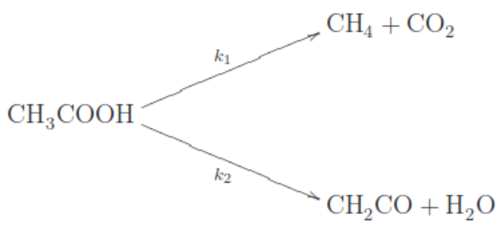
1. Sulfuryl chloride (SO_2Cl_2, ideal gas) is being heated in a closed container on 320 °C and with 1 bar initial pressure. The $SO_2Cl_2 \rightarrow SO_2 + Cl_2$ reaction follows first order kinetics. The rate constant on 320 °C is $k = 0.0792\ \mathrm{h}^{-1}$.
   (a) What % of the sulfuryl chloride has been decomposed after 30 minutes?
   (b) How much time is necessary for the 90 % of the sulfuryl chloride to be decomposed, and what will be the pressure in the container?

2. In a A → P first order reaction 22 % of A converts into P after 18.7 minutes.
   (a) Given 1.5 mM of A, what percentage of it will convert after an hour?
   (b) How much time is necessary for 80.5 % to convert?

3. The dimerization of butadiene (C_4H_6) into cyclooctadiene (C_8H_{12}) is a second order reaction with a rate constant of $k = 1.43\ 1/(\mathrm{M}\cdot\mathrm{h})$. We measure 8 g of butadiene into a 2 dm^3 container. How much time is necessary for 75 % of it to convert? ($M = 54$ g/mol)

4. Ethyl iodide (C_2H_5I) reacts with base (OH^-) in a second order reaction: $C_2H_5I + OH^- \rightarrow C_2H_5OH + I^-$. The rate of reaction can be written in the form of $v = k[\mathrm{A}][\mathrm{B}]$. Mixing 10 dm^3, 0.1 M ethyl iodide with 5 dm^3, 0.25 M base solution and waiting 5 minutes we measure a iodide concentration of 0.025 M. What is the rate constant (k) ?

5. On high temperatures (500-1000 °C) acetic acid decomposes to carbon dioxide and methane, and at the same time it also decomposes to ketene and water:



   Both reactions follow first order kinetics. At 1189 K temperature the rate constant for the first reaction is 3.74 1/s, while for the other it is 4.65 1/s. Calculate how much time is needed for 93 % of the acetic acid to decompose, and what is the maximal concentration of ketene we can gain from 1 M acetic acid in these circumstances.

6. Substances A and B are in an opposing reaction: $\mathrm{A} \rightleftharpoons \mathrm{B}$. We start from 0.33 M of pure A, and wait 2 hours at 150 °C . The concentration of A becomes 0.2 M. We know that at this temperature the equilibrium constant is 2.3 .
   (a) What are the equilibrium concentrations?
   (b) What are the rate constants?
   (c) What is the half-life of A?

7. N-methylaniline reacts with ethyl iodide in the following consecutive reactions

$$C_6H_5NHMe + EtI \xrightarrow{k_1} C_6H_5NMeEt + HI \text{ and}$$

$$C_6H_5NMeEt + EtI \xrightarrow{k_2} C_6H_5NMeEt_2{}^+ + I^- \ .$$

   Both reactions are pseudo first order because of the high surplus of the ethyl iodide. The half-life of N-methylaniline is 52.6 minutes, and $k_1/k_2 = 0.483$.
   (a) After how much time will the intermediate reach its maximal concentration?
   (b) What % of the precursor was converted into intermediate by this time? How about the final product?

8. We investigate the reaction between the myoglobin protein and carbon monoxide: $\mathrm{Mb} + \mathrm{CO} \xrightarrow{k_1} \mathrm{MbCO}$. First we mix 0.1 dm^3, 1 mM Mb solution with 0.3 dm^3, 0.5 mM CO solution, then measure the half-life of Mb. In a following experiment we mix the same type of Mb solution with 0.3 dm^3, 2 mM CO solution. We find the half-life of Mb to be 10 seconds shorter in this case. Finally, in a third experiment we mix the same Mb solution with 0.3 dm^3, 0.5 M CO solution.
   (a) What is the half-life of Mb in the second experiment?
   (b) What is the half life of Mb in the third experiment with and without the pseudo first order approximation?

1. N-methylaniline reacts with ethyl iodide in the following consecutive reactions

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Both reactions are pseudo first order because of the high surplus of the ethyl iodide. Starting from pure N-methylaniline we find that its half-life is 52.6 minutes, and $k_1'/k_2' = 0.483$, where primes denote the rate constants for the pseudo first order reactions.

   (a) After how much time will the intermediate reach its maximal concentration?

   (b) What % of the precursor was converted into intermediate by this time? How about the final product?

2. Acetonedicarboxylic acid in its aqueous solution decomposes in a first order reaction:

$$CO(CH_2COOH)_2 \xrightarrow{k} CO(CH_3)_2 + 2\ CO_2$$

The half-life of the acid at 0 °C is 470 minutes, while at 50 °C it is 37 seconds. What is the activation energy of the reaction?

3. 1-Fluoropentane reacts with sodium ethoxide in a second order reaction:

$$C_5H_{11}F + NaOC_2H_5 \xrightarrow{k} NaF + C_5H_{11}OC_2H_5$$

At 20 °C we mix 45 cm^3, 1.8 M fluoropentane with 40 cm^3, 4 M ethoxide, and find that the concentration of the fluoropentane is 0.87 M after 12 minutes. Repeating the experiment at 65 °C the concentration after 10 minutes turns out to be 0.35 M. What is the activation energy?

4. In a parallel reaction substance A converts into either B or C. The activation energy of the reaction yielding B and C is 123 kJ/mol and 101 kJ/mol, respectively. In an experiment we start from pure A, and wait half an hour at 300 °C . After this time the molar fraction of A is 0.6, while for B this is 0.15. The mixture is an ideal gas and the volume does not change during the process.

   (a) At what temperature will there be an equal amount of B and C?

   (b) What will be the half-life of A at this temperature?

5. The decomposition of substance A follows second order kinetics (2 A $\rightarrow$ P + ... type reaction). In the presence of a catalyst the kinetics of the reaction changes to first order, and the activation energy decreases by 10 kJ/mol. According to a measurement at 250 K and without a catalyst the concentration of A decreases to half of its original value in 10 minutes if we start from 1 M of A. The value of the preexponential factor in this case is $3.6489 \cdot 10^6 \frac{1}{\mathrm{Ms}}$. Using a catalyst at the same temperature 90 % of the substance converts in 10 minutes. Starting from 1 M of A what temperature do we have to apply if we want 95 % of A to convert in 10 minutes

   (a) without the catalyst?

   (b) with the catalyst?

6. We investigate the reaction between the myoglobin protein and carbon monoxide: $Mb + CO \xrightarrow{k_1} MbCO$. First we mix 0.1 dm^3, 1 mM Mb solution with 0.3 dm^3, 0.5 mM CO solution, then measure the half-life of Mb. In a following experiment we mix the same type of Mb solution with 0.3 dm^3, 2 mM CO solution. We find the half-life of Mb to be 10 seconds shorter in this case. Finally, in a third experiment we mix the same Mb solution with 0.3 dm^3, 0.5 M CO solution.

   (a) What is the half-life of Mb in the second experiment?

   (b) What is the half life of Mb in the third experiment with and without the pseudo first order approximation?

7. The radioactive decay of ^{238}U is a consecutive reaction, but since one of the steps is much slower than the others it can be treated as if it followed first order kinetics:

$$^{238}U \xrightarrow{k} {}^{206}Pb$$

We want to determine the age of a sample which contains 1.5 mg of ^{238}U and 460 μg of ^{206}Pb. The half-life of ^{238}U is $4.51 \cdot 10^9$ years, and we can assume that the volume of the sample has remained constant.

   (a) What is the age of the sample?

   (b) How much uranium did it contain 250 million years ago?

(Hint: do not forget to convert the masses into mols! 1 g of U does not turn into 1 g of Pb)

1. Determine the electromotive force of the

$$Sn(s) \mid Sn^{2+}(aq, a = 0.01) \mid\mid Pb^{2+}(aq, a = 0.1) \mid Pb(s)$$

galvanic cell, and also the electrode potentials at 25 °C . What is the cell reaction, and what is its equilibrium constant?

(Standard electrode potentials at 25 °C : $\varepsilon^0_{Sn/Sn^{2+}} = -0.1364$ V, $\varepsilon^0_{Pb/Pb^{2+}} = -0.1263$ V)

2. Determine the solubility constant of $PbSO_4$ in water at 25 °C !

(Standard electrode potentials at 25 °C : $\varepsilon^0_{Pb+SO_4^{2-}/PbSO_4} = -0.356$ V, $\varepsilon^0_{Pb/Pb^{2+}} = -0.1263$ V, measured with aqueous solutions)

3. We construct the following galvanic cell

$$Ag(s) \mid AgCl(s) \mid Cl^-(EtOH, a = 0.012) \mid\mid Cl^-(H_2O, a = 0.07) \mid AgCl(s) \mid Ag(s)$$

at 25 °C . The electromotive force is 0.2578 V. What is the solubility constant of AgCl in EtOH?

(Standard electrode potentials at 25 °C : $\varepsilon^{0,EtOH}_{Ag/Ag^+} = 0.7490$ V, $\varepsilon^{0,H_2O}_{Ag+Cl^-/AgCl} = 0.2223$ V, $\varepsilon^{0,H_2O}_{Ag/Ag^+} = 0.7996$ V)

4. In a galvanic cell the cathode is a saturated calomel electrode [Hg(l) | Hg_2Cl_2(s) | Cl^- (aq)], and the anode is a tin chloride redox electrode [Pt(s) | Sn^{2+} / Sn^{4+}(aq)]. At 25 °C the electrode potential of the cathode is 0.2438 V, and the electromotive force is 0.1 V. What percentage of the tin ions is in the oxidized form (Sn^{4+}) ? The activity coefficients of the Sn^{2+} and the Sn^{4+} ions are 1.

($\varepsilon^0_{Sn^{2+}/Sn^{4+}} = 0.15$ V)

5. A galvanic cell consists of two hydrogen gas electrodes dipping into a common hydrogen chloride solution. The electromotive force at 25 °C is 0.0464 V, and the partial pressure of H_2 on the anode is 100 kPa. What is the pressure of H_2 on the cathode?

6. At 15 °C the electromotive force of a

$$Zn(s) \mid Zn^{2+}(aq) \mid\mid Cu^{2+}(aq) \mid Cu(s)$$

type cell is 1.0934 V, and $(\partial E/\partial T)_{p,15°C} = -4.3 \cdot 10^{-4}$ V/K. What is the reaction that takes place, and what is the molar Gibbs free energy, entropy, and entalphy change of this reaction?

7. An Ag/AgCl electrode and a hydrogen gas electrode with 1 bar pressure is dipped into a common electrolyte with 0,1 M of HCl at 25 °C . We measure an electromotive force of 0.3535 V. What is the cell reaction? What is the mean activity coefficient of the HCl?

($\varepsilon^0_{Ag+Cl^-/AgCl} = 0.2223$ V)

1. We mix 200 cm^3 of a 0.09 mol/dm^3 HCl solution and 100 cm^3 of a 0.06 mol/dm^3 NaCl one. What is the conductivity of the mixture?

   (You can exploit the law of independent migration of ions. $\lambda_{Na^+} = 5.01 \cdot 10^{-3} Sm^2/mol$, $\lambda_{H^+} = 3.498 \cdot 10^{-2} Sm^2/mol, \lambda_{Cl^-} = 7.635 \cdot 10^{-3} Sm^2/mol$.)

2. We put 0.1 mol of acetic acid (CH_3COOH) into 1 dm^3 of water. Not all of the acetic acid molecules dissociate. In a cell with a cell constant of 30 1/m we measure a conductance of 19.535 mS for our solution. What percentage of the acetic acid is in dissociated form? Ignore the amount of H_3O^+ and OH^- coming from the autoprotolysis of water.

   (You can exploit the law of independent migration of ions. $\lambda_{CH_3COO^-} = 4.09 \cdot 10^{-3} Sm^2/mol$, $\lambda_{H^+} = 3.498 \cdot 10^{-2} Sm^2/mol$.)

3. We would like to determine the solubility constant of the poorly soluble ferrous hydroxide ($Fe(OH)_2$) in water at 25 °C . We put distilled water in our measuring cell, and measure a conductance of 5 μS. After saturating the water in the cell with ferrous hydroxide the measured conductance is 21.3 μS. In a separate experiment we measure the conductance of a KCl solution with a conductivity of 0.3 S/m, and it turns out to be 12 mS. What is the solubility constant of $Fe(OH)_2$?

   (You can exploit the law of independent migration of ions. $\lambda_{Fe^{2+}} = 1.07 \cdot 10^{-2} Sm^2/mol$, $\lambda_{OH^-} = 1.983 \cdot 10^{-2} Sm^2/mol$.)

4. We wish to determine the amount of alcohol in a blood sample. For this purpose, we mix 10 cm^3 of blood with 90 cm^3 of a buffer solution which maintains the pH at 6 and contains 0.07 mol/dm^3 of acetaldehyde. We put this mixture into a device, which immerses two platinum electrodes into the solution, and pumps 1 bar of oxygen gas at one of the plates. The measurement is based on the reaction:

   $$CH_3CHO + 2H^+ + 2e^- = CH_3CH_2OH \ , \ \varepsilon^0 = 0.221V$$

   The other half reaction is:

   $$\frac{1}{2}O_2(g) + 2H^+ + 2e^- = H_2O \ , \ \varepsilon^0 = 1.229V$$

   The first of the above two processes goes in the oxidative direction (oxidation of CH_3CH_2OH), in the second case reduction takes place (reduction of O_2 to H_2O). After connecting the cell, we measure an electromotive force of 0.9595 V at 25 °C . What was the concentration of ethanol in the blood? The mean activity coefficients are one.

5. We construct the following galvanic cell at 15 °C:

   $$Ni(s) \mid Ni(NO_3)_2(aq) \mid\mid KCl(aq,\ 0.25M) \mid AgCl(s) \mid Ag(s)$$

   After 3.5 minutes the electromotive force decreases by 14.39 mV, and the Ni^{2+} concentration becomes 1.417 times its original value. The mean activity coefficients are 1.

   a) What are the half-cell reactions and the total cell reaction?

   b) What was the original concentration of the Ni^{2+} ions?