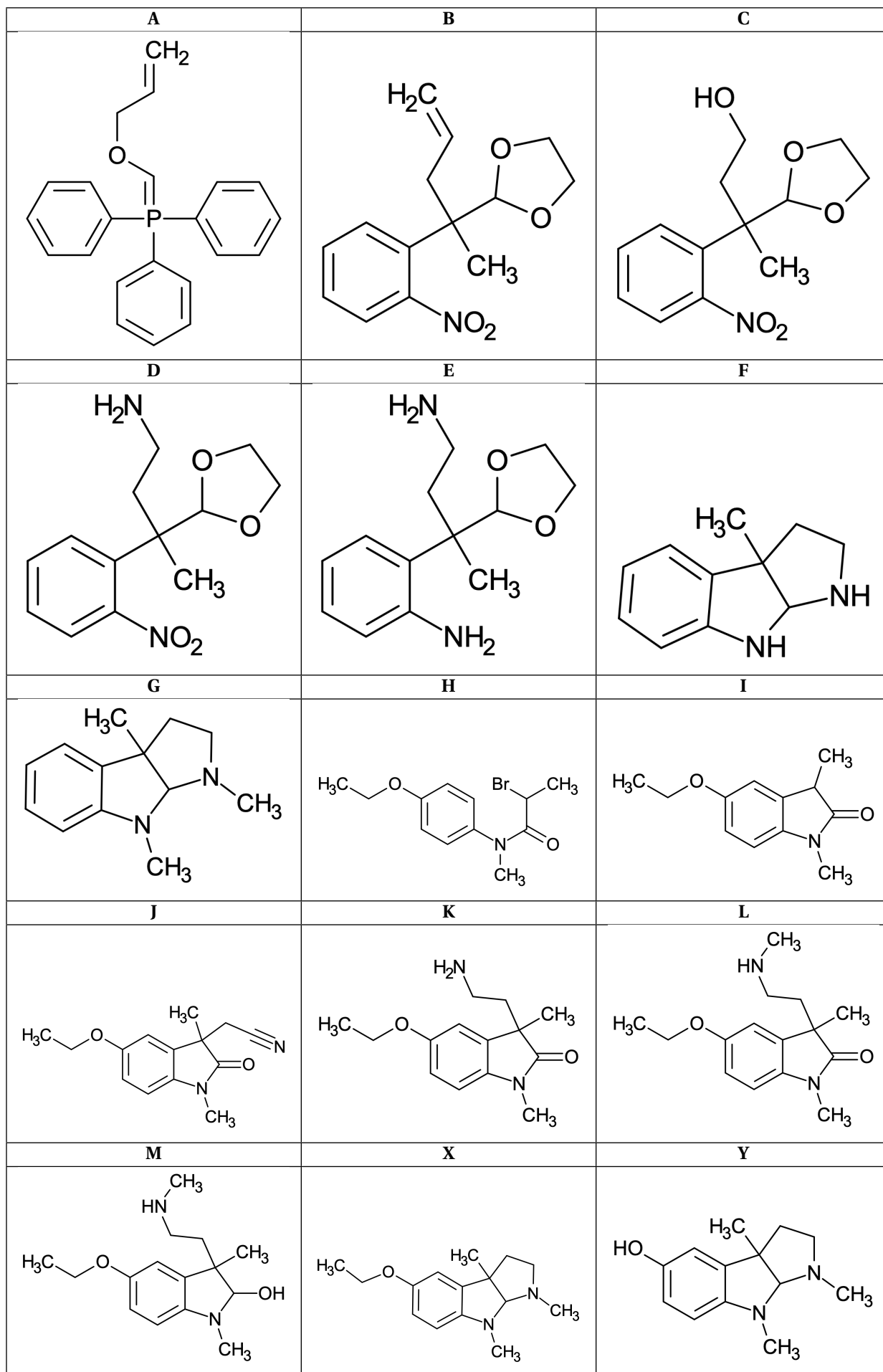
(b) Provide mechanisms for the biosynthesis of compound F and the transformation of 1 to 2.

(c) Write down the number of possible physostigmine stereoisomers.

Physostigmine has 2 chiral centers, which means it has $2^2 = 4$ stereoisomers.

Problem 5. A national drink

It may seem that famous Russian chemist Dmitri I. Mendeleev (1834–1907) dedicated his life to the periodic table of elements. However, Mendeleev wrote his doctoral thesis, "A Discourse on the Combination of Alcohol and Water," where he investigated the relationship between the density and composition of solutions. Mendeleev's experiment was repeated using data available on the web, and the graph shown in Figure 1 was obtained. It shows derivatives of the density against the volume fraction of the ethanol in solution plotted as a function of the volume fraction of the ethanol. In the graph, there are several extreme points, and one of them is marked as **Z**. Mendeleev explained such extreme points by the formation of ethanol–water hydrates. The density of the ethanol is $0.789\,\mathrm{g\,cm^{-3}}$.
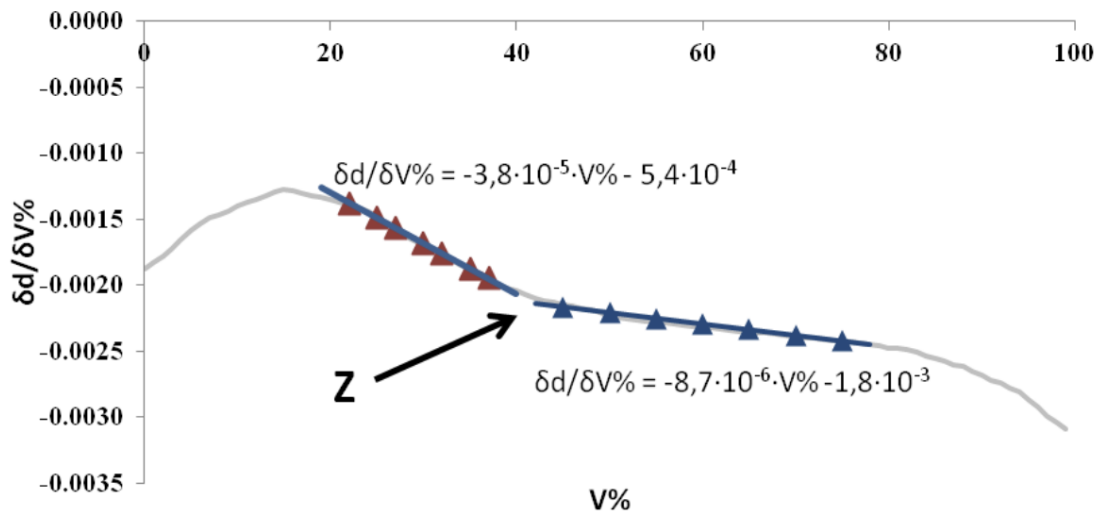

Figure 1: Derivative of density against volume fraction of ethanol in solution plotted as a function of the volume fraction of the ethanol

(a) Calculate the composition of ethanol–water hydrate **Z**, where the composition is expressed as the volume fraction of ethanol in water. Does it fit the Russian vodka standard of 40 %?

> Let $x = V\%$. The x value for the point **Z** is the x value where two given lines intercept.
>
> $$-3.8 \cdot 10^{-5} \cdot x - 5.4 \cdot 10^{-4} = -8.7 \cdot 10^{-6} \cdot x - 1.8 \cdot 10^{-3}$$
>
> $$2.93 \cdot 10^{-5} \cdot x = 1.26 \cdot 10^{-3}$$
>
> $$x \approx 43\%$$
>
> It does not fit the Russian vodka standard, but as the percentage is higher, it can be easily diluted.

(b) Calculate the composition of hydrate **Z** expressed as mass fraction and molar fraction of ethanol in solution. If you were unable to solve question 1, you may assume that **Z** corresponds to 40 % ethanol (volume fraction).

> V - solution volume, p_v ethanol volume fraction, p_m ethanol mass faction p_{mol} ethanol molar fraction. Used water density $1.00\,\mathrm{g\,cm^{-3}}$.
>
> $$m_{\mathrm{ethanol}} = p_v V \rho_{\mathrm{ethanol}}$$
>
> $$m_{\mathrm{H_2O}} = (1 - p_v) V \rho_{\mathrm{H_2O}}$$
>
> $$p_m = \frac{m_{\mathrm{ethanol}}}{m_{\mathrm{ethanol}} + m_{\mathrm{H_2O}}} = \frac{p_v V \rho_{\mathrm{ethanol}}}{p_v V \rho_{\mathrm{ethanol}} + (1 - p_v) V \rho_{\mathrm{H_2O}}} =$$
>
> $$= \frac{p_v \rho_{\mathrm{ethanol}}}{p_v \rho_{\mathrm{ethanol}} + (1 - p_v) \rho_{\mathrm{H_2O}}} = \frac{0.43 \cdot 0.789\,\mathrm{g\,cm^{-3}}}{0.43 \cdot 0.789\,\mathrm{g\,cm^{-3}} + (1 - 0.43) \cdot 1.00\,\mathrm{g\,cm^{-3}}} \approx 0.37 = 37\%$$
>
> $$n_{\mathrm{ethanol}} = \frac{p_v V \rho_{\mathrm{ethanol}}}{M_{\mathrm{ethanol}}}$$
>
> $$n_{\mathrm{H_2O}} = \frac{(1 - p_v) V \rho_{\mathrm{H_2O}}}{M_{\mathrm{H_2O}}}$$

$$p_{\text{mol}} = \frac{n_{\text{ethanol}}}{n_{\text{ethanol}} + n_{\text{H}_2\text{O}}} = \frac{\frac{p_v V \rho_{\text{ethanol}}}{M_{\text{ethanol}}}}{\frac{p_v V \rho_{\text{ethanol}}}{M_{\text{ethanol}}} + \frac{(1-p_v)V\rho_{\text{H}_2\text{O}}}{M_{\text{H}_2\text{O}}}} = \frac{\frac{p_v \rho_{\text{ethanol}}}{M_{\text{ethanol}}}}{\frac{p_v \rho_{\text{ethanol}}}{M_{\text{ethanol}}} + \frac{(1-p_v)\rho_{\text{H}_2\text{O}}}{M_{\text{H}_2\text{O}}}}$$

$$= \frac{\frac{0.43 \cdot 0.789\,\text{g cm}^{-3}}{46.07\,\text{g mol}^{-1}}}{\frac{0.43 \cdot 0.789\,\text{g cm}^{-3}}{46.07\,\text{g mol}^{-1}} + \frac{(1-0.43)\cdot 1.00\,\text{g cm}^{-3}}{18.02\,\text{g mol}^{-1}}} \approx 0.19 = 19\,\%$$

Mass fraction 37 %, molar fraction 19 %.

(c) Point out the main intermolecular forces acting between the ethanol and the water molecules in the hydrate.

Hydrogen bonding

Pure ethanol is a colorless liquid with a boiling point of 78.37 °C (pressure $p = 101.33\,\text{kPa}$), while at 20.00 °C temperature, its vapor pressure is 5.95 kPa. Assume that all enthalpy and entropy changes given and calculated in this problem are temperature-independent.

(d) Using the data given above, calculate the molar enthalpy and entropy of vaporization of ethanol.

$$\ln\left(\frac{p}{p_v}\right) = -\frac{\Delta H_{\text{vap}}}{R}\left(\frac{1}{T_b} - \frac{1}{T_1}\right)$$

$$\ln\left(\frac{101.33\,\text{kPa}}{5.95\,\text{kPa}}\right) = -\frac{\Delta H_{\text{vap}}}{8.314\,\text{J K}^{-1}\,\text{mol}^{-1}}\left(\frac{1}{351.52\,\text{K}} - \frac{1}{293.15\,\text{K}}\right)$$

$$\Delta H_{\text{vap}} \approx 41\,611\,\text{J mol}^{-1} \approx 41.61\,\text{kJ mol}^{-1}$$

$$\Delta S_{\text{vap}} = \frac{\Delta H_{\text{vap}}}{T_b} = \frac{41\,611\,\text{J mol}^{-1}}{351.52\,\text{K}} \approx 118.4\,\text{J mol}^{-1}\,\text{K}^{-1}$$

(e) Compare the obtained value with the molar enthalpy of vaporization of water, which is $44.0\,\text{kJ mol}^{-1}$ at 80 °C. Explain why the obtained enthalpy value is greater / smaller than the enthalpy of vaporization of water. If you were not able to calculate the enthalpy value in question **d)**, you may answer the second part of this question by suggesting the possible enthalpy value and explaining it.

The obtained value of the molar enthalpy of vaporization of ethanol is smaller than water's because the hydrogen bonding is weaker between ethanol molecules due to structural differences.

Ethanol is widely used in homemade window cleaning solutions, but it is not very effective as ethanol quickly evaporates. It also may be used as a window cleaner for cars during the winter.

(f) Calculate the melting point for 35 % (mass fraction) ethanol solution. The cryoscopic constant for water is $1.85\,\text{K kg mol}^{-1}$.

m_m - molality

$$m_m = \frac{\frac{0.35 \cdot m_{\text{sol}}}{46.07\,\text{g mol}^{-1}}}{\frac{1\,\text{kg}}{1000\,\text{g}} \cdot (1-0.35) \cdot m_{\text{sol}}} \approx 11.688\,\text{mol kg}^{-1}$$

$$\Delta T = 1.85\,\text{K kg mol}^{-1} \cdot 11.688\,\text{mol kg}^{-1} \cdot 1 \approx 21.6\,\text{K}$$

As pure water has a melting point of 0 °C, the solution's melting point is -21.6 °C.

Ethanol is also used as an additive in biofuel. Brazil is the leading country in using ethanol as a gasoline additive, where fuel E25 contains 25 % (volume fraction) ethanol while the rest is petrol. Let us assume that the petrol consists of pure octane (the density of octane is $0.703\,\text{g cm}^{-3}$).

(g) Calculate the enthalpy of combustion for octane and ethanol (in kJ per mol) using average bond enthalpies given in Table 1. Calculate the heat ratio between the combustion of 1.0 kg of ethanol and the combustion of 1.0 kg of octane.

Chemical bond	C–H	C–C	C–O	O=O	H–O	C=O
ΔH (bond), kJ mol^{-1}	413	348	358	498	463	804

Table 1: Average bond enthalpies

1. $2\,C_8H_{18} + 25\,O_2 \longrightarrow 16\,CO_2 + 18\,H_2O$
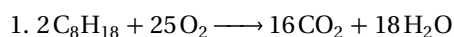
Bonds broken:

- 7 C–C bonds per octane molecule
- 18 C–H bonds per octane molecule
- 1 O=O bonds per oxygen molecule

Bonds created:

- 2 C=O bonds per CO_2 molecule
- 2 O–H bonds per H_2O molecule

$$\Delta H_r = 25 \cdot 1 \cdot 498\,\text{kJ mol}^{-1} + 2 \cdot 18 \cdot 413\,\text{kJ mol}^{-1} + 2 \cdot 7 \cdot 348\,\text{kJ mol}^{-1} - 16 \cdot 2 \cdot 804\,\text{kJ mol}^{-1} - 18 \cdot 2 \cdot 463\,\text{kJ mol}^{-1} =$$

$$= -10\,206\,\text{kJ mol}^{-1}$$

$$\Delta H_c = \frac{1}{2} \cdot -10\,206\,\text{kJ mol}^{-1} = -5103\,\text{kJ mol}^{-1}$$

$$Q_1 = 5103\,\text{kJ mol}^{-1} \cdot \frac{1000\,\text{g}}{114.22\,\text{g mol}^{-1}} \approx 44\,675\,\text{kJ}$$

2. $C_2H_5OH + 3\,O_2 \longrightarrow 2\,CO_2 + 3\,H_2O$
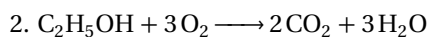
Bonds broken:

- 1 C–C bond per ethanol molecule
- 5 C–H bonds per ethanol molecule
- 1 C–O bond per ethanol molecule
- 1 O–H bond per ethanol molecule
- 1 O=O bond per oxygen molecule

Bonds created:

- 2 C=O bonds per CO_2 molecule
- 2 O–H bonds per H_2O molecule

$$\Delta H_c = \Delta H_r = 1 \cdot 1 \cdot 348\,\text{kJ mol}^{-1} + 1 \cdot 5 \cdot 413\,\text{kJ mol}^{-1} + 1 \cdot 1 \cdot 358\,\text{kJ mol}^{-1} + 1 \cdot 1 \cdot 463\,\text{kJ mol}^{-1} + 3 \cdot 1 \cdot 498\,\text{kJ mol}^{-1} -$$

$$- 2 \cdot 2 \cdot 804\,\text{kJ mol}^{-1} - 3 \cdot 2 \cdot 463\,\text{kJ mol}^{-1} = -1266\,\text{kJ mol}^{-1}$$

$$Q_2 = 1266\,\text{kJ mol}^{-1} \cdot \frac{1000\,\text{g}}{46.07\,\text{g mol}^{-1}} \approx 27\,480\,\text{kJ}$$

$$\frac{Q_2}{Q_1} = \frac{27\,480\,\text{kJ}}{44\,675\,\text{kJ}} \approx 0.62$$

(h) Enthalpy of the chemical reactions can be calculated using the standard enthalpies of formation. Using the data from Table 2, calculate the enthalpy of ethanol combustion and identify the main reason for the differences between values calculated here and in question **g)**.

Compound	Ethanol (liquid)	Carbon dioxide (gas)	Water (liquid)
ΔH°, kJ mol^{-1}	-277.0	-393.5	-285.0

Table 2: Standard enthalpies of formation

$$C_2H_5OH \text{ (l)} + 3\,O_2 \text{ (g)} \longrightarrow 2\,CO_2 \text{ (g)} + 3\,H_2O \text{ (l)}$$
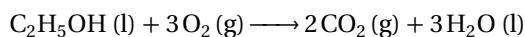
$$\Delta H_c = 3 \cdot (-285.0) + 2 \cdot (-393.5) - 3 \cdot 0 - 1 \cdot (-277.0) = -1365\,\text{kJ mol}^{-1}$$

Main reason of differences is state of water as here it is liquid while using bond enthalpy it is in gas phase.

At low temperatures, ethanol exists in a solid state, and two different polymorphic modifications of ethanol have been detected. Gibbs energy curves for different phases of ethanol are given in Figure 2.
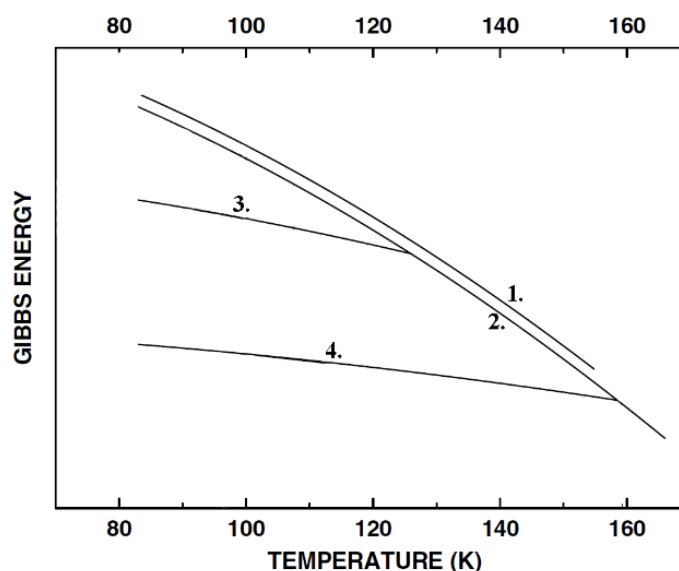
Figure 2: Gibbs energy curves for different phases of ethanol.

(i) Identify these curves as corresponding to **i)** liquid ethanol, **ii)** thermodynamically stable solid form, **iii)** metastable solid form, and **iv)** supercooled liquid and explain your choice.

Due to their shapes, 1./2. are liquids, 3./4. are solids. As lower Gibbs energy means more stable, 4. is thermodynamically stable solid form and 3. is metastable solid form. Because 1. ends at a lower temperature and has a bit higher Gibbs energy, it is a supercooled liquid, and the remaining 2. is liquid ethanol.

(j) Determine the melting point of the thermodynamically stable and metastable forms.

Melting points are the transition points between two curves. For the metastable form, the melting point is about 125 K, and for the stable form, about 160 K.

(k) Which of the following phase diagrams can correspond to ethanol? What are the limitations for pressure for selected diagrams, if there are any? Show these limitations by marking the pressure which corresponds to data given in Figure 2.
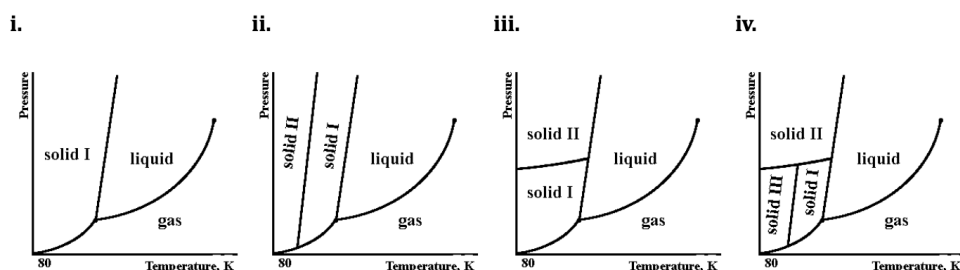
i.   ii.   iii.   iv.

> Phase diagrams **i**, **iii** (and also **iv** if there exists also third polymorphous phase) can correspond to ethanol. One phase is thermodynamically stable in the whole range from 80 K up to the melting point which is the factor that eliminates phase diagram **ii**) as the correct answer and does not allow all pressure values from solid-liquid-gas triple point up to the critical pressure in diagrams **i**, **ii** and **iii**.
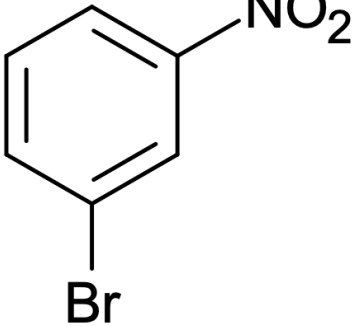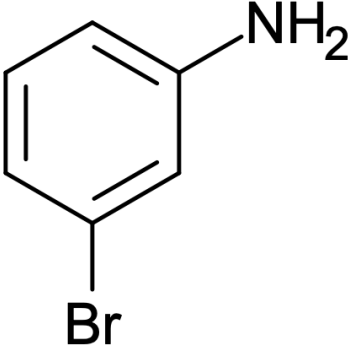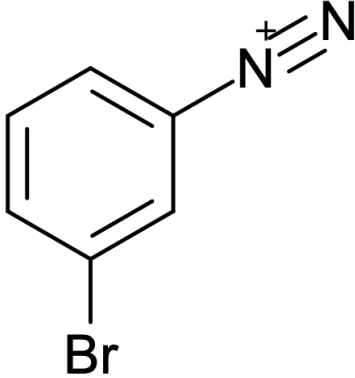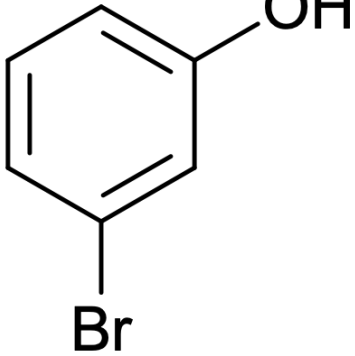
Problem 6. Benzyne

benzyne
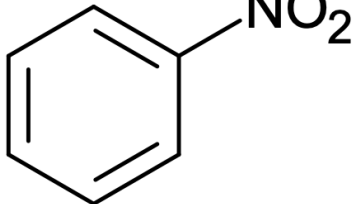
Some of the most fascinating types of reactions are those involving the intermediacy of benzyne. Benzyne is benzene minus two adjacent hydrogens, producing a formal triple bond – C_6H_4. The structure of benzyne has been examined both experimentally and theoretically, and the alkyne representation is most widely accepted, although two other structures are considered significant resonance contributors. Using IR spectroscopy, the vibrational frequency of the triple bond in benzyne was assigned to be $1846\,cm^{-1}$, an unstrained alkyne has a vibrational frequency of approximately $2150\,cm^{-1}$.

(a) What does this say about the relative strength of the benzyne triple bond compared to unstrained alkyne? Choose correct answer(s).

  ○ stronger   √ **longer**   √ **weaker**   ○ shorter

Due to the extreme reactivity of arynes, they must be generated in situ. In the early days of benzyne chemistry, harsh conditions were needed to generate benzynes from aryl halide and a strong base. Consider the following scheme for the synthesis of m-bromoanisole, which is then used as a substrate for an experiment involving a benzyne intermediate.
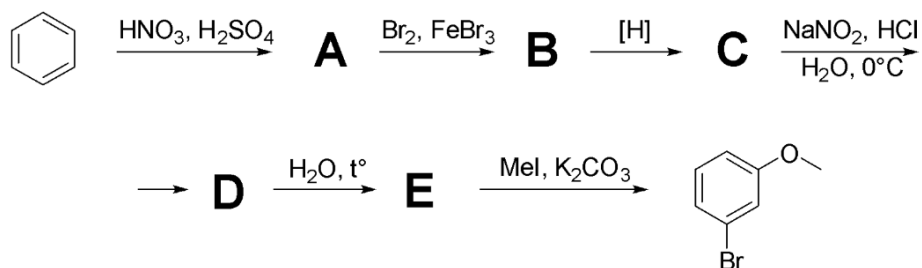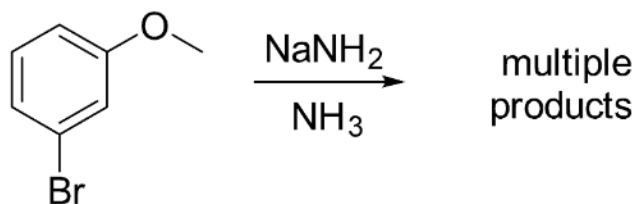

(b) Suggest structures for **A**, **B**, **C**, **D**, and **E**.

A	B	C
NO_2	NO_2 / Br	NH_2 / Br
D	E	
$N \equiv N^+$ / Br	OH / Br	

The reaction of m-bromoanisole with amide anion in liquid ammonia could potentially give multiple benzyne intermediates and multiple products.

(c) Suggest structures for all possible intermediate benzyne(s) and all possible final products after the workup step!

| Intermediate benzyne I	Intermediate benzyne I	Final product I
Final product II	**Final product III**	

A hexadehydro-Diels-Alder (HDDA) reaction was developed for generating benzyne intermediates in a very sensitive manner. HDDA involves the cycloaddition of 1,3-diyne and alkyne.

(d) Draw the structure for resonance structure **R**. To what class of unsaturated compounds does the open-chain analog of **R** belong?
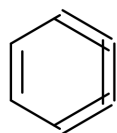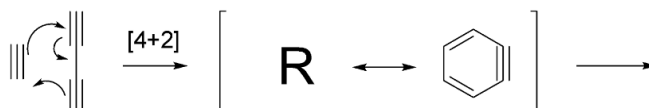
 Open-chain analogue of **R** is cumulene.

Consider the following scheme, in which a novel benzyne generation approach was used.
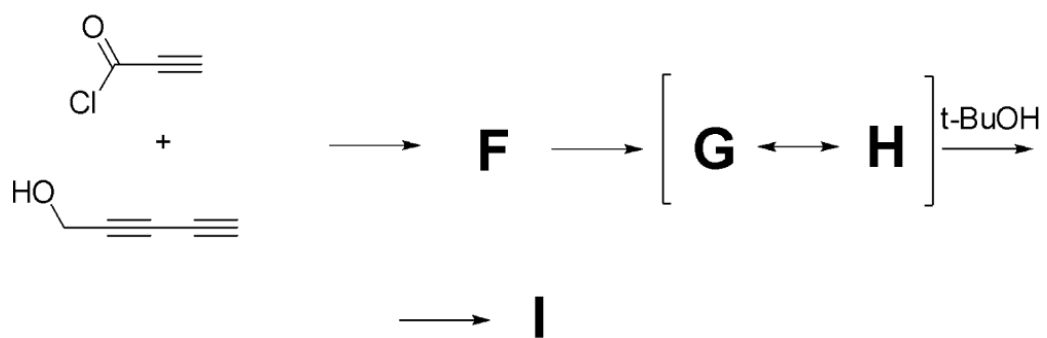
(e) Suggest the structures for **F**, **G**, **H**, and **I**.

F	G	H
I		