

Solutions to Preparatory problems

Problem 1. Graphite oxide

- 1) In GO the interplane spacing is larger. This facilitates exfoliation of GO. Graphite is hydrophobic, whereas GO is hydrophilic due to the formation of the functional groups. This makes GO soluble in water, which is very important for chemical exfoliation. The grave disadvantage of GO as a precursor of graphene is the necessity of reduction of single sheets after exfoliation. Graphene produced from GO is always defective.
- 2) 25% of carbon atoms retain the sp^2 hybridization, which means that they are not bonded to oxygen atoms. 75% of carbon atoms form chemical bonds with oxygen. Each oxygen atom is bonded to the pair of carbon atoms. The net formula is $CO_{0.375}$. Maximum X in the Hoffman model is 0.5. The net formula is $CO_{0.5}$.
- 3) The four groups are the phenol (OH sp^2), hydroxyl (OH sp^3), and epoxide groups in the basal plane, and the carboxylic acid groups at the edges.
- 4) Each hydrogen atom corresponds to one oxidized carbon atom. 22% of carbon atoms are bonded to the hydroxyl or phenol group, or are in the carboxylic acid group. Let all the hydrogen atoms be in the carboxylic acid groups. Then 44% of oxygen atoms are in the carboxylic acid groups and 2% are in the epoxy groups. In this case $22\% + 2 \cdot 2\% = 26\%$ of all the carbon atoms are oxidized. 74% of the total amount of carbon atoms do not form chemical bonds with oxygen. This is the upper limit. Let all the hydrogen atoms be in the hydroxyl or phenol groups. This means that there are no carboxylic acid groups in the particular GO sample! Then 24% of oxygen atoms are in the epoxy groups. In this case $22\% + 2 \cdot 24\% = 70\%$ of all the carbon atoms are bonded to oxygen. 30% of carbon atoms are not oxidized. This is the lower limit.
- 5) Acid groups do not participate in the hydrogen bonding network (Fig. 3). It means that maximum degree of water absorption will be reached in case of the absence of such groups in GO. Then each pair of hydrogen atoms holds one molecule of H_2O (0.11), and each pair of epoxy groups also holds one molecule of H_2O $(0.46 - 0.22) / 2 = 0.12$. Altogether there are 0.23 molecules of water per one carbon atom. The chemical formula of GO hydrate is $CH_{0.22}O_{0.46} \cdot 0.23H_2O$.

Problem 2. Efficiency of photosynthesis



The process is reverse to combustion of 1/6(glucose), hence:

$$\Delta_r H_{298}^\circ = -\frac{1}{6} \Delta_c H_{298}^\circ (\text{C}_6\text{H}_{12}\text{O}_6) = \mathbf{467.5 \text{ kJ}\cdot\text{mol}^{-1}}.$$

Standard entropy change in the reaction:

$$\Delta_r S_{298}^\circ = \frac{1}{6} S_{298}^\circ (\text{C}_6\text{H}_{12}\text{O}_6) + S_{298}^\circ (\text{O}_2) - S_{298}^\circ (\text{H}_2\text{O}) - S_{298}^\circ (\text{CO}_2) = -43.7 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}.$$

Standard Gibbs energy change:

$$\Delta_r G_{298}^\circ = \Delta_r H_{298}^\circ - 298 \Delta_r S_{298}^\circ = 467.5 - 298 \cdot (-43.7 \cdot 10^{-3}) = \mathbf{480.5 \text{ kJ}\cdot\text{mol}^{-1}}.$$

Energy of 1 mol of photons with wavelength of 680 nm:

$$E_m = \frac{hcN_A}{\lambda} = \frac{6.63 \cdot 10^{-34} \cdot 3.00 \cdot 10^8 \cdot 6.02 \cdot 10^{23}}{680 \cdot 10^{-9}} \cdot 10^{-3} = 176 \text{ kJ}\cdot\text{mol}^{-1}.$$

The minimum number of photons necessary to supply more energy than $E = 480.5 \text{ kJ}\cdot\text{mol}^{-1}$ is **3**.

(Instead of $E = \Delta_r G_{298}^\circ$, one can use $E = \Delta_r H_{298}^\circ = \Delta_r U_{298}^\circ$ – the result is the same: 3 photons.)

2.
$$\Delta_r G_{298} = \Delta_r G_{298}^\circ + RT \ln \frac{p_{\text{O}_2}}{p_{\text{CO}_2}} = 480.5 + 8.314 \cdot 298 \cdot 10^{-3} \cdot \ln \frac{0.21}{3 \cdot 10^{-4}} = \mathbf{496.7 \text{ kJ}\cdot\text{mol}^{-1}}.$$

The correction from non-standard pressures is not large – about 1/30 of the standard Gibbs energy.

3. Energy of 10 mol of photons absorbed by green plants is $176 \cdot 10 = 1760 \text{ kJ}$. Of this amount 480.5 kJ is converted to Gibbs energy. The efficiency of the solar energy conversion by green plants can be estimated as $480.5 / 1760 \cdot 100\% = \mathbf{27\%}$.

4. Total solar energy absorbed:

a) Moscow area: $E = 1070 \cdot 10^6 \text{ m}^2 \cdot 150 \text{ J}\cdot\text{s}^{-1}\cdot\text{m}^{-2} \cdot (10 \cdot 86400) \text{ s} = 1.4 \cdot 10^{17} \text{ J}.$

b) MSU campus: $E = 1.7 \cdot 10^6 \text{ m}^2 \cdot 150 \text{ J}\cdot\text{s}^{-1}\cdot\text{m}^{-2} \cdot (5 \cdot 3600) \text{ s} = 4.6 \cdot 10^{12} \text{ J}.$

$$\text{Number of photons } N = (E / E_m) \cdot N_A:$$

a) Moscow area: $N = \mathbf{4.8 \cdot 10^{35}}.$

b) MSU campus: $N = \mathbf{1.6 \cdot 10^{31}}.$

Solar energy utilized by green plants and converted to chemical energy:

a) Moscow area: $E_{\text{util}} = 1.4 \cdot 10^{17} \cdot (18\%/100\%) \cdot (10\%/100\%) \cdot (27\%/100\%) = 6.8 \cdot 10^{14} \text{ J}$

b) MSU campus: $E_{\text{util}} = 4.6 \cdot 10^{12} \cdot (54\%/100\%) \cdot (10\%/100\%) \cdot (27\%/100\%) = 6.7 \cdot 10^{10} \text{ J}$

Quantity of photosynthesis products $n(\text{CH}_2\text{O}) = E_{\text{util}} / \Delta_r G_{298}^\circ$

a) Moscow area: $n(\text{CH}_2\text{O}) = n(\text{O}_2) = 1.4 \cdot 10^9 \text{ mol}$

$$m(\text{CH}_2\text{O}) = n \cdot M = 1.4 \cdot 10^9 \text{ mol} \cdot 0.03 \text{ kg/mol} = \mathbf{4.2 \cdot 10^7 \text{ kg}}$$

$$V(\text{O}_2) = n \cdot V_m = 1.4 \cdot 10^9 \text{ mol} \cdot 0.0244 \text{ m}^3/\text{mol} = \mathbf{3.4 \cdot 10^7 \text{ m}^3}$$

b) MSU campus: $n(\text{CH}_2\text{O}) = n(\text{O}_2) = 1.4 \cdot 10^5 \text{ mol}$

$$m(\text{CH}_2\text{O}) = n \cdot M = 1.4 \cdot 10^5 \text{ mol} \cdot 0.03 \text{ kg/mol} = \mathbf{4200 \text{ kg}}$$

$$V(\text{O}_2) = n \cdot V_m = 1.4 \cdot 10^5 \text{ mol} \cdot 0.0244 \text{ m}^3/\text{mol} = \mathbf{3400 \text{ m}^3}$$

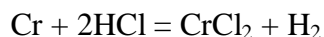
5. Percent of solar energy converted to chemical energy:

a) Moscow area: $(18\%/100\%) \cdot (10\%/100\%) \cdot (27\%/100\%) = 0.005 = \mathbf{0.5\%}$

b) MSU campus: $(54\%/100\%) \cdot (10\%/100\%) \cdot (27\%/100\%) = 0.015 = \mathbf{1.5\%}$

Problem 3. Ammine complexes of transition metals

1. Chrome is dissolved in a diluted sulfuric or hydrochloric acid:



The experiment is conducted under inert atmosphere.

2. $4[\text{Cr}(\text{NH}_3)_6]\text{Cl}_2 + 4\text{NH}_4\text{Cl} + \text{O}_2 = 4[\text{Cr}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2 \downarrow + 4\text{NH}_3 + 2\text{H}_2\text{O}$

The formula of the precipitate is $\text{CrCl}_3\text{N}_5\text{H}_{15}$.

3. H_2O_2 . The compound $[\text{Cr}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ is formed because the oxidation takes place via the η_2 -bridging peroxocomplex, followed by the hydrolysis when the leaving peroxo-group is replaced by the chloride-ion from the solution.

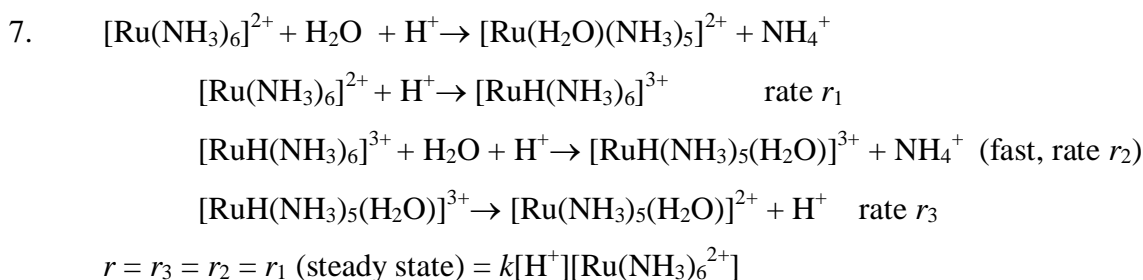
4. $2[\text{Cr}(\text{NH}_3)_6]\text{Cl}_2 + 2\text{NH}_4\text{Cl} = 2[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3 + \text{H}_2 + 2\text{NH}_3$

5. The chromium(3+) complexes are inert, thus the substitution process occurs slowly. This is due to the d^3 configuration.

6. $\text{Fe}(\text{NH}_3)_6^{2+} < \text{Ru}(\text{NH}_3)_6^{2+} < \text{Cr}(\text{NH}_3)_6^{2+}$

The coordinated ammonia has no vacant electron pair and therefore cannot interact with a proton. The iron(2+) complex is labile, that is, ammonia ligands can be easily substituted by water molecules, which have a free electron pair even when linked to a metal atom. The ruthenium(2+) complex is inert, but due to high atomic radius of ruthenium has a possibility to

form an intermediate complex with an enhanced coordination number. The chromium(3+) complex is inert and has no possibility to bind a proton. Therefore it is the most stable complex in the acidic media.



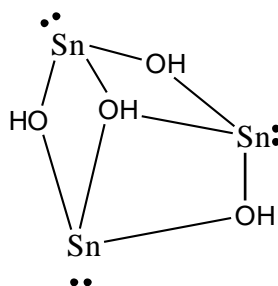
See J.D. Atwood, Inorganic and organometallic reaction mechanisms, 2nd edition, Wiley-VCH, pp.85-86 and P.C. Ford et al, Inorg. Chem., 1968, 7, 1976.

Problem 4. Preparation of inorganic compound

1. The common mineral of tin is cassiterite, SnO_2 . Thus, 1.05 g of X after decomposition give 0.8664 g of SnO_2 that contains 5.738 mmol of tin. Under decomposition 0.069 g (3.833 mmol) of water form. As the ratio $n(\text{Sn}) : n(\text{H}_2\text{O})$ is equal to 1.5 (or 3 : 2), the brutto formula of X contains 3 equivalents of SnO_2 , 4 of H and 2 of O (from 2 water molecules). In addition, it also contains nitrogen and probably more oxygen. Their mass is $1.05 - 0.8664 - 0.069 = 0.1146$ g and the average molar mass is $M = 0.1146 / (0.00383/2) = 60$ g/mol, which corresponds to N_2O_2 . Thus, the formula of X is $\text{Sn}_3\text{O}_{10}\text{N}_2\text{H}_4$, or $\text{Sn}_3\text{O}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2$.

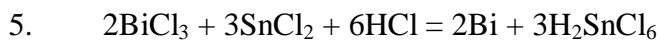
2. All the operations should be performed in an inert atmosphere, because tin(II) hydroxide is oxidized in air.

3. If all the metal atoms in the cation are equivalent they have the same coordination sphere. So, we may suppose the formula $[\text{Sn}_3(\text{OH})_4]^{2+}$, that is a combination of three pyramids linked by joint edges in a cycle (See J.D. Donaldson et al, JCS Dalton Trans, 1995, 2273.):



The pyramidal nonplanar geometry is due to the electron pair on each tin atom.

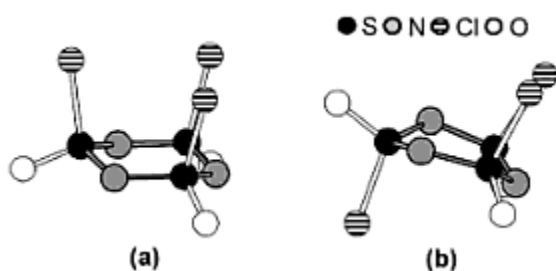
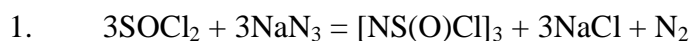
4. In the acidic solution the hydrated tin(2+) ions are formed, in the basic media – the anions $[\text{Sn}(\text{OH})_3]^-$, $[\text{Sn}(\text{OH})_6]^{4-}$ and oligonuclear species such as $[\text{Sn}_2\text{O}(\text{OH})_4]^{2-}$, $[\text{Sn}_4\text{O}(\text{OH})_{10}]^{4-}$.



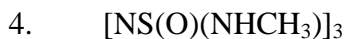
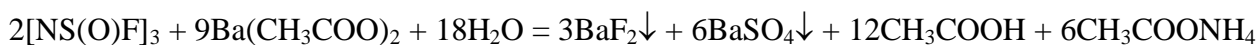
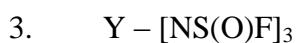
$$E^\circ = 0.317 - 0.15 = 0.167 \text{ V,}$$

$$K = \exp\left(\frac{nFE^\circ}{RT}\right) = \exp\left(\frac{6 \cdot 96500 \cdot 0.167}{8.314 \cdot 298}\right) = 8.90 \cdot 10^{16}$$

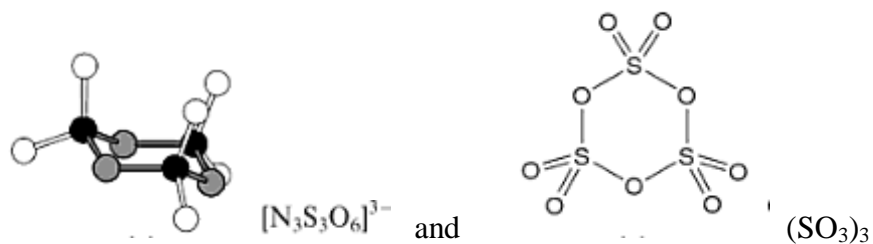
Problem 5. Inorganic chains and rings



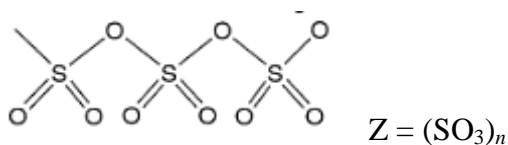
2.



5.



6.



Problem 6. Transition metal compounds

1. Anhydrous salt **D** is the main constituent of compound **B**. We may suppose that **B** is a hydrate of **D**. The Na : **X** molar ratio in **D** is 3:1. **D** is not a binary compound Na_3X as in this case $M_{\text{X}} = (29.3 \cdot 69 / 70.7) = 28.6$. There is no such element. So, **D** contains some other element(s) too. Oxygen is the most probable element, *i.e.*, **D** is Na_3XO_n (salt **D** cannot have formulae of $\text{Na}_3\text{H}_m\text{XO}_n$ type as all volatiles should be removed under reaction conditions used for synthesis of **D** (heating at 800°C)). High content of **X** in compound **C** allows one to suppose that **C** is a binary compound, *i.e.*, it is an oxide of **X**. Now we can determine **X**.

Oxide	X_2O	XO	X_2O_3	XO_2	X_2O_5	XO_3	X_2O_7	XO_4
M_{X}	13.74	27.48	41.22	54.96	68.70	82.43	96.17	109.91

Therefore, **X** is Mn and **C** is MnO_2 . From the content of Mn in **D** we derive its formula, Na_3MnO_4 . The manganese oxidation state in this compound is +5. Under heating or cooling, the alkaline solution of **D** disproportionates, giving solid MnO_2 and a green solution. Solutions of manganese(VII) derivatives are usually purple but not green. Therefore, the solution contains a salt of manganese (VI). The analogous green solution is formed in the last procedure. We may conclude that this procedure leads to manganate, K_2MnO_4 . Indeed, the content of Mn in K_2MnO_4 (compound **E**) is 27.9%.

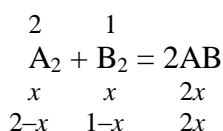
Compound **B** (a Mn(V) derivative) is obtained by the reaction of **A** with sodium sulfite which is a well-known reducing agent. Heating of the alkaline solution of **A** affords K_2MnO_4 . It is possible only if **A** is a Mn(VII) derivative. Indeed, the Mn content in **A** corresponds to the formula of KMnO_4 . The remaining unknown compound is **B**. Above we supposed that **B** is a hydrate of **D**. Calculations using the formula of $\text{Na}_3\text{MnO}_4 \cdot n\text{H}_2\text{O}$ lead to $M_{\text{B}} = 413.5$. It corresponds to $n = 12.5$. However, $M_{\text{B}} = 381.2$ from the Na content. In other words, Na : Mn ratio in **B** is not 3 : 1 but 3.25 : 1. This additional sodium appears due to the presence of some other Na compound(s) in the solvate. To determine this compound, the analysis of the synthetic procedure is required. During the synthesis of **B** solvate is washed with NaOH solution. So, the possible formula of **B** is $\text{Na}_3\text{MnO}_4 \cdot 0.25\text{NaOH} \cdot n\text{H}_2\text{O}$. From Na and Mn content we conclude that $n = 12$. Finally, **B** is $[4\text{Na}_3\text{MnO}_4 \cdot \text{NaOH} \cdot 48\text{H}_2\text{O}]$.

2. Four reactions are discussed in the text. They are:

- 1) $4 \text{KMnO}_4 + 4 \text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O} + 13 \text{NaOH} + 16 \text{H}_2\text{O} = [4\text{Na}_3\text{MnO}_4 \cdot \text{NaOH} \cdot 48\text{H}_2\text{O}]_{\downarrow} + 4 \text{Na}_2\text{SO}_4 + 4 \text{KOH}$
 $(4\text{KMnO}_4 + 4\text{Na}_2\text{SO}_3 + 13\text{NaOH} + 44\text{H}_2\text{O} = [4\text{Na}_3\text{MnO}_4 \cdot \text{NaOH} \cdot 48\text{H}_2\text{O}]_{\downarrow} + 4\text{Na}_2\text{SO}_4 + 4\text{KOH})$
- 2) $2 \text{Na}_3\text{MnO}_4 + 2 \text{H}_2\text{O} = \text{Na}_2\text{MnO}_4 + \text{MnO}_2 + 4 \text{NaOH}$
- 3) $12 \text{NaOH} + 4 \text{MnO}_2 + \text{O}_2 = 4 \text{Na}_3\text{MnO}_4 + 6 \text{H}_2\text{O}$
- 4) $4 \text{KMnO}_4 + 4 \text{KOH} = 4 \text{K}_2\text{MnO}_4 + \text{O}_2 + 2 \text{H}_2\text{O}$

Problem 7. Simple equilibrium

1. The initial ratio $A_2 : B_2 = 2 : 1$

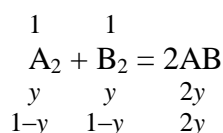


$$n(AB) = 2x = n(A_2) + n(B_2) = (2-x) + (1-x),$$

$$x = 0.75$$

$$K_1 = \frac{n(AB)^2}{n(A_2)n(B_2)} = \frac{1.5^2}{1.25 \cdot 0.25} = 7.2$$

2. The initial ratio $A_2 : B_2 = 1 : 1$



$$K_1 = \frac{n(AB)^2}{n(A_2)n(B_2)} = \frac{(2y)^2}{(1-y) \cdot (1-y)}$$

The ratio of heteronuclear to homonuclear molecules:

$$\frac{n(AB)}{n(A_2) + n(B_2)} = \frac{2y}{(1-y) + (1-y)} = \frac{y}{1-y} = \sqrt{\frac{K_1}{4}} = 1.34$$

3. New equilibrium constant: $K_2 = K_1 / 2 = 3.6$.

Equilibrium amounts: $n(AB) = 1.5 \text{ mol}$, $n(A_2) = 1.25 \text{ mol}$, $n(B_2) = 0.25+x \text{ mol}$,

$$K_2 = \frac{1.5^2}{1.25 \cdot (0.25+x)} = 3.6,$$

$x = 0.25 \text{ mol} = 25\%$ of initial amount of B_2 should be added.

4. Consider two initial mixtures: $A_2 : B_2 = x : 1$ and $A_2 : B_2 = 1/x : 1 = 1 : x$. It is clear that in both cases the equilibrium yield is the same, hence $\eta(x) = \eta(1/x)$. The value $x = 1$ for such functions is the extremum point. We can prove it in the following way. Consider the identity:

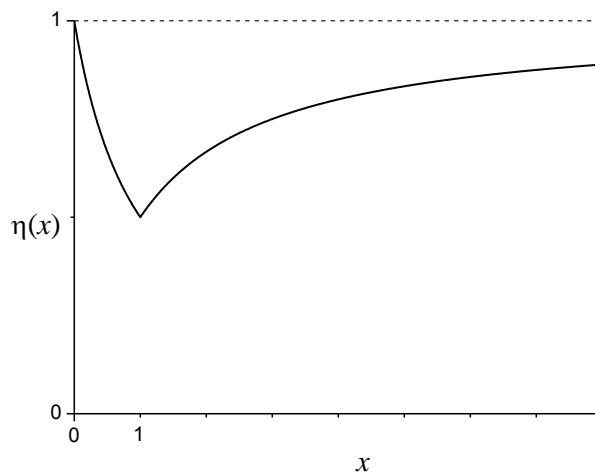
$$\eta(1) - \eta(x) = \eta(1) - \eta\left(\frac{1}{x}\right)$$

near the point $x = 1$. If $\eta(x)$ is an increasing or decreasing function at $x = 1$, then near this point both sides of the identity will have opposite signs. Hence, either $\eta(x) = \text{const}$ (which is chemical nonsense), or $x = 1$ is the point of extremum.

5. a) At $x \rightarrow \infty$ the very large amount of A_2 will almost completely shift the equilibrium $A_2 + B_2 = 2AB$ to the right, and almost all B_2 will be converted to AB , the yield will tend to 1, $\eta(x \rightarrow \infty) \rightarrow 1$.

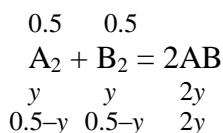
b) At $x \rightarrow 0$ ($1/x \rightarrow \infty$) the situation is the same as in (a) if we interchange A_2 and B_2 , that is $\eta(x \rightarrow 0) \rightarrow 1$.

6. From question 5 it follows that at $x = 1$ the function $\eta(x)$ has a minimum, because at $x = 0$ or $x = \infty$ it approaches the maximum possible value of 1. Qualitatively, the graph is as follows:



7. Suppose we have in total 1 mol of A_2 and B_2 , and the molar ratio $A_2 : B_2 = x : 1$. Then, the initial amounts of reagents are: $n(A_2) = x/(x+1)$, $n(B_2) = 1/(x+1)$. It follows from the symmetry between A_2 and B_2 that the equilibrium amount of AB will be the same for the molar ratios x and $1/x$, hence $x = 1$ corresponds to the maximum or minimum $n_{\text{eq}}(AB)$.

If x is very large (small), then the initial amount of B_2 (A_2) will be small and so will be $n_{\text{eq}}(AB)$. Therefore, the maximum amount of AB will be obtained at $A_2 : B_2 = 1 : 1$. The equilibrium calculation for this case is as follows.



$$K = \frac{n(\text{AB})^2}{n(\text{A}_2)n(\text{B}_2)} = \frac{(2y)^2}{(0.5-y)^2}$$

$$y = \frac{\sqrt{K}}{4 + 2\sqrt{K}}$$

$$n_{\text{eq}}(\text{AB}) = \frac{\sqrt{K}}{2 + \sqrt{K}}$$

Problem 8. Copper sulfate and its hydrates

1. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.
2. The Clausius-Clapeyron equation for the decomposition of a solid hydrate:



has the form:

$$\frac{dp_h}{dT} = \frac{\Delta H_d}{T\Delta V} \approx \frac{p_h \Delta H_d}{2RT^2},$$

where p_h is the vapor pressure of water over the hydrate, ΔH_d is the enthalpy of decomposition.

The solution of this equation is:

$$p_h = p_{h0} \exp\left(\frac{\Delta H_d}{2R} \left(\frac{1}{T_0} - \frac{1}{T}\right)\right),$$

where $p_{h0} = 1047$ Pa is the saturated vapor pressure over $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $T_0 = 298\text{K}$. Enthalpy of decomposition of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is: $\Delta H_d = 2 \cdot (-241.83) - 1688.7 + 2277.4 = 105.04 \text{ kJ} \cdot \text{mol}^{-1}$.

The similar equation describes the temperature dependence of the vapor pressure of water p_w :

$$p_w = p_{w0} \exp\left(\frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_0} - \frac{1}{T}\right)\right).$$

The enthalpy of vaporization of water is: $\Delta H_{\text{vap}} = -241.83 + 285.83 = 44.0 \text{ kJ} \cdot \text{mol}^{-1}$. The humidity is the ratio of two vapor pressures:

$$\frac{p_h}{p_w} = \frac{p_{h0}}{p_{w0}} \exp\left(\frac{\Delta H_d / 2 - \Delta H_{\text{vap}}}{R} \left(\frac{1}{T_0} - \frac{1}{T}\right)\right) = 0.35.$$

From this equation we find the required temperature:

$$\frac{1}{T} = \frac{1}{T_0} - \frac{R}{\Delta H_d / 2 - \Delta H_{\text{vap}}} \ln \frac{0.35 p_{w0}}{p_{h0}} = \frac{1}{298} - \frac{8.314}{(105.04 / 2 - 44) \cdot 10^3} \ln \frac{0.35 \cdot 3200}{1047} = 0.00329$$

$$T_0 = \frac{1}{0.00329} = 304 \text{ K or } 31 \text{ }^\circ\text{C}.$$

3. b)

4. After several repetitions of the procedure, the equilibrium is established between the anhydrous copper sulfate and its monohydrate: $\text{CuSO}_4 \cdot \text{H}_2\text{O} = \text{CuSO}_4 + \text{H}_2\text{O}$. In this case the saturated vapor pressure of water over its solution in ethanol is equal to the saturated vapor pressure of water over $\text{CuSO}_4 \cdot \text{H}_2\text{O}$. Thus, $p_h = p_w \gamma x$, $x = \frac{p_h}{p_w \gamma} = 0.0136$, the mass fraction of water is:

$$w(\text{H}_2\text{O}) = \frac{xM(\text{H}_2\text{O})}{xM(\text{H}_2\text{O}) + (1-x)M(\text{C}_2\text{H}_5\text{OH})} = 0.0054, \text{ or } 0.54\%.$$

5. Enthalpy of decomposition of $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ is: $\Delta H_d = -241.83 - 770.4 + 1084.4 = 72.17$ $\text{kJ} \cdot \text{mol}^{-1}$. From the equations above it follows that:

$$x = \frac{p_h}{p_w \gamma} = \frac{p_{h0}}{\gamma p_{w0}} \exp \left(\frac{\Delta H_d - \Delta H_{\text{vap}}}{R} \left(\frac{1}{T_0} - \frac{1}{T} \right) \right).$$

At $T = 273 \text{ K}$, $x = 0.0048$, $w = 0.19 \%$; at $T = 313 \text{ K}$ $x = 0.0235$, $w = 0.93 \%$.

Problem 9. TOF and TON

1. The *TOF* unit is $\{\text{time}^{-1}\}$. SI unit for *TOF* is $\{\text{s}^{-1}\}$.

TOF relates to *TON* by the equation

$$TOF \times t = TON,$$

where t is the time till the moment of inactivation of a catalyst. The formula gives the upper limit for *TON*. It assumes that the catalyst works with its best efficiency (*TOF*) all the time and becomes inactivated suddenly, in a moment. It is more realistic to assume that *TOF* goes down gradually. Then the following relation is valid:

$$TOF \times t \geq TON.$$

2. a) *TOF* is a maximum value of

$$\frac{\Delta N_B}{\Delta t \cdot 10^{15}} \quad (1)$$

Maximum of $\Delta N_B/\Delta t$ corresponds to the initial linear part of the curve in Fig. 1a and is equal to

$$\frac{\Delta N_B}{\Delta t} = \tan \alpha = \left(\frac{7}{2}\right) \cdot 10^{-8} \frac{\text{mol}}{\text{cm}^2 \cdot \text{s}} = 21 \cdot 10^{15} \frac{\text{molec}}{\text{cm}^2 \cdot \text{s}}$$

TOF is equal to

$$TOF = \frac{\Delta N_B}{\Delta t \cdot 10^{15}} = 21$$

b) There are several curves in Fig. 1b. It is obvious that the value of $\Delta N_B/\Delta t$ for the initial linear parts of the curves goes up with the increase of the initial pressures of the reagent A. However for curves (10) and (11) the initial slopes $\Delta N_B/\Delta t$ are the same. It means that the maximum efficiency of the catalyst is achieved. Now $\Delta N_B/\Delta t$ is independent of the reagent pressure and no more A can be converted into products per unit of time per catalytic site. The initial slopes of the curves (10) and (11) should be used to calculate *TOF* and *TON*

$$\frac{\Delta N_B}{\Delta t \cdot 10^{15}} = 210 \text{ s}^{-1}; \quad TON \leq TOF \times t = 210 \cdot 40 \cdot 60 = 5 \cdot 10^5$$

3. a) The slope of the linear dependence in Fig. 2a should be used to calculate *TOF*:

$$TOF = \tan \alpha = 6 \text{ s}^{-1}$$

It is assumed that every single atom of the metal forms a catalytic site and works independently. *TOF* is independent of the amount of atoms deposited.

b) In this case a group of n atoms, rather than a single atom, forms a catalytic site. The number of catalytic sites is

$$k = \frac{N_B}{TOF} = \frac{18 \cdot 6.02 \cdot 10^{23} \cdot 10^{-11}}{35} = 3.1 \cdot 10^{12} \text{ molec} / \text{cm}^2,$$

and the number of atoms n in one catalytic site is equal to:

$$n = \frac{N_{\text{Cat}}}{k} = \frac{N_{\text{Cat}}}{N_B} TOF = \frac{7 \cdot 10^{12}}{3.1 \cdot 10^{12}} = 2.2 \approx 2$$

4) The authors of this study considered every single Au atom to be a catalytic site. One has to calculate the number of Au atoms involved in the catalytic process in Fig. 3a and 3b. In the case (b), all yellow spheres are taking part in the reaction. In the case (a), 1/3 of the yellow spheres from the lower monolayer are involved together with all red spheres. 2/3 of the yellow

spheres are blocked by the red spheres from the top and do not participate in the catalytic reaction.

Let N_{Au} be the number of the yellow spheres in Fig. 3b. The number of the red spheres in Fig. 3a is equal to $1/3 N_{\text{Au}}$. The total number of Au atoms involved in catalytic reaction in Fig. 3a is $1/3 N_{\text{Au}}(\text{red}) + 1/3 N_{\text{Au}}(\text{yellow})$. The rate of the reaction in case (a) is:

$$r_2 = 4r_1 = r_2(\text{red}) + \frac{1}{3}r_1,$$

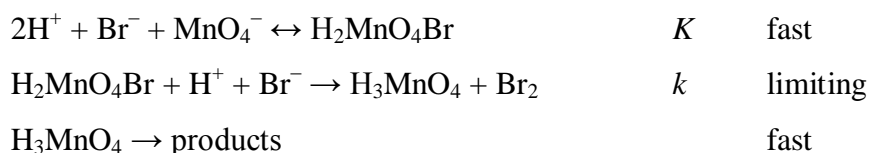
where $r_2(\text{red})$ and $1/3r_1$ are partial rates for the red and yellow spheres, respectively.

$$\text{Finally, } \frac{TOF(\text{a})}{TOF(\text{b})} = \frac{4r_1 - \frac{1}{3}r_1}{\frac{1}{3}N_{\text{Au}}} : \frac{r_1}{N_{\text{Au}}} = \frac{3(11/3r_1)}{r_1} = 11$$

Problem 10. Kinetic puzzles

Below are given the mechanisms of these reactions, established by various experimental methods. However, the limited data given in the text of a problem allow multiple mechanisms. Therefore the only two criteria for the correct solutions are: 1) the consistency of the mechanism with the rate law; 2) the chemical sense.

1. The schematic mechanism is:



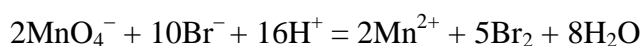
At low concentrations of proton and bromide the equilibrium of the first reaction is shifted to the left, hence the concentration of the complex $\text{H}_2\text{MnO}_4\text{Br}$ is

$$[\text{H}_2\text{MnO}_4\text{Br}] = K[\text{MnO}_4^-][\text{Br}^-][\text{H}^+]^2 \approx Kc(\text{MnO}_4^-)c(\text{Br}^-)c^2(\text{H}^+)$$

At high concentrations of proton and bromide the equilibrium of the first reaction is shifted to the right, hence the concentration of complex $\text{H}_2\text{MnO}_4\text{Br}$ equals the total concentration of permanganate:

$$[\text{H}_2\text{MnO}_4\text{Br}] \approx c(\text{MnO}_4^-)$$

The rate of the reaction



is half of that of the rate-determining step:

$$r = \frac{1}{2} k[\text{H}_2\text{MnO}_4\text{Br}][\text{H}^+][\text{Br}^-]$$

in the case (a)

$$r = \frac{1}{2} k[\text{H}_2\text{MnO}_4\text{Br}][\text{H}^+][\text{Br}^-] \approx k_{\text{eff}}c(\text{MnO}_4^-)c^2(\text{Br}^-)c^3(\text{H}^+)$$

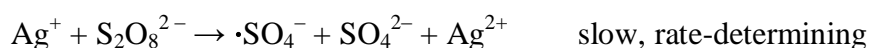
where $k_{\text{eff}} = \frac{1}{2} kK$.

In the case (b)

$$r = \frac{1}{2} k[\text{H}_2\text{MnO}_4\text{Br}][\text{H}^+][\text{Br}^-] \approx k_{\text{eff}}c(\text{MnO}_4^-)c(\text{Br}^-)c(\text{H}^+)$$

where $k_{\text{eff}} = \frac{1}{2} k$.

2. The catalytic effect of silver is due to formation of silver(II) ions and sulfate ion radicals upon reaction of Ag^+ with persulfate. The mechanism is:



The first reaction is the rate-determining step; therefore the overall oxidation reaction has the same order as the rate-determining step:

$$r = k[\text{Ag}^+][\text{S}_2\text{O}_8^{2-}]$$

3. The minimal mechanism includes the following steps:



The second and the third reaction make a chain process involving consumption of peroxydisulfate and formate. The first reaction is very slow, so most of peroxydisulfate is consumed in the third reaction. Applying the steady-state approximation to $\cdot\text{SO}_4^-$ and $\cdot\text{CO}_2^-$ we get:

$$2r_1 - r_2 + r_3 - r_4 = 0$$

$$r_2 - r_3 - r_4 = 0$$

Hence

$$r_1 = r_4$$

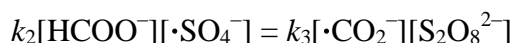
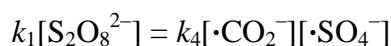
$$r_2 - r_3 = r_1$$

Since the rate of the first reaction is very low, then

$$r_1 = r_4$$

$$r_2 = r_3$$

Applying the rate laws we get:



Hence

$$[\cdot\text{CO}_2^-] = (k_1 k_2)^{1/2} (k_3 k_4)^{-1/2} [\text{HCOO}^-]^{1/2}$$

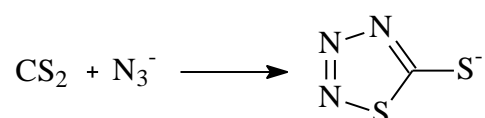
$$[\cdot\text{SO}_4^-] = (k_1 k_3)^{1/2} (k_2 k_4)^{-1/2} [\text{S}_2\text{O}_8^{2-}] [\text{HCOO}^-]^{-1/2}$$

The rate of the reaction is equal to the rate of formate consumption:

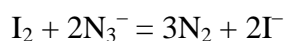
$$r = r_2 = k_2[\text{HCOO}^-][\cdot\text{SO}_4^-] = (k_1 k_2 k_3)^{1/2} k_4^{-1/2} [\text{HCOO}^-]^{1/2} [\text{S}_2\text{O}_8^{2-}] = k_{\text{eff}} [\text{HCOO}^-]^{1/2} [\text{S}_2\text{O}_8^{2-}]$$

A more complex mechanism includes the formation of OH radicals and several chain termination reactions. That's why the given rate law is valid only for a limited range of reactant concentrations.

4. The rate-determining step is the addition of azide ion to the solvent, carbon disulfide:



The oxidation of this ion by iodine is a series of fast reactions. The overall rate of the reaction



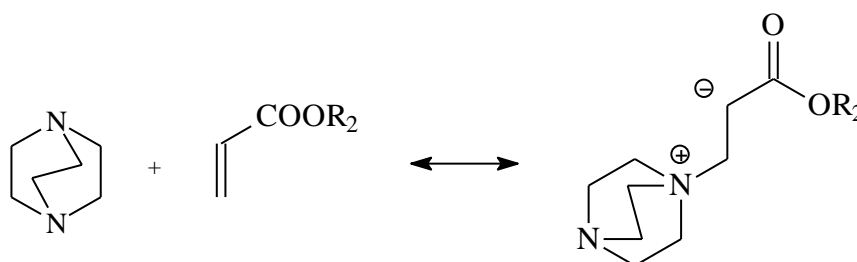
is half of that of the azide-CS₂ reaction:

$$r = \frac{1}{2} k[\text{N}_3^-][\text{CS}_2].$$

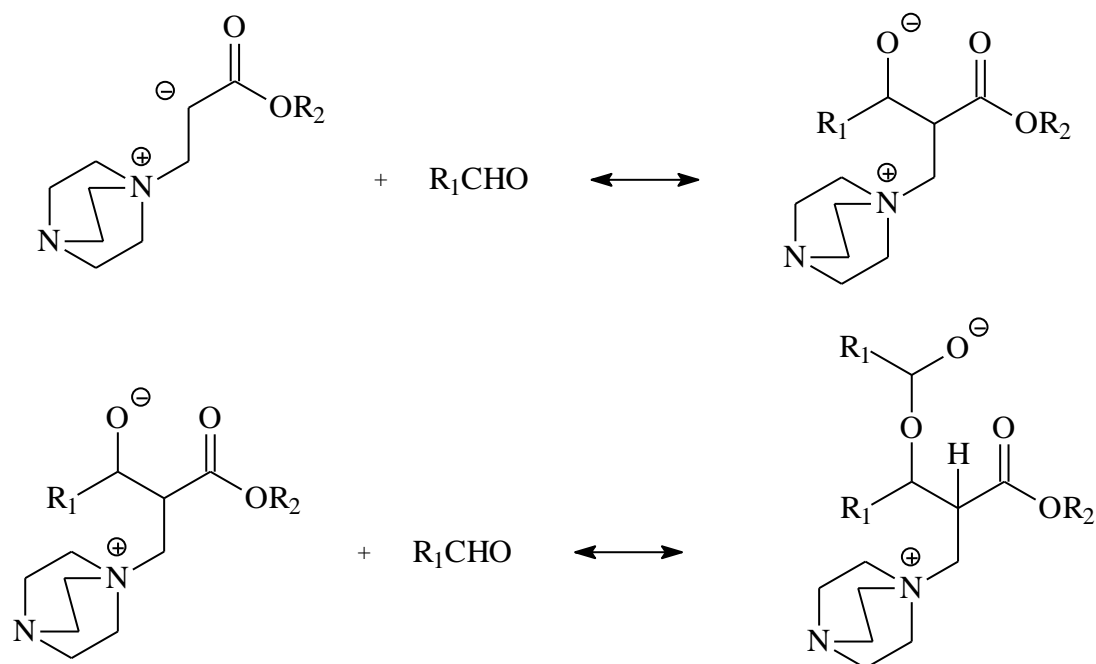
Introducing the effective constant $k_{\text{eff}} = \frac{1}{2} k[\text{CS}_2]$ we get:

$$r = k_{\text{eff}}[\text{N}_3^-].$$

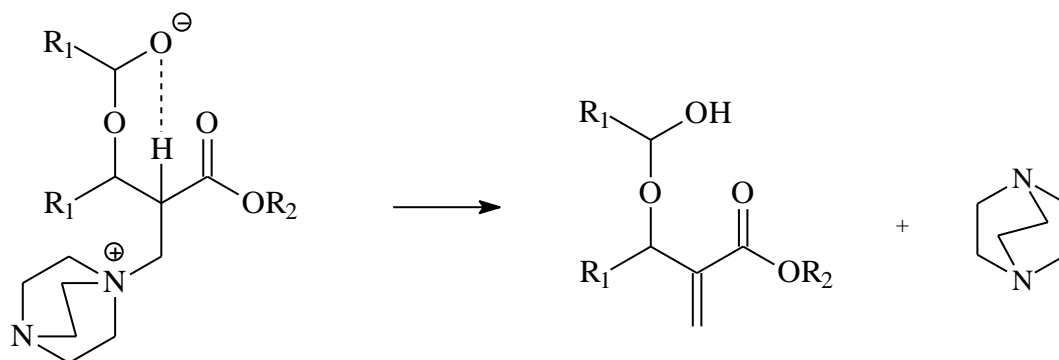
5. The reaction mechanism includes several steps. The first step is the reversible addition of DABCO to ester:



The next two steps are the reversible additions of two molecules of aldehyde to the zwitter ion formed in the previous step:



The rate-determining step is an intramolecular proton transfer followed by the elimination of DABCO:

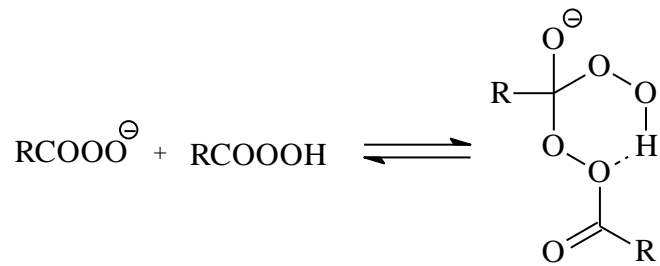


After that, the product rapidly eliminates one molecule of aldehyde. Applying quasi-equilibrium conditions to the first three steps, we get:

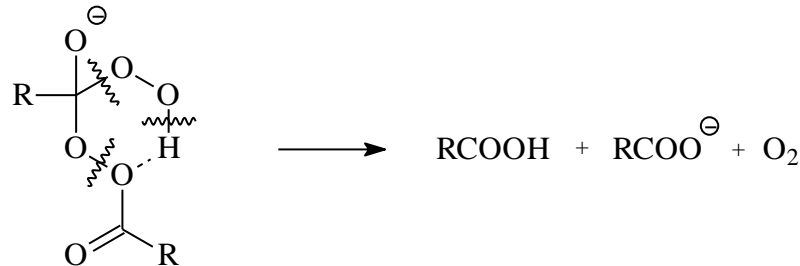
$$r = k_{RDS}K_1K_2K_3[\text{aldehyde}]^2[\text{ester}][\text{DABCO}] = k_{\text{eff}}[\text{aldehyde}]^2[\text{ester}][\text{DABCO}]$$

It is worth mentioning that in protic solvents the rate-determining step is the solvent-assisted proton transfer in DABCO-ester-aldehyde adduct, hence the reaction order is one with respect to either aldehyde, or ester or base.

6. The first step of the reaction is the reversible addition of peroxyacid anion to the carboxylic group of peroxyacid:



The next, rate-determining step is a decomposition of the addition product:



Applying a quasi-equilibrium approximation, we get:

$$r = k_{\text{eff}}[\text{RCO}_3\text{H}][\text{RCO}_3^-]$$

The concentrations of peroxyacid and its anion are related to the total concentration of peroxy compound $c(\text{RCO}_3\text{H})$ and proton concentration $[\text{H}^+]$ as follows:

$$[\text{RCO}_3\text{H}] = \frac{[\text{H}^+]}{K_a + [\text{H}^+]} c(\text{RCO}_3\text{H}) \quad [\text{RCO}_3^-] = \frac{K_a}{K_a + [\text{H}^+]} c(\text{RCO}_3\text{H}),$$

where K_a is the acidity constant of peroxyacid. Substituting these concentrations to the rate law we obtain:

$$r = c^2(\text{RCO}_3\text{H}) \frac{k_{\text{eff}} K_a [\text{H}^+]}{(K_a + [\text{H}^+])^2} = c^2(\text{RCO}_3\text{H}) \frac{k_1 [\text{H}^+]}{(k_2 + [\text{H}^+])^2}$$

Note that at given $c(\text{RCO}_3\text{H})$ the reaction rate is maximum if $[\text{RCO}_3\text{H}] = [\text{RCO}_3^-]$ (and $[\text{H}^+] = K_a$).

Problem 11. Black box

Since this is a reactor with ideal stirring, the concentrations of substances in the output flow are equal to the concentrations inside the reactor. In a stationary state, the concentrations and quantities of substances in the reactor are constant. Consider the material balance with respect to X, Y and P.

Stationary conditions are:

$$\frac{\Delta V_{X,R}}{\Delta t} = 0 \quad \frac{\Delta V_{Y,R}}{\Delta t} = 0 \quad \frac{\Delta V_{P,R}}{\Delta t} = 0, \quad (1)$$

where $\Delta V_{X,R}$, $\Delta V_{Y,R}$, $\Delta V_{P,R}$ are the changes of the quantities for the substances X, Y and P in the reactor during time Δt . The quantity of the substance in the reactor may change due to input flow, chemical reaction, and output flow:

$$\frac{\Delta V_{X,R}}{\Delta t} = \left(\frac{\Delta V_{X,R}}{\Delta t} \right)_{input} + \left(\frac{\Delta V_{X,R}}{\Delta t} \right)_{reaction} + \left(\frac{\Delta V_{X,R}}{\Delta t} \right)_{output} \quad (2)$$

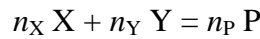
The same is true for Y and P.

Input flow rates of the substances are

$$\left(\frac{\Delta V_{X,R}}{\Delta t} \right)_{input} = f_X c_{X,I} \quad \left(\frac{\Delta V_{Y,R}}{\Delta t} \right)_{input} = f_Y c_{Y,I} \quad \left(\frac{\Delta V_{P,R}}{\Delta t} \right)_{input} = 0, \quad (3)$$

where f_X and f_Y are the input volumetric flows of the solutions of X and Y, $c_{X,I}$ and $c_{Y,I}$ – concentrations of X and Y in the respective solutions.

Let the balanced reaction equation be



where n_X , n_Y and n_P are the stoichiometric coefficients for the corresponding substances. Due to a chemical reaction the quantities of the substances in the reactor change with the rates

$$\left(\frac{\Delta V_{X,R}}{\Delta t} \right)_{reaction} = -n_X r V_R \quad \left(\frac{\Delta V_{Y,R}}{\Delta t} \right)_{reaction} = -n_Y r V_R \quad \left(\frac{\Delta V_{P,R}}{\Delta t} \right)_{reaction} = n_P r V_R, \quad (4)$$

where r – the reaction rate, V_R – the reactor volume.

The output flows of the substances are:

$$\left(\frac{\Delta V_{X,R}}{\Delta t} \right)_{output} = f_O c_{X,R} \quad \left(\frac{\Delta V_{Y,R}}{\Delta t} \right)_{output} = f_O c_{Y,R} \quad \left(\frac{\Delta V_{P,R}}{\Delta t} \right)_{output} = f_O c_{P,R}, \quad (5)$$

where f_O is the volumetric output flow, $c_{X,R}$, $c_{Y,R}$ and $c_{P,R}$ – the concentrations of substances X, Y and P in the reactor. Since the process is stationary and the reaction proceeds in the liquid phase, the output volumetric flow equals the sum of input volumetric flows:

$$f_O = f_X + f_Y \quad (6)$$

Thus the material balance equations (2) considering expressions (1) and (3)-(6) are

$$\frac{\Delta V_{X,R}}{\Delta t} = f_X c_{X,I} - n_X r V_R - c_{X,R} (f_X + f_Y) = 0$$

$$\frac{\Delta V_{Y,R}}{\Delta t} = f_Y c_{Y,I} - n_Y r V_R - c_{Y,R} (f_X + f_Y) = 0$$

$$\frac{\Delta V_{P,R}}{\Delta t} = n_P r V_R - c_{P,R} (f_X + f_Y) = 0$$

Hence

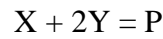
$$n_X rV_R = f_X c_{X,I} - c_{X,R} (f_X + f_Y)$$

$$n_Y rV_R = f_Y c_{Y,I} - c_{Y,R} (f_X + f_Y)$$

$$n_P rV_R = c_{P,R} (f_X + f_Y)$$

Exp. no.	$n_X rV_R$, mol/s	$n_Y rV_R$, mol/s	$n_P rV_R$, mol/s	$n_X:n_Y:n_P$
1	10.02	20.04	10.02	1:2:1
2	10.04	20.07	10.05	1:2:1
3	15.73	31.47	15.72	1:2:1
4	19.68	39.34	19.68	1:2:1

Hence the balanced reaction equation is



Now consider the rate dependence on concentrations

Exp. no.	$c_{X,R}$, mol/m ³	$c_{Y,R}$, mol/m ³	$c_{P,R}$, mol/m ³	rV_R , mol/s
1	299	48.2	501	10.02
2	732	30.9	335	10.04
3	8.87	351	524	15.73
4	308	66.6	492	19.68

The rate law is

$$r = k c_{X,R}^x c_{Y,R}^y c_{P,R}^p$$

or, after multiplying by reactor volume,

$$rV_R = kV_R c_{X,R}^x c_{Y,R}^y c_{P,R}^p$$

Take the logarithm of both parts of the equation

$$\ln(rV_R) = \ln(kV_R) + x \ln c_{X,R} + y \ln c_{Y,R} + p \ln c_{P,R} \quad (7)$$

The coefficients in this equation are given in the table below:

Exp. no.	$\ln c_{X,R}$	$\ln c_{Y,R}$	$\ln c_{P,R}$	$\ln(rV_R)$
1	5.70	3.88	6.22	2.30
2	6.60	3.43	5.81	2.31
3	2.18	5.86	6.26	2.76
4	5.73	4.20	6.20	2.98

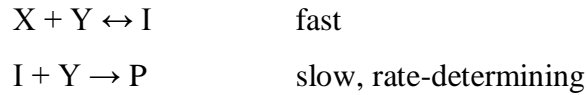
Solving the system of equations (7) we get:

$$x = 1.00 \quad y = 2.00 \quad p = 0.01 \quad \ln(kV_R) = -11.20$$

Hence the orders of the reaction are one in X, two in Y, and zero in P. The product kV_R is:

$$kV_R = \exp(-11.20) = 1.37 \cdot 10^{-5} \text{ m}^9 \text{ mol}^{-2} \text{ s}^{-1}.$$

One of the possible mechanisms that match the obtained rate law is:



Summarizing, the obtained results are:

- ◆ the reaction equation: $X + 2Y = P$;
- ◆ the reaction orders: 1, 2, and 0 with respect to X, Y, and P respectively;
- ◆ the product of the rate constant and reactor volume: $kV_R = 1.37 \cdot 10^{-5} \text{ m}^9 \cdot \text{mol}^{-2} \cdot \text{s}^{-1}$.

Problem 12. Chlorination of styrenes

1. Since all reaction pathways obey the same rate law, the quantity of the product is proportional to the respective rate constant. The overall constant equals the sum of constants for different pathways. Hence

for 1,2-dichloro:

$$k = 1.45 \cdot 10^4 \frac{61\%}{100\%} = 8.8 \cdot 10^3 \text{ M}^{-1} \text{ s}^{-1}$$

for 1-acetoxy-2-dichloro:

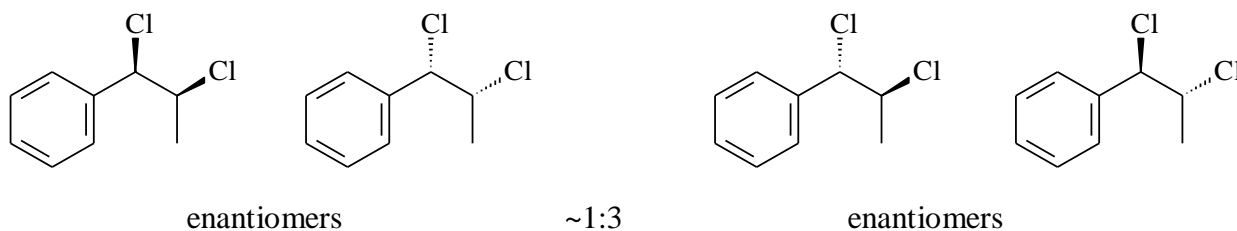
$$k = 1.45 \cdot 10^4 \frac{30\%}{100\%} = 4.4 \cdot 10^3 \text{ M}^{-1} \text{ s}^{-1}$$

for 2-chlorostyrene:

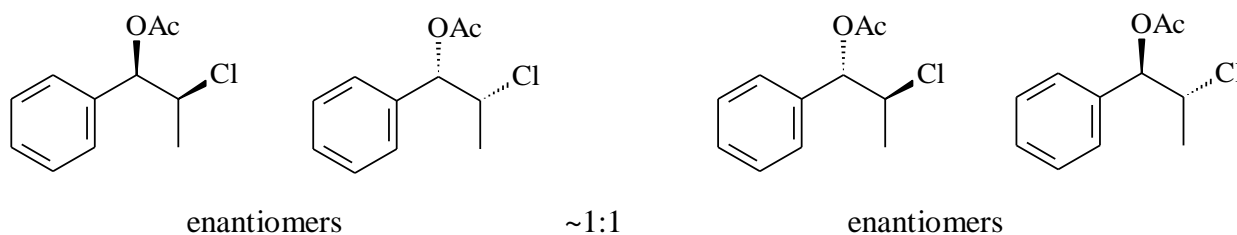
$$k = 1.45 \cdot 10^4 \frac{9\%}{100\%} = 1.3 \cdot 10^3 \text{ M}^{-1} \text{ s}^{-1}$$

2. This reaction is not stereospecific and leads to the formation of diastereomeric addition products in comparable amounts. The following products are obtained (approximate ratios of product quantities at 25°C are given as an illustration):

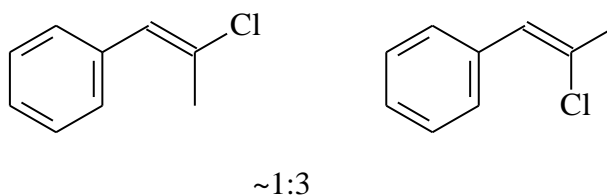
1,2-dichloro:



1-acetoxy-2-chloro:



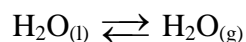
2-chlorostyrene:



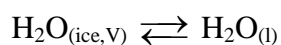
The achiral sorbent is unable to separate enantiomers, so only 6 different fractions can be obtained. The chiral sorbent allows full separation, so in this case the determined number of products is 10.

Problem 13. The dense and hot ice

1. The boiling point of water and the melting point of ice V increase, and the melting point of ordinary ice decreases with the increasing pressure. This can be easily explained using the Le Chatelier principle. In the phase transitions

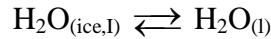


and



the volume increases and heat is absorbed ($\Delta V > 0$, $\Delta H > 0$). Hence, with the increasing pressure both equilibria are shifted to the left; consequently, temperature should be increased to keep the equilibria.

In the phase transition



the volume decreases and heat is absorbed ($\Delta V < 0$, $\Delta H > 0$). Hence, with the increasing pressure the phase equilibrium is shifted to the right, and temperature should be decreased to keep the equilibrium.

2. a) 250 K: vapor \rightarrow ice I \rightarrow ice III \rightarrow ice V \rightarrow ice VI
- b) 400 K: vapor \rightarrow liquid \rightarrow ice VII
- c) 700 K: only vapor (at high pressure it may be called “supercritical fluid”), no phase transitions occur.

3. Phase transitions between condensed phases are described by the Clapeyron equation:

$$\frac{dp}{dT} = \frac{\Delta H}{T\Delta V},$$

or, in approximate form:

$$\frac{\Delta p}{\Delta T} = \frac{\Delta H}{T\Delta V}.$$

We calculate the right side of this equation for the ice I \rightleftharpoons water transition. The volume change is determined from the densities:

$$\Delta V = V(\text{water}) - V(\text{ice}) = \frac{M(\text{H}_2\text{O})}{\rho(\text{water})} - \frac{M(\text{H}_2\text{O})}{\rho(\text{ice})} = \frac{18}{1.000} - \frac{18}{0.917} = -1.63 \text{ cm}^3/\text{mol}$$

$$\frac{\Delta p}{\Delta T} = \frac{\Delta H}{T\Delta V} = \frac{6010 \text{ J/mol}}{273 \text{ K} \cdot (-1.63 \cdot 10^{-6} \text{ m}^3/\text{mol})} = -1.35 \cdot 10^7 \text{ Pa/K} = -13.5 \text{ MPa/K}.$$

If this slope does not depend on pressure and temperature then at the pressure of 210 MPa the temperature of liquid water in equilibrium with ice I and Ice III is approximately:

$$T = 273 + \Delta T = 273 + \frac{210 - 0.1}{-13.5} = -257.5 \text{ K} = -15.5 \text{ }^\circ\text{C}.$$

This is an estimate; the real value is $-22 \text{ }^\circ\text{C}$. The difference between the estimated and real values is due to the fact that the enthalpy of fusion and densities vary with pressure. For example, at 210 MPa the enthalpy of fusion of ice I is 4230 J/mol (instead of 6010 at normal pressure), and the volume change is $\Delta V = -2.43 \text{ cm}^3/\text{mol}$ (instead of $-1.63 \text{ cm}^3/\text{mol}$ at normal pressure).

4. From the Clapeyron equation it follows that the slope of the $p(T)$ dependencies for the melting points of ice III to ice VII is determined by ΔH , T , and ΔV . The first quantity is assumed to be the same for all transitions, the temperature is comparable in all cases, hence the main contribution to the slope comes from ΔV . For ice VII, the slope is the smallest, hence, the $\Delta V = V(\text{water}) - V(\text{ice})$ is the largest, whereas $V(\text{ice})$ is the smallest. It means that ice VII is the densest form of ice (among those forms that are shown on the phase diagram).

From the phase diagram we see that the melting point of ice VII at a pressure of 10 GPa is about 630 K. This is, indeed, a very “hot” ice.

5. Determine the molar volume of ice VII. One mole contains $N_A/2$ cubic unit cells:

$$V_m = \frac{N_A}{2} d^3 = 3.01 \cdot 10^{23} \cdot (0.335 \cdot 10^{-7})^3 = 11.3 \text{ cm}^3/\text{mol}.$$

The density of ice VII is:

$$\rho = M / V_m = 18 / 11.3 = 1.59 \text{ g/cm}^3.$$

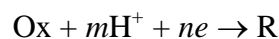
6. Knowing the density of ice VII, we use the Clapeyron equation to estimate its enthalpy of fusion. Comparing the triple point “water – ice VI – ice VII” and the melting point of ice VII at pressure 10 GPa we estimate the slope: $\Delta p / \Delta T = (10^4 - 2200) / (630 - 355) = 28 \text{ MPa / K}$. The volume change during melting is: $\Delta V = (18/1.00) - 11.3 = 6.7 \text{ cm}^3/\text{mol}$. Substituting these data into the Clapeyron equation, we get:

$$\Delta H = T \Delta V \frac{\Delta p}{\Delta T} = 355 \text{ K} \cdot (6.7 \cdot 10^{-6} \text{ m}^3/\text{mol}) \cdot (28 \cdot 10^6 \text{ Pa/K}) = 66000 \text{ J/mol}.$$

This value is by an order of magnitude larger than the exact value 6400 J/mol. The reason is probably due to a low resolution of the phase diagram at high pressures, which leads to a rough estimate of the slope. This result also shows that the approximations used are not valid at high pressures and temperatures.

Problem 14. Redox reactions in photosynthesis

1. Applying the Nernst equation for a half-reaction

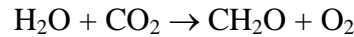


and putting $[\text{H}^+] = 10^{-7}$, we get a standard biochemical redox potential:

$$E^{o'} = E^\circ + \frac{0.0591}{n} \lg(10^{-7})^m = E^\circ - 0.414 \frac{m}{n}$$

Half-reaction	E° (V)	$E^{\circ\prime}$ (V)
$\text{O}_2 + 4\text{H}^+ + 4\text{e} \rightarrow 2\text{H}_2\text{O}$	1.23	0.82
$\text{S} + 2\text{H}^+ + 2\text{e} \rightarrow \text{H}_2\text{S}$	0.14	-0.27
$\text{Plastoquinone} + 2\text{H}^+ + 2\text{e} \rightarrow \text{Plastoquinone}\cdot\text{H}_2$	0.52	0.11
$\text{Cytochrome f}(\text{Fe}^{3+}) + \text{e} \rightarrow \text{Cytochrome f}(\text{Fe}^{2+})$	0.365	0.365
$\text{NADP}^+ + \text{H}^+ + 2\text{e} \rightarrow \text{NADP}\cdot\text{H}$	-0.11	-0.32
$\text{P680}^+ + \text{e} \rightarrow \text{P680}$	1.10	1.10
$\text{Chlorophyll}^+ + \text{e} \rightarrow \text{Chlorophyll}$	0.78	0.78

2. The standard electromotive force for the reaction



is the difference between standard redox potentials for oxidant and reductant.



For this reaction, the standard Gibbs energy is 480.5 kJ/mol, and 4 electrons are transferred from H_2O to CO_2 . Hence, the standard emf is:

$$E^\circ = -\frac{\Delta G^\circ}{nF} = -\frac{480500}{4 \cdot 96500} = -1.24 \text{ V} = E_1^\circ - 1.23 \text{ V}$$

For CO_2 reduction to carbohydrates the standard redox potential is $E_1^\circ = -0.01 \text{ V}$. The standard

biochemical potential is: $E_1^{\circ\prime} = -0.01 - 0.414 \frac{4}{4} = -0.42 \text{ V}$.

3. The overall reaction: $\text{CO}_2 + 2\text{H}_2\text{S} \rightarrow \text{CH}_2\text{O} + 2\text{S} + \text{H}_2\text{O}$



Standard emf: $E^\circ = -0.01 - 0.14 = -0.15 \text{ V}$

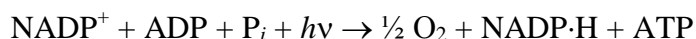
Standard Gibbs energy: $\Delta G^\circ = -nFE^\circ = -4 \cdot 96500 \cdot (-0.15) \cdot 10^{-3} = 57.9 \text{ kJ/mol}$.

Energy of light with wavelength 840 nm:

$$E_m = \frac{hcN_A}{\lambda} = \frac{6.63 \cdot 10^{-34} \cdot 3.00 \cdot 10^8 \cdot 6.02 \cdot 10^{23}}{840 \cdot 10^{-9}} \cdot 10^{-3} = 143 \text{ kJ/mol}$$

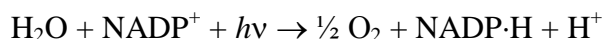
One quantum gives enough energy to oxidize two molecules of H_2S .

4. Both NADP^+ reduction and ATP formation require one proton, and during H_2O oxidation two protons are released. Hence, the overall reaction equation of light stages is:

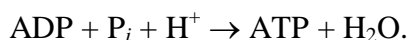


(water is not present in this reaction, because the number of H_2O molecules oxidized to O_2 is equal to the number of H_2O molecules formed during ADP phosphorylation).

5. The overall reaction is the sum of two reactions:



and



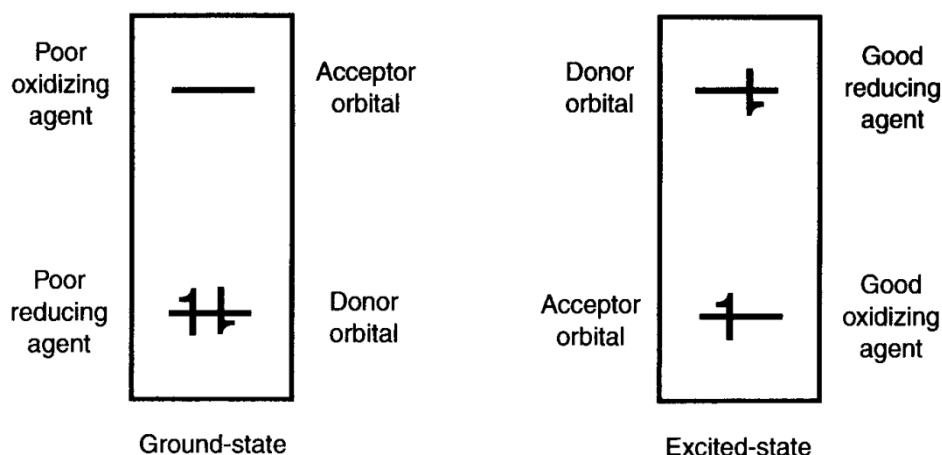
For the latter, the standard biochemical Gibbs energy is known (30.5 kJ/mol) and for the former it can be determined from the standard biochemical redox potentials.

$$\Delta G^{\circ'} = -nFE^{\circ'} = -2 \cdot 96500 \cdot (0.82 - (-0.32)) \cdot 10^{-3} = 220 \text{ kJ/mol}.$$

The overall light stages reaction contains no protons, hence the standard Gibbs energy is the same as the standard biochemical Gibbs energy:

$$\Delta G^{\circ} = \Delta G^{\circ'} = 220 + 30.5 = 250.5 \text{ kJ/mol}$$

6. This effect is easily understood using a simple orbital diagram (see Appendix in "Molecular Mechanisms of Photosynthesis" by R.E. Blankenship). In the ground state, a lost electron comes from the low-energy HOMO, while an acquired electron enters the high-energy LUMO. As a result, the molecule is neither a strong oxidant nor a good reductant. In the excited state, the situation is different: a lost electron leaves the high-energy LUMO, and the acquired electron comes to low-energy HOMO: both processes are energetically favorable, and the molecule can act both as a strong oxidant and a powerful reductant.



7. Consider two half-reactions:



and $\text{Ox} + e \rightarrow \text{R}^*$ (standard redox potential $E_{\text{Ox/R}^*}^{\circ}$).

The difference in their Gibbs energies is equal to the excitation energy:

$$F \left(E_{\text{Ox/R}}^{\circ} - E_{\text{Ox/R}^*}^{\circ} \right) = E_{\text{ex}} = \frac{hcN_{\text{A}}}{\lambda},$$

whence it follows:

$$E_{\text{Ox/R}^*}^{\circ} = E_{\text{Ox/R}}^{\circ} - \frac{hcN_{\text{A}}}{\lambda F}.$$

$$\text{For P680}^+: \quad E_{\text{P680}^+/\text{P680}^*}^{\circ} = 1.10 - \frac{6.63 \cdot 10^{-34} \cdot 3.00 \cdot 10^8 \cdot 6.02 \cdot 10^{23}}{680 \cdot 10^{-9} \cdot 96500} = -0.72 \text{ V}$$

$$\text{For Chlorophyll}^+: \quad E_{\text{Chl}^+/\text{Chl}^*}^{\circ} = 0.78 - \frac{6.63 \cdot 10^{-34} \cdot 3.00 \cdot 10^8 \cdot 6.02 \cdot 10^{23}}{680 \cdot 10^{-9} \cdot 96500} = -1.04 \text{ V}$$