Physical chemistry laboratory practice

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1 Foreword

Today, automatization of measurements seems to reduce the role of human operators in a lot of areas of science and industry. To understand and improve these methods, however, a closer interaction with the measured phenomena is necessary. It is the authors' hope that these practices will help students to understand the fundamental aspects of measurements in physical chemistry, and the derivation of important parameters from recorded data in general.

This handout is primarily written for the physical chemistry laboratory practice of Chemistry BSc. and pharmacy students. In each practice, you will measure physical and chemical properties, and then use basic relationships in physical chemistry to calculate important parameters such as heat of dissolution, rate constant, pK, selectivity coefficient of ion-selective electrodes, and others.

During the course, the you will familiarize yourself with basic and intermediate level methods in physical chemical measurements. The authors however, assume a basic knowledge of general and analytical chemistry, regarding simple concentration calculations, titrimetric methods, basic electrochemistry, and photometric methods.

The effort on each practice should be divided into three more or less equal parts. First, it is essential for a successful practice to prepare in advance. Second, the practice itself should be carried out with great care and precision. Good laboratory practice (GPL) is advised for all students, and regardless of the topic. And third, a laboratory notebook should be prepared during, and finished after the practice to make it complete with the necessary calculations, figures, and conclusions.

The authors wish a successful course for each student undertaking these practices and hope to contribute to their laboratory skills and their understanding of physical chemistry.

Pécs, 2018 December The authors

2 Investigating the temperature dependence of drug decomposition

2.1 Introduction

During this practice we study the pseudo first-order hydrolysis reaction of acetilsalicilic acid. The rate constant of a first-order reaction can be written as:

$$k = \frac{1}{t} \ln \frac{z}{z-x} \tag{2.1}$$

where t is time, z is the initial concentration of the reagent, x is the concentration of the product at time t.

The reaction rate depends on temperature, which is stated in the *Arrhenius law*:

$$\frac{d \ln k}{dT} = \frac{E}{\mathrm{R}T^2} \tag{2.2}$$

after integration:

$$k = Ae^{-E/(\mathrm{R}T)} \tag{2.3}$$

and

$$\lg k = \lg A - \frac{E}{2.303\mathrm{R}T} \tag{2.4}$$

A is the preexponential factor, E is the activation energy, and R is the universal gas constant (R= 8.314 J/Kmol). The factor 2.303 is the conversion form ln to lg. Activation energy can be obtained graphically if we take the slope of the function $\lg k - 1/T$ and multiply it by 2.303×8.314. The dimension in this case for E is J/mol. If we measure k on two different temperatures (k_1 and k_2 on T_1 and T_2 temperature), activation energy can be calculated as follows:

$$E = 2.303 \times 8.314 \lg \frac{k_1}{k_2} \frac{T_1 T_2}{T_1 - T_2} \tag{2.5}$$

2.2 Practice procedures

Alkaline hydrolysis of acetylsalicylic acid (Fig. 2.1) is a pseudo first-order reaction. The reaction is quite slow on room temperature, therefore we conduct our measurements at a higher temperature. To determine the rate constant k, we need to know the change in concentration of the reactants or the products as a function of time. In this practice, we will use spectrophotometry after forming an Fe^{3+} salicilate complex by adding $FeCl_3$ to the samples. The complex has a deep violet color, and its absorbance is directly proportional

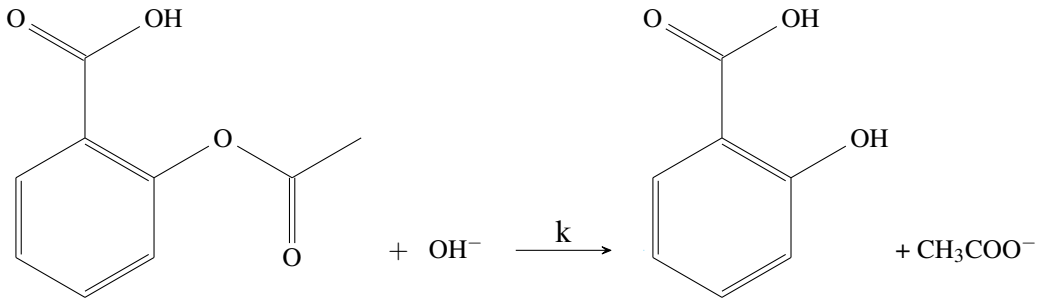

Figure 2.1: Alkaline hydrolysis of acetylsalicylic acid.

to the concentration of the complex, therefore to the concentration of the product salicilate as stated by *Lambert-Beer's law*:

$$A = \varepsilon l c \tag{2.6}$$

where A is absorbance, ε is the molar decadic absorption coefficient, l is the length of the solution block the light is passing through, and c is the concentration. We take known volumes of samples from the alkaline reaction vessel, and suddenly decrease [OH^-] and temperature by adding NaOH and putting the samples on ice. If the measured absorbance is above 2 A.U., dilution is necessary, since over this value the relationship between c and A is not linear anymore. To determine the product concentration at $t = \infty$ (which equals to the reactant concentration at $t = 0$), we take samples at the and of the practice. We carry out the measurements at two different temperatures, determined by the instructor (usually 313 and 353 K).

Pulverize an *Aspirin* tablet in a mortar with the help of a pestle, dissolve it a small amount of deionized water, then filter it into a 100 cm^3 measuring flask, and fill it up to 100 cm^3. This will be the stock solution. The stock solution obtained in this way will be most likely saturated[1]

Starting and following the reaction:

(a) Determining the initial concentration z of acetylsalicylic acid. Pipette 2-2 cm^3 sample from the stock solution into two Erlenmeyer flasks with bottlecaps (low and high temp.), and add 3-3 cm^3 0.25 M NaOH solution to them. Put them into the two thermostats after labeling them. At the end of the practice we stop the reaction. It should be complete, but we should treat these solutions as the others to rule out any artifacts. „Stop the reactions” by adding 2-2 cm^3 0.25 M HCl solution and 3-3 cm^3 $FeCl_3$, then fill the flasks up to 100 cm^3 with deionized water.

[1] An *Aspirin* tablet has 500 mg acetylsalicylic acid in it, and its solubility in water is 2 - 4 g / L, depending on temperature.

(b) Determining concentration x at time t. Put one half of the remaining stock solution into an Erlenmeyer and the other half into another Erlenmeyer flask. Close the flasks, label them, and put them into their respective thermostats. Add 5 cm^3 buffer solution (ask the technician), and start a stopwatch. By adding the buffer solution the reaction starts ($t = 0$). Without taking out the flask, take 2 cm^3 samples from them at 15, 20, 25, 30 and 35 minutes after the reaction has started, and put them into separate, labeled 25 cm^3 measuring flasks you prepared beforehand. Prepare them by adding 0.5 cm^3 0.25 M HCl solution (this will stop the *alkaline hdydrolysis*), and 0.5 cm^3 0.1 M $FeCl_3$ solution (to form the complex and make the product visible for spectrophotometry). Fill the remaining volume in the 25 cm^3 flasks with deionized water. Start the two reactions by shifting one by $1-2$ minutes, so you don't have to take samples at the same time from the two reactions.

Measuring absorbance and calculating concentration. Both the initial and the instantaneous concentration at time t will be measured spectrophotomertically. Find the users manual next to the instrument, or ask the instructor to help. To calculate the concentration from absorbance use the factor $b = 8.3\ (mol/dm^3)/AU$. This is the concentration of the theoretical solution, whose absorbance is 1 AU, if $d = 1\ cm$, where d is the length of solution block in the path from source to detector.

2.3 Results to submit

1. Measured and calculated data in table (use table 2.1 as reference).
2. Calculate the rate constants (table 2.2.) for both temperatures, and calculate standard deviation[2].
3. From the temperature dependence of the rate constant, calculate the rate constant for 20 °C-on (293 K) graphically by plotting $\lg k$ as a function of $1/T$.
4. Calculate E and A by substituting into the integrated form of the Arrhenius equation:
   (a) E [kJ mol^{-1}]
   (b) lg A [s^{-1}]
   (c) A [s^{-1}]

[2]Standard deviáció, $s = \sqrt{\frac{\Sigma(x_i-\bar{x})^2}{n-1}}$

Table 2.1: Measured and calculated data.
T = ... K, z = ... mg/100 cm^3

reaction time, s	dilution	A	x, mg / 100 cm^3	(z-x), mg / 100 cm^3	k, s^{-1}
...	...	...	...	...	...

Table 2.2: Temperature dependence of the rate constant.

T, K	1/T	$\bar{k}$ (average), s^{-1}	lg k	standard deviation
...	...	...	...	...

3 Determination of selectivity coefficient of ion-selective electrode

3.1 Introduction

Ion-selective electrodes are potentiometric sensors, that allow the selective determination of the activity of certain ions. They are widely used in the clinical diagnostics for routine measurements: automatic blood analisators measure the Na^+ and K^+-ion activity in blood samples. One more example is the determination of F^--ion in tap water, even if there are interfering ions such as Cl^- or OH^-. Their function is based on a selective membrane, which can be ionophore based (Na^+ and K^+), or lattice vacancy based (F^-). An example for the latter is the F^- ion-selective electrode, which is based on a europium doped lanthanum fluoride crystal.

The equation that describes the behaviour of these electrodes is the Nernst-equation:

$$E = E^0 + \frac{RT}{z_i F} ln(a_i) \tag{3.1}$$

where z_i is the signed valence of the primary ion (the ion that the electrode is selective to), a_i is its activity. According to the equation, for cation elective electrodes the electrode potential (E) is increasing with increasing actvity, and for anion selective ones, it decreases. Because of deviations from the theoretical behaviour, in practice, we use the following, experimental equation:

$$E = E^0 \pm Sln(a_i) \tag{3.2}$$

where S is the slope of the linear part of the electrode calibration curve, which can be measured. In real, multi-component samples, the potential of the ion-selective electrodes is influenced by the so-called *interfering ions*, but in fact, more or less by every ion in the sample to some (small) extent. For this reason, using eqs. 3.1 and 3.2 will introduce error during evaluation. To take into account these deviations we use the concept of *selectivity coefficient* (k_{pot}). With this we can rewrite the equations as such:

$$E = E^0 + \frac{RT}{z_i F} \ln \left[a_i + \sum_j \left(k_{ij} a_j^{z_i/z_j} \right) \right] \tag{3.3}$$

This is the Nikolsky equation. a_j is the activity of the jth interfering ion, z_j is its charge, k_{pot} i, j is the selectivity coefficient of the jth ion. The selectivity coefficient shows how much more sensitive is the electrode towards the primary ion, then towards to the interfering ion. For instance, if $k = 10^{-2}$, the activity of the j ion must be hundredfold of the i primary ion to have the same effect on the electrode potential (increase or de-

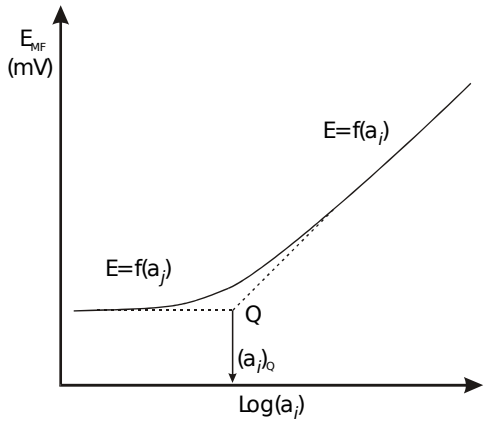

Figure 3.1: Using the mixed solution method to determine the selectivity coefficient.

crease it to the same extent). There are two main methods for determining the selectivity coefficient: the mixed and the separate solution methods.

In the mixed solution method, ion activity of the j interfering ion is constant, and we increase the activity i primary ion, and measure the potential response. After plotting the data fig. 3.1, we find Q. Then, we calculate the selectivity coefficient as follows:

$$k_{i,j}^{pot} = \frac{(a_i^{z_j})_Q}{a_j^{z_i}} \tag{3.4}$$

When using the separate solution method, we need to record two calibration curves. First, at zero interfering ion activity, we make a calibration of primary ion i, then at zero primary ion i activity, we make a calibration plot of interfering ion j. After obtaining these two curves, the selectivity coefficient can be obtained as seen in fig. 3.2, taking either

(a) activities corresponding to the same potentials:

$$k_{i,j}^{pot} = \frac{a_i}{a_j^{z_i/z_j}} \tag{3.5}$$

(b) or potentials corresponding to the same activities:

$$\lg k_{i,j}^{pot} = \frac{(E_2 - E_1)zF}{2.303RT} = \frac{\Delta E}{S} \tag{3.6}$$

There are a number of factors that influence the selectivity coefficient: ionic strength, method, etc... As it can be seen, from relationships 3.5 and 3.6, the drawback of the separate solution method is that it assumes, that the valence of the primary and interfering ion is equal, and that the sensitivity towards them is the same. For this reason, selectivity coefficients obtained with this method are regarded as approximations, and the much better mixed solution method is preferred.

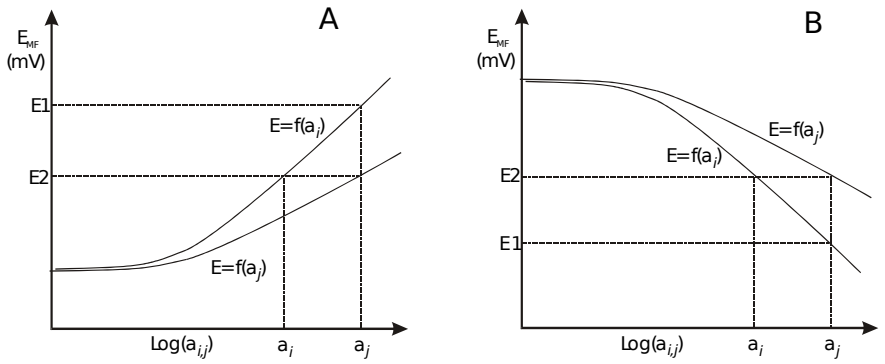

Figure 3.2: Determining the selectivity coefficient with the separate solution method for positive (A) and negative (B) ions.

3.2 Practice procedures

The purpose of this practice is to study the function of potassium or fluoride ion-selective electrodes (ask the instructor which one). Your first task is to prepare a dilution series of soluions of the primary ion. Use salts KCl or NaF. Prepare 100 ml 10^{-2} mol·dm^{-3} solution using a salt of the primary ion. Then make a tenfold dilution by taking out 10 ml from this solution, and putting it in another, clean 100 ml measuring flask. Fill it up to 100 ml with deionized water. Continue making dilution by always using the previous solutions, until you reach a concentration of 10^{-6} mol·dm^{-3}. Pour a small amount of each into separate, labeled beakers, so that the electrodes can submerse into them with their active area. Then start with the most dilute solution by putting the measuring and the reference electrodes into it. Wait 1 minute, and write down the potential. Move on to the next solution ($10\times$ more conc.), wait another 1 minute, and record the data. Carry out measurements in all five solutions advancing from dilute to concentrated, repeat it altogether 3 times. Carefully rinse the electrodes between series.

3.2.1 Determining the selectivity coefficient using the separate solution method

Repeat the previous procedure, but use a salt of the interfering ion to prepare the first solution, the do the dilutions. It’s important to use deionized water free of potassium, sodium, chloride and fluoride ions as much as possible. Ask the technician for ultrapure water.

3.2.2 Determining the selectivity coefficient using the mixed solution method

For this method prepare another dilution series by using a salt of the primary ion, but instead of deionized water, use a 10^{-2} M solution of the interfering ion as solvent. In this way, the interfering ion concentration will be constant in all of the solutions, but the

primary ion concentration will vary just like in the first experiment.

3.3 Evaluation

1. Find the activity coefficients for the primary and interfering ions online, and calculate the activities from the concentrations.
2. Plot the $\lg a_i - E$ functions as seen in the diagrams above.
3. Determine the slope of the linear part by linear fitting for each graph.
4. Determine the lower limit of detection of the electrode towards the primary ion (Q when there is no interfering ion).
5. Calculate the selectivity coefficients using all 3 methods (1 mixed solution method and 2 separate solution methods).
6. For the separate solution method, plot the two curves in the same diagram.

3.4 Results to submit

Lower limit of detecction towards the primary ion, 2 selectivity coefficients from the separate solution method, and 1 from the mixed solution method. Five calibration diagrams, each with linear fits on the linear section.

4 Determination of dissociation constants of weak acids with conductometry

4.1 Introduction

According to Ohm's law, the current passing through between two points and the potential difference between those two points are in linear relationship:

$$U = I \cdot R \tag{4.1}$$

where R is the factor of proportionality, called **electrical resistance**. Its dimension is ohm (■).

Specific resistance is the longitudinal resistance of a conductor which is 1 m long and has a cross section of 1 m^2 (1 mm^2 in practice).

In electrochemistry it is often more simple to use the reciprocal of these quantities. The reciprocal of resistance is conductivity, its dimension is Siemens, S = 1/■. The reciprocal of specific resistance is specific conductivity. The specific conductivity of an electrolyte is the conductivity we measure if the two electrodes have a surface area of 1 cm^2, they are 1 cm apart, they are made of an inert metal (gold, platinum), and they are submersed in the electrolyte. Its dimension is $S \cdot cm^{-1}$. It depends on concentration, temperature, and it's a unique property of every material.

Molar specific conductivity (Λ_m) is the ratio of the specific conductivity and the concentration:

$$\Lambda_m = \frac{\kappa 1000}{c} = \kappa V \tag{4.2}$$

where c is concentration (mol·dm^{-3}), and V is dilution.

Kohlrausch found that the limiting molar conductivity (molar conductivity of an infinitely dilute solution) of anions and cations are additive: the conductivity of a solution of a strong electrolyte is equal to the sum of conductivity contributions from the cation and anion:

$$\Lambda_m^0 = \lambda_a^0 \nu_a z_a + \lambda_k^0 \nu_k z_k \tag{4.3}$$

where z_a, z_k are the valence of the ions, ν_a, ν_k are stochiometric factors, λ_a^0 and λ_k^0 are the limiting molar conductivities for the anions and the cations.

The conductivity of weak electrolytes can be described as follows:

$$\lambda_c = \alpha \lambda_0 \tag{4.4}$$

where α is the degree of dissociation, λ_0 is the limiting molar conductivity. The dissociation constant K_d of a weak acid can be calculated from its concentration and its degree of dissociation:

$$K_d = \frac{\alpha^2 c}{1-\alpha} \tag{4.5}$$

It is worth noting however, that K_d – based on the Debye-Hückel theory – depends on the permittivity of the media and temperature.

If we express α from 4.4, we get *Ostwald's law of dilution*:

$$K_d = \frac{\lambda_c^2 c}{\lambda_0^2 - \lambda_0 \lambda_c} \tag{4.6}$$

That means we can determine K_d from conductometric measurements. λ_c can be measured directly, while λ_0 can be obtained with the following method. By rearranging eq. 4.6 we get

$$\frac{1}{\lambda_c} = \lambda_c c \frac{1}{K_d \lambda_0^2} + \frac{1}{\lambda_0} \tag{4.7}$$

If we plot $1/\lambda_c$ as a function of $\lambda_c c$ (which is nothing but κ), we get a straight line whose y interception is $1/\lambda_0$. And knowing λ_c and λ_0 we can calculate K_d.

Additionally, we have to consider these:

(a) The solvent also contributes to the conductivity of the solution. Therefore we substract the conductivity of the pure solvent (G_{solvent}) from each measurement carried out in the solutions of that solvent.

(b) In practice, we don't use the conductivity cell from the definition of specific conductivity. Instead, the more practical „bell electrodes” are used. To obtain specific conductivity from the conductivity values measured with these cells, we multiply every value with the cell constant C (dimension: m^{-1} or cm^{-1}).

The cell constant shows the relationship between solution with a known specific conductivity (κ_{ref}) and the conductivity measured with cell used in practice (G_{measured}):

$$C = \kappa_{\text{ref}} / G_{\text{measured}} \tag{4.8}$$

Based on this, we can calculate the contribution of solute to the conductivity of the solution: $\kappa_{\text{korr}} = (G_{\text{solution}} - G_{\text{solvent}})C$, where κ_{korr} is the specific conductivity of the solution taking into account that of the solvent and the cell constant.

Therefore, specific molar conductivity of a weak acid is:

$$\lambda = \kappa_{korr} V \tag{4.9}$$

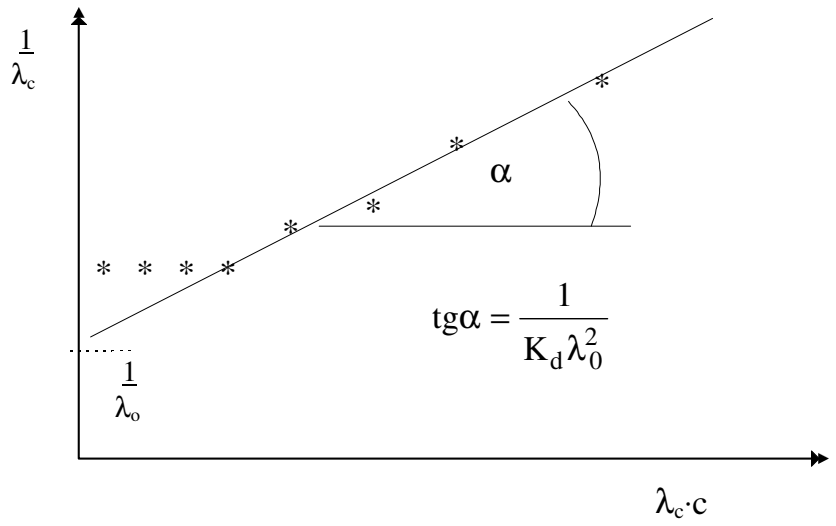

Figure 4.1: Obtaining the limiting molar conductivity (λ_0).

4.2 Practice procedures

Rinse the electrode of the conductometer several times (4 - 5) with deionized water, the with ultrapure water ($\kappa < 1$ μS/cm). Ask the technician for ultrapure deionized water.

Prepare 20 v/v% solution from an alcohol selected by the instructor. Then prepare two weak acid solutions (the weak acid is also selected by the instructor), from the stock solution (1 mol·dm^{-3}) by pipetting 2.00 cm^3 into two 100 cm^3 measuring flasks, and then filling one with the 20 v/v% alcohol solution, the other with ultrapure deionized water up to 100 cm^3.

Carry out the conductivity measurements in a measuring cilinder. Pour the water based solution into the cilinder and measure its conductivity. Then, pipette 25 cm^3 from the cilinder into a clean 50 cm^3 measuring flask, fill it up with ultrapure deionized water (2× dilution), and measure the conductivity of the new solution after carefully rinsing it with ultrapure deionized water. Repeat the dilution and measurement 3 times. Then do the same with the alcohol based solution, but using the 20 v/v% alcohol solution for the dilutions and rinsing.

Note and record the temperature measured by the built-in thermometer of the electrode for each measurement.

Finally, measure the conductivity of the solvents as well (for the correction). Then, to obtain the cell constant, measure the conductivity of 0.01 M KCl solution, and write down the temperature as well. Based on table

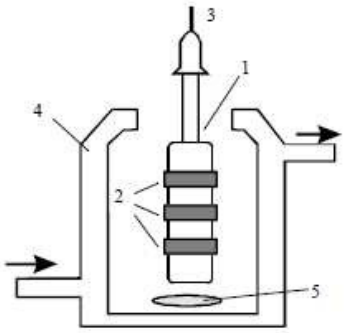

Figure 4.2: Schematics of a conductometric cell. 1 - „bell electrode”, 2 - platinized platinum rings, 3 - electrical connection, 4 - double walled vessel, 5 - magnetic stirrer.

Figure 4.2 shows the schematics of a conductometric cell. A well-defined, inert electrode pair is submersed into an electrolyte, and the voltage drop between them is measured. Alternating current is used to avoid polarization and electrolysis.

4.3 Evaluation

1. Calculate the cell constant. Present the recorded data in such a table:

c ($\mathrm{mol \cdot dm^{-3}}$)	$G_{measured}$	κ_{korr} ($\mathrm{S \cdot cm^{-1}}$)	λ_c	$1/\lambda_c$	$\lambda_c c$	α	K_d
...	...	...	...	...	...	...	...

2. Determine λ_0 graphically. Knowing λ_c and λ_0, calculate α and K_d for each concentration.

5 Electrochemical study of the catalytic oxidation of vitamin C

5.1 Introduction

In this practice we will use an electrochemical method, voltammetry to study the catalytic oxidation of vitamin C. It is an essential vitamin for humans. Its spontanaeous oxidation is well known:

$$C_6H_8O_6 + 1/2O_2 = C_6H_6O_6 + H_2O \tag{5.1}$$

The reaction is catalyzed by multivalent metal ions. If there is excess oxygen, the reaction becomes pseudo first-order. In this case, the measured rate constant is an *apparent rate constant*. Let's look at a simple reaction:

$$A + B = P \tag{5.2}$$

In this reaction, product P is formed from reactants A and B. The rate equation is

$$v = \frac{d[A]}{dt} = -\frac{d[P]}{dt} = k[A] \tag{5.3}$$

To determine k, we can either measure the change in $[A]$, $[B]$ or $[P]$ as a function of time t. Consider the change in $[A]$. Assume, that the initial ($t = 0$) concentration is $[A_0]$. Then we can solve the differential equation 5.3 by integrating:

$$\int_{[A_0]}^{[A]} \frac{d[A]}{dt} = -k \int_0^t dt \tag{5.4}$$

The solution is:

$$ln\frac{[A]}{[A_0]} = -kt \tag{5.5}$$

and

$$[A] = [A_0]e^{-kt} \tag{5.6}$$

In a first-order reaction, concentration changes exponentially in time, and the logarithm of concentration changes linearly as a function of time. By using eq. 5.6, we can decide if a reaction is first-order or not. This can be done by plotting $\ln[A]$ as a function of time, and see if the points fit on a line or not. If they do, it's a first-order reaction, and the slope is the rate constant k.

5.2 Practice procedures

We will use voltammetry to determine the concentration of ascorbic acid at any time t. First, make a calibration plot:

1. Start by preparing 50 ml 10 mM stock solution, dissolved in deionized water.
2. Then take a clean 20 - 50 ml beaker, and measure 10 ml of 0.1 M NaCl solution into it. Place the beaker on a magnetic stirrer, and put a magnet into the beaker. Put the electrodes into the solution. We will use carbon paste working electrode, Ag/AgCl reference electrode, and a platinum auxiliary electrode.
3. Record a cyclic voltammogramm from 0 to 0.8 V, with a scanrate of 100 mV/s. Adjust the current range if necessary.
4. Then start increasing the ascorbic acid concentration (now it's zero), by adding small volumes (30 µl) from the stock solution. Record a CV after every addition. Repeat it 10 times, so you have 11 measurements. Now you have data for the calibration curve. Calculate the concentrations at home. (For example if you add 100 µl, $c = n/V = (0.1\ mol \cdot L^{-1} \times 0.0001\ L)/0.0101\ L = 9.9 \cdot 10^{-3}\ mol \cdot L^{-1}$.) Prepare a table to record the data in. (First column: added total volume of ascorbic acid, second column: anodic peak current, i_{pa}.)

Then, we will follow the catalytic oxidation of ascorbic acid by measuring its concentration with voltammetry:

1. To study the catalytic oxidation of ascorbic acid, we will use a double walled, thermostatted reaction vessel. Start the thermostat. Put 80 ml of 0.1 M NaCl solution into it. Add 100 µl of 0.1 M $CuCl_2$. This will serve as a catalyst.
2. Start the oxygen pump. This serves two purposes. First, it supplies the reaction with plenty of oxygen, so it becomes pseudo first-order. Additionally, it stirs the solution.
3. Take a small sample out, and record a CV the same way you did in the calibration measurements. The volume doesn't matter, but it should be enough for the electrodes to have their acitve area submersed. Put the sample back into the reaction vessel after the measurement is complete.
4. Add 1 ml of stock solution to the reaction vessel. Start a stopwatch at the moment of addition. This is when the reaction starts.
5. At $t = 5, 10, 15, 20, 25, 30, 35, 40$ minutes, take samples and record a CV in them. Always put the sample back into the reaction vessel.

5.3 Results to submit

1. Cyclic voltammogramms of the calibration measurements.
2. Cyclic voltammogramms of the measurements for the catalytic breakdown.
3. Calibration plot ($c - i_{pa}$). i_{pa} is the anodic peak on the CV. Its magnitude is proportional to the concentration of ascorbic acid. This relationship is what we will use in the determination of the concentration. From the calibration plot, the concentration of ascorbic acid in an unknown solution can be determined from the anodic peak.
4. $t - c$ table for the catalytic breakdown. First column: time, second column: concentration of ascorbic acid calculated from the anodic peak currents, using on the calibration plot.
5. $lnc - t$ plot. This is the plot on which you should fit a linear equation. Its slope will be the **rate constant**. This is the end result of the practice. Write a conlcusion: „Rate constant of the catalytic breakdown of ascorbic acid, based on my measurements in these conditions (list conditions here) is $k = ...s^{-1}$.

6 Investigation of sucrose inversion with polarimetry

6.1 Introduction

The purpose of the studies in reaction kinetics is to reveal the underlying mechanisms, for which the knowledge of the order or partial order regarding the reactants is really helpful. The general rate equation for homogeneous reactions is:

$$r = k[A]^{\beta_a}[B]^{\beta_b}...[N]^{\beta_n} \tag{6.1}$$

where β_a, β_b and β_n are the partial order of the respective reactants, and $\beta = \beta_a + \beta_b + ... + \beta_n$ is the overall order of the reaction.

If there is concentration – time data available and we know the order of the reaction, the rate constant can be calculated.

Using the rate equations. It is possible to use the indefinite integral form of first order reactions for graphical evaluations:

$$\ln \frac{[A]}{[A]_0} = -kt \tag{6.2}$$

Plotting $\ln[A]$ as a function of time we get a staright line, whose slope is $-k$, the rate constant (fig. 6.1). Note that the slope of the $\ln([A]/[A]_0) - t$ and $\ln[A] - t$ functions are the same, since $\ln([A]/[A]_0) = \ln[A] - \ln[A]_0$ and $\ln[A]_0$ is constant.

Usually concentration is not measured directly, but a quantitiy that is proportional to concentration is measured. We will denote this quantitiy as z in general. It is easy to see that the difference between z_0 at time $t = 0$ and z_∞ at time $t = \infty$ is proportional to $[A]_0$ and the product concentration at the end of the reaction ($t = \infty$), if there is a linear relationship between z and $[A]$. Then, it is possible to express the concentration $[A]$ at any time t if the

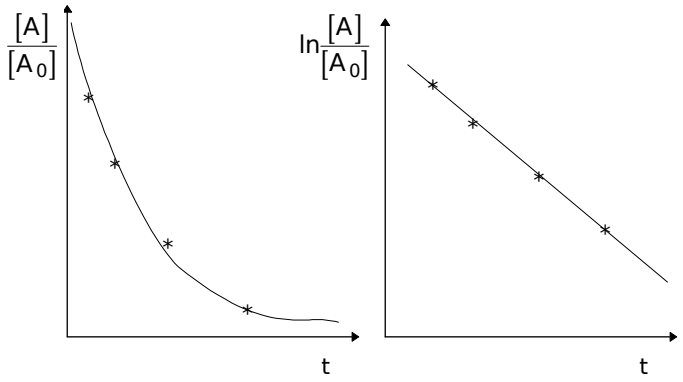

Figure 6.1: Determining the rate constant of a first order reaction.

measured signal z_t at time t and z_∞ is known. Substituting to eq. 6.2, we get

$$\ln \frac{z_\infty - z_t}{z_\infty - z_0} = -kt \tag{6.3}$$

Guggenheim's method. To use eq. 6.3, to determine the rate constant of a first order reaction, the knowledge of the physical parameter z at both $t = 0$ and $t = \infty$ is necessary. When the reaction is too fast or too slow however, measuring z_0 or z_∞ might prove to be problematic due to technical difficulties. To circumvent these difficulties one could use *Guggenheim's method*. To do this, measure z_t at $t_1, t_2, t_3, ..., t_n$ and at $t_1 + \Delta t, t_2 + \Delta t, t_3 + \Delta t, ..., t_n + \Delta t$, where Δt is a constant time interval. For instance if we measured z at $t = 12, 18$ and 27 seconds, and $\Delta t = 30s$, we measure z at 42, 48 and 57 seconds as well.

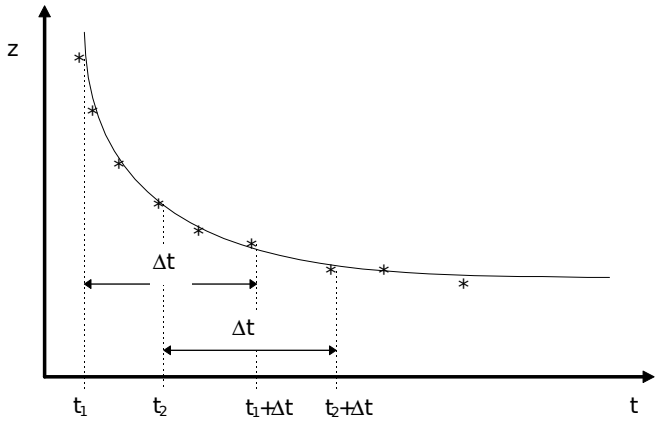

Figure 6.2: Determining the rate constant of a first order reaction using *Guggenheim's method*.

First we substitute t and $t + \Delta t$ into the exponential form of eq. 6.3, then rearrange the resulting equation:

$$z_t - z_\infty = (z_0 - z_\infty)e^{-kt} \tag{6.4}$$

$$z_{t+\Delta t} - z_\infty = (z_0 - z_\infty)e^{-k(t+\Delta t)} \tag{6.5}$$

Then substract eq. 6.5 from 6.4 to get

$$\ln(z_t - z_{t+\Delta t}) = -kt + \ln(z_0 - z_\infty)(1 - e^{-k\Delta t}) \tag{6.6}$$

The second term on the right side is constant, since z_0 and z_∞ does not change during the reaction (we don't add or remove reactants or products), and $\Delta t - t$ was chosen to be constant. Thus, if we plot the left side as a function of t, we get a linear equation, whose

slope is k, the rate constant. Notice that for this method to work, we don't need to know either z_0 nor z_∞. It must be mentioned however that one should choose Δt carefully, preferably it should be as big as possible. The estimation will be more precise if we measure in a small range of conversion, and Δt approaches the half life ($t_{1/2}$) of the reaction.

Method of initial rates. Usually it's not possible to follow the concentration changes of all components in a reaction, nevertheless, the reaction order and rate constant is possible to measure anyway. Let's take a logarithm of both sides of eq. 6.1:

$$\ln r = \ln k + \beta_a \ln[A] + \beta_b \ln[B] + ... + \beta_n \ln[N] \tag{6.7}$$

If we keep the concentration of every component constant except for example A, and we measure the rate constant at several different $[A]_0$, the we get a linear equation when we plot $\ln r$ as a function of $\ln[A]_0$. The slope of this equation is β_a, the partial order with respect to A. This is true only at low conversion range, ie. the initial part of the reaction. The measurements must be done at time instances when $t << 0.05 t_{1/2}$.

6.2 Investigating the inversion reaction of sucrose

Sucrose is a disaccharide, which undergoes hydrolysis in acidic medium. As a result, D-glucose and D-fructode are being produced:

$$C_{12}H_{22}O_{11} + H_2O = C_6H_{12}O_6 + C_6H_{12}O_6 \tag{6.8}$$

If the solution is dilute enough, this becomes a pseudo first order reaction, because the „concentration of water” does not change significantly. The reaction occures in neutral solutions as well, but very slowly. Dilute acids will catalyse the reaction, and the reaction rate will be proportional with the concentration of the acid. Since the reaction can be regarded as first order reaction, with eq. 6.3 the rate constant can be calculated if we measure a physical parameter that is proportional with the concentration of any of the components in the reaction. In this practice we will use rotation of light that is passing through the solution. In our system there are several optically active components: the solution of sucrose rotates light to the right ($+$), the products rotate light to the left ($-$). This phenomenon is a result of the chirality of chemical compounds. The speed of light in the optically active media is different for light polarized to the right and left. Thus, there is a shift in phase when light hits the detector. If we use *polarized* light, there is only light with a certain rotational angle, and it's possible to measure the phase shift.

In a cuvette with a length l, rotation is defined by

Table 6.1: Reaction mixtures to study sucrose inversion as a function of time.

#	sucrose solution, ml	HCl solution, ml	deionized water
1	10	10	0
2	10	8	2
3	10	5	5
4	10	2	8

$$\alpha = \frac{10\pi l}{\lambda}(n_l - n_d) \tag{6.9}$$

where λ is the wavelength of light in cm, n_l is the refractive index of light polarized to the left, n_d is that of light polarized to the right. Specific rotation is the rotation angle which is observed in a solution with a concentration of 1 g/cm^3 when $l = 1$ dm. Since rotation depends on waveength and temperature, usually it is referenced to the *D line* of sodium for either 20 or 25 °C.

6.3 Practice procedures

Prepare 100 cm^3 30 m/m% sucrose solution and 50 cm^3 5 M HCl. To have a complete reaction at the end of the practice, first assemble the following reaction: 10 cm^3 sucrose solution + 10 cm^3 HCl. Put it in a 50 °C thermostat. By the end of the practice, the reaction should have been undergone completely. Leave it there for now, and continue with the $t = 0$ solution. Do this by creating a solution of 10 cm^3 sucrose solution + 10 cm^3 H_2O. In this solution the reactions proceeds quite slowly, and it will not change significantly during the practice. This is the initial state, since there is only sucrose in the solution, and no glucose or fructose. You can take your time and familiarize yourself with the polarimeter.

Turn on the *Krüss P1000-LED* polarimeter. This instrument is using LEDs as light source, therefore there is no need for warmup. Ask the instructor or the technician if you don’t know how to use it. Measure the rotation of light in the $t = 0$ solution. Start recording in such a table:

t, minutes	z, degrees
...	...

Prepare 2 of reaction mixtures from table 6.1 (ask the instructor which 2).

Prepare the solutions in a large enough, clean beaker. Stir the mixture thoroughly and start the stopwatch when you pour tha last component into the beaker (it should be the sucrose or the HCl solution, but NOT water). This is when the reaction starts. Then quickly fill the cuvette of the polarimeter with the reaction mixture and put it into the

polarimeter (don’t forget the caps). Start reading rotational angles at a 60, or if you can handle it a 30 s interval. Write down in the table the time and the angle at that time. Collect altogether 25 points for each reactions.

6.4 Evaluation

Evaluate the collected data according to this table:

# of reaction: ... , $z_0 =$ ... degrees, $z_\infty =$ ... degrees

t, minutes	z_t, degrees	$z_t - z_\infty$	$\ln(z_0 - z_\infty) - \ln(z_t - z_\infty)$, degrees	k, 1/s
...	...	...	...	...

Plot the 4th column as a function of time t, and determine k graphically as well. Calculate k with Guggenheim’s method too. Choose at least 15 minutes for Δt. Plot $\ln(z_t - z_{t+\Delta t})$ as a function of t, and determine k from the slope.

7 Using the Langmuir isotherm to calculate the maximal adsorption capacity of a solid adsorbent

7.1 Introduction

Adsorption is a physicochemical process, during which atoms, ions or molecules adhere to a surface. The result is a thin layer of the adsorbate that is formed on the adsorbent surface (Fig. 7.1). The original media from which the adsorbate originates can be gas or liquid. The reverse process is called desorption. Adsorption is an important process, and it is present in many areas of everyday life, industry, research, pharmacy. It is an important step – among many – in heterogeneous catalysis, water treatment, removal by activated carbon. Adsorption by activated carbon is used to remove toxins or unwanted dangerous substances from the gastrointestinal tract after poisonings. Adsorption can be used in pharmaceutical industry to modulate the rate at which specific components are being released. It is the basis of many types of chromatography.

The first theoretical model to describe adsorption was developed by Irving Langmuir:

$$\theta = \frac{Kp}{1+Kp} \tag{7.1}$$

It is called the *Langmuir isotherm*, and its plot can be seen in Fig. 7.2. θ is the *fractional coverage*, K is k_d/k_a, the ratio of the rate of desorption and adsorption. p is the partial pressure of the adsorbate.

This equation was derived to describe the adsorption of gases at solid surfaces. However, it also describes the adsorption of a solute from a solution, if the solvent has little or no adsorption to the adsorbent, compared to the solute. After replacing the partial pressure p and multiplying both sides with the *maximal adsorption capacity* n_{max} we get:

$$n = n_{max}\frac{c}{c+K_{half}} \tag{7.2}$$

where c is the equilibrium concentration of the adsorbate in the solution, K_{half} is the *half-saturation constant*, that equals to $1/K$. The half-saturation constant is the equilib-

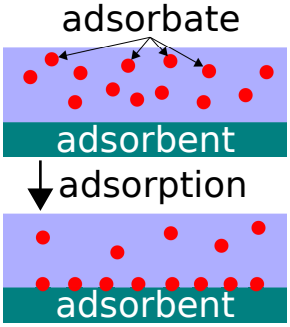

Figure 7.1: During adsorption, a thin adhered layer of the adsorbate is produced on the surface of the adsorbent.

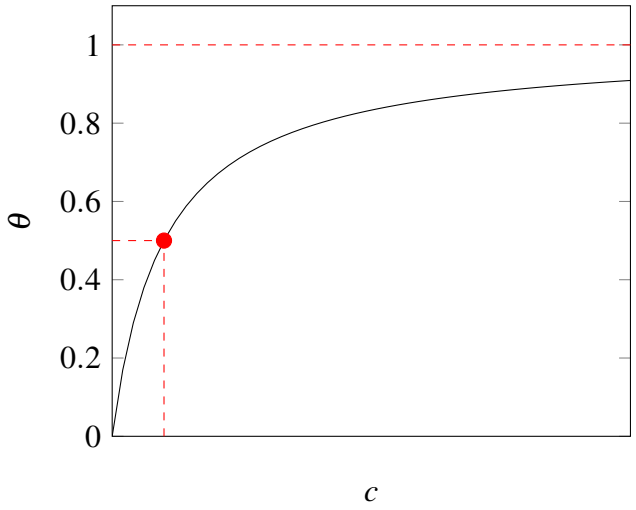

Figure 7.2: The Langmuir isotherm. Red dot: K, the *half-saturation constant*. θ eventually reaches 1 (maximal coverage), as c approaches infinity. In practice, maximal coverage is reached much sooner.

rium concentration of the adsorbate, when half of the available surface is covered, so $\theta = 0.5$. Note that if $c = K_{half}$, then $c/(c + K_{half})$ is $1/2$ and therefore $n = 0.5\, n_{max}$.

Specific adsorbance (n^*_{max}) is the amount of adsorbate adsorbed by 1 g of adsorbent. Its unit is mol/g. The maximal specific adsorption capacity of an adsorbent can be determined from the linearized form of Eq. 7.1:

$$\frac{1}{n^*} = \frac{1}{n^*_{max}} + \frac{K'}{c} \tag{7.3}$$

If we plot $1/n^*$ as a function of $1/c$, then the y-interception will be $1/n^*_{max}$. Determining it is the goal of the practice.

7.2 Practice procedures

Prepare a dilution series from known concentration methylene blue stock solution. The series should feature the following concentrations: $2 \cdot 10^{-4}$, 10^{-4}, $5 \cdot 10^{-5}$, $2 \cdot 10^{-5}$, 10^{-5}, $5 \cdot 10^{-6}$ M. Use 50 ml volumetric flasks to prepare the solutions. Record a spectrum of the $2 \cdot 10^{-5}$ solution, and determine the absorption peak in the visible range. Measure the absorbance of all the solutions. This dataset will be used to prepare the calibration curve.

Pipette 25–25 ml from each solution into a 100 ml Erlenmeyer flask. Put 0.3–0.5 g of adsorbent into each of flasks. The mass should be known in each case. The absorbent will be cellullose (filter paper or cotton swab) on the practice. Shake the solutions for 30 minutes, then filter them, and measure their absorbance.

Calculate the adsorbed amount, and prepare the $1/n^*$–$1/c$ plot based on Eq. 7.3. Correct for the differences in adsorbent mass by using the specific adsorbance. After doing a linear regression (line fitting) on the dataset, use the y–interception to calculate n^*_{max}.

8 Investigating the iodine clock reaction. Determination of the initial rate and reactions orders

8.1 Introduction

As seen during the investigation of the first order process, the order of a reaction with respect to a selected component can be determined by the method of initial rates: the concentration of the selected component must be varied within a series of experiments while the concentrations of all others must be kept constant. Under acidic conditions, iodate and ioidide ions react in a process described by the following chemical equation:

$$IO_3^- + 5I^- + 6H^+ \longrightarrow 3I_2 + 3H_2O \tag{8.1}$$

This is not a simple reaction. Three different reactants are necessary, and all of them have different stoichiometric coefficients. If the reaction obeys power law kinetics, the rate law can be given in the following form:

$$r_0 = \frac{d[IO_3^-]}{dt} = k[IO_3^-]^{\beta IO_3^-}[I^-]^{\beta I^-}[H^+]^{\beta H^+} \tag{8.2}$$

Brackets in this equation mean the (molar) concentration of the species enclosed.

The reaction can be monitored as follows: the iodine produced forms a highly colored inclusion compound with starch. However, iodine is reacted with an auxiliary reactant, which is used at the same initial concentration in all experiments, but this is a lot lower than the initial concentrations of all other recatants. This allows a low conversion for the reaction we wish to study, so the inital rate and other kinetic parameters can be determined releatively simply. As long as the auxiliary substance (arsenous acid in this particular case) is present, iodine does not accumulate but reacts further in a fast reaction. If the order of reaction with respect to iodate ion is to be determined, the initial concentration of iodate ion is varied systematically in the presence of arsenous acid. The amount of this auxiliary substance sets a constant conversion of the process at which the color of the iodine starch complex becomes visible. The color chagne is sudden and time from the mixing to the observable change can be measured easily. Iodine and arsenous acid react as follows:

$$H_3AsO_3 + I_2 + H_2O \longrightarrow HAsO_4^{2-} + 2I^- + 4H^+ \tag{8.3}$$

The initial concentraton of arsenous acid can also be used to control the time at which iodine appears, so this reaction is sometimes called a clock reaction.

8.2 Practice procedures

Prepare the following solutions:

1. 0.2 M KI solution (100 cm^3)

2. 0.1 M KIO_3 solution (50 cm^3)

3. 0.75 M $NaCH_3COO$ solution (250 cm^3)

4. 0.2 M CH_3COOH solution (250 cm^3)

5. Buffer A: Measure 100 cm^3 0.75 M $NaCH_3COO$ solution and 100 cm^3 0.2 M CH_3COOH solution into a 500 cm^3 volumetric flask. Fill up the flask to the mark. (This will give $[H^+] = 1 \times 10^{-5}$ M.)

6. Buffer A: Measure 20 cm^3 0.75 M $NaCH_3COO$ solution and 40 cm^3 0.2 M CH_3COOH solution into a 100 cm^3 volumetric flask. Fill up the flask to the mark. (This will give $[H^+] = 2 \times 10^{-5}$ M.)

Prepare the solutions given in the following table in dry beakers except the KI solution, which should be measured in a separate beaker. Initiate the reaction by pouring the KI solution suddenly into the mixture and start the stopwatch. You can do the ten experiments necessary relatively quickly if you prepare all the necessary samples and intiate them in one-minute intervals. Record the time at which the violet color of the iodine starch complex suddenly appears for each experiment.

After the first series of measurements, repeat experiments 1, 8, 9, and 10 but use distilled water instead of the KIO_3 solution. Measure the pH of these samples with a pH-meter calibrated using two buffers and calculate the hydrogen ion concentrations.

Table 8.1: Composition of individual experiments

Sample number	KI cm^3	KIO_3 cm^3	H_3AsO_3 cm^3	starch cm^3	H_2O cm^3	Buffer A cm^3	Buffer B cm^3
1	6.0	2.0	0.5	1.0	7.5	33	-
2	6.0	3.0	0.5	1.0	6.5	33	-
3	6.0	4.0	0.5	1.0	5.5	33	-
4	6.0	5.0	0.5	1.0	4.5	33	-
5	8.0	2.0	0.5	1.0	5.5	33	-
6	10.0	2.0	0.5	1.0	3.5	33	-
7	12.5	2.0	0.5	1.0	1.0	33	-
8	6.0	2.0	0.5	1.0	7.5	22	11
9	6.0	2.0	0.5	1.0	7.5	11	22
10	6.0	2.0	0.5	1.0	7.5	-	33

8.3 Evaluation

Give the experimentally measured reaction times and the calculated initial rates in the from of a table:

Number	t s	r_0 mol dm^{-3} s^{-1}	$\log_{10} r_0$
1			
2			
...			

To find the individual orders of reaction, use the following series of data: measurements 1, 2, 3, and 4 for iodate ion dependence; measurements 1, 5, 6, and 7 for iodide ion dependence; measurements 1, 8, 9, and 10 for hydrogen ion dependence.

In the usual power law kinetics, there is a linear relationship between the logarithms of the initial rates and the logarithms of the concentrations of the component studied. The order of reaction is given by the slope. For example, for iodide ions:

$$\log_{10} r_0 = \log_{10} k' + \beta \mathrm{I}^- \log_{10}[\mathrm{I}^-] \tag{8.4}$$

The intercept of the fitted straight line is k', it contains the product of the orders of reactions and initial concentrations of the remaining components and the value of the rate constant. Enumerate your results in the following tabular form:

Number	$\log_{10} r_0$	$[IO_3^-]$ mol dm^{-3}	$\log_{10}[IO_3^-]$	$[I^-]$ mol dm^{-3}	$\log_{10}[I^-]$	$[H^+]$ mol dm^{-3}	$\log_{10}[H^+]$

Plot r_0 as a function of the appropriate concentration and determine the individual reaction orders.

9 Investigating the kinetic salt effect

9.1 Introduction

Reactions in solution phase are significantly different from gas phase reactions. The identity of the solvent has a very marked influence on the rate of reaction and in most cases, the solvent also interacts with the reactants in some direct manner. This is also the case when ionic reactions proceed in aqueous solution. Water promotes the dissociation of the dissolved salts as energy is gained in the process of hydration (or solvation in non-aqueous solvents). Although activities were only defined for thermodynamic purposes, it is actually quite customary to interpret such kinetic salt effects through the activity coefficients of dissolved ions.

In transition state theory (or absolute rate theory), the rate constant of a bimolecular process between reactants A and B is given by the following form of the Eyring equation:

$$k = \frac{k_\mathrm{B} T}{h} K^* \frac{\gamma_\mathrm{A} \gamma_\mathrm{B}}{\gamma_{\mathrm{M}^*}} \tag{9.1}$$

In this equation, k_B is the Boltzmann constant, T is the absolute temperature, h is the Planck constant, K^* is the concentration-based equilibrium constant of the formation of the activated complex and the γ values are the activity coefficients.

Aqueous reactions are almost never ideal processes primarily because of the interaction between the solute and water molecules. The difference from the ideal case is often given by a ΔG_i^n free energy change between the real and ideal cases. This ΔG_i^n is related to the γ_i activity coefficient of ionic species i through the following equation:

$$\Delta G_i^\mathrm{n} = k_\mathrm{B} T \ln \gamma_i \tag{9.2}$$

The Debye-Hückel theory gives the following estimation for the activity coefficients:

$$k_\mathrm{B} T \ln \gamma_i = \frac{z_i^2 e^2}{2\varepsilon a} - \frac{z_i^2 e^2}{2\varepsilon(1+\beta a)} \tag{9.3}$$

In this equation, z_i values are the ionic charges, ε is the dielectric constant of the medium, e is the charge of an electron, β is the ionic strength, and a is the smallest distance between two ions.

At constant pressure and temperature, the difference between the real and ideal cases is expresses by the ratio of the real and ideal equilibrium constants:

$$\Delta G_i^\mathrm{n} = RT \ln \frac{K_\mathrm{real}}{K_\mathrm{ideal}} \tag{9.4}$$

Combining the Eyring equation with Debye-Hückel theory gives the following equa-

tion:

$$\ln k = \ln k_0 - \frac{z_1 z_2 e^2}{k_B T \varepsilon a} + \frac{z_1 z_2 e^2}{k_B T \varepsilon (1+\beta a)} \tag{9.5}$$

In this equation, k_0 is the value of the rate constant in the ideal (reference) state. In ion reactions, the reference state is $\varepsilon \to \infty$ and $\beta \to 0$. Under these conditions, the following relations hold:

$$\frac{z_1 z_2 e^2}{k_B T \varepsilon a} \to 0 \quad \text{if} \quad \varepsilon \to \infty \qquad \text{and} \qquad \frac{z_1 z_2 e^2 \beta}{k_B T \varepsilon (1+\beta a)} \to 0 \quad \text{if} \quad \beta \to 0 \tag{9.6}$$

So the $k_0 = k_B T K^* / h$ equation refers to this hypothetical state.

In dilute aqueous solutions, the previous formulas can be transformed into a somewhat simplified version:

$$\log_{10}\left(\frac{k}{k_0}\right) = 1.02 z_1 z_2 \sqrt{\beta} \tag{9.7}$$

$$\beta = \frac{1}{2}\sum c_i z_i^2 \tag{9.8}$$

Equation (9.7) is often referred to as the Bønsted equation in the literature of chemical kinetics.

During the calculation of the ionic stregnth, the contributions of all ionic species must be summed including reactants and non-reactive ions as well. According to equation (9.7), a plot of $\log_{10} k$ as a function of $\sqrt{\beta}$ will give a straight line. This has been experimentally confirmed in many ionic reactions at relatively small ionic strengths. The applicability of this equation is limted by the validity range of the extended Debye-Hückel theory, which means that deviations from linearity are expected at higher ionic stengths.

In this practice, a relatively simple reaction between iodide amd peroxodisulfate ions will be studied. The stoichimetry of the process is given as:

$$2\mathrm{I}^- + \mathrm{S_2O_8^{2-}} \longrightarrow \mathrm{I_2} + 2\mathrm{SO_4^{2-}} \tag{9.9}$$

The appearnce if iodine in the system can be conveniently monitored in time by titration with sodium thiosulfate (iodometry).

A modification of this monitoring method is when thiosulfate ion is added before initiating the reaction and a simple iodine clock reaction is created in this way. The time when iodine begins to appear visibly marks the moment when thiosulfate ion is completely used up. Therefore, if the initial thiosulafte ion conentration is kept constant and low compared to other reactant concentrations in a series of experiments, the initial rate of the process

can be estimated easily.

In the iodine clock reaction, the reduction of iodine with thiosulfate ions occurs at the same time as the studied reaction between iodide and peroxodisulfate ions progresses:

$$I_2 + 2S_2O_3^{2-} \longrightarrow 2I^- + S_2O_3^{2-} \tag{9.10}$$

This process is much faster than the studied reaction between iodide and peroxodisulfate ions, so iodine cannot accumulate until thiosulfate ion is completely used up. When iodine accumulation begins, the starch added to the solution forms an intense blue inclusion complex with the iodine, which can be easily detected visually. Thiosulafte ion is used in large deficiency compared to the other two reagents, so the conversion of the studied reaction is sufficiently low at the moment of iodine appearance to calculate the initial rate directly from the measured time.

From the chemical literaure, the reaction between iodide and peroxodisulfate ions is known to be first order with respect to both reagents. Iodide ion concentration does not change in the initial (clock) stage of the reaction because of the addition of thiosulfate ions, so the rate law of the process can be formulated as follows:

$$-\frac{d[S_2O_8^{2-}]}{dt} = k_\Psi [S_2O_8^{2-}] \tag{9.11}$$

In this equation, k_Ψ is a pseudo-first order rate constant, which is given as the product of the second order rate constant k and the iodide ion concentration:

$$k_\Psi = k[I^-] \tag{9.12}$$

As discussed before, the initial rate of the reactions can be estmaited based on differences:

$$-\frac{d[S_2O_8^{2-}]}{dt} = \frac{\Delta[S_2O_3^{2-}]}{\Delta t} \tag{9.13}$$

In this equation, $\Delta[S_2O_3^{2-}]$ is the concentration of initially added thiosulfate ion and Δt is the clock time measured. In principle, the value of k could be determined based on a single experimens as the rate law is already known. However, it is typically advisable to carry out several measurements with different initial concentrations so that the reproducibility of the results is also assessed.

9.2 Practice procedures

You will need the following equipment:

1. 1000 cm^3 volumetric flask (1)

2. 500 cm^3 volumetric flask (2)
3. 250 cm^3 volumetric flask (2)
4. 250 cm^3 Erlenmeyer flask (10)
5. 50 cm^3 burette (5)
6. 10 cm^3 graduated pipette (2)
7. 200 cm^3 beaker (1)
8. stand with burette clamp (3)
9. heater (1)
10. stopwatch (3)

You will need the following chemicals:

1. Potassium iodide
2. Potassium peroxodisulfate
3. Potassium nitrate
4. Sodium thiosulfate
5. Ethylene diamine tetraacetic acid (EDTA)
6. concentrated hydrochloric acid
7. starch
8. iodine

Prepare the following stock solutions:

1. 0.1 M KI solution (500 cm^3)
2. 0.001 M $Na_2S_2O_3$ solution (250 cm^3)
3. 0.01 M $K_2S_2O_8$ solution (500 cm^3)
4. 10^{-5} M EDTA in 0.001 M HCl (1000 cm^3) as the general solvent
5. 1 M KNO_3 solution in the general solvent (250 cm^3)

6. Starch solution: suspend 1 g starch in 20 cm^3 water thoroughly, then add another 80 cm^3 water. Heat this solution rapidy to boiling then cool it back to room temperature.

Take 10 Erlenmeyer flasks and prepare the sample solutions listed in the table below.

Be careful. The last component that you add must always be the solution of potassium peroxodisulfate. The starting time of the reaction is the moment when this last portion is added. Shake the flasks occasionally to ensure good mixing. Start the first three samples (where no extra electrolyte is added) first, wait for the end of these reactions, record your results and then start the remaining seven samples.

Table 9.1: Composition of individual experiments

Sample number	0.01 M KI cm^3	0.001 M $Na_2S_2O_3$ cm^3	1 M KNO_3 cm^3	solvent cm^3	starch cm^3	0.01 M $K_2S_2O_8$ cm^3
1	20.0	10.0	0	59.0	1.0	10
2	20.0	10.0	0	44.0	1.0	25
3	20.0	10.0	0	34.0	1.0	35
4	20.0	10.0	1.0	43.0	1.0	25
5	20.0	10.0	3.0	40.0	1.0	25
6	20.0	10.0	5.0	38.0	1.0	25
7	20.0	10.0	10.0	33.0	1.0	25
8	20.0	10.0	20.0	23.0	1.0	25
9	20.0	10.0	25.0	18.0	1.0	25
10	20.0	10.0	35.0	8.0	1.0	25

9.3 Evaluation

Give the experimentally measured reaction times and the calculated initial rates in the from of a table:

Sample Number	Clock time s	$[S_2O_3^{2-}]$ mol dm^{-3}	$[S_2O_8^{2-}]$ mol dm^{-3}	$[I^-]$ mol dm^{-3}	r_0 mol dm^{-3} s^{-1}
1					
2					
...					

Give the calculated rate constants in the from of a table:

Sample Number	k_Ψ / s^{-1}	k / mol^{-1} dm^3 s^{-1}	$\log_{10}$ (k / mol^{-1} dm^3 s^{-1})	ionic strength, β, mol dm^{-3}	$\sqrt{\beta}$ / $mol^{1/2}$ $dm^{-3/2}$
1					
2					
...					

Plot $\log_{10} k$ as a function of $\sqrt{\beta}$.

10 Investigating a ternary system

10.1 Introduction

Ternary systems pose interesting questions not only form a theoretical point of view, but they also have practical importance for instance in metallurgy or the plastic industry. Just consider alloys, in which several different solid phases could be present, or mutually insoluble liquid phases which contain a common dissolved substance, for instance a drug dissolved in fat and water. In a ternary system, the mutual solubility of the components could be different. In every ternary system there is a pressure and/or temperature at which at least two components are only partially soluble in each other. The presence of a third component – in case it mixes partially or completely in the other two – could modifiy the mutual solubility of the two other components.

If the components are not reacting with each other, then to describe the state of a ternary system, knowing the temperature and the pressure is necessary. Since knowing the molefraction of two components determines the molefraction of third, the degree of freedom in such a system is 4. Therefore, at a given temperature and pressure, we only have to know the molefraction of two of the components to know the exact state of the system. To plot the phase diagram of a ternary system on a plane, it is useful to take pressure and temperature constant. By doing this, the phase diagram of the system can be plotted on an equilateral triangle. The corners of the triangle represent a system composed of only one of the three components. For easier reading, there is a convention regarding the orientation of the axes of the ternary triangle; it is always counter-clockwise. The sides (axes) of the triangle, the mole or weigth fraction or percentage of the components are represented (Fig. 10.1.).

Point *„P”* inside the triangle represents a system with all three components. We can read the composition by finding the respective molefraction values on the axes. The sides

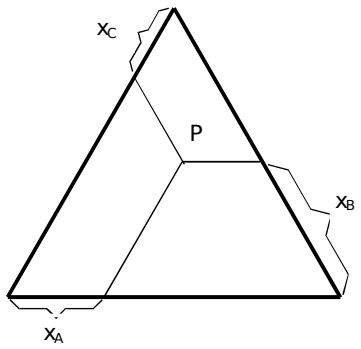

Figure 10.1: Composition of a ternary system on a ternary diagram. The mole fraction of the components increases couter-clockwise.

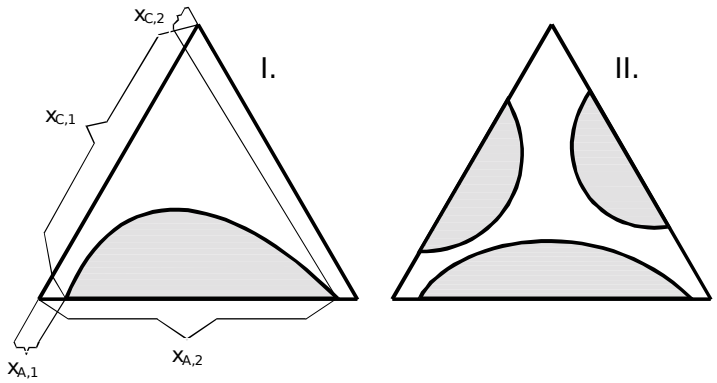

Figure 10.2: Phase diagrams of ternary systems. (I.) Only one component pair is partially miscible: the gray area under the curve is heterogeneous, the rest (white area) is homogeneous. (II.) All three component pairs are only partially miscible in each other.

give the composition of the pairwise two-component systems as well (Fig. 10.2 I.). In Fig. 10.2. (I.) we show the composition of a ternary system, in which two components mix partially (water–chloroform), while the third (acetic acid for instance) dissolves completely in both. The area below the curve marks the heterogeneous systems. In such a state, the system will have two, so-called *„conjugated phases”*. Any point in the triangle outside of this area represents a homnogeneous system. Where the curve intersects any side of the triangle, the system has two components; $x_{A,1}$ and $x_{C,1}$ mean the solubility of water in chloroform, $x_{A,2}$ and $x_{C,2}$ mean the solubility of chloroform in water, if A is water, B is acetic acid and C is chloroform. If all the component pairs are only partially soluble in each other, then we get a diagram similar to Fig. 10.2. (II.).

From now on we discuss the water–chloroform–acetic acid ternary system. As we have mentioned already, any point below the curve will mean a system with two conjugated phases. Connecting the two points that are representing the conjugated phases we get the so called *„tie line”*. All the tie lines will have a common intersection, usually outside of the triangle (point *P*, Fig. 10.3). The tie lines are usually not parallel with the base of the triangle, because the third component doesn't dissolve equally in the two conjugated phases. Drawing a tangent from pont P to the curve we get point *K*, the *plait point* for a given temperature and pressure. If not all one but two or three component pairs are only partially miscible in each other, the we get two or three plait points, respectively. In the practice we will investigate the water-chloroform-acetic acid ternary system.

10.2 Practice procedures

Prepare 20 cm^3 15, 30, 50, 60, 70, 80, 85, 90 and 95 volume% mixtures of chloroform and acetic acid. The volume% is given with respect to chloroform. Measure the compo-

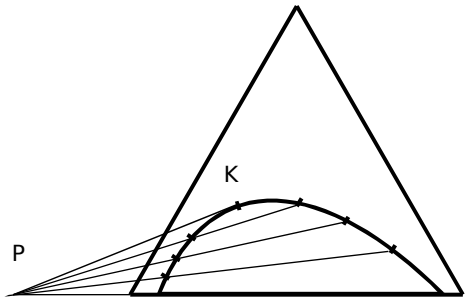

Figure 10.3: Determining the plait point in a system in which only one component pair's solubility is limited. P: intersection of the tie lines. K: plait point.

nents with an automatic burette into clean, water-free Erlenmeyer flasks, and close them. Titrate the mixtures with water using a graduated (0.05 cm^3) 10 cm^3 automatic burette until you observe a slight opaque white color throughout the mixture. Find the density of the components from the table below, and using these and the volumes used until the endpoints (opaque color) calculate the mole fraction and mass fractoin of all three components for all 9 mixtures. Draw the two phase diagrams, using both mole and mass fraction as well (two separate diagrams) to get the equilibrium diagram. Give the results of the calculations in a table such as the following:

organic solvent M = ... g $mole^{-1}$ ρ = ... g cm^{-3}				weak acid M = ... g $mole^{-1}$ ρ = ... g cm^{-3}				water M = ... g $mole^{-1}$ ρ = ... g cm^{-3}			
cm^3	mole	x	m%	cm^3	mole	x	m%	cm^3	mole	x	m%
2											
4											
...											

To determine the plate point, prepare a mixture which has two conjugated phases (system under the curve). Separate them, and titrate a known mass of both of them with NaOH to get the mass of acetic acid in both of them. Then calculate the mass fraction of acetic acid in the conjugated phases. After this step we can draw a tie line. Repeat it with another mixture with different composition, to get an additional tie line. Draw a tangent from the intersection of the tie lines to get the plait point. Give the mass fraction composition of this point as a final result of the practice.

Recommendations for the two systems:

- A: 20 ml water, 25 ml chloroform, 1 ml acetic acid
- B: 25 ml water, 25 ml chloroform, 3 ml acetic acid

Close the flasks, shake them for about 5 minutes to reach equilibrium. Separate the phases in a separation funnel, and titrate 5 ml of the organic and 10 ml of the water phase,

after measuring the mass of both. Use either 0.1 M or 1 M NaOH fot titration and a few drops of phenolphthalein as indicator. Prepare the following table:

phase	titrant volume (ml) for organic phase	m_{acid} (g)	m_{phase} (g)	m%
A organic				
A water				
B organic				
B water				

Knowing the mass of the phases you can calculate the mass fraction of acetic acid in both phases. Using these, find the intersection with the equlibrium line to get the conjugated phases' composition. Draw both tie lines. Find point P, the intersection of the tie lines. Draw the tangent to the equilibrium line from point P, to get the plait point K. Read the mass fraction composition of the plait point and write it down in your notebook as a final conclusion.

Table 10.1: Solvent molar mass and density.

	M g mole^{-1}	Density at 20 ^{o}C g cm^{-3}
acetic acid	60.05	1.0497
chloroform	119.38	1.4891
water	18.02	0.9982

Safety Instructions and General Guide for the Physical Chemistry Laboratory Practice

Working in a chemistry laboratory can be dangerous. You are exposed to a wide range of chemicals, flame, high temperature devices ie. hotplate, high pressure containers, sharp tools, fragile glassware. Safe laboratory practice is essential to prevent any injure in yourself, and others.

First and foremost, you should always be prepared for your current laboratory practice. You should be familiar with the topic. Prepare for the practice in advance. Depending on the subject spend at least 1 to 2 hours with preparations by studying the handout carefully in the day before the pactice, and about 15 minutes before the practice. Understand the task at hand. If you don't know what you are doing, you will make mistakes, unnecessarily prolong the practice, endanger yourself and others, and ultimately fail. With good preparation however, the practice will be useful, succesful, and even fun.

1. You may carry to the laboratory only the following items:
    - your notebook,
    - pen,
    - marker,
    - calculator,
    - labcoat,
    - your own spatula if you have one.
2. You may NOT carry these to the laboratory:
    - food,
    - drinks,
    - your bag,
    - jacket,

- umbrella.

3. You may NOT do these in the laboratory:

   - eat,
   - drink,
   - smoke,
   - do any other practice than your own,
   - be alone in the laboratory.

Always wait for the supervising teacher to arrive before you enter the laboratory. Be punctual, arrive at least 5 minutes before the practice starts, at the entrance, ready for the work. Leave your bag, jacket, umbrella etc. in your locker at the designated area. Do not leave anything at the entrance.

Start your work by cleaing your work area. Then wash everything (eg. glassware, electrodes, cuvettes, beakers, flasks, spatulas, pipettes, burettes) first by tapwater, use detergents and scrubber if necessary. Then, flush it with ionized water, or double deionized water, depending on the requirements of the practice. For example to determine the solubility product of a sparingly soluble salt, both the electrodes, and the glassware have to be extremely clean. Wash glassware with great care for these practices. The quality of your work will depend on your effectiveness of cleaning.

It is VERY important to write down everything you do in the laboratory. A short guide about this can be found in the foreword of your practice handouts. Precise record keeping is essential for the evaluation of your work. Write down your observations, measured data, the precise time if possible, and even the results of unsuccesful work. These might turn out to be "succesful" experiments later.

Always label every solution you prepare with a marker. If you are unsure about the content of an unlabeled container, don't use it! Use only labeled chemicals. It is strongly advised to bring your own marker to the practice instead of constantly keep borrowing someone else's.

Never use broken equipment. If you notice a crack or even the smallest one, dispose it in the designated waste container. Always notify the laboratory supervisor about broken equipment.

Dispose aqeous solutions with low environmental hazard into the sink. Use excess water to wash it down. Neutralize concentrated acids and bases before disposing. There is an organic solvent waste located below the fume hood. You may dispose organic waste into this container only. Do not throw solids in the sink eg. pieces of broken glass, spatulas. Do not pour fluids into the sink if there is a magnetic stirrer in it. Remove the stirrer first.

Use protective equipment if necessary. Latex gloves and safety glasses will be in your drawer. Always wear your labcoat during the entire practice. It is advised to button your coat. Do not wear open shoes. Keep your hair up.

Do not smell chemicals directly. Use your hands as a fan instead to smell the chemical. Do not taste any chemical under any circumstances! If a chemical is accidentally swallowed, wash it with excessive water, and notify the supervisor immediately!

We won't use open flame during this practice. If there is a fire however, you can find fire extinguishers in the lab, and in the corridor. There is an emergency shower located above the door in the laboratory. Use this immediately if your cloth catches on fire. Stand below the shower, and pull the lever. The elevators may not be used during a fire alarm. In case of a fire alarm, use the emergency stairs ti exit the building.

Fire will persist of there is flammable material, enough oxygen, and high enough temperature. Remove any of these, and the fire will stop. The building has an automatic ventillation system, the windows cannot be opened. You can cover the fire with a blanket or a piece of wet clothing to prevet oxygen resupply to the fire. Depending on the fire, use different fire extinguishers. To extinguish electric fire, do not use water based extinguishers! Use only dry chemical extinguiser in these cases.

There is a first aid kit in the laboratory to provide basic medical assistance. If acids or bases are spilled on your skin, use plenty of water to wash it, then use 2% sodium-hydroge-carbonate and 2% acetic acid for injuries caused by acids and bases, respectively. If these are spilled into your eyes, use 2% sodium-borate (borax), and 2% boric-acid for acids and bases, respectively, after washing it with plenty of water.

In case of gas intoxication, get fresh air immediately. As the windows are not openable in our laboratory, you should get out of the building immediately accompanied by at least two other persons. Notify the ambulance in any case of intoxication or injury! Use fume hood for the practices using volatile chemicals (chloroform, cc. acetic-acid). If acid is swallowed, DO NOT swallow sodium-carbonate to neutralize it, as a huge amount of carbon-dioxide could potentially evolve, and the injures stomach might rupture. In case of electrical shock, notify the supervisor, and seek medical assistance immediately!

Figure 10.4: Old chemical hazard symbols.

Figure 10.5: New chemical hazard symbols.

Appendix A – Ionic conductivity at infinite dilution

The following table includes the molar ionic conductivities at infinite dilution for certain ions, that are necessary for evaluations in certain practices. The values refer to aqueous solutions at 25 °C.

Table 10.2: Molar ionic conductivity at infinite dilution. Source: CRC Handbook of Chemistry and Physics 76th edition, David R. Lide editor in chief, 1995-1996 ISBN: 0-8493-0476-8.

Ion	$\lambda_{\pm}^{0}$, $\cdot 10^{-4} \cdot m^2 \cdot S \cdot mol^{-1}$
Ag^{+}	61.9
1/3 Al^{3+}	61
1/2 Ba^{2+}	63.6
1/2 Be^{2+}	45
1/2 Ca^{2+}	59.47
1/2 Cd^{2+}	54
1/3 Ce^{3+}	69.8
1/2 Co^{2+}	55
1/2 Cu^{2+}	69.3
1/2 Fe^{2+}	54
1/3 Fe^{3+}	68
H^{+}	67.3
1/2 Hg^{2+}	68.6
K^{+}	73.48
1/2 Mg^{2+}	53.0
1/2 CO_3^{2-}	69.3