Physical chemistry laboratory practice

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A Conductometry

Ohm's law states that the current (I) through a conductor between two points is directly proportional to the voltage (U) across the two points. The constant of proportionality is called electric resistance (R_{el}):[1]

$$U = R_{\mathrm{el}} I \tag{A.1}$$

The SI units of resistance is ohm (Ω), which can also be written with other SI units: $\Omega = \mathrm{V/A} = \mathrm{kg\ m^2\ s^{-3}\ A^{-2}}$. The resistance depends on the dimensions of the object: it is directly proportional to the length and inversely proportional to the cross-section. The specific resistance is characteristic of the material, and it can be obtained by dividing the resistance by the length and multiplying by the surface.

It is advantageous in electrochemistry to use reciprocals of the above quantities: the reciprocal of resistance is called conductance (G, units: Siemens, $\mathrm{S} = 1/\Omega$), the reciprocal of specific resistance is called specific conductivity (κ, units: $\mathrm{S\ m^{-1}}$).

In the case of solutions, the geometric parameters are determined by the shape of the electrode. Since this is never a rectangular shape (its name is often a bell electrode), it would be a rather complex task to compute the specific resistance from the dimensions of the electrode. So the usual method to determine the electrode-specific C cell constant is the measuring of the conductivity (G_{KCl}) of a solution with well-known specific conductivity (κ_{KCl}) and using Equation A.2. For each further measurement, the specific conductivity can already be calculated as the product of the measured conductivity and the cell constant. For such a calibration, the most commonly used solution is 0.0100 mol $\mathrm{kg^{-1}}$ or 0.100 mol $\mathrm{kg^{-1}}$ KCl solution. Temperature dependent specific conductivity values are shown in Table A.1.

$$C = \frac{\kappa_{\mathrm{KCl}}}{G_{\mathrm{KCl}}} \tag{A.2}$$

When performing conductometric measurements, it is important that no electrolysis occurs in the solution, so it would not be a good way to measure with direct current: alternating current should be used instead. Its frequency is much higher than that of the grid (50 Hz), typically 1-3 kHz. Thus, a conductometer is basically a high-frequency resistance measuring device, which usually displays directly the measured conductivity or resistance.

The electrical conductance of an electrolyte solution generally increases significantly with increasing temperature, following ionic mobility. For this reason, a tem-

[1] The usual symbol of resistance in physics is R, however, in this book, R_{el} is used to distinguish it from the universal gas constant that is very often used in chemistry, and also labeled R.

Table A.1: Specific conductivities of standard KCl solutions as a function of temperature

T (℃)	$\kappa_{0.0100\ \mathrm{mol\ kg^{-1}KCl}}$ (S m^{-1})	$\kappa_{0.100\ \mathrm{mol\ kg^{-1}KCl}}$ (S m^{-1})
0	0.077292	0.711685
5	0.089096	0.818370
10	0.101395	0.929172
15	0.114145	1.04371
20	0.127303	1.16159
25	0.140823	1.28246
30	0.154663	1.40592
35	0.168779	1.53160
40	0.183127	1.65910
45	0.197662	1.78806
50	0.212343	1.91809

perature sensor is often built into the modern conductometric electrodes.

The quality of distilled or deionized water is often characterized by conductance. The presence of a very small amount of impuritiy can have a significant effect on the value of G, so it is especially important for conductometric measurements to use ultrapure water and rinse the electrode as thoroughly as possible with ultrapure water.

B Spectrophotometry and Beer's law

Spectrophotometry studies the light absorption of materials, most often in the solution phase. There are a large number of different instruments available commercially today, the principles behind their operation are the same.

The extent of light absorption depends on the wavelength, so some light dispersion device is always necessary. Most commercial instruments today can measure not only in the visible range of the electromagnetic radiation, but also in the near ultraviolet and near infrared region, typically between the wavelengths 200 and 1000 nm. A typical spectrophotometer contains two lamps that can be switched on and off independently: a deuterium lamp mostly for the UV region and a halogen lamp. In a few instruments, there is only one lamp (sometimes a xenon lamp), but this results in a limited useful wavelength range.

The light absorption of a solution is generally measured in a suitably sized, transparent cell called a *cuvette*. There are two important properties of a cuvette. The first is the optical path length (l), which is the distance between the two transparent walls. Most often this is 1,000 cm, but cuvettes with path lengths between 5,00 cm to 0,0010 cm are readily available from vendors. The second important property is the material of the cuvette: quartz, glass and plastic are typically used. Quartz cuvettes can be used in the entire wavelength region of spectrophotometry. Glass and plastic cuvettes typically absorb all UV radiation below 300 nm. On the walls of the cuvettes, the path length and the material is often displayed: QS is a common notation for quartz, whereas OS means glass.

The light absorption of a sample is often measured not only at a single wavelength, but in an entire wavelength region, this is called a *spectrum*. Depending on its construction, a spectrophotometer can carry out this sort of measurement in two different ways:

1. *Scanning spectrophotometers* only measure at a single wavelength at any time. They lead a light beam to the cuvette that contains radiation with a single wavelength (monochromatic), and the light dispersion device rotates to vary the wavelength of the measurement. The scanning speed shows how fast the wavelength is varied, it determines the time necessary to record a spectrum (typically 1-5 minutes). A lower scanning speed lets more measurement time for a single wavelength so results in a spectrum with enhanced precision. The detector, which measures light intensity, does not differentiate between wavelengths. Therefore, the sample compartment has to be isolated from external light for the time of the measurement, this is simply done by closing its lid. The main advantage of a scanning spectrophotometer is that it is capable of

providing high wavelength resolution (absorbance can in principle be measured in intervals as small as 0,1 nm), and the precision for single wavelength measurements is usually much better than in other instruments.

2. *Diode array spectrophotometers* lead intense light with many wavelengths (polychromatic) onto the sample, which is then decomposed by the dispersion unit into monochromatic beams that are led to the diode array. A high number of different detectors operate simultaneously in this case, so rotating the dispersion unit is not necessary. An entire spectrum can be recorded in a very short time (about a tenths of a second), which is the greatest advantage of this instrument type. Ambient light is usually quite faint compared to the intense beam passing through the sample, so the cell compartment does not need to be closed. The disadvantage is that the number of diodes in the array limits the wavelength resolution. In addition, single-wavelength measurements are less precise because these detectors are not as sensitive as the single large detector in a scanning spectrophotometer.

To measure the absorption of a solution, the light intensity must be measured before (I_0) and after (I) the sample. Depending on the timing of these measurements, there are two types of spectrophotometers:

1. In a *single beam spectrophotometer*, I_0 and I are measured in a single light beam at different times. Most diode array spectrophotometers work in a single beam mode.

2. In a *double beam spectrophotometer*, the light beam is divided into two parts, a measuring beam and a reference beam. The instrument measures I_0 and I simultaneously. Sometimes, there are two identical detectors in the instrument, but the two beams can also be led to the same detector in an alternating fashion. Most scanning spectrophotometers work in the double beam mode.

A baseline measurement in a single beam instrument means the determination of I_0. The cuvette should contain the pure solvent without any solute in this case, so that conditions are as similar to the measured sample as possible. The baseline measurement has to be repeated quite frequently as the intensity of even a carefully stabilized radiation source might vary significantly in time.

In principle, no baseline measurement is necessary in double beam instruments as they measure I_0 continuously on the reference beam. Most sample compartments make it possible to place a cuvette into the reference beam as well, this should be filled with the pure solvent. However, carrying out a baseline correction is advisable

even in this case to avoid the corruption of measurements because of some differences between the two light beam geometries or detector characteristics. With baseline correction, it is not very important that the reference beam should contain a cuvette with the pure solvent: the only thing that matters is that the reference beam should be unchanged during the entire series of measurements.

In spectrophotometry, the concentration of the absorbing species is deduced directly from the *absorbance* (A) of the sample. *Beer's law* states the following:

$$A = \lg \frac{I_0}{I} = \epsilon c l \tag{B.1}$$

The new quantities in this equation are the molar absorbance (ϵ) and the concentration of the absorbing species (c). It is easily seen that absorbance is dimensionless. The path length l is typically measured in cm, the units of c is mol dm^{-3}, therefore the most common units for ϵ are dm^3 mol^{-1} cm^{-1}. Yet the most consistent SI units for ϵ would be m^2 mol^{-1}, so this value is sometimes thought of as an effective molar cross section.

If the solution contains several absorbing species, their absorbance contributions are simply added:

$$A = \sum \epsilon_i c_i l \tag{B.2}$$

Here ϵ_i is the molar absorbance of absorbing component i, whereas c_i s the concentration of component i.

The literature often mentions that deviations from Beer's law are possible. This is a common but imprecise statement: the law itself is of mathematical nature, no exceptions are possible. However, it may happen that the law is applied in an incorrect manner.

The detector in most modern spectrophotometers measures light intensity precisely within two orders of magnitude (a factor of 100). It follows that the instrument does not measure the value of I reliably above the absorbance value of 2.0, therefore, the displayed value of A does not reflect reality. Because of this phenomenon, it is often said that Beer's law is not valid above absorbance 2.0. Nonetheless, this is clearly a practical limitation arising from the imperfect instrumentation and not a property of the law itself. Some commercially available instruments can measure light intensity precisely over four orders of magnitude, so an absorbance around 4.0 can still be measured precisely in this way.

It is not uncommon to speak of deviations from Beer's law when in fact the concentration of the absorbing species is not known correctly. This is typical when the absorbing species is involved in fast equilibrium reactions. In cases like this,

sometimes even the number of absorbing species may be incorrectly known to the experimenter.

Occasionally, Beer's law is corrected by a term that contains the refractive index of the solution. Yet, the law itself still remains valid as it gives the intensity of *absorbed* light. The refraction index correction is rationalized by the fact that part of the light beam in an instrument may not reach the detector not because it is absorbed, but because its direction changes as a consequence of refraction. The impact of the phenomenon may be minimized by baseline correction using the solvent, as its refractive index is typically very close to those of the samples, so the refraction correction is already taken care of in the value of I_0.

C Potentiometric measurements

In potentiometric measurements, the voltage[2] between two electrodes (U) is measured to determine some characteristics of the system. Typically, the system is a solution and the concentration of the components is to be determined.

The electric potential of a given point (E) is defined in physics as the work by which a singly charged body can be moved to this point from an infinite distance. The unit of potential is volt (V), which is by definition the same as J/C, or with SI base units: kg m^2 s^{-3} A^{-1}. Potential is the ratio of two extensive quantities, *i.e.* an intensive one.

It is important to note that, by definition, the direct measurement of potential is neither possible nor necessary. Only the potential difference between the two points, *i.e.* the voltage is measured in every procedure.[3]

In physical chemistry, an electrochemical half-cell is a heterogeneous system: it usually consists of an electrolyte and some separate phase(s); the latter must always have an electrically conductive part, most often made of metal. In such a system, there is a potential difference between the electrolyte and the metallic phase, but this is not easy to measure. It is much easier to determine the voltage between the metallic outlets of two different electrodes that are immersed into the same electrolyte. Such a system is commonly referred to as an electrochemical cell: the electrolyte of the two electrodes is in contact with each other either because they are the same or in a way that allows charge transfer.

It was important to define a reference point for studying electrodes. For the sake of consistency with other conventions of physical chemistry, the standard hydrogen electrode (SHE) was chosen for this purpose. The electrolyte of SHE is a solution containing hydrogen ion with an activity of 1, in contact with hydrogen gas of 10^5 Pa fugacity, and an electrical connection provided by a platinum plate.[4] The potential of a SHE is defined as zero, so the voltage measured in an electrochemical cell composed of a SHE and another electrode is entirely attributed to the potential of the other electrode.

[2]"Voltage" and "potential difference" are sometimes used interchangeably. Strictly speaking, voltage refers to the parameter that is measured by the voltmeter, thus it is not a well defined formal term. The term emphpotential difference is to be used instead in cases when theoretical background is implied.

[3]In the textbooks and in the literature, this is somewhat contradictory: constant potential or absolute potential are quite often mentioned (*e.g.* Galvanic potential, zeta potential, ...). This is because it is so natural for experienced scientists that only potential differences can be measured that reference points are not even specified in everyday communication.

[4]Note that platinum is really only necessary for its metallic conduct, it is not involved in the chemical process at all, although it acts as a catalyst for hydrogen reduction. The inertnes of platinum is one of the reasons why it is suitable for building a SHE.

If an electrochemical cell is created to study the electrolyte, one of the two electrodes should be chosen so that its potential does not depend on the composition of the electrolyte. This reference electrode is often an electrode of the second kind (*e.g.*, calomel electrode, Ag/AgCl electrode). The potential of the other electrode is influenced by the composition of the studied electrolyte solution: this is called the indicator electrode or a measuring electrode. It is advisable to construct this electrode in such a way that, as far as possible, its potential is determined by a single process, *i.e.* it is selective. Electrodes of the first kind (metal dipped in an electrolyte containing its own ions) are often used for this purpose: the concentration of the metal ion in the solution determines the electrode potential.

Most modern electrochemical cells are much more complex, usually with several different phases with electrical connections. The reference electrode and the indicator electrode are often incorporated into a single electrode body, *i.e.*, a combined electrode is built having two metallic outlets, and the voltage is measured between these. During the measurement, it is important that current should not flow in the system, that is, to measure the equilibrium electrode potential.[5] In the case of an ideal, reversible electrochemical cell, the dependence of the potential (E) on the activity of the component which is selectively sensed by the electrode (a_i) is given by the Nernst equation:

$$E = E^\circ + \frac{RT}{z_i F} \ln(a_i) \tag{C.1}$$

In this formula, E° is the standard electrode potential (*i.e.* the value of E under standard conditions), R is the universal gas constant (8.314 J mol^{-1} K^{-1}), T is the temperature, z_i is the electron number change of the electrode process,[6] F is Faraday's constant *i.e.* the charge of 1 mol of electron (96485 C mol^{-1}).

[5]Of course, between any two points with different potentials that are connected through a conductor of non-infinite resistance, current will flow. In potentiometry, however, the reference and indicator electrodes are measured with a high input-impedance voltmeter (R_{in} approximately 10^{15} Ω). The resulting current is non-zero, but negligible. It is also possible to measure under strictly zero-current conditions with a compensation method: in this way, the potential difference necessary to stop any current is measured.

[6]For electrodes of the first kind, this is the same as the charge of the metal ion in the solution. For more complex electrodes, it is not always easy to find.

D Measuring the density of a solution

By definition, density (ρ) is the ratio of mass (m) and volume (V). The density of a liquid is far easier to measure than that of a solid or gas, since the volume of a solid can be difficult to obtain, while the mass of a gas can rarely be measured directly. However, the volume and mass of a liquid can be measured directly and, for most applications, simultaneously. There are several different methods to measure or estimate the density of a solution. The most important ones used in laboratory practices are listed here:

1. *Measuring the density of a solution with a Mohr-Westphal balance (hydrostatic balance)*: The Mohr-Westphal balance is a non-symmetric, direct-reading instrument for determining the densities of liquids. Its parts are described by Figure D.1.

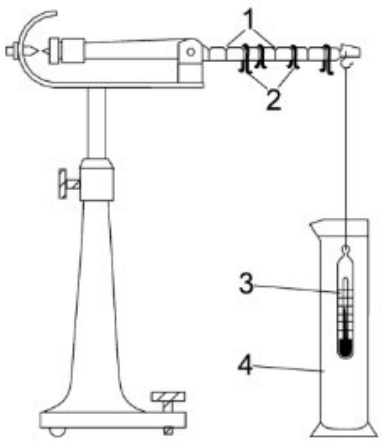

Figure D.1: Parts of a Mohr-Westphal balance: 1: beam, 2: weights, 3: bouyancy body (or plummet), 4: liquid sample

At the free end of the arm of the balance, a *bouyancy body* (3) is suspended in air. The bouyancy body is normally made of glass and can have a built-in thermometer. It has a well-known mass and volume. When performing a measurement, the bouyancy body is immersed into the *liquid of interest* (4). Because of the effect of bouyancy, the weight of the submersed glass body will appear lower than it was in air, and will bring the balance out of zero. The bouyancy force can be measured by successively adding small *weights* (2) to the arm until the balance is restored to zero. The density value of the liquid sample can be read directly from the positions of the weights.

2. *Measuring density with a pycnometer*: It is the most accurate method for measuring the density of a liquid, especially when an analyticel balance is used for measuring masses. A pycnometer (also called pyknometer or specific gravity bottle) is a flask with a close-fitting ground glass stopper or thermometer. If the pycnometer is weighed empty (m_{pyc}), full of water ($m_{\text{pyc+water}}$), and full of a liquid whose density is to be determined ($m_{\text{pyc+liquid}}$), the volume of the pycnometer (V_{pyc}) and the density of the liqiud (ρ_{liquid}) can be calculated using the temperature dependent density of water:

$$V_{\text{pyc}} = \frac{m_{\text{pyc+water}} - m_{\text{pyc}}}{\rho_{\text{water}}} \tag{D.1}$$

$$\rho_{\text{liquid}} = \frac{m_{\text{pyc+liquid}} - m_{\text{pyc}}}{V_{\text{pyc}}} \tag{D.2}$$

Table D.1: Density of water at different temperatures around room temperature

T (℃)	ρ_{water} (g cm^{-3})	T (℃)	ρ_{water} (g cm^{-3})
15	0.9991026	23	0.9975415
16	0.9989460	24	0.9972995
17	0.9987779	25	0.9970479
18	0.9985986	26	0.9967867
19	0.9984082	27	0.9965162
20	0.9982071	28	0.9962365
21	0.9979955	29	0.9959478
22	0.9977735	30	0.9956502

3. *Measuring/estimating density with a pipette*: Since pipettes can measure the volumes of liquids quite accurately, the density of a liqiud can be estimated by measuring the mass of a well-knovn volume of liquid (e.g. 10.00 cm^3) poured out from a pipette. For mass measurement, you should use an analytical balance, and the measurement procedure should be repeated at lest 3 times to get an accurate density value.

E Relationship between equilibrium constants given by activities and concentrations

In thermodynamics, the exact definition of the equilibrium constant (K) includes activities. All chemical reactions can be described by the following general equation:

$$0 = \sum \nu_i \mathrm{X}_i \tag{E.1}$$

Here, X_i denotes the reactants and products and ν_i is the stoichiometric coefficient with an appropriate sign, which is negative for reactants and positive for products.[7] Based on the law of mass action, the following equilibrium constant is defined for the chemical reaction given by Equation E.1:

$$K = \prod a_i^{\nu_i} \tag{E.2}$$

In this formula, a_i is the activity of component X_i. As a more specific example, consider the following reaction:

$$\mathrm{A} + \mathrm{B} = \mathrm{C} + \mathrm{D} \tag{E.3}$$

The corresponding equilibrium constant is as follows:

$$K = \frac{a_\mathrm{C} a_\mathrm{D}}{a_\mathrm{A} a_\mathrm{B}} \tag{E.4}$$

The thermodynamic equilibrium constant expressed by activities is connected to the standard Gibbs free energy change of the reaction ($\Delta_r G^\circ$):

$$\Delta_r G^\circ = -RT \ln K \tag{E.5}$$

It can be seen that K is always dimensionless, and that the standard state is of great importance to its definition (since $\Delta_r G^\circ$ also depends on it). Standard state means standard pressure and ideal behavior at all temperatures, so the value of K may only depend on the temperature, not on pressure and other state functions.

In thermodynamics, molality-based activity is the most commonly used for solutes:

$$a_i = \gamma_i \frac{m_i}{m^\circ} \tag{E.6}$$

In this formula, γ_i is the activity coefficient, m_i is the molality of component X_i and m° is the standard molality ($1.0000\ldots\,\mathrm{mol\ kg^{-1}}$). In the case of gases, pressure

[7] The stoichiometric coefficients are not necessarily integers.

(p) is used instead of the molality, and fugacity coefficient (Φ_i) should be used instead of activity. The product of $\Phi_i p_i$ is often referred to as fugacity f_i.

Molality is defined as the ratio of the amount of material dissolved and the mass of the solvent. Its advantage compared to concentration c (or molarity) is that its value does not depend on the temperature. For relatively dilute solutions, concentration can be calculated by multiplying the density (ρ) with the molality:[8]

$$c_i = \rho m_i \tag{E.7}$$

Thus, the relationship between activity and molarity is as follows:

$$a_i = \gamma_i \frac{c_i}{\rho m^\circ} \tag{E.8}$$

Substituting into the definition of equilibrium constant gives the following:

$$K = (\rho m^\circ)^{-\sum \nu_i} \prod \gamma_i^{\nu_i} \prod c_i^{\nu_i} \tag{E.9}$$

In this formula, the last product is basically the equilibrium constant expressed as concentrations (K_c) for which the following formula can be given:

$$K_\mathrm{c} = K \frac{(\rho m^\circ)^{\sum \nu_i}}{\prod \gamma_i^{\nu_i}} \tag{E.10}$$

The formula clearly shows that K_c has a physical dimension, and its value depends not only on the temperature, but on everything else that influences the activity coefficients and the density of the solution. Therefore, the concentration-based equilibrium constant is often interpreted in the literature as a solvent-dependent quantity; in aqueous solutions, K_c depends on temperature and ionic strength. It is worth noting that for a chemical reaction described by Equation E.3, $\sum \nu_i = 0$ is valid so Equation E.11 simplifies to the following form:

$$K_\mathrm{c} = K \frac{\gamma_\mathrm{A}\gamma_\mathrm{B}}{\gamma_\mathrm{C}\gamma_\mathrm{D}} \tag{E.11}$$

That is, in reactions that do not involve any change in the total amount of substance, the relationship between K and K_c depends only on the activity coefficients, not on the density of the solution and the choice of the standard state.

[8]For more concentrated solutions containing a single solute, the term is more complex. The value of M_i (molar mass of the solute) is also necessary in this formula in addition to density: $c_i = \rho m_i/(1 + m_i M_i)$. However, in the case of such concentrated solutions, it is preferable to use the usual description of mixtures, *i.e.*, mole fraction based activity.

1 Temperature dependent decomposition of acetylsalicylic acid

1.1 Check your previous studies

1. First order processes (lecture course)
2. Arrhenius equation (lecture course)
3. Spectrophotometry and Beer's law (this book, Section B.)

1.2 Theoretical background

During this practice, you will study the pseudo-first order hydrolysis reaction of acetylsalicylic acid under alkaline conditions (Figure 1.1). This compound is the active ingredient of the well-known drug Aspirin.

If a reactant S decomposes in a pseudo-first order reaction with the stoichiometry $S \rightarrow P$, the time dependence of its concentration ($[S]_t$) can be given by the following exponential formula (t is time, $[S]_0$ is the concentration of the reactant at time zero, k is the pseudo-first order rate constant):

$$[S]_t = [S]_0 e^{-kt} \tag{1.1}$$

If $[S]_0$ is known and the remaining reactant concentration $[S]_t$ is measured at time instance t, the pseudo-first order rate constant can be calculated as follows:

$$k = \frac{1}{t} \ln \frac{[S]_0}{[S]_t} \tag{1.2}$$

If product P is not present at the beginning, the time dependence of its concentration ($[P]_t$) can simply be calculated from mass balance:

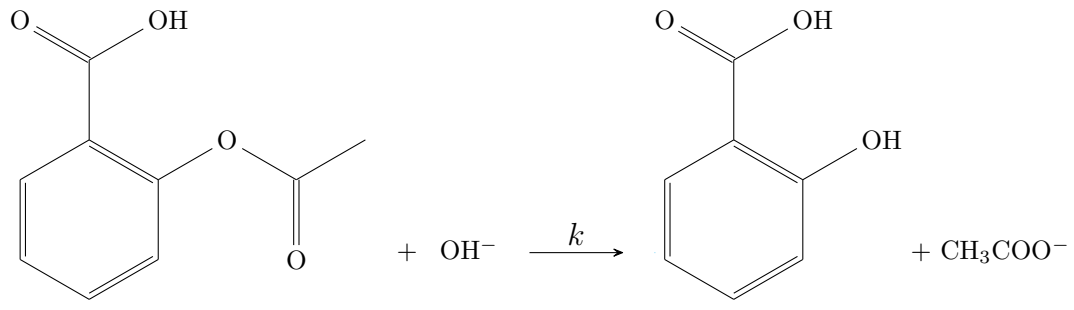

Figure 1.1: Alkaline hydrolysis of acetylsalicylic acid

$$[\mathrm{P}]_t = [\mathrm{S}]_0 - [\mathrm{S}]_t = [\mathrm{S}]_0(1 - \mathrm{e}^{-kt}) \tag{1.3}$$

When the concentration of a product is monitored in a process, the following equation can be used to calculate the pseudo-first order rate constant:

$$k = \frac{1}{t} \ln \frac{[\mathrm{P}]_\infty}{[\mathrm{P}]_\infty - [\mathrm{P}]_t} \tag{1.4}$$

The new quantity $[\mathrm{P}]_\infty$ in this last equation is the product concentration at the end of the process, it is usually identical to $[\mathrm{S}]_0$.

Reaction rates are known to depend on temperature very sensitively. Hence, measuring and maintaining constant temperature is of primary importance in chemical kinetics. The temperature dependence of a rate constant[9] is often well described by the *Arrhenius equation*, which can be stated in several different forms. The first is the differential form which can be given in two, mathematically identical ways:

$$\frac{\mathrm{d} \ln k}{\mathrm{d}T} = \frac{E_\mathrm{a}}{RT^2} \qquad \frac{\mathrm{d} \ln k}{\mathrm{d}(1/T)} = -\frac{E_\mathrm{a}}{RT} \tag{1.5}$$

The second is the most common form, which is obtained by integrating the previous equation:

$$k = A\mathrm{e}^{-E_\mathrm{a}/(RT)} \tag{1.6}$$

The linearized form of the Arrhenius equation is also frequently used, and can be given by taking the natural logarithms of both sides of the integrated form:

$$\ln k = \ln A - \frac{E_\mathrm{a}}{RT} \tag{1.7}$$

In these equations, A is called the pre-exponential factor, E_a is the activation energy, and R is the universal gas constant. Note that A and E_a do not depend on the temperature.[10]

Activation energy can be obtained graphically by plotting a series of measured $\ln k$ values as a function of $1/T$. This sort of graph is called an *Arrhenius plot* (Figure 1.2). If the process follows the Arrhenius equation, this plot gives a straight line with a negative slope, from which the activation energy is obtained upon multiplication by $-R$. The pre-exponential factor can be calculated from the extrapolated intercept

[9] Note a subtlety here: the Arrhenius equation gives the temperature dependence of a rate constant and *not a reaction rate*. Therefore, for an attempt to characterize the temperature dependence of the kinetics of a reaction, the form of the rate law must be determined first.

[10] Textbooks often give a general definition of the activation energy based on the differential form shown above so that it may depend on temperature. However, a temperature-dependent E_a automatically implies that the process *does not follow* the integrated Arrhenius equation.

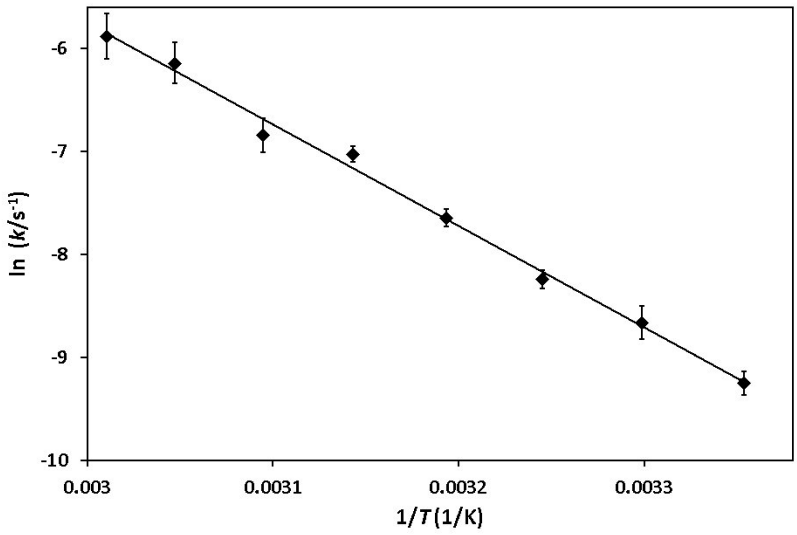

Figure 1.2: A typical Arrhenius plot

of the straight line.

Usually, it is not advisable to measure the value of k at only two temperatures because the adherence to the Arrhenius equation for the studied process is not verified in this way. However, if the validity of the formula is certain for some other reason, then the activation energy and pre-exponential factor can be calculated from two data points (k_1 at T_1 and k_2 at T_2) as follows:

$$E_\mathrm{a} = R\frac{T_1 T_2}{T_1 - T_2} \ln \frac{k_1}{k_2} \tag{1.8}$$

$$A = {k_1}^{T_1/(T_1-T_2)} {k_2}^{T_2/(T_2-T_1)} \tag{1.9}$$

1.3 Practice procedures

During this practice, pseudo-first order conditions will be used to study the alkaline hydrolysis of acetylsalicylic acid. The reaction is a simple ester hydrolysis from an organic chemistry point of view and first order with respect to the organic reagent from a kinetic point of view. Its rate also depends on the pH of the solution in a complicated manner. Fortunately, the use of a buffer ensures that the pH is kept constant throughout the entire process and this dependence is eliminated during our experiments.

The reaction is quite slow at room temperature, so the measurements will be conducted at somewhat elevated temperatures. The time and the equipment available will only allow you to measure at two different temperatures.

Spectrophotometry will be used to monitor the process. You will see that both the reactant and the product are colorless in solution (although there is in fact some absorption in the UV). To overcome this problem, a color forming reagent, $FeCl_3$ will be added to the solution, which gives a Fe^{3+} salicylate complex with the product salicylic acid, but does not react with acetylsalicylic acid at all.

Samples with a known volume are taken from the alkaline reaction vessel, and cold acid is added suddenly to decrease both $[OH^-]$ and the temperature, which stops the process (in other words, it *quenches the reaction*).

To determine the product concentration at $t = \infty$ (which is equal to the reactant concentration at $t = 0$), separate samples are prepared. The measurements are carried out at two different temperatures: 40 ℃ and 60 ℃.

First, pulverize an *Aspirin* tablet in a mortar with a pestle, add approximately 80 cm^3 of deionized water and keep this solution on a magnetic strirrer for 10 minutes. When the stirring is over, filter the solution into a 100 cm^3 volumetric flask, add 5.00 cm^3 of buffer solution, and fill the flask up to its mark. This is the stock solution. The stock solution obtained in this way will be close to saturated.[11]

When the stock solution is ready, you will have to use it in two different series of experiments:

(1) *Determining the final concentration of salicylic acid:* Pipette 2.0-2.0 cm^3 samples from the stock solution into two 100.0 cm^3 volumetric flasks (40 ℃ and 60 ℃), and add 3.0-3.0 cm^3 0.25 mol dm^{-3} NaOH solution to them. After labeling, put them into the two thermostats and leave them there for an hour. Then add 3.0-3.0 cm^3 0.25 mol dm^{-3} HCl solution and 2.0-2.0 cm^3 0.10 mol dm^{-3} $FeCl_3$, then fill the flasks up with deionized water and measure their absorbances as described later.

(2) *Monitoring the concentration in kinetic experiments:* Put one half of the remaining stock solution into an Erlenmeyer flask and the other half into another one. Close the flasks, label them, and put them into their respective thermostats, and start a stopwatch. Start the two reactions by a time shift of $1-2$ minutes, so that you can do the sampling in this time shift. Take ten labeled 25.0 cm^3 volumetric flasks and add 0.50-0.50 cm^3 0.25 mol dm^{-3} HCl solution, and 0.50-0.50 cm^3 0.10 mol dm^{-3} $FeCl_3$ solution into them. Without taking out the Erlenmeyer flasks from the thermostat, take 2.0 cm^3 samples from them after 15, 20, 25, 30 and 35 minutes, and put them into the labeled 25.0 cm^3 volumetric flasks (already

[11] Typically, an *Aspirin* tablet contains a dose of 500 mg acetylsalicylic acid, which has a solubility in water around 2 - 4 g dm^{-3}, depending on temperature. Most of the stuff that remains undissolved are other, non-active ingredients of *Aspirin*.

containig the HCl and $FeCl_3$ solutions). Fill the volumetric flasks with deionized water and measure their absorbances as described in the next paragraph.

When all the 12 samples are ready, measure their absorbance (A)[12] in a spectrophotometer at 526 nm using a cell with 1.000 cm path length.

1.4 Evaluation

1. Give the measured and calculated data in the format of Table 1.1. Prepare a separate table for each temperature. Note that the dilution factor is different in the two series of experiments. During the determination of the final concentration of salicylic acid, 2.0 cm^3 of stock solution is used to prepare 100.0 cm^3 of measured solution, which gives a dilution factor of 50, so $c = [P]_\infty/50$. During the kinetic experiments, 2.0 cm^3 of stock solution is used to prepare 25.0 cm^3 of measured solution, which gives a dilution factor of 12.5, so $c = [P]_t/12.5$. In the evaluation, using the measured absorbance values only (without converting them to concentrations) is sufficent provided that the path length is unchanged:

$$k = \frac{1}{t} \ln \frac{[P]_\infty}{[P]_\infty - [P]_t} = \frac{1}{t} \ln \frac{\epsilon l [P]_\infty}{\epsilon l [P]_\infty - \epsilon l [P]_t} = \frac{1}{t} \ln \frac{4A_\infty}{4A_\infty - A_t} \tag{1.10}$$

Here A_∞ is the final absorbance measured in the first series of experiments (characteristic of the final concentration of salicylic acid), whereas A_t is the absorbance measured after time t in the second series of experiments.

Table 1.1: Measured and calculated data. T = ... K, A_∞ = ...

reaction time, t (s)	A_t	k (s^{-1})
...	...	...

2. Calculate the averages and the standard deviations[13] for the rate constants at both temperatures.

Table 1.2: Temperature dependence of the rate constant

T (K)	$\overline{k}$ (s^{-1})	standard deviation (s^{-1})
313	...	...
333	...	...

[12] Unfortunately, the commonly used symbol of absorbance, A, is the same as the pre-exponential factor of the Arrhenius equation. Be careful not to mix the two quantities.

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

3. Calculate the activation energy and the pre-exponential factor.

4. From the calculated values of E_a and A, find an extrapolated value for the pseudo-first order rate constant of the reaction at 20 ℃.

1.5 Advanced discussion points

1. Based on the available data, estimate the conversion up to which you have monitored the decomposition process and think about the following:

   (a) Would these data be suitable for validating the claimed pseudo-first order nature of the process?

   (b) Could the rate constant be determined using the initial rate method?

2. In addition to cooling back the reaction mixture to room temperature, acid was also added. Is there any reason to do so other than stopping the reaction? Could the color-developing $FeCl_3$ solution be added before the acid?

3. When the final concentration of salicylic acid is determined, the reaction time is 60 minutes, which is not much longer than the 35-minute monitoring time for the kinetic experiments. Why is it certain that the reaction reaches completion in this case?

4. Another equation that is in widespread used for describing the temperature dependence of rate constants is called the Eyring equation. What is the difference between this and the Arrhenius equation? Why is it often possible to use both equations to evaluate the same data set?

5. Why is it unnecessary to convert the measured absorbance values to concentrations during the evaluation?

2 Determination of the dissociation constant of a weak acid by conductometry

2.1 Check your previous studies

1. Physical properties related to ionic conduction in solution (lecture course)
2. Kohlrausch law of independent migration of ions (lecture course)
3. Ostwald's dilution law (lecture course)
4. Conductometry (this book, Section A.)
5. Relationship between equilibrium constants given by activities and concentrations (this book, Section E.)

2.2 Theoretical background

The electrical resistance (R_{el}) or its reciprocal, the conductivity (G) of an electrolyte solution can be measured very easily in electrochemistry. Conductivity itself is not a very useful property in physical chemistry because it depends on the geometry of the electrodes used in the experiments. Therefore, after determining a suitable cell constant, the property of specific conductivity (κ) is introduced, which does not depend on the geometry of the electrodes and is only characteristic of the studied solution. Molar specific conductivity (Λ_m) is the ratio of the specific conductivity and the concentration (c):[14]

$$\Lambda_\mathrm{m} = \frac{\kappa}{c} \tag{2.1}$$

Friedrich Kohlrausch found that the limiting molar conductivity (Λ_0, the molar conductivity of an infinitely dilute solution) can be calculated by adding the individual contributions of anions and cations:

$$\Lambda_0 = \lambda^0_\mathrm{a}\nu_\mathrm{a} + \lambda^0_\mathrm{c}\nu_\mathrm{c} \tag{2.2}$$

Here $\nu_\mathrm{a}, \nu_\mathrm{c}$ are stochiometric factors, λ^0_a and λ^0_c are the limiting molar conductivities for the anions and the cations. This equation is stated for a solution containing a single type of anion with a single type of cation. If more than two kinds of ions occur in a system, more additive terms must be included in Equation 2.2.

[14] Note that many earlier literature sources display a multiplying factor of 1000 in this equation. When SI units are used consistently, this is unnecessary. However, keep track of the correct units used for the various physical and chemical properties you encounter in this practice very carefully.

The specific conductivity of weak electrolytes can be directly calculated from the limiting molar conductivity and the degree of dissociation (α):

$$\kappa = \Lambda_{\mathrm{m}} c = \alpha \Lambda_0 c \tag{2.3}$$

The dissociation constant K_{d} of a weak acid can be calculated from its concentration and its degree of dissociation:

$$K_{\mathrm{d}} = \frac{\alpha^2 c}{1 - \alpha} \tag{2.4}$$

It is worth noting that K_{d} is an equlibrium constant for a process in solution, so it depends on the temperature, and also (slightly) on the pressure and on the permittivity of the medium.

If we express α from Equation 2.3 and substitute it into Equation 2.4, a famous expression is obtained that is called *Ostwald's law of dilution*:

$$K_{\mathrm{d}} = \frac{\Lambda_{\mathrm{m}}^2 c}{\Lambda_0^2 - \Lambda_0 \Lambda_{\mathrm{m}}} \tag{2.5}$$

In earlier times, it was customary to linearize this equation by the following rearrangement:

$$\frac{1}{\Lambda_{\mathrm{m}}} = \Lambda_{\mathrm{m}} c \frac{1}{K_{\mathrm{d}} \Lambda_0^2} + \frac{1}{\Lambda_0} \tag{2.6}$$

If $1/\Lambda_{\mathrm{m}}$ is plotted as a function of $\Lambda_{\mathrm{m}} c$ (which is identical to κ), the intercept of the resulting straight line is $1/\Lambda_0$, whereas the slope is $1/(K_{\mathrm{d}} \Lambda_0^2)$. Therefore, K_{d} can be calculated in a simple fashion: the square of the intercept must be divided by the slope (Figure 2.1).

2.3 Practice procedures

During this practice, you will determine the dissociation constant of a weak acid in two different media (water and a water-alcohol mixture). There are several possible choices for both the weak acid and the alcohol. Agree with the instructor on a particular pair of choices.

Rinse the electrode of the conductometer several times (4 - 5) with water. For this purpose, use ultrapure deionized water with low conductivity ($\kappa < 1$ μS cm^{-1}), and not the usual deionized water. Ask the technician for ultrapure water.

Prepare two solutions of the selected weak acid from the stock solution (1.0 mol dm^{-3}) by pipetting 2.00 cm^3 into two 100.0 cm^3 volumetric flasks, and then filling one with the 20 V/V% alcohol-water mixture, the other with ultrapure deionized

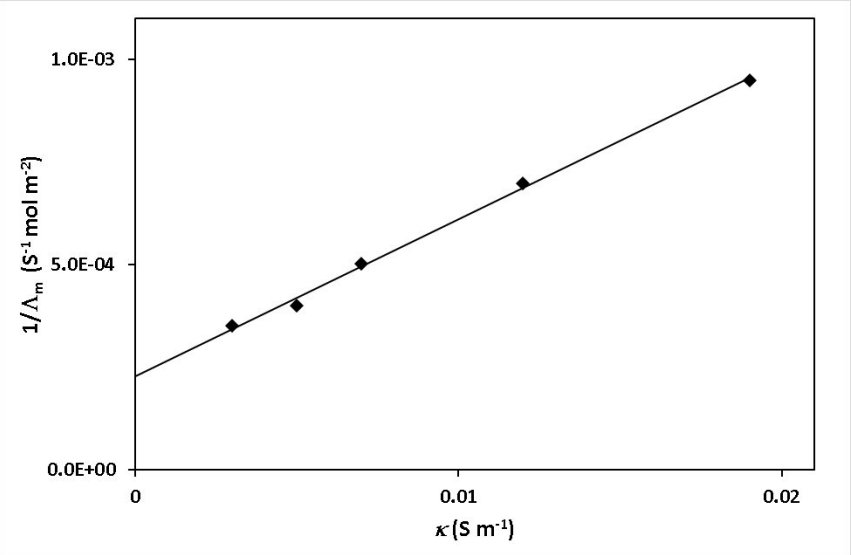

Figure 2.1: A typical plot based on Ostwald's law of dilution

water up to the mark.

First, measure the conductivity of the ultrapure water (G_{water}) and the 20 V/V% alcohol-water mixture ($G_{\text{alcohol-water}}$). These will be necessary later for correcting the measured conductivities.

In order to obtain the cell constant, measure the conductivity of 0.0100 mol dm^{-3} KCl solution, and record it along with the temperature.

Carry out the conductivity measurements in a measuring cylinder. Pour the water-based solution into the cylinder and measure its conductivity. Then, pipette 25.0 cm^3 from the cylinder into a clean 50.0 cm^3 volumetric flask, fill it up with ultrapure deionized water (2× dilution), and measure the conductivity of the new solution after carefully rinsing the electrode with ultrapure deionized water. Repeat the dilution and measurement 3 times (so that you have a total of five data points with different concentrations).

Then do the same to the alcohol-based solution, but now use the 20 V/V% alcohol-water mixture for all the dilutions and rinsing.

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

2.4 Evaluation

1. Calculate the cell constant (C) of your electrode. To do this, you will need the standard specific molar conductivity of the 0.0100 mol dm^{-3} KCl solution (κ_{KCl}), the conductivity measured for this solution in your instrument (G_{KCl}) and the conductity of ulptrapure water (G_{water}). You can use the following

formula:

$$C = \frac{\kappa_{\mathrm{KCl}}}{G_{\mathrm{KCl}} - G_{\mathrm{water}}} \tag{2.7}$$

2. Calculate the specific conductivites (κ) from all your measured conductivity data (G) in aqueous medium. To do this, you will need the cell constant (C) and the conductity of ultrapure water (G_{water}):

$$\kappa = C(G - G_{\mathrm{water}}) \tag{2.8}$$

Do the same for the series of measurements in 20 V/V% alcohol-water solution:

$$\kappa = C(G - G_{\mathrm{alcohol\text{-}water}}) \tag{2.9}$$

3. Calculate the molar specific conductivity values (Λ_{m}) for all your measured data using Equation 2.3.

4. Summarize all your data in the format of Table 2.1. You will need two tables: one for aqueous solution and another for the 20 V/V% alcohol-water solution. You can use more convenient units if you wish (*e.g.* μS instead of S, mmol dm^{-3} instead of mol dm^{-3}, or mS cm^{-1} instead of S m^{-1}).

Table 2.1: Measured and calculated conductometric data

c (mol dm^{-3})	G (S)	κ (S m^{-1})	Λ_{m} (S mol^{-1} m^2)	$1/\Lambda_{\mathrm{m}}$ (S^{-1} mol m^{-2})
...	...	...	...	...

5. Plot $1/\Lambda_{\mathrm{m}}$ as a function of κ. Determine the intercept and the slope of the straight line that can be fitted to these points. Calculate Λ_0 and K_{d} from the appropriate combinations of the intercept and slope. You will need two plots: one for aqueous solution and another for the 20 V/V% alcohol-water solution.

2.5 Advanced discussion points

1. What sort of error would it cause if the actual concentration of your stock solution, unknown to you, would be different from the value displayed on the label (1.0 mol dm^{-3})?

2. The evaluation in this practice uses a linearization method (Ostwald's law of dilution is transfomed). Devise a nonlinear formula that shows G (the directly

measured dependent variable) as a function of c (the directly controlled independent variable). This equation should contain G_{solvent}, C, K_{d} and Λ_0 as parameters. Two of these parameters (G_{solvent} and C) are measured in independent experiments. How would you determine the remaining two parameters based on the measurements without linearization?

3. Discuss why correction with G_{solvent} is necessary in conductometric measurements.

4. Is Equation 2.3 valid for strong electrolytes as well ($\alpha = 1$)?

5. The theoretical background mentioned the Kohlrausch law of independent migration of ions. Is there another law that is named after Kohlrausch in conductometry?

3 Quantitative description of an adsorption process by the Langmuir isotherm

3.1 Check your previous studies

1. Adsorption (lecture course)
2. Langmuir isotherm (lecture course)
3. Spectrophotometry and Beer's law (this book, Section B.)

3.2 Theoretical background

Adsorption is a physico-chemical process during which atoms, ions or molecules adhere to a surface.[15] The result is a thin layer of the adsorbate that is formed on the adsorbent surface (Figure 3.1).

The first major theoretical model to describe adsorption was developed by Irving Langmuir and the corresponding formula is called the *Langmuir isotherm*:

$$\theta = \frac{Kp}{1 + Kp} \tag{3.1}$$

Here θ is the *fractional coverage*, K is the equilibrium constant of adsorption and p is the partial pressure of the adsorbate in the gas phase.

This equation was originally introduced to describe the adsorption of gases at solid surfaces. However, it also describes the adsorption of a solute from a solution provided that the solvent has little or no adsorption to the adsorbent compared to the solute. In this case, the amount of adsorbed species (n) is given as a function of concentration using n_{max}, the *maximal adsorption capacity*:

[15] Make sure you clearly distinguish adsorption from absorption and absorbance. *Adsorption* is a surface phenomenon, *absorption* is an interaction with the entire volume of the other substance and *absorbance* is a quantity measured in spectrophotometry.

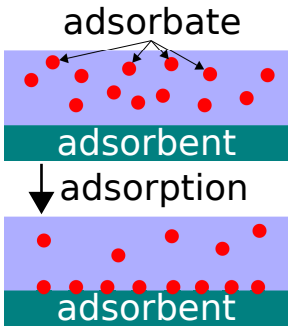

Figure 3.1: During adsorption, a thin adhered layer of the adsorbate is produced on the surface of the adsorbent.

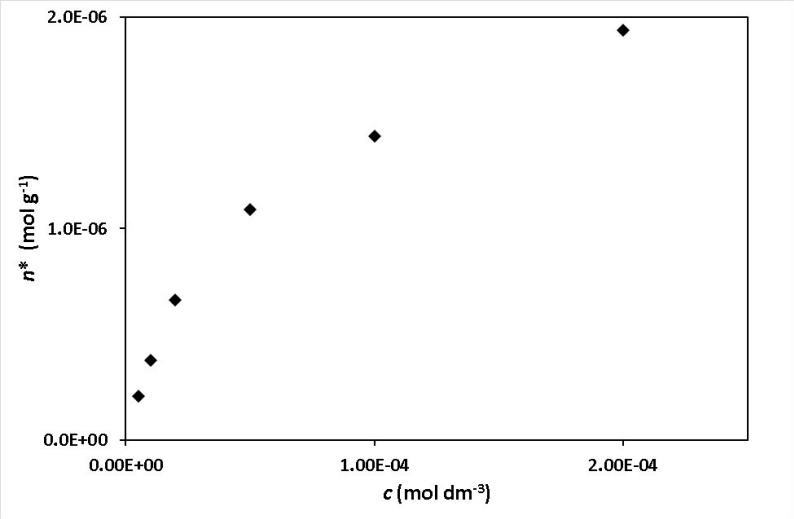

Figure 3.2: The Langmuir isotherm

$$n = n_{max}\frac{c}{c+K} \tag{3.2}$$

Here c is the equilibrium concentration of the adsorbate in the solution, whereas – similarly to gas adsorption – K is called the equilibrium constant of adsorption.

Both the amount of adsorbed species and the maximal adsorption capacity are extensive physical properties. To obtain intensive values, both can be divided by the mass of the adsorbent. In this way, the specific adsorbance (n^*, units: mol g^{-1}) and the maximal specific adsorption capacity (n^*_{max}) are introduced into the formula:

$$n^* = n^*_{max}\frac{c}{c+K} \tag{3.3}$$

This equation describes a saturation curve (Figure 3.2): as the concentration of the adsorbate in the solution increases, first the specific adsorbance increases in a fashion that is close to linear. As c keeps increasing further, n^* gradually levels off, and finally becomes independent of c as all adsorption sites become occupied. Before computers became widely available, it was quite customary to use the linearized from of the Langmuir isotherm:

$$\frac{1}{n^*} = \frac{1}{n^*_{max}} + \frac{K}{n^*_{max}}\frac{1}{c} \tag{3.4}$$

In the linearized plot, $1/n^*$ is shown as a function of $1/c$, then the intercept will be $1/n^*_{max}$, the reciprocal of the maximal specific adsorption capacity (Figure 3.3).

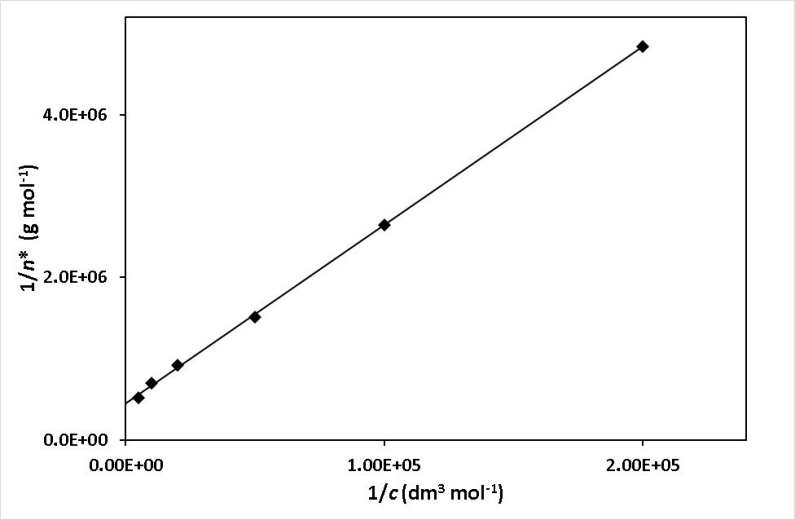

Figure 3.3: The linearized Langmuir isotherm

3.3 Practice procedures

In this practice, you will study the adsorption of the dye methylene blue onto a very common adsorbent, filter paper.

A methylene blue stock solution of known concentration is available. Prepare a dilution series with the following concentrations: $2 \cdot 10^{-4}$, 10^{-4}, $5 \cdot 10^{-5}$, $2 \cdot 10^{-5}$, 10^{-5}, $5 \cdot 10^{-6}$ mol dm^{-3} in 50.0 cm^3 volumetric flasks. Record the absorbance values of all the solutions at 664 nm for calibration purposes in a cell with a path length of 1.000 cm (only do this later, together with the adsorption samples).

Pipette 25.0-25.0 cm^3 from each solution into a 100 cm^3 Erlenmeyer flask. Put adsorbent into each of flasks: the adsorbent masses should be between 0.10 g and 0.15 g for all solutions. They need not be the same for every solution, but the exact masses must be recorded in your laboratory notebook. Shake all the solutions for 30 min, then take 3.0 cm^3 samples from each and measure measure their absorbance at 664 nm in a cell with a path length of 1.000 cm. After these measurements, pour back the samples to their Erlenmeyer flasks of origin, and shake them for another 15 minutes. Measure the absorbance of the adsorbent-free solutions at 664 nm in a cell with a path length of 1.000 cm.

3.4 Evaluation

1. Decide which of the measured absorbance values are suitable for quantitative evaluation. Remember that absorbance values above 2.0 are typically not measured reliably.

2. Prepare a calibration curve in which you plot the reliably known absorbances

for the solutions before adsorption as a function of concentration. Beer's law states that the points should fit reasonably well to a straight line that goes through the origin. Calculate the slope of this straight line; this divided by the path length ($l = 1.000$ cm) will be the molar absorption coefficient of methylene blue in water at the selected wavelength (ϵ, units: dm^3 mol^{-1} cm^{-1}).

3. Compare the absorbance values measured after 30 and 45 minutes of shaking. Decide which series is more suitable for further evaluation and use only those values in your later calculations.

4. Using the ϵ value, calculate the concentrations for all solutions in the selected series. These must be smaller than the concentrations before adsorption as the process removes some fo the dye from the solution. Calculate the specific adsorbance for each sample as follows:

$$n^* = \frac{(c_{\text{before}} - c_{\text{after}})V_{\text{sol}}}{m_{\text{adsorbent}}} \tag{3.5}$$

Here c_{before} is the concentration of the dye before adsorption, c_{after} is the concentration of the dye after adsorption, V_{sol} is the volume of the solution (25.0 cm^3) and $m_{\text{adsorbent}}$ is the mass of the adsorbent. Give your data in the format of Table 3.1.

Table 3.1: Measured and calculated data for the adsorption of methylene blue. Absorbance measured at $\lambda = ...$ nm

c_{before} (mol dm^{-3})	$m_{\text{adsorbent}}$ (g)	A	c_{after} (mol dm^{-3})	n^* (mol g^{-1})
$2 \cdot 10^{-4}$	...	...	...	...
$1 \cdot 10^{-4}$	...	...	...	...
$5 \cdot 10^{-5}$	...	...	...	...
$2 \cdot 10^{-5}$	...	...	...	...
$1 \cdot 10^{-5}$	...	...	...	...
$5 \cdot 10^{-6}$	...	...	...	...

5. Plot n^* as a function of c_{after}. This is the non-linearized Langmuir plot. Observe the features of this graph. Try to estimate the maximal specific adsorption capacity (n^*_{max}) and the equilibrium constant of adsorption (K).

6. Prepare a linearized graph by plotting $1/n^*$ as a function of $1/c_{\text{after}}$. Fit a straight line to the points and estimate the maximal specific adsorption capacity from the intercept.

3.5 Advanced discussion points

1. Why is the linearization of the Langmuir isotherm undesirable for evaluation? What is the modern method that should be followed?

2. The equilibrium constant of adsorption (K) – like every equilibrium constant – is a temperature dependent quantity, this is the reason why the formula is called an *isotherm*. Why is the lack of thermostatting acceptable in this practice?

3. Try to evaluate the reliability of the maximal specific adsorption capacity (n^*_{max}) and the equilibrium constant of adsorption (K) you have determined. What changes in the experimental design could lead to an improvement of this reliability?

4. Examine the glassware you have used in your experiments. Suggest an explanation for your observations.

4 Partition equilibrium of I_2 between two phases

4.1 Check your previous studies

1. Partition equilibrium between two phases (lecture course)
2. Relationship between equilibrium constants given by activities and concentrations (this book, Section E.)

4.2 Theoretical background

If substance X is soluble in two different liquids (A and B) which are immiscible and the two solvents are in contact with each other, the substance is said to be involved in a *partition process*. After reaching thermodynamic equilibrium, the chemical potential of substance X is equal in the two solvents:

$$\mu_{\mathrm{X,A}} = \mu_{\mathrm{X,B}} \tag{4.1}$$

The chemical potential of a substance is directly connected to its activity in the following way:

$$\mu^*_{\mathrm{X},A} + RT \ln a_{\mathrm{X,A}} = \mu^*_{\mathrm{X,B}} + RT \ln a_{\mathrm{X,B}} \tag{4.2}$$

Here $\mu^*_{\mathrm{X},i}$ is the standard chemical potential of substance X in solvent i, and $a_{\mathrm{X},i}$ is the thermodynamic activity of substance X in solvient i. Rearranging this equation shows that the ratio of the thermodynamic activities of substance X in the two phases can be given as:

$$\frac{a_{\mathrm{X,A}}}{a_{\mathrm{X,B}}} = \mathrm{e}^{(\mu^*_{\mathrm{X,B}} - \mu^*_{\mathrm{X,A}})/(RT)} \tag{4.3}$$

It can be seen that at a given temperature, the right side of the equation is constant.[16] Therefore, the ratio $K = a_{\mathrm{X,A}}/a_{\mathrm{X,B}}$ is also constant and is called the *partition ratio of substance X between solvents A and B*. The derivation assumes that substance X does not dissociate or form adducts in any of the solvents.

4.3 Practice procedures

During this practice, you will determine the partition ratio of iodine between water and toluene by measuring the concentration of the solute in each phase directly through iodometric titration.

[16] The word "constant" here means that the ratio is independent of the activities or concentrations, but as it is analogous to an equilibrium constant, it depends on temperature.

Measure 0.1 g of elemental iodine on an analytical balance (you do not need to measure 0.1000 g precisely, but should record the exact mass in your laboratory notebook). Dissolve it in 20 cm^3 toluene in an Erlenmeyer flask. Add 150 cm^3 distilled water, close the flask, then put it onto a shaker device for 20 min. When the shaking time is over, transfer the content of the flask into a separatory funnel, and then separate the two phases very carefully. Take a 5.0 cm^3 sample from the organic phase and a 100.0 cm^3 sample from the aqueous phase. Titrate the organic phase with a 0.01 mol dm^{-3} solution of sodium thiolsulfate, then titrate the aqueous phase with a 0.001 mol dm^{-3} solution of sodium thiolsulfate. In the organic phase, the end point of the titration will be easily detectable through the disappearance of the intense color of iodine. In the aqueous phase titration, add some starch solution toward the end of the titration when the solution is light yellow in order to detect the end point better by the disappearance of the intense blue.[17] The exact concentrations of the titrating solutions might be slightly different from the values given above; you will learn these from your supervisor during the practice.

Transfer the remaining (non-titrated) parts of the two phases back to the original Erlenmeyer flask, add 5 cm^3 of toluene and 100 cm^3 of water and repeat the entire previous procedure from the beginning (*i.e.* from the shaking) two more times. In this way, you will have three data pairs for evaluation.

4.4 Evaluation

1. Calculate the concentrations of both the aqueous and organic phase from the titration results. Remember that the titrated volumes were different. The stoichiometry of the iodometric titration is given as:

$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-} \tag{4.4}$$

2. Calculate the partition ratio of iodine between water and toluene from all three experiments assuming that the activities and the concentrations are the same. Give your results in the format of Table 4.1.

Table 4.1: Concentrations of iodine in different phases and partition ratios

experiment number	$c_{I_2,\text{water}}$ (mol dm^{-3})	$c_{I_2,\text{toluene}}$ (mol dm^{-3})	K
1	...	...	...
2	...	...	...
3	...	...	...

[17] This color is caused by the reversible formation of a complex between starch and iodine.

3. Calculate the average and the standard deviation[18] of the three estimates of the partition ratio.

4.5 Advanced discussion points

1. Why does the concentration of iodine change between the three experiments?
2. During the calculation, it is assumed that the activities and the concentrations are the same. Actually, this is not really necessary as an assumption. Find a weaker condition that the activity coefficients must satisfy in the evaluation of this experiment.
3. Iodine is a non-polar substance, water is a highly polar solvent. Explain how iodine can still be dissolved in water.

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

5 Catalysis, inhibition and promoter effect in the decomposition reaction of hydrogen peroxide

5.1 Check your previous studies

1. Rate equation of first order reaction (lecture course)
2. Definitions of catalyst, inhibitor and promoter (lecture course)
3. Gas laws (lecture course)

5.2 Theoretical background

The main objective of reaction kinetics is to determine the rate equation of a reaction and in order to explore the mechanism. In a homogeneous system, the rate equation of a reaction without a significant intermediate can often be given in the form of a power law, *i.e.* with the following formula:

$$r = k[\mathrm{A}]^{\beta_a}[\mathrm{B}]^{\beta_b} \dots [\mathrm{N}]^{\beta_n} \tag{5.1}$$

In this equation, β_a, β_b, ..., β_n are the reaction orders with respect to different components, $\beta = \beta_a + \beta_b + \ldots + \beta_n$ is the net reaction order. The rate constant can be determined from the experimental kinetic (concentration-time) curves, using the known reaction orders and initial concentrations. An obvious way to do this is to use the initial rate method: the rate constant can be calculated if the reaction rate at zero time (r_0) is divided by the product of the initial concentrations raised to the appropriate powers:

$$k = \frac{r_0}{[\mathrm{A}]_0^{\beta_a}[\mathrm{B}]_0^{\beta_b} \dots [\mathrm{N}]_0^{\beta_n}} \tag{5.2}$$

In reaction kinetics, (pseudo-)first order reactions are quite common. One such example is the decomposition of hydrogen peroxide, which occurs according to the following stoichiometry:

$$2\mathrm{H_2O_2} \rightarrow 2\mathrm{H_2O} + \mathrm{O_2} \tag{5.3}$$

In spite of the simple rate equation, the mechanism of the process is in fact complicated, with many elementary reactions.

The rate of decomposition of hydrogen peroxide is also influenced by substances that are not included in the stoichiometric equation: *e.g.* heavy metal ions catalyze

the process even at very low concentration levels. Other substances, such as phosphoric acid, decrease the rate of decomposition by reacting with traces of catalytic impurities. Due to this phenomenon, commercially available high-quality hydrogen peroxide often contains stabilizers to slow down the decomposition. The presence of these stabilizers should be taken into account when a hydrogen peroxide solution is used for various chemical purposes.

The rate of catalyzed processes may also be influenced by promoters and inhibitors. The promoters alone have no effect on the reaction rate, but can significantly increase the catalytic effect of a suitable catalyst (this is also called synergism). For example, in the presence of $CuCl_2$, iron(III)ions catalyze the decomposition of hydrogen peroxide more efficiently. Inhibitors prevent the catalysts from working. In the studied process, *e.g.* acetanilide has an inhibitory effect on iron(III) catalysis.

Experimental findings show that the decomposition of hydrogen peroxide is a first order process:

$$\frac{\mathrm{d}\xi}{\mathrm{d}t} = -\frac{1}{2}\frac{\mathrm{d}n_{\mathrm{H_2O_2}}}{\mathrm{d}t} = -\frac{V_{\mathrm{sol}}}{2}\frac{\mathrm{d}[\mathrm{H_2O_2}]}{\mathrm{d}t} = -k[\mathrm{H_2O_2}] \tag{5.4}$$

Here V_{sol} is the volume of the solution, $n_{\mathrm{H_2O_2}}$ is the molar amount of hydrogen peroxide. The solution of the rate equation (*i.e.* the shape of the kinetic curve) is as follows:

$$[\mathrm{H_2O_2}]_t = [\mathrm{H_2O_2}]_0 \mathrm{e}^{-k_1 t} \tag{5.5}$$

The definition of the new parameter in the formula is: $k_1 = 2k/V_{\mathrm{sol}}$. The decomposition of hydrogen peroxide is easy to follow by measuring the volume of oxygen gas formed, as the following equation is valid:

$$-\frac{1}{2}\frac{\mathrm{d}n_{\mathrm{H_2O_2}}}{\mathrm{d}t} = \frac{\mathrm{d}n_{\mathrm{O_2}}}{\mathrm{d}t} \tag{5.6}$$

When the pressure is constant and oxygen is considered an ideal gas ($n_{\mathrm{O_2}} = pV_{\mathrm{O_2}}/(RT)$), the equation can be given in the following form:

$$-\frac{\mathrm{d}[\mathrm{H_2O_2}]}{\mathrm{d}t} = \frac{2p}{RTV_{\mathrm{sol}}}\frac{\mathrm{d}V_{\mathrm{O_2}}}{\mathrm{d}t} = a\frac{\mathrm{d}V_{\mathrm{O_2}}}{\mathrm{d}t} \tag{5.7}$$

Thus, if the initial rate of oxygen volume change is known at zero time, the initial rate of hydrogen peroxide decomposition can be calculated through multiplying it by a factor of $a = 2p/(RTV_{\mathrm{sol}})$.

The easiest way to estimate the initial rate is to follow the process up to a relatively small conversion. In this case, the volume of oxygen produced is plotted

as a function of time, and a straight line is fitted to the points. Its slope is equal to the initial rate.

5.3 Practice procedures

In this experiment, the effect of iron(III) and copper(II) ions on the decomposition reaction of hydrogen peroxide will be examined.

The amount of oxygen formed in the reaction can be measured with a gas burette. The gas burette is a vertically mounted glass tube with splits, filled with a liquid, and attached to a leveling vessel through a flexible rubber tube at the lower end. To the upper end, also with a flexible tube, a round-bottom flask (*i.e.* the reaction vessel) is connected *via* a T-joint. Reagents can be added to the round-bottom flask through a stopper on the top.

First, open the T-joint so that the outside air can flow into both the reaction vessel and the gas burette. Take off the separator funnel and pipette 10.0 cm^3 of 3% hydrogen peroxide into the carefully cleaned reaction vessel. Place a stirring magnet into the vessel and close it. Turn the magnetic stirrer on. Do not change the revolution setting of the magnetic stirrer during the laboratory practice to ensure the same experimental conditions.

Prepare 40.0 cm^3 solution containing the appropriate reagents (catalyst, promoter and/or inhibitor) in a beaker. Set the level of the liquid in the burette to zero using the leveling vessel. Add the reagent to the hydrogen peroxide solution through the inlet, quickly close the stopper and start the stopwatch. Adjust the T-joint so that this time only the reaction vessel and the gas burette are connected. Read the volume of oxygen formed on the gas burette so that the pressure of the formed gas equals the external air pressure. To do this, the leveling vessel should be lifted so that the liquid level in the burette and in the leveling vessel is the same.

During each kinetic experiment, record the volume-time data point pairs every minute in the first ten minutes of the reaction (thus, a total of 11 data points will be recorded for each detected curve) or until the volume of the oxygen formed exceeds the volume of the gas burette. Thermostatting is not possible in the current experimental setup, so note and record the temperature of the laboratory as well.

You have to complete a total of eight series of measurements. The compositions of the appropriate reagent solutions is summarized in Table 5.1. Prepare the appropriate reagent solutions from the stock solutions. In Table 5.1, give exactly how each solution was prepared. At the beginnig of the measurements, record the temperature and pressure of the laboratory.

Table 5.1: Composition of reagent solutions ($V = 40.0$ cm^3) in the kinetic experiments

experiment number	[Fe(III)] (mol dm^{-3})	[Cu(II)] (mol dm^{-3})	$V_{\mathrm{Fe(III)}}$ (mol dm^{-3})	$V_{\mathrm{Cu(II)}}$ (cm^3)	V_{water} (cm^3)
1	0	0	...	...	...
2	0.00125	0	...	...	...
3	0.00375	0	...	...	...
4	0.00750	0	...	...	...
5	0	0.00750	...	...	...
6	0.00125	0.00125	...	...	...
7	0.00125	0.00375	...	...	...
8	0.00125	0.00750	...	...	...

5.4 Evaluation

1. For each of the eight kinetic measurements, plot the volume of oxygen formed as a function of time (you may plot all the eight data series in a single figure, not all of them should be shown on separate figures). Fit a straight line to each kinetic curve (ignore some points if necessary), then determine the slopes of the lines. This will be the initial rate of oxygen formation.

2. Use Equation 5.7 to calculate the initial rate of hydrogen peroxide concentration change from the initial rate of oxygen formation. Its numerical value will be negative as the reactant concentration decreases.

3. Summarize your measurement results in a Table similar to Table 5.2.

Table 5.2: Initial rate of hydrogen peroxide decomposition kinetic experiments. $T = \ldots$ K, $p = \ldots$ Pa

[Fe(III)] (mol dm^{-3})	[Cu(II)] (mol dm^{-3})	$\mathrm{d}V_{\mathrm{O_2}}/\mathrm{d}t$ (cm^3 s^{-1})	$\mathrm{d}[\mathrm{H_2O_2}]/\mathrm{d}t$ (mol dm^{-3} s^{-1})
...	...	...	...

4. Calculate the concentration of each reagent in the reaction mixture (*i.e.*, after mixing 10.0 cm^3 of 3% hydrogen peroxide with 40.0 cm^3 reagent solution), for each kinetic experiment.

5. Plot the initial rate of hydrogen peroxide decomposition as a function of iron(III) concentration. To do this, you can use the measurements where copper(II) was not present in the solution, *i.e.*, together with the comparative experiment without iron(III), there will be four measured points in the figure. Draw your conclusions on the reaction order with respect to iron(III).

6. From the result of the experiment containing only copper(II) without iron(III), draw your conclusions about the catalytic effect of copper(II).

7. Compare the results of the three experiments in which the concentration of copper(II) was changed so that the iron(III) concentration was kept constant (including the experiment when copper(II) was not present at all). Draw your conclusions on the promoter effect of copper(II).

5.5 Advanced discussion points

1. In the first two to three minutes of the measured kinetic curves, the increase in the volume of oxygen gas may be slower than at later times. This is not caused by a decrease in the concentration of hydrogen peroxide in the solution, as it should slow down the process in time rather than accelerating it. What may be the reason for the phenomenon?

2. Why is it not possible to calculate the pseudo-first-order rate constant reliably from the measured kinetic curves?

3. How could we still calculate the pseudo-first-order rate constants from the data obtained during the practice if we also use the fact that – based on literature data – hydrogen peroxide decomposition is first order with respect to H_2O_2?

6 Determination of the selectivity coefficient of an ion selective electrode

6.1 Check your previous studies

1. Electrode potential and its definition (lecture course)
2. Nernst equation (lecture course)
3. Debye–Hückel limiting law (lecture course)
4. Potentiometric measurements (this book, Section C.)

6.2 Theoretical background

The potential of ion selective electrodes (in the absence of interfering ions) can be given by the *Nernst equation*:

$$E = E^0 + \frac{RT}{z_i F} \ln(a_i) = E^0 + \frac{RT \ln 10}{z_i F} \lg(a_i) \tag{6.1}$$

In this equation, z_i is the charge of the primary ion i (with a positive or negative sign), a_i is the activity of the primary ion. In the case of cation sensitive electrodes, the potential of the electrode increases, and for anion selective electrodes, it decreases with increasing primary ion activity. Ion selective electrodes are almost never reversible electrodes, so often the following equation is used to give their potential:

$$E = E^0 \pm S \lg(a_i) \tag{6.2}$$

Here S is the slope of the electrode, which can be determined in separate experiment. In the case of real, multi-component sample solutions, the potential of the ion selective electrode is influenced not only by the activity of the primary ion, but also more or less by all other ions in the solution. These are commonly called interfering ions because they also affect the measured electrode potential. For this reason, using Equations 6.1 and 6.2 for calculating the activity of the primary ion is not accurate. The effect of other ions present in the sample solution on the electrode potential can be described with the so-called potentiometric selectivity coefficient (k^{pot}). With this, the electrode potential of an electrode is described by the *Nikolskij equation*:[19]

[19]The number 2.303 often occurs in the Nernst and Nikolskij equations instead of $\ln 10$.

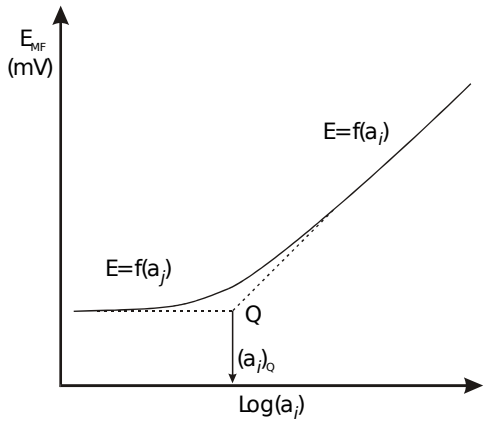

Figure 6.1: Determination of selectivity coefficient of a cation selective electrode by the mixed solution method

$$E = E^0 + \frac{RT \ln 10}{z_i F} \lg \left[a_i + \sum_j \left(k_{i,j}^{pot} a_j^{z_i/z_j} \right) \right] \tag{6.3}$$

Here a_j is the activity of the interfering ion j , z_j is its charge and $k_{i,j}^{pot}$ is the selectivity coefficient of interfering ion j. The value of the selectivity coefficient gives how many times more sensitive the electrode is for the primary ion i than for the interfering ion j. For example, $k_{i,j}^{pot} = 10^{-2}$ means that the activity of interfering ion j should one hundred times higher than the activity of primary ion i to have the same effect on the electrode potential.

There are two methods for determining the selectivity coefficient: the mixed solution and the separate solution methods.

In the mixed solution method, the activity of primary ion i is changed while the activity of interfering ion j is kept constant. From the graph obtained by plotting the measured data (Figure 6.1), the intersection Q is determined. From the actvity corresponding to Q, the selectivity coefficient can be calculated with the following formula:

$$k_{i,j}^{pot} = \frac{(a_i^{z_j})_Q}{a_j^{z_i}} \tag{6.4}$$

For the separate solution method, two separate curves are required. First, in the absence of interfering ion j, the calibration curve for primary ion i is measured, and in another measurement, in the absence of primary ion i, the calibration curve for interfering ion j is determined. As shown in Figure 6.2, the two curves can be used to determine the value of the selectivity coefficient in two ways. One is the ratio of activities at the same potential:

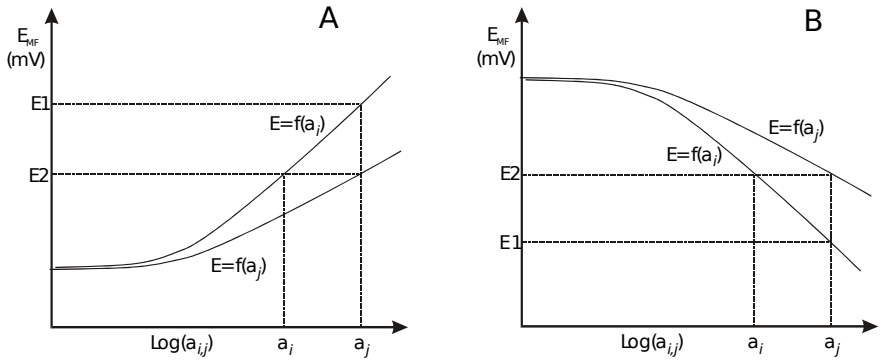

Figure 6.2: Determination of the selectivity coefficients by the separate solution method for single positively (A) and single negatively charged (B) ions

$$k_{i,j}^{pot} = \frac{a_i}{a_j^{z_i/z_j}} \tag{6.5}$$

The selectivity coefficient can also be estimated from the potential values corresponding to the same activities:

$$\lg k_{i,j}^{pot} = \frac{(E_2 - E_1)zF}{RT \ln 10} = \frac{\Delta E}{S} \tag{6.6}$$

The value of the selectivity coefficient is influenced by several factors: the ionic strength of the solution, the method of determination, *etc.* You can see the drawback of the separate solution method from Equations 6.5 and 6.6: it relies on the assumption that the primary and interfering ions have the same charges. In the separate solution method, the conditions of determination may be different from those in practice, so the selectivity coefficients determined this way are considered to be approximate values.

Electrolytes are usually far from ideal solutions, so concentrations (c) are typically not the same as thermodynamic activities (a). In strong electrolytes, the Debye–Hückel limiting law is widely used to estimate the mean activity coefficient ($\gamma_\pm$):

$$\lg \gamma_\pm = -A|z_+ z_-|\sqrt{I} \tag{6.7}$$

In this formula, I is the ionic strength of the solution (mol kg^{-1}), A is a combination of universal constants and some physical properties of the solvent, its value is 0.509 mol$^{-1/2}$ kg$^{1/2}$ in water and at 25 °C.

6.3 Practice procedures

The aim of the practice is to investigate a halide ion (fluoride or bromide ion) selective electrode. The exact type of electrode and the interfering ion to be used will be given by your supervisor prior to starting the laboratory practice.

First, you need to determine the detection limit, which is the minimal measureable activity of the electrode for primary ion i . To do this, set up a dilution series from the corresponding primary ion salt: use the 10^{-2} mol dm^{-3} primary salt stock solution, and make a ten times dilution by pipetting 10.0 cm^3 of the stock solution into a 100.0 cm^3 volumetric flask and filling the volumetric flask with deionized water up to the mark. Repeat the dilution in new volumetric flasks, always using the previous solution, until the concentration 10^{-6} mol dm^{-3} is reached. Pour the solutions into labeled beakers.

Immerse the measuring electrode and the reference electrode into the beaker with the most dilute solution and connect the electrodes to the voltmeter. After about 1 min, record the voltage value. After reading, immerse the electrodes in the next, ten times more concentrated solution, and read the voltage again after 1 min. Perform the measurement with all five solutions, beginning from the most dilute one and reaching the most concentrated one at the end. Do this three times (first set of measurements). Rinse the electrodes carefully between and after the series with deionized water. During the measurements, no thermostatting can be used in the current experimental setup, so record the laboratory temperature in your notebook.

Then make a series of solutions in which the i primary ion concentration varies in the 10^{-2} mol dm^{-3} – 10^{-6} mol dm^{-3} concentration range but also in each solution, the j interfering ion is present at a concentration of 10^{-2} mol dm^{-3}. To do this, measure 0.00100 mol of the solid salt of the i primary ion into a 100.0 cm^3 volumetric flask, using an analytical balance for mass measurement. Fill the flask up to the mark with the 10^{-2} mol dm^{-3} stock solution of the j interfering ion. Pipette 10.0 cm^3 of the solution thus prepared into another 100.0 cm^3 volumetric flask and fill the volumetric flask up to the mark with the 10^{-2} mol dm^{-3} stock solution of the j interfering ion. Repeat the dilution in new volumetric flasks, always using 10.0 cm^3 of the previous solution. Instead of water, always use the stock solution of the j interfering ion to fill the volumetric flask up to the mark. Repeat the dilution until the concentration 10^{-6} mol dm^{-3} for the i primary ion is reached (second series of measurements).

Finally, make a dilution series from the 10^{-2} mol dm^{-3} stock solution containing the salt of the interfering ion j, using distilled water. The concentration range of this third dilution series is from 10^{-2} mol dm^{-3} to 10^{-6} mol dm^{-3} (similarly to the first set of measurements). Determine the voltage values of the solutions three times

(third set of measurements).

6.4 Evaluation

1. In each of the 15 solutions, calculate all ion concentrations as well as the ionic strengths of the 15 solution. Then, use the Debye–Hückel limiting law to estimate the mean activity coefficients in each case. Finally, calculate the activities of the primary and the interfering ions. The densities of the diluted solutions used in this practice are 1.00 g cm^{-3}. The results should be summarized in the format of Table 6.1.

Table 6.1: Calculated and measured potentiometric data. primary ion: ...; interfering ion: ...; $T = \ldots$ K

c_i (mol dm^{-3})	c_j (mol dm^{-3})	I (mol kg^{-1})	$\gamma_\pm$	a_i	a_j	E (V)
...	...	...	...	...	...	...

2. Plot the results of the first and second set of measurements on a single graph such that the 10-based logarithm of the activity of the primary ion is on the horizontal axis, the measured voltage is on the vertical axis.

3. Determine the detection limit of the electrode graphically from the first set of measurements. This should be done in the same way as the determination of Q in Figure 6.1, but in the absence of the interfering ion. The detection limit is the resulting $(a_i)_Q$ activity value.

4. Determine the slopes (S values) from the linear parts of the first and second series of measurements (in the presence and absence of interfering ion).

5. From the second set of measurements, determine the selectivity coefficient as it is shown by Figure 6.1. Use Equation 6.4 in the calculation.

6. The data of the third set of measurement should be plotted as follows: the 10-based logarithm of the activity of the interfering ion is on the horizontal axis, the measured voltage is on the vertical axis. Determine the slope S from the linear part of the figure.

7. From the third set of measurements, estimate the selectivity coefficient from Eqations 6.5 and 6.6, using carefully choosen activity and potential values.

6.5 Advanced discussion points

1. The Debye–Hückel limiting law is not valid in the complete concentration range used in this practice. What kind of error does this fact cause? How would you modify the practice procedure so that you do not have to estimate the mean activity coefficients with the Debye–Hückel limiting law?

2. In this laboratory practice, you obtained three different estimates for the same selectivity coefficient. How reliable are these estimates? Which one do you think is the most accurate?

7 Determination of solubility product and enthalpy of solution by conductometry

7.1 Check your previous studies

1. Physical quantities associated with electrolytic conduction (lecture course)
2. The Kohlrausch law of independent migration of ions (lecture course)
3. Equilibrium constant of heterogeneous processes (lecture course)
4. van't Hoff equation (lecture course)
5. Conductometry (this book, Section A.)

7.2 Theoretical background

The electrical resistance (R_{el}) of an electrolyte solution or its reciprocal, the conductance (G) can be easily measured in electrochemistry. Conductance itself is not a very useful property in physical chemistry as it depends on the geometry of the electrode used in the experiments. Therefore, it is necessary to determine the cell constant characteristic of the electrode and then use it to introduce the so-called specific conductivity (κ), which is no longer dependent on the electrode geometry, but only on the properties of the solution. The molar specific conductivity (Λ_m) is the ratio of the specific conductivity and the concentration (c):[20]

$$\Lambda_\mathrm{m} = \frac{\kappa}{c} \tag{7.1}$$

Friedrich Kohlrausch found that the molar specific conductivity of an infinitely dilute solution (Λ_0) is the sum of the individual contributions of anions and cations:

$$\Lambda_0 = \lambda^0_\mathrm{a}\nu_\mathrm{a} + \lambda^0_\mathrm{c}\nu_\mathrm{c} \tag{7.2}$$

Here ν_a and ν_c are the stoichiometric coefficients, λ^0_a and λ^0_c are the molar specific conductivities of an infinitely dilute solution for the cation and anion, respectively. This equation is valid for solutions in which there is only one kind of anion and one kind of cation. If there are more than two kinds of ions in the system, equation 2.2 contains more additive terms.

[20]It should be noted that the literature often includes a multiplication factor of 1000 in this formula. If you use SI units consistently, this is unnecessary. However, take extra care the correct SI units for all physical and chemical quantities during this laboratory practice.

The combination of the two equations makes it possible to estimate the concentration of a strong electrolyte from conductivity measurement: if the concentration is small enough, it can be calculated by dividing the experimentally measured specific conductivity with the molar specific conductivity of the infinitely dilute solution of the anion and cation given in equation 7.2.

From the concentration of a saturated solution of strong electrolyte with poor solubility in water, the equilibrium concentration of the ions in the solution, and thus, the K_{sol} solubility product of the $\mathrm{M}_p\mathrm{X}_q$ electrolyte can be calculated as follows:

$$K_{\mathrm{sol}} = [\mathrm{M}]^p[\mathrm{X}]^q \tag{7.3}$$

The solubility product is an equilibrium constant, so its temperature dependence is described by the van't Hoff equation:

$$\frac{\mathrm{d}\ln K_{\mathrm{sol}}}{\mathrm{d}T} = \frac{\Delta H^\circ}{RT^2} \tag{7.4}$$

In this formula, T the temperature, R is the gas constant, ΔH° is the standard enthalpy of solution. This equation is valid without exception, but the value of enthalpy in it may also depend on the temperature. If a process is studied in a sufficiently small temperature range to make the standard enthalpy constant, the following integrated form can be written:

$$\ln K_{\mathrm{sol}} = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \tag{7.5}$$

The new quantity in the equation is the ΔS° standard entropy of solution. In the usual van't Hoff plot, the natural-based logarithm of the equilibrium constant is plotted against the inverse temperature. If the enthalpy change and the entropy change do not depend on the temperature, then the points are a staright line with a slope proportional to ΔH° and an intercept proportional to ΔS°.

7.3 Practice procedures

During this laboratory practice, you will determine the solubility product of calcium carbonate at four temperatures and then estimate the standard enthalpy of solution from these data.

Turn the thermostat on and set the temperature to 30 ℃. While the thermostat warms up, perform the room temperature measurements.

Rinse the electrode of the conductometer several times (4 - 5) with water. For this purpose, use ultrapure deionized water with low conductivity ($\kappa < 1$ μS cm^{-1}), and not the usual deionized water. Ask the technician for ultrapure water. The same

careful washing procedure should be performed before every measurement during this laboratory practice to avoid contamination of the solutions when using the electrode.

Prepare a solution of calcium carbonate from solid calcium carbonate by immersing solid $CaCO_3$ into ultrapure deionized water (the solution should be cloudy). The conductivity of this solution will be measured at each temperature.

First, measure the conductance of the ultrapure deionized water (G_{water}) and record it together with the temperature of the solution. These data will later be needed to correct the measured conductance values.

In order to obtain the cell constant, measure the conductance of 0.0100 mol dm^{-3} KCl solution (G_{KCl}), and record it along with the temperature.

Then measure the conductance of the saturated calcium carbonate solution at room temperature. Wait for the measured conductance value to stabilize. Do not forget to record the temperature either.

Next, measure the conductance of the ultrapure deionized water and the saturated calcium carbonate solution by placing the beaker with the solutions in the 30 ℃-thermostat. In your notebook, record the temperature value displayed by the sensor of the electrode rather than the value set on the thermostat. Then set the thermostat to 40 ℃, wait until this temperature is reached, re-measure the conductivity and temperature of the ultrapure deionized water and the saturated calcium carbonate solution as well. Finally, do the same after setting the thermostat to 50 ℃.

When you are done with all your measurements, reset the thermostat to 30 ℃ to help the next student.

7.4 Evaluation

1. Calculate the cell constant (C) of your electrode. To do this, you will need the specific conductivity of the 0.0100 mol dm^{-3} KCl solution (κ_{KCl}), the conductance measured for this solution in your instrument (G_{KCl}) and the conductance of ultrapure water (G_{water}). You can use the following formula:

$$C = \frac{\kappa_{\text{KCl}}}{G_{\text{KCl}} - G_{\text{water}}} \tag{7.6}$$

2. Calculate the specific conductivity (κ) of the saturated calcium carbonate solution at each temperature from the conductance (G) values. For these calculations, you need the cell constant (C) and the conductance of ultrapure water (G_{water}):

$$\kappa = C(G - G_{\text{water}}) \tag{7.7}$$

3. Determine the molar specific conductivity of calcium and carbonate ion in infinite dilution at each measured temperature. To do this, use the following equations:

$$\lambda^0 = a + bT + cT^2 \tag{7.8}$$

Constants for calcium ion: $a = 570.3$ S cm^2 mol^{-1}, $b = -5.678$ S cm^2 mol^{-1} K^{-1} and $c = 0.01397$ S cm^2 mol^{-1} K^{-2}. Constants for carbonate ion: $a = 735.6$ S cm^2 mol^{-1}, $b = -7.157$ S cm^2 mol^{-1} K^{-1} and $c = 0.01730$ S cm^2 mol^{-1} K^{-2}.

4. Calculate the concentration of the saturated calcium carbonate solution at each temperature. Pay close attention to the units used in this equation.:

$$c = \frac{\kappa}{\lambda^0_{\text{Ca}^{2+}} + \lambda^0_{\text{CO}_3^{2-}}} \tag{7.9}$$

5. Calculate the solubility product of calcium carbonate at each temperature.

6. Give all your data in the form of Table 7.1. You can use more convenient units if you wish (*e.g.* μS instead of S, mmol dm^{-3} instead of mol dm^{-3}, or mS cm^{-1} instead of S m^{-1}).

Table 7.1: Measured and calculated conductometric data

T (K)	G (S)	G_{water} (S)	κ (S m^{-1})	$\lambda^0_{\text{Ca}^{2+}}$ (S m^2 mol^{-1})	$\lambda^0_{\text{CO}_3^{2-}}$ (S m^2 mol^{-1})	c (mol dm^3)	K_{sol}
...	...	...	...	...	...	...	...

7. Plot the $\ln K_{\text{sol}}$ values as a function of $1/T$. Determine the standard enthalpy of solution for calcium carbonate from the figure.

7.5 Advanced discussion points

1. Why is correction with G_{water} necessary in conductometric measurements carried out in aqueous solutions?

2. The molar specific conductivity of strong electrolytes – as described in one of the Kohlrausch laws – depends on the concentration. Give the mathematical equation that describes this dependence. During this laboratory practice, why is this dependence neglicted?

3. How could you deduce equation 7.5 from basic thermodynamic functions, without the use of equation 7.4 (*i.e.* the van't Hoff equation)?

4. Observe how the conductance of water depends on the temperature. Suggest an explanation for your observations.

5. Why is it unnecessary to measure the C cell constant at each temperature?

8 Determination of acid dissociation constant of a weak acid by pH-potentiometry

8.1 Check your previous studies

1. Electrode potential and its definition (lecture course)
2. Nernst equation (lecture course)
3. Definition of pH (lecture course)
4. Potentiometric measurements (this book, Section C.)
5. Relationship between equilibrium constants given by activities and concentrations (this book, Section E.)

8.2 Theoretical background

For the experimental determination of equilibrium constants defined by concentrations, the equilibrium concentration of at least one component must be measured. The reliability of the determination generally improves if more than one component is measured, but this is not necessary because the measurement of one equilibrium concentration is enough to calculate all other concentrations from the balance equations.

These principles are easy to apply to describe acid-base titrations. If a hydrochlodic acid solution with V_0 initial volume and concentration c_a is titrated with a NaOH solution of concentration c_b, then, after the addition of titrant with a volume of V_b, the concentrations of all four ions in the solution (sodium ion, chloride ion, hydrogen ion, and hydroxide ion) present can be given using three different types of equations:

1. *Mass balance equations*: sodium and chloride ions are not involved in any chemical reactions, so only dilution should be taken into account when calculating their concentrations:

$$[\mathrm{Cl}^-] = c_\mathrm{a}\frac{V_0}{V_0 + V_\mathrm{b}} \tag{8.1}$$

$$[\mathrm{Na}^+] = c_\mathrm{b}\frac{V_\mathrm{b}}{V_0 + V_\mathrm{b}} \tag{8.2}$$

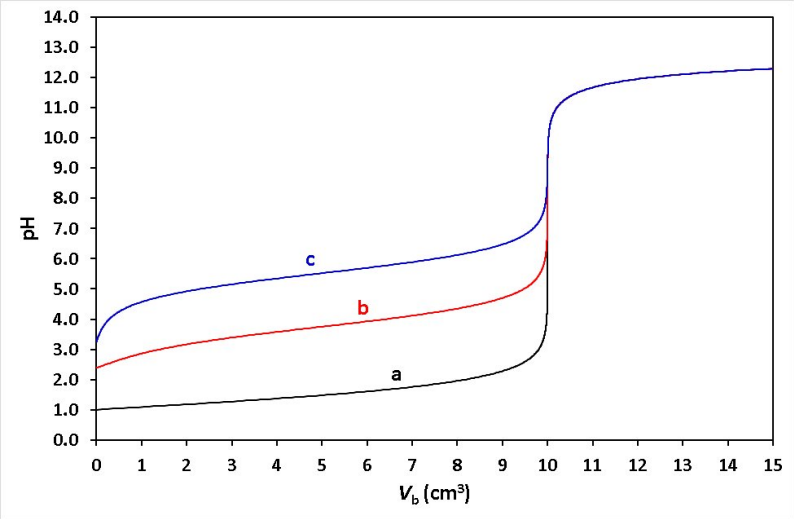

Figure 8.1: Typical titration curves. $V_0 = 10{,}0$ cm^3; $c_a = 0{,}10$ mol dm^{-3}; $c_b = 0{,}10$ mol dm^{-3}; titrant: Strong base; titrated substance: strong acid (a), weak acid $K_d = 1,8 \cdot 10^{-4}$ (b); weak acid $K_d = 3,0 \cdot 10^{-6}$ (c)

2. *Charge balance*: since the solution is prepared by mixing electrically neutral components, the mixed solution must also be neutral:

$$[\mathrm{Na^+}] + [\mathrm{H^+}] = [\mathrm{Cl^-}] + [\mathrm{OH^-}] \tag{8.3}$$

3. *Equilibrium constant(s)*: The only equilibrium process in the solution is the self-dissociation of water, which can be characterized by the ion product of water:

$$K_w = [\mathrm{H^+}][\mathrm{OH^-}] \tag{8.4}$$

Thus, this is a system of four equations with four unknown equilibrium concentrations, from which the unknown equilibrium concentrations can be determined. In the above case, this is particularly easy as Equations 18.2 and 8.2 contain only one equilibrium concentration, so these are known without any separate operations. From Equation 8.4, the equilibrium concentration of hydroxide ion can easily be expressed ($[\mathrm{OH^-}] = K_w/[\mathrm{H^+}]$). Substituting this into Equation 8.3 yields a new formula that contains only $[\mathrm{H^+}]$ as an unknown:

$$c_b \frac{V_b}{V_0 + V_b} + [\mathrm{H^+}] = c_a \frac{V_0}{V_0 + V_b} + \frac{K_w}{[\mathrm{H^+}]} \tag{8.5}$$

This equation makes it possible to calculate the points of a titration curve, which shows pH as a function of V_b. Sample titration curves are displayed in Figure 8.1.

Hydrogen ion concentration is usually easy to determine with a pH meter. By definition, the pH is the negative ten-based logarithm of the activity of hydrogen ion (a_{H}), and (using the activity coefficient γ_{H}) connected to the concentrations in a dilute aqueous solution as follows:

$$\mathrm{pH} = -\lg a_{\mathrm{H}} = -\lg\left(\gamma_{\mathrm{H}}\frac{m_{\mathrm{H}}}{m^{\circ}}\right) = -\lg\left(\gamma_{\mathrm{H}}\frac{[\mathrm{H}^{+}]}{\rho m^{\circ}}\right) \tag{8.6}$$

In this equation, m_{H} is the molality of hydrogen ion, m° is the standard molality, ρ is the density of water (the solution is dilute, so it is equal to the density of the solution). Using a new parameter $\iota = \rho m^{\circ}/\gamma_{\mathrm{H}}$, the concentration of hydrogen ion can be given from the pH as follows:

$$[\mathrm{H}^{+}] = \iota 10^{-\mathrm{pH}} \tag{8.7}$$

This formula can be substituted into Equation 8.5. Based on the characteristics of titrations, two cases are distinguished. Before the equivalence point, the solution is acidic so $[\mathrm{H}^{+}] \gg K_{\mathrm{w}}/[\mathrm{H}^{+}]$. Thus, after some rearrangement, the following formula is obtained:

$$(V_0 + V_{\mathrm{b}})10^{-\mathrm{pH}} = \frac{c_{\mathrm{a}}}{\iota}V_0 - \frac{c_{\mathrm{b}}}{\iota}V_{\mathrm{b}} \tag{8.8}$$

The left side of this equation is called the *Gran function of the acidic part*: its value can always be calculated durng the titration from the well-known pH, V_0 and V_{b} values. The Gran function of the acidic part plotted as a function of titrant volume (V_{b}) gives a straight line with the x axis intercept equal to the volume of the equivalence point (V_{eq}). The concentration of the titrant (base) divided by the absolute value of the slope of the straight line gives the value of ι.

The same rearrangement can be done for the basic data points after the equivalence point, when $K_{\mathrm{w}}/[\mathrm{H}^{+}] \gg [\mathrm{H}^{+}]$. This is called the *Gran function of the basic part*:

$$(V_0 + V_{\mathrm{b}})10^{\mathrm{pH}} = \frac{\iota c_{\mathrm{b}}}{K_{\mathrm{w}}}V_{\mathrm{b}} - \frac{\iota c_{\mathrm{a}}}{K_{\mathrm{w}}}V_0 \tag{8.9}$$

When the left side of this Gran function is plotted against the titrant volume (V_{b}), another straight line can be obtained, which gives a new estimate of the volume of the equivalence point (V_{ekv}) as x axis intercept. The slope of the line divided by the base concentration and ι gives the ion product of water (K_{w}).

The same derivation can also be performed when titrating a solution of a weak acid (HA) with NaOH. In this case, there is one more equilibrium concentration, since the undissociated form of the weak acid is also present in significant amounts.

The first of the conservation equations (18.2) is therefore modified:

$$[\mathrm{HA}] + [\mathrm{A}^-] = c_\mathrm{a} \frac{V_0}{V_0 + V_\mathrm{b}} \tag{8.10}$$

Equation 8.2 remains unchanged. In the charge cosnervation equation (Equation 8.3), A^- should be written instead of chloride ion:

$$[\mathrm{Na}^+] + [\mathrm{H}^+] = [\mathrm{A}^-] + [\mathrm{OH}^-] \tag{8.11}$$

Equation 8.4 (ionic product of water) can be given in the same form for a weak acid titration, but one more equilibrium constant needs to be taken into consideration including the acid dissociation constant of the weak acid:

$$K_\mathrm{d} = \frac{[\mathrm{H}^+][\mathrm{A}^-]}{[\mathrm{HA}]} \tag{8.12}$$

Altogether, there are five equilibrium concentrations and five equations. After expressing the values of four concentrations similarly as in the previous derivations, the formula analogous to 8.5 takes the following form:

$$\frac{c_\mathrm{b} V_\mathrm{b}}{V_0 + V_\mathrm{b}} + [\mathrm{H}^+] = \frac{K_\mathrm{d}}{[\mathrm{H}^+] + K_\mathrm{d}} \frac{c_\mathrm{a} V_0}{V_0 + V_\mathrm{b}} + \frac{K_\mathrm{w}}{[\mathrm{H}^+]} \tag{8.13}$$

This equation is suitable for determining the points of a weak acid–strong base titration curve.[21] Figure 8.1. displays two titration curves for weak acids with different dissociation constants.

Interestingly, the *Gran function of the acidic part* is simpler than for strong acid–strong base titration since – except for the first points of titration – not only $[\mathrm{H}^+] \gg K_\mathrm{w}/[\mathrm{H}^+]$ but also $[\mathrm{Na}^+] \gg [\mathrm{H}^+]$ holds:

$$V_\mathrm{b} 10^{-\mathrm{pH}} = \frac{K_\mathrm{d} c_\mathrm{a}}{\iota c_\mathrm{a}} V_0 - \frac{K_\mathrm{d}}{\iota} V_\mathrm{b} \tag{8.14}$$

Plotting the left side as a function of volume (V_b) gives a straight line, whose intercept with the x axis is the volume of the equivalence point (V_ekv). K_d can also be determined as the product of the absolute value of the slope and ι.

The *Gran function of the basic part* can also be derived. Its mathematical form is the same as for the strong acid–strong base titration (Equation 8.9).

[21] If the unknown hydrogen ion concentration is sought for a known V_b in this formula, a cubic equation results. It is a lot easier to calculate the volume of titrant necessary to reach a set hydrogen ion concentration.

8.3 Practice procedures

Measure 20.0 cm^3 of 0.1 mol dm^{-3} hydrochloric acid solution into a beaker. Fill the burette with NaOH of known concentration. Place the magnetic stirring bar and the pH electrode in the solution, then place the beaker on the magnetic stirrer so that you can add the titrant from the burette without moving the beaker. The pH electrode is a combined electrode. It encorporates the pH sensitive electrode, and a (usually Ag/AgCl/KCl) reference half-cell. Find the ceramic plug (frit) that couples the reference half-cell to the sample. This must be immersed in the sample solution as well.

Perform the titration by adding 1.00 cm^3 NaOH solution in each step. Wait for the electrode signal to stabilize (about half a minute) and then write down the pH. Continue the titration until there are at least 6 points with pH readings greater than 7.

Titrate 20.0 cm^3 of the 0.05 mol dm^{-3} solution of the weak acid with NaOH solution, but use 0.50 cm^3 increments of the titrant at this time.

For both titrations, perform at least one parallel measurement.

8.4 Evaluation

1. Collect the data for each titration in the format specified in Table 8.1. For the acidic points of the strong acid titration, calculate Gran function 8.8, and for the acidic points of the weak acid titration, calculate Gran function 8.14. For the basic points of both titrations, calculate Gran function 8.9.

Table 8.1: Titration data. V_0 = 20.0 cm^3, c_a = ... mol dm^{-3}, c_b = ... mol dm^{-3}

V_b (cm^3)	pH pH	acidic Gran function (cm^3)	basic Gran function (cm^3)
...	...	...	...

2. For each titration, plot the measured pH as a function of the volume of titrant. Show all the titration curves in a single figure.

3. For each titration, plot the Gran functions of the acidic and basic parts as a function of the volume of titrant (but the Gran function of the acidic part should be given only for acidic pH points and the Gran function of the basic part only for alkaline pH points). Find the linear section in these figures, fit a straight line, and determine the x axis intercepts and slopes of the lines.

4. The x axis intercepts give the volumes of the equivalence points for all titrations. Using these volumes, calculate the exact concentrations of the NaOH

titrant and the titrated weak acid as well (it is no a coincidence that 0.1 mol dm^{-3} was given earlier as acid concentration: the low number of significant figures given reflects that this is only an approximate value.)

5. Calculate the value of ι from the slope of the Gran function of the acidic part of the strong acid–strong base titration.

6. Calculate the ionic product of water (K_w) from the slope of the Gran function of the basic part of the strong acid–strong base titration.

7. Calculate the acid dissociation constant of the wak acid (K_d) from the slope of the Gran function of the acidic part of the weak acid–strong base titration.

8.5 Advanced discussion points

1. What is the reason why pH cannot be measured reliably close to the equivalence point of the titrations?

2. What is the advantage of Gran plots compared to the use of acid-base indicators?

3. How can you explain that the Gran function of the basic part is the same for the strong acid–strong base and weak acid–strong base titrations?

4. Both the acidic and the basic points of the same titration can be used to estimate the same equivalence point using Gran plots. There is often a small but significant difference between the two equivalence points. What could be the reason for this?

5. The derivation of the equations assumes that the activity coefficient of hydrogen ion does not change during the titrations. The activity coefficient is mainly influenced by ionic strength. How does the ionic strength of the solution change in the case of a strong acid–strong base and a weak acid–strong base titration? What changes in the experimental design could keep the ionic strength (and thus the activity coefficient) constant?

9 Determination of the dissociation constant of a pH-indicator

9.1 Check your previous studies

1. Use of indicators in chemistry (lecture course)
2. Definition of pH (lecture course)
3. Spectrophotometry and Beer's law (this book, Section B.)
4. Potentiometric measurements (this book, Section C.)
5. Relationship between equilibrium constants given by activities and concentrations (this book, Section C.)

9.2 Theoretical background

Indicators are organic dye molecules that are weak acids or bases. At least one of the two different forms (acidic and basic) has a very intense color. The pH = pK ±1 of the indicator (also referred to as the transition range of the indicator) shows a mixture of the color of the acidic and basic form. At more acidic pH values, only the acidic form, and at more basic pH values, only the basic form of the indicator exists. Many different indicators are known with different pK values, so they can cover the entire pH range.

Like for other weak acids, the pK of an indicator is the ten-fold negative logarithm of its acid dissociation constant, K_a. If the indicator is a weak acid, its protonated form is denoted by HInd, and its deprotonated form is Ind^-. The activity-based definition of and the definition of K_a is as follows:

$$K_\mathrm{a} = \frac{a_{\mathrm{H}^+} a_{\mathrm{Ind}^-}}{a_{\mathrm{HInd}}} \tag{9.1}$$

If the indicator is a weak base, the same formula can be used, only the Ind form will be neutral, and HInd^+ will be positively charged.

In most cases, a sufficiently accurate approximation is that the activity coefficient of HInd and Ind^- is the same in the solution, so the ratio of activities equals to the ratio of molar concentrations. With this approximation, equation 9.1 can be converted to the following form:

$$K_\mathrm{a} = \frac{a_{\mathrm{H}^+} [\mathrm{Ind}^-]}{[\mathrm{HInd}]} \tag{9.2}$$

The activity of hydrogen ion in a solution can be measured relatively easily with a suitable glass electrode and a pH meter. For the determination of the dissociation constant, it would be enough to measure these data in proper experimental design (see *8. Determination of acid dissociation constant of a weak acid by pH-potentiometry*). However, several measurements by different methods generally increase the reliability of the result as well as the scientific value of the determination. In this case, due to the intense color of the indicator, it is obvious that the ratio of the acidic and basic forms is determined by spectrophotometry using absorbance values at two different wavelengths.

The derivation presented here uses the general case when both the acidic and the basic forms absorb at both wavelengths. In this case – based on Beer law – absorbance values at the two wavelengths is given by the following formulas:

$$A_1 = \epsilon_{1,\mathrm{Ind}}[\mathrm{Ind}^-]l + \epsilon_{1,\mathrm{HInd}}[\mathrm{HInd}]l \tag{9.3}$$

$$A_2 = \epsilon_{2,\mathrm{Ind}}[\mathrm{Ind}^-]l + \epsilon_{2,\mathrm{HInd}}[\mathrm{HInd}]l \tag{9.4}$$

In these equations, $\epsilon_{1,\mathrm{Ind}}$ is the molar absorbance of the basic form at wavelength 1, $\epsilon_{2,\mathrm{Ind}}$ is the molar absorbance of the basic form at wavelength 2, $\epsilon_{1,\mathrm{HInd}}$ is the molar absorbance of the acidic form at wavelength 1, and $\epsilon_{2,\mathrm{HInd}}$ is the molar absorbance of the acidic form at wavelength 2.

$[\mathrm{Ind}^-]$ and [HInd] concentrations can be determined from the two equations by knowing the molar absorbances and the measured absorbances. Actually, we do not need them alone, only for their ratio:

$$\frac{[\mathrm{HInd}]}{[\mathrm{Ind}^-]} = \frac{A_2\epsilon_{1,\mathrm{Ind}} - A_1\epsilon_{2,\mathrm{Ind}}}{A_1\epsilon_{2,\mathrm{HInd}} - A_2\epsilon_{1,\mathrm{HInd}}} \tag{9.5}$$

Note that when calculating the concentration ratio of the two forms, you do not need to know the value of the optical path length (l). The only important thing is that l is unchanged during the experiment.

Equation 9.2 can be re-arranged as follows:

$$\frac{[\mathrm{HInd}]}{[\mathrm{Ind}^-]} = \frac{1}{K_\mathrm{a}} a_{\mathrm{H}^+} \tag{9.6}$$

From this equation, it follows that if we plot the $[\mathrm{HInd}]/[\mathrm{Ind}^-]$ values from the spectrophotometric measurements as a function of hydrogen ion activity, the slope of the resulting straight line is the reciprocal of the acid dissociation constant.

9.3 Practice procedures

Your teacher will select which indicator to perform the experiments with. You will find the stock solution of this indicator on your laboratory desk.

Use some analytical chemistry books or the Internet to search for literature data for the pK of the selected indicator. Select three pH values (separated by at least 0.4 pH units from each other) from table 9.1 describing the prepartion of Britton–Robinson buffer solutions that overlap with the transition range of your indicator. Prepare these three buffers in three beakers. If the volume of the solutions is less than 25 cm^3, add some distilled water to make the volume 25 cm^3. Measure the pH of the three buffer solutions with a pH meter.

Table 9.1: Preparation of Britton–Robinson buffer solutions. Add the given volume (in cm^3) of solution B (basic component) to 20.0 cm^3 of solution A (acidic component)

pH	V_B (cm^3)	pH	V_B (cm^3)	pH	V_B (cm^3)	pH	V_B (cm^3)
1.81	0.0	4.10	5.0	6.80	10.0	9.62	15.0
1.89	0.5	4.35	5.5	7.00	10.5	9.91	15.5
1.98	1.0	4.56	6.0	7.24	11.0	10.38	16.0
2.09	1.5	4.78	6.5	7.54	11.5	10.88	16.5
2.21	2.0	5.02	7.0	7.96	12.0	11.20	17.0
2.36	2.5	5.33	7.5	8.36	12.5	11.40	17.5
2.56	3.0	5.72	8.0	8.69	13.0	11.58	18.0
2.87	3.5	6.09	8.5	8.95	13.5	11.70	18.5
3.29	4.0	6.37	9.0	9.15	14.0	11.82	19.0
3.78	4.5	6.59	9.5	9.37	14.5	11.92	19.5

Pipette 1.00-1.00 cm^3 from the stock solution into three different 25.0 cm^3 volumetric flasks (labeled 1, 2, 3) and fill them up to the mark with the three different pH buffer solutions.

Pipette 0.30 cm^3, 0.60 cm^3 and 1.00 cm^3 indicator solution into three different 25.0 cm^3 volumetric flasks (labeled 4, 5, 6) and fill them up with 0.010 mol dm^{-3} hydrochloric acid solution. Similarly, pipette 0.30 cm^3, 0.60 cm^3 and 1.00 cm^3 indicator solution into three further 25.0 cm^3 volumetric flasks (labeled 7, 8, 9), then fill them up with 0.010 mol dm^{-3} NaOH solution.

Measure the spectrum of each of the nine prepared solutions between 350 and 700 nm.

9.4 Evaluation

1. Calculate the concentration of the indicator in all prepared solutions.

2. Plot the spectra of solutions 1, 2 and 3 in a single figure. Find the point at which all three spectra pass. This is called the izo(s)bestical point.

3. Plot the spectra of solutions 4, 5 and 6 in a diagram. Determine the absorption maxima of the acidic form of the indicator. Choose one of them for evaluation (λ_1).

4. Plot the spectra of solutions 7, 8 and 9 in a diagram. Determine the absorption maxima of the basic form of the indicator. Choose one of them for evaluation (λ_2).

5. From each of the nine spectra, determine the measured absorbance values at λ_1 and λ_2 wavelengths. Do this on the computer connected directly to the spectrophotmeter because otherwise this is more time consuming. Summarize your data in the format specified in Table 9.2.

Table 9.2: Measured pH and absorbance data. Indicator: ..., $\lambda_1 = \ldots$ nm, $\lambda_2 = \ldots$ nm

experiment number	c_{ind} (mol dm^{-3})	pH	A_1	A_2
...	...	...	...	...

6. Plot the absorbance values measured in solutions 4, 5 and 6 at both wavelengths as a function of the indicator concentration. Plot straight line through the dots starting from the origo and determine the $\epsilon_{1,\text{HInd}}$ and $\epsilon_{2,\text{HInd}}$ molar absorbances.

7. Plot the absorbance values measured in solutions 7, 8 and 9 at both wavelengths as a function of the indicator concentration. Plot straight line through the dots starting from the origo and determine the $\epsilon_{1,\text{Ind}}$ and $\epsilon_{2,\text{Ind}}$ molar absorbances.

8. Calculate the hydrogen ion activity from the pH values of solutions 1, 2 and 3. Use equation 9.5 to calculate the [HInd]/[Ind$^-$] ratio from the absorbance measurements.

9. Plot the [HInd]/[Ind$^-$] value as a function of hydrogen ion activity. Plot a straight line to the points crossing the origin and determine the K_{a} and pK for the indicator.

9.5 Advanced discussion points

1. What kind of error would the result be if the concentration of the indicator stock solution is witten incorrectly to its bottle?

2. The deviation of the three selected pH values from the pK of the indicator should not be large (± 1 range) so that the evaluation can be performed reliably. Why?

3. How could you determine the pK from absorbance measurements performed at one single wavelength?

4. What should be changed in the experiments and evaluation in order to avoid the need to measure molar absorbances in separate experiments?

5. At what wavelength is the absorbance measured to determine the concentration of the indicator without knowing the pH?

6. Check the Internet for the composition of the Britton–Robinson buffer. Why can it be used practically in the entire pH range?

7. Would it be possible to obtain the pK without knowing the concentration of the stock solution? How?

10 Measuring the viscosity of solutions with Ostwald viscometer

10.1 Check your previous studies

1. Viscosity (lecture course)
2. Electrolytic conduction (lecture course)
3. Measuring the density of a solution (this book, Section D.)

10.2 Theoretical background

By increasing the amount of a dissolved substance, certain parameters of the solution change proportionally. For example, in the case of colored solutes, it is easy to see with the naked eye that the higher the concentration of the solution, the more intense the color is.

The flow properties of the solutions also change with increasing the amount of solute. The study of the flow matter is called *rheology*. From a rheological point of view, materials can be grouped in a number of ways, but during this laboratory practice, we only deal with ideally viscous (so-called Newtonian) fluids.

If there is an ideal fluid between two parallel walls with A area and y distance, and one wall is moved relative to the other one at a given speed (v_x) parallel to the plane of the wall, then a permanent work should be exerted to overcome the friction forces and to maintain the desired speed (Figure 10.1).

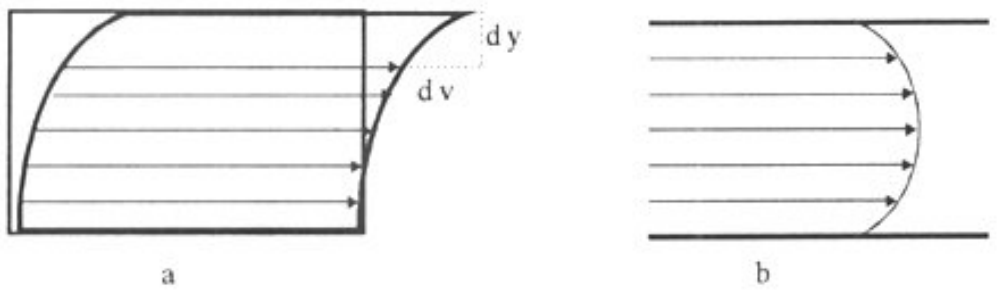

Figure 10.1: (a) Flow of a Newtonian fluid, (b) laminar flow in a capillary

The F friction force is proportional to the size of the moving surface (A), and the ratio of the v_x speed to the y distance of the two surfaces. This relationship is expressed by the *Newton equation*:

$$F = -\eta A \frac{\mathrm{d}v_x}{\mathrm{d}y} \tag{10.1}$$

Here, the η proportionality factor is the internal friction coefficient, *i.e.* the dynamic viscosity of the fluid. The sign is negative because the friction force is opposite to the fluid velocity vector. Thus, internal friction is the force required to move two layers of unit area at a unit speed. On the surface of the walls, the medium does not flow, so the friction occurs between the neighbouring layers of the fluid, each layer being slowed down by the adjacent layer. The unit of η is Pa s (formerly, the unit poise (P) has been used, 1 P = 0.1 Pa).

Kinematic viscosity is the ratio of the dynamic viscosity to the density of the medium (ρ). Its unit is $\mathrm{m}^2\ \mathrm{s}^{-1}$.

The flow of liquids in capillaries is shown in Figure 10.1. Since the velocity of the adhesive layers (called Prandtl-layers) on both sides of the capillary is 0, the flow rate will be at the maximum in the center of the capillary. In the case of laminar (layered) flows, the movement of the fluid can be considered as the movement of parallel layers, where the layers do not mix with each other. From the Newton equation, the Hagen–Poiseuille law can be derived, which is valid for a fluid flow in a r radius and l length capillary. The equation gives the volume (V) of liquid moving during t time as a result of a Δp difference in pressure:

$$V = \frac{1}{\eta} \frac{\pi r^4 \Delta p t}{8l} \tag{10.2}$$

Thus, for Newtonian liquids, there is a linear correlation between the flow velocity and hydrostatic pressure. The viscosity of dilute solutions is usually referred to the viscosity of the pure solvent at the same temperature. This ratio is called the relative viscosity of the solution: $\eta_r = \eta/\eta^0$ where η is the viscosity of the solution and η^0 is the viscosity of the pure solvent. The so-called specific viscosity is also used to characterize the viscosity of solutions. This is the difference of viscosity for the solution and the solvent, relative to the viscosity of the pure solvent:

$$\eta_{\mathrm{sp}} = \frac{\eta - \eta^0}{\eta^0} = \eta_r - 1 \tag{10.3}$$

As can be seen from the formula, the specific and relative viscosity values are dimensionless numbers.

The viscosity of an ideal fluid mixture can be calculated from the viscosities of each components by weighting with the molar fractions:

$$\eta = x_1\eta_1 + x_2\eta_1 + \cdots = \sum x_i\eta_i \tag{10.4}$$

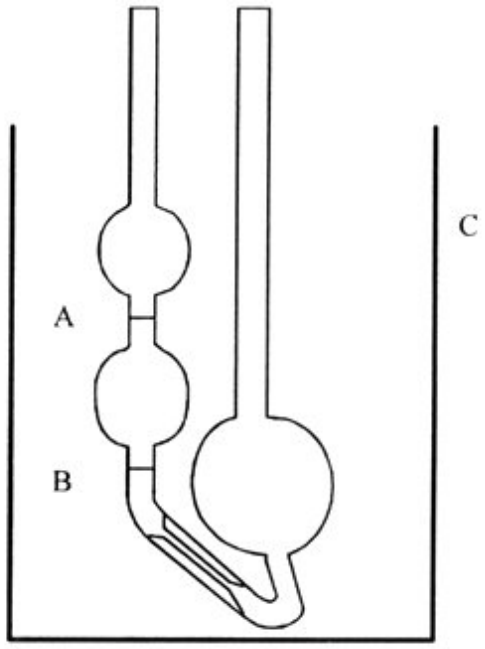

Figure 10.2: The construction of the Ostwald viscometer. A and B: signs for flow-out time measurement, C: tempering beaker (liquid bath - during your practice, air replaces the liquid bath)

In real mixtures, *e.g.* in aqueous solutions of electrolytes and nonelectrolytes, this relationship is usually not valid. In dilute solution, the electrolyte increases the viscosity only to a small extent, but in their concentrated solutions, the viscosity can be much higher as it is for the solvent. This is partly due to the fact that the electrolyte transforms the structure of the water through its solvation and, on the other hand, the size of the ions is relatively large because of the solvate shell. In the case of a non-electrolyte dissolved in water, the increase in the size of the ion caused by the solvation is negligable, but – due to the disruption of the water structure – the viscosity of the solution is also increased with increasing concentration.

During the laboratory practice, we use the Ostwald viscometer (see Figure 10.2) based on the Hagen–Poiseuille equation. In this equipment, the V volume of fluid is sucked over the "sign A" in the capillary, and then the t flow-out time is measured which is required for the V volume of fluid in an r radius and l length capillary to flow from "sign A" to "sign B" in a $\Delta p = \rho V g h$ difference in pressure.

From Equation 10.2, the viscosity of the liquid can theoretically be calculated. However, since accurate results require the accurate knowledge of the device's dimensions, the viscometer is primarily used for comparative measurements: when η_1 is the well-known viscosity of a reference solution and η_2 is the unknown viscosity of an unknown solution densities (ρ_1 and ρ_2) and flow-out times of the two fluids (t_1

and t_2) can be used to determine the unknown viscosity:

$$\frac{\eta_2}{\eta_1} = \frac{\rho_2 t_2}{\rho_1 t_1} \tag{10.5}$$

Due to the high temperature dependence of the viscosity, it is important to keep the temperature constant by using a liquid bath or be keeping the air temperature constant.

10.3 Practice procedures

During the laboratory practice, you will measure the viscosity of various aqueous solutions and mixtures with a Ostwald viscometer.

(1) *Determination of an unknown concentration by viscometry:* Prepare a series of solutions of 50.0-50.0 cm^3 with the following relative concentrations: 5, 10, 25 and 75% (where the concentration of the stock solution is 100%). Use deionized water for the dilution. Use pipettes and volumetric flasks. Determine the density of all the diluted solutions, the stock solution and water.

Use the Ostwald viscometer to measure the flow-out time of all solutions (including the stock solution) and of water as well. Start your measurements with the most dilute solution progressing toward the more concentrated solutions. After rinsing the device with distilled water, rinse it with a small portion of the new solution as well. The flow-out time for each solution should be determined from three parallel measurements when youe measure the concentration dependence, and then averaged for each solution. Be sure to use the same volume of samples for the measurements, because at different volumes, the hydrostatic pressure will be different, which can corrupt the measurement. Measure the temperature of the laboratory and write it down into your laboratory notebook.

Measure the viscosity and density of the solution of unknown concentration as well. (This solution is only unknown as its *concentration* is not known. The solute in it is the same as for the stock solution!)

(2) *Examining different alcohols:* Measure the viscosity and density of alcohol solutions with different lengths of alkyl chains. Measure and note the laboratory temperature as well.

(3) *Investigation of dissolved electrolyte and non-electrolyte solutions:* Study the effect of dissolved electrolytes (NaCl, NH_4Cl) and non-electrolyte (glucose, urea) on viscosity by measuring 1.0 mol dm^{-3} concentration aqueous solutions of these materials.

Table 10.1: Viscosity of water at different temperatures around room temperature

temperature (℃)	20	25	30
η (Pa s)	$1.003 \cdot 10^{-3}$	$0.891 \cdot 10^{-3}$	$0.797 \cdot 10^{-3}$

10.4 Evaluation

1. From the measured flow-out times for the solutions with different concentrations as well as the measured density values, use equation 10.5 to determine the viscosities of all solutions. This will require a reference solution with known viscosity. Use deionized water as reference solution. The temperature-dependent viscosity values of water are given in Table 10.1. If the temperature of your measurements does not match one of the temperatures in the table, use linear interpolation to calculate the viscosity of water.

2. Calculate the viscosity–concentration calibration curve from the viscosity values calculated for different concentrations of solutions.

3. Determine the exact concentration of the unknown solution based on the calibration curve.

4. From the flow-out times for alcohol solutions with different lengths of alkyl chain and the measured density values, use Equation 10.5 to determine the viscosity of all alcohols. To do this, use the data for deionized water again as a reference.

5. Plot both the viscosity and the density values for the different alcohol solutions as a function of their alkyl chain length.

6. From the flow-out times for different electrolyte and non-electrolyte solutions in the same concentration (1.0 mol dm^{-3}), and from the measured density values, use Equation 10.5 to determine the viscosity of all electrolyte and non-electrolyte solutions. To do this, use the data for deionized water again as a reference.

7. Compare the viscosity values of the different electrolyte and non-electrolyte solutions in the same concentration (1.0 mol dm^{-3}).

10.5 Advanced discussion points

1. How does the viscosity of a solution change as a function of concentration? How does the density of a solution change as a function of concentration? Why? What could this dependence be used for?

2. How does the viscosity and density of alcohols depend on the length of the alkyl chain? Why? What could you use this dependency for?

3. How does a dissolved electrolyte or non-electrolyte change the viscosity of a solution? What general conclusion could you draw from the data?

11 Determination of the enthalpy of neutralization by calorimetry

11.1 Check your previous studies

1. The definition of internal energy, enthalpy, heat capacities at constant volume and constant pressure (lecture course)

2. Calorimetry (lecture course)

11.2 Theoretical background

Calorimetric measurements aim to determine the heat transfer of chemical reactions or phase transitions. Heat is an exceptional form of energy because, unlike all other forms, it cannot be transformed into other forms of energy entirely. In a process at constant volume in a cosed system, the heat of the reaction is equal to the change in internal energy (ΔU). At constant pressure in a closed system, the heat of the reaction is equal to the change in enthalpy (ΔH). It is much more common to carry out experiments at constant pressure in chemistry, therefore enthalpy is a more useful property than internal energy. When 'heat of reaction' is mentioned casually, that usually means enthalpy change. A process is termed *exothermic* if it releases heat into the surroundings, whereas heat is trasported from the surroundings into the system in an *endothermic* process.

The SI units of energy, therefore heat as well, joule (J = kg m^2 s^{-2}). Previously, the units calorie (cal) was also in widespread use, it can be converted into joule using the proportianlity 1 cal = 4.184 J. The heat required for raising a body's temperature by 1 K is called heat capacity (C) and has the units of J K^{-1}. Because heat is not a state function, two different versions of heat capacity is commonly used: heat capacity at constant volume (C_V) and heat capacity at constant pressure (C_p). The former is the partial derivative of internal energy (U) with respect to temperature at constant volume, the latter is the partial derivative of enthalpy (H) with respect to temperature at constant pressure. These heat capacities are extensive quantities. To obtain physical properties that are characteristic of the material, heat capacities are often divided by another extensive property. Specific heat (c_V and c_p) is the ratio of the heat capacity and mass of an object, it has the units J kg^{-1} K^{-1}. Molar heat capacities ($C_{V,\mathrm{m}}$ and $C_{p,\mathrm{m}}$) are obtained by dividing heat capacities by the amount of substance and have the units of J mol^{-1} K^{-1}.[22]

[22]Notice that the same units are used for molar entropy and the universal gas constant.

A calorimeter is isolated from it surroundings so that heat exchange cannot occur (at least the heat exchange is slow compared to the measurements). Therefore, if a process is carried out in a calorimeter, its heat will raise the temperature of the system (i.e. the calorimeter) only. If the heat capacity of the calorimetric system (C_{sys}) is known, the heat of the process can be deduced from measuring the temperature change.

The heat capacity of the calorimetric system is usually composed of two additive terms. The first is the heat capacity of the fixed parts of the (empty) calorimeter (C_{fix}), the second is the heat capacity of the substances added to it (C_{add}). C_{fix} is the same in every measurement, whereas C_{add} needs to be calculated for each experiment seperately. As already mentioned, the heat capacity of the calorimetric system is than calculated by simple addition:

$$C_{\text{sys}} = C_{\text{fix}} + C_{\text{add}} \tag{11.1}$$

The calorimeter used in this practice is a very simple device: a commercially available thermos bottle with some extra fittings (Figure 11.1.). It is composed of two parts: the lower part B is the actual calorimeter, while the upper unit A of is a removable cap that makes it possible to add materials and has inlet holes for the thermometer and a stirring device. The device is not entirely closed because of the intentionally loose fittings: the pressure always remains identical to the atmospheric pressure in it. Therefore, strictly speaking, enthalpy changes are measured in this way.[23]

The heat capacity of the substances added to the calorimeter can be calculated from the specific heats and the masses of the added materials. However, the heat capacity of the fixed parts must be determined experimentally. One possible way to do this is to carry out a chemical reaction in the calorimeter for which the enthalpy of reaction is known. Another possibility, which will be used in this practice, is to prepare a thermally imbalanced system in the calorimeter where the temperature of the different parts is known before homogenization begins and measuring the final temperature. A simple way to do this is to add water (mass m_1) to the calorimeter, let it reach thermal equilibrium with the device and measure their common temperature (T_{cold}), then add a known amount (mass m_2) of hotter water (T_{hot}). The calorimeter reaches a new thermal equilibrium, the temerature of which is measured (T_{final}). Let c_{w} be the specific heat of water. There is no chemical reaction in this system, and it is isolated from the surroundings, so the sum of the enthalpy changes of the parts

[23] In solution processes, the typical volume changes are really tiny because liquids are practically incompressible. Therefore, changes in enthalpy and changes in internal enegry are not very much different, the difference between the two quantitites is often smaller than experimental errors.

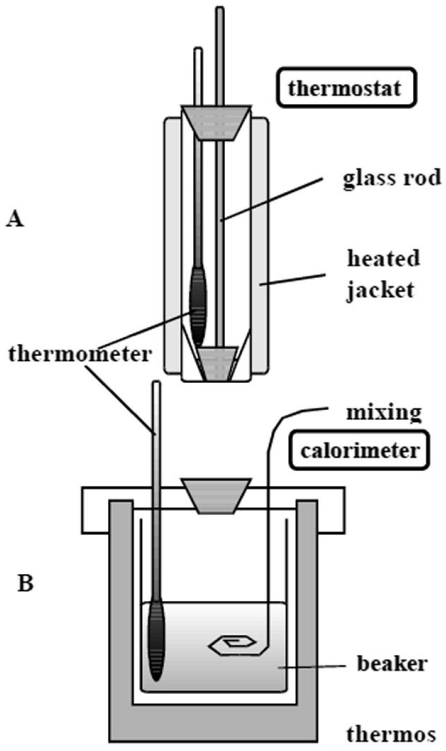

Figure 11.1: Scheme of the calorimeter used in this practice

of this system is zero:

$$C_{\text{fix}}(T_{\text{final}} - T_{\text{cold}}) + m_1 c_{\text{w}}(T_{\text{final}} - T_{\text{cold}}) + m_2 c_{\text{w}}(T_{\text{final}} - T_{\text{hot}}) = 0 \tag{11.2}$$

From the measured data, C_{fix} is calculated by rearranging the above equation:

$$C_{\text{fix}} = m_2 c_{\text{w}} \frac{T_{\text{hot}} - T_{\text{final}}}{T_{\text{final}} - T_{\text{cold}}} - m_1 c_{\text{w}} \tag{11.3}$$

Neutralization reactions are chemical processes between acids and bases. It is an interesting fact that their enthalpy of neutralization in dilute solution does not depend on the identities of the acids and bases as long as they are both strong. This observation is interpreted by the fact that the actual chemical reaction taking place under such conditions is always the reaction between H^+ and OH^- ions, and the rest of the ions remain unchanged:

$$H^+ + OH^- = H_2O \tag{11.4}$$

11.3 Practice procedures

During this practice, you will determine the enthalpy change of neutralization using the reaction between dilute solutions of hydrochloric acid and sodium hydroxide.

Turn on the thermostat at your workstation and begin heating it up to 65 ℃. Put some water in it in a beaker or flask: you will use this for determining the heat capacity of the fixed parts of the calorimeter. It will take considerable time until the thermostat reaches the desired temperature, so first you will do the measurements on the neutralization reaction and then return to the heat capacity determination.

In your mesaurements, a plastic cup will be used as a reaction vessel. Be careful, there are several such cups at your workstation and their mass is different. Weigh one empty cup (m_{cup}) and then add 40,0 cm^3 of 1.00 mol dm^{-3} hydrochloric acid to it. Weigh the cup again and record the mass of the hydrochloric acid solution (m_{HCl}). Place the cup into the thermos flask, put the lid on, and begin monitoring the temperature. Read the temperature every minute until it stabilizes (the last two readings are within 0,1 ℃). The stabilized temperature is denoted T_{before} in your calculations. Prepare 40,0 cm^3 of 1.00 mol dm^{-3} sodium hydroxide solution. Measure its temperature quickly (T_{NaOH}), then add it into the calorimeter. Begin monitoring the temperature again: read it in every minute until the values begin to decrease. The highest temperature reading is denoted T_{after} during the evaluation. Take the lid off, and weigh the cup with the total amount of solution in it (m_{total}).

Repeat the whole procedure twice so that you have three parallel measurements for the enthalpy of neutralization.

To determine the heat capacity of the fixed parts of the calorimeter, weigh the plastic cup (m_{cup}) and fill it with about 50 g room-temperature water. The mass does not need to be precisely 50 g, but the exact mass (m_1) should be recorded in your notebook. Place the cup onto the thermos flask, put the lid on, and begin monitoring the temperature. Read the temperature every minute until it stabilizes (the last two readings are within 0,1 ℃). The stabilized temperature is denoted T_{cold} in your calculations. Then add about 50 cm^3 hot water (with temperature T_{hot}) to the calorimeter. Begin monitoring the temperature again: read it in every minute until the values begin to decrease. The highest temperature reading is denoted T_{final} during the evaluation. Take the lid off, and weigh the cup with the total amount of water in it (m_{total}).

Repeat this procedure twice so that you have three parallel measurements for the heat capacity of the fixed parts of the calorimeter.

11.4 Evaluation

1. Calculate the heat capacity of the fixed parts of the calorimeter from your measurements using Equation 11.3. Use the $c_w = 4.184$ J g^{-1} K^{-1} as the specific heat of pure water. Summarize your data in the format of Table 11.1. Calculate the average and standard deviation[24] for C_{fix} from the three parallel measurements.

Table 11.1: Determination of the heat capacity of the fixed parts of the calorimeter

experiment number	m_1 (g)	m_2 (g)	T_{cold} (°C)	T_{hot} (°C)	T_{final} (°C)	C_{fix} (J K^{-1})
...	...	...	...	...	...	...

2. Calculate the concentration of the NaCl solution (c_{NaCl}) you prepared in the neutralization experiments. Find the specific heat of this solution ($c_{p,NaCl}$) by interpolation based on the data shown in Table 11.2.

Table 11.2: Specific heats of NaCl solutions as a function of concentration

c (mol dm^{-3})	c_p (J g^{-1} K^{-1})
0.18	4.113
0.55	4.020
1.35	3.822

3. Calculate the amount of substance for the NaCl formed in the neutralization experiments (n).

4. Calculate the molar neutralization heat from all three of your measurements with the following formula:

$$\Delta H_{neutr} = \frac{C_{fix} + c_{p,NaCl}(m_{total} - m_{cup})}{n}(T_{after} - T_{before}) + \frac{c_{p,NaOH}(m_{total} - m_{cup} - m_{HCl})}{n}(T_{before} - T_{NaOH}) \quad (11.5)$$

There is a new property in this equation: $c_{p,NaOH}$, the specific heat of the 1.00 mol dm^{-3} sodium hydroxide solution. You can use $c_{p,NaOH} = 3.977$ J g^{-1} K^{-1} in your calculations. Summarize your data in the format of Table 11.3. Calculate the average and standard deviation for ΔH_{neutr} from the three parallel measurements.

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

Table 11.3: Determination of the enthalpy of neutralization

experiment number	m_{cup} (g)	m_{HCl} (g)	m_{total} (g)	T_{before} (°C)	T_{NaOH} (°C)	T_{after} (°C)	$\Delta H_{\mathrm{neutr}}$ (kJ mol^{-1})
...	...	...	...	...	...	...	...

11.5 Advanced discussion points

1. Would it be possible to determine the heat capacity of the fixed parts of the calorimeter by adding water that is colder than the calorimeter?

2. You will see that parallel measurements for the heat capacity of the fixed parts of the calorimeter are likely to have quite a bit of scatter. What could be the reason for this phenomenon? How does this impact the reliability of your final results for the enthalpy of neutralization?

12 Measuring the surface tension of liquids

12.1 Check your previous studies

1. Definition of surface tension (lecture course)

2. Typical surface tension values for liquids and gases (lecture course)

3. Measuring the density of a solution (this book, Section D.)

12.2 Theoretical background

Surface tension is a phenomenon which appears at the surface of different phases. It is a characteristic of any material whose particles interact with each other in addition to the collision. Depending on the phases that come into contact with each other, we distinguish liquid-gas, liquid-liquid, solid-gas and solid-liquid surfaces and surface tensions. Although the considerations of surface tension can be generalized, only the phenomena associated with the liquid-gas surface are described below.

A distinction can be made between particles forming a phase depending on whether they are in the bulk phase (inside) or on the surface of the phase. Compared to the bulk phase, particles on the surface are in an asymmetric field, and therefore their energy differs from that of the bulk phase. As a result, the formation or termination of the surface involves work. When creating a unit surface of a pure fluid, the work needed under isothermal reversible conditions is called *surface tension* (Γ), so its unit is J m^{-2}, N m^{-1} or with base SI units kg s^{-2}.

The surface tension of mixtures and solutions differs from the tension of the pure solvent, since these systems consist of more than one type of molecules, so the interaction between the different molecules will be different from the interaction between the solvent molecules only. Substances that lower the surface tension are called surfactants or capillary active agents (detergents, wetting agents, emulsifiers, foaming agents, dispersants, alcohols, etc.), while compounds increasing the surface tension (e.g., sugars or strong electrolytes) are capillary inactive agents. Capillary active substances accumulate in the surface layer. The excess concentration on the surface is denoted by Γ. Based on the Gibbs equation, the relationship between surface tension change and excess surface concentration can be described for dilute solutions in the following form, when the actual concentration (c) and activity of the solution are considered to be the same:

$$\Gamma = -\frac{c}{RT}\frac{\mathrm{d}\gamma}{\mathrm{d}c} \tag{12.1}$$

If we determine the concentration dependence of the surface tension, then the value of Γ can be calculated, so the adsorption isotherm of the solute on the surface layer can also be determined.

Surface tension can be determined by direct or relative methods. In the latter case, there is a need for a reference solution, for which the value of γ is already known. One of the direct methods is calle Lenard frame method. It is a widespread method, but requires precise work and a lot of experience. In this technique, the F force is measured which requires to cut off a l long wire frame or ring from the surface of the sample. The surface tension can be calculated using the $\gamma = F/(2l)$ formula.

Relative methods are usually simpler and more accurate. In this laboratory practice, the stalagmometric method is used. The principle of the method is to allow a sample of known volume to be drained slowly through a capillary drilled into a polished glass disc. A drop just breaks from the disk when the gravitational force and the surface tension are equal. Counting the droplets and knowing the volume and density of the liquid and the radius of the disc, the weight of a drop, and from it, the surface tension can be calculated using the following formula:

$$2r\pi\gamma = \frac{V\rho g}{n} \tag{12.2}$$

In this formula, r is the radius of the droplet, V is the volume of the liquid, ρ is the density of the liquid, g is the gravity constant and n is the number of droplets in V volume of liquid. When using this method, the device should be calibrated by determining the number of droplets for the reference solvent with known surface tension, so the diameter of the disk is not required for the calculation. If you use the same V volume from the reference solution (with n_{ref} droplets, γ_{ref} surface tension and ρ_{ref} density), the surface tension of the unknown liquid can be given by the following formula:

$$\gamma = \frac{\gamma_{\text{ref}}\rho n_{\text{ref}}}{\rho_{\text{ref}} n} \tag{12.3}$$

The Traube stalagmometer used in this laboratory practice is shown in 12.1.

12.3 Practice procedures

During this laboratory practice, the surface tension of aqueous solutions will be determined by a Traube stalagmometer.

The technical implementation of the measurement is very simple: transfer the liquid into the stalagmometer and count the number of droplets that flow between

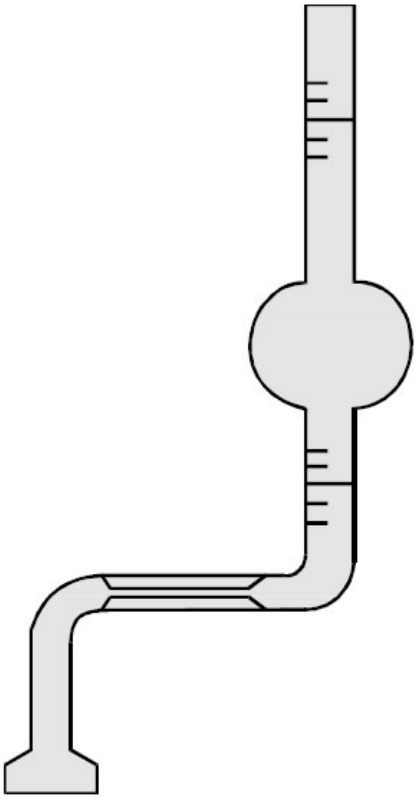

Figure 12.1: Traube stalagmometer

the two marks. The resulting number is the number of droplets for the measured solution (n). Perform each measurement three times and use the average of the three number of dropkets obtained for the calculations. Determine the densities of each solution tested as well.

First, determine the number of droplets for distilled water; this will be the reference value (n_{ref}). Measure the density of water. Write down the temperature of the laboratory as well.

(1) *Determination of an unknown concentration by surface tension:* Prepare a series of alcohol solutions of 50.0-50.0 cm^3 with the following relative concentrations: 5, 10, 25 and 75% (where the concentration of the stock solution is 100%). Measure the number of droplets and the densities of each solution. This alcohol also has a solution of unknown concentration: measure the number of droplets and the density for this unknown solution as well.

(2) *Examining different alcohols:* Measure the the number of droplets and densities of alcohol solutions with different lengths of alkyl chains. Measure and note the laboratory temperature as well.

(3) *Investigation of dissolved electrolyte and non-electrolyte solutions:* Study the effect of dissolved electrolytes (NaCl, NH_4Cl) and non-electrolyte (glucose, urea) on surface tension by measuring 1.0 mol dm^{-3} concentration aqueous solutions of these materials.

12.4 Evaluation

1. Calculate the surface tension of water at laboratory temperature. Use the following formula:

$$\gamma_{\text{water}} = a - bT \tag{12.4}$$

   In this equation, constant a is 118.0 kg s^{-2} and constant b is 0.155 kg s^{-2} K^{-1}. (The relationship can be used near room temperature.)

2. Knowing the numbers of droplets and densities, use equation 12.3 to calculate the surface tensions of all samples. Summarize your data in the format specified in table 12.1.

Table 12.1: Measured surface tensions. $T = \ldots$ K, $\rho_{\text{ref}} = \ldots$ kg m^{-3}, $n_{\text{ref}} = \ldots$, $\gamma_{\text{ref}} = \ldots$ kg s^{-2}

experiment number	solution constitution	n	ρ (kg m^{-3})	γ (kg s^{-2})
...	...	...	...	...

3. Plot the surface tension values for the alcohol samples (calibration series) as a function of concentration. Based on this graph, estimate the concentration of the unknown sample.

4. Based on the calibration plot, estimate the concentration derivative of the surface tension at each point by expressing the concentration in volume fraction (x_V). Based on this derivatives, use equation 12.1 to calculate the excess concentration on the surface. The data should be summarized in the format specified in table 12.2. Plot the excess concentration on the surface as a function of volume fraction.

Table 12.2: Excess surface concentration as a function of volume fraction. Alcohol: ..., $T = \ldots$ K

experiment number	γ (kg s^{-2})	x_V	$d\gamma/dx_V$ (kg s^{-2})	Γ (mol m^{-2})
...	...	...	...	...

5. Compare the surface tensions of the solutions of different alcohols. How it changes with changing the number of carbon atoms? Try to find a trend in the data.

6. Compare the surface tensions of the 1.0 mol dm^{-3} concentration NaCl, NH_4Cl, glucose and urea solutions and deduce the properties of these materials.

12.5 Advanced discussion points

1. If only the concentration is to be determined for the unknown solution, is it necessary to measure its density and calculate the actual surface tension?

2. Could other concentration units be chosen when calculating the derivative of the surface tension and the excess surface concentration?

3. In which case can the excess surface concentration be negative?

13 A phase study of the chloroform–acetic acid–water ternary system

13.1 Check your previous studies

1. Gibbs phase rule (lecture course)
2. Thermodynamics of ternary systems (lecture course)
3. Use of triangle diagrams (lecture course)

13.2 Theoretical background

According to the Gibbs phase rule, a three-component system has four degrees of freedom. These are usually chosen as the temperature, pressure, and two composition parameters, which can be molar fractions, volume fractions, weight percent, or other concentration units. When using the molar fractions, it is easy to see that two parameters are sufficient to describe the composition of the system: if two molar fractions are known, then the third one is obtained by subtracting the sum of the first two from 1.

In systems that have four degrees of freedom, graphing any feature would require a five-dimensional representation for a complete description. In practice, therefore, two degrees of freedom (typically pressure and temperature) are kept constant: the figures thus produced can only be used with the given values of these parameters. Fortunately, in practice, this does not limit the usability of the graph that much because experiments are performed at room temperature and atmospheric pressure in most cases.

In fact, even in this simplified case, we would still need to create a three-dimensional graph, since the property under investigation should be represented as a function of two independent variables (two concentrations). This can be further simplified if the tested property is simple: for example, the number of phases present in the system. In this case, one, two, three, or multiphase systems can be labeled on the appropriate areas of the diagram. If the amount studied can assume a lot of different values, then the use of contour lines (*i.e.*, connecting the points with the same values for some selected cases) is also possible to make an informative two-dimensional representation.

Although it would be possible to create figures from a three-component system in a rectangular coordinate system, triangular diagrams are in more widespread use instead, mainly because they reflect the symmetry properties better. The traiangle

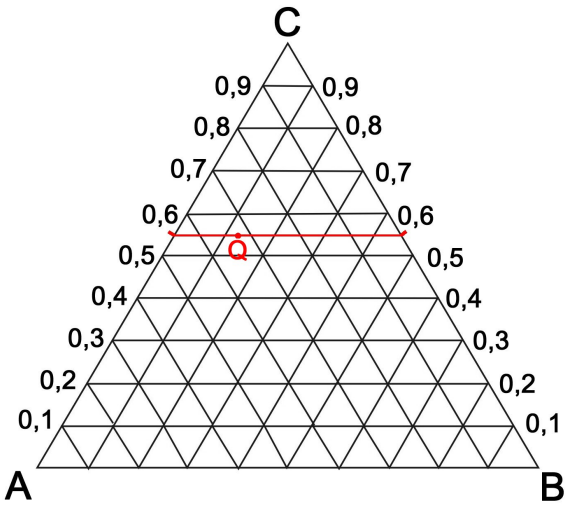

Figure 13.1: Reading the molar fraction for component C from a triangle diagram

diagrams are basically coordinate systems in which the two axes meet at an angle of 60° instead of 90°. Molar fractions are always between 0 and 1, so we can draw a third, non-independent, but actually equivalent axis for the third component by connecting the endpoints of the first two axes at their at molar fractions of 1. In this way, triangular diagrams are created, the shape of which is indeed a regular triangle. One such is shown in Figure 13.1.

In contrast to charts using a rectangular coordinate system, it is advisable to label the verteces of the triangle diagram rather than the sides. When the three components are denoted as A, B, and C, each vertex of the triangle corresponds to pure A, pure B, and pure C. On the side connecting the vertices A and B, there is no C in the mixture. Points assigned to systems with all three components are inside the triangle. In these cases, the molar fraction (of course, may also be mass fraction or volume fraction) of an individual component can be read by the following procedure: *e.g.* we are interested in the molar fraction of component C (Figure 13.1). Then we draw a line parallel with the side AB. This line intersects both the CA and the CB sides, and the molar fraction of component C can be read from each of the two by writing the value 1 to vertex C and 0 to the other one. [25] One can read the molar fraction of component A and B in the same way. Thus, the molar fraction values of points Q on Figure 13.2 are $x_{\mathrm{A}} = 0.33$, $x_{\mathrm{B}} = 0.12$ and $x_{\mathrm{C}} = 0.55$.

In the case of three different liquids, the triangle diagram is usually used to show the mixing conditions. It is rare that three liquids do not mix with each other in all three pairs as the mixing properties are usually relted to the polar or nonpolar nature, where there is no third category. Thus, two typical mixing triangle diagrams

[25] The laws of Euclidean geometry guarantee that the same value can be read on both axes.

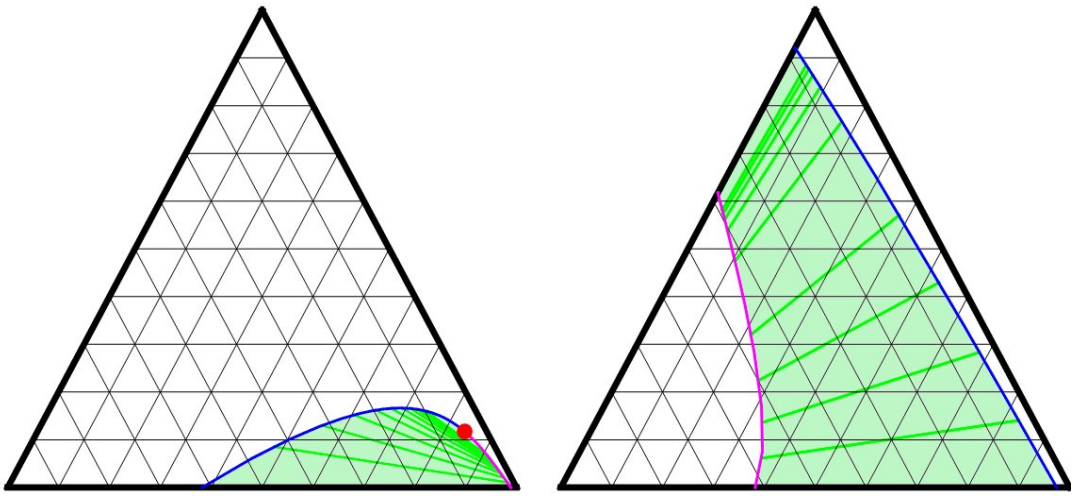

Figure 13.2: Two typical mixing triangle diagrams: one pair of liquids is not miscible (left side), two pairs of liquids are not miscible (right side)

can be drawn, examples of which are shown in Figure 13.2. On the left side, one pair of liquids is not miscible, and on the right, two pairs of liquids are not miscible.

The areas with light green color in Figure 13.2 represent th system compositions where two different phases are present. The composition of these two phases can be determined by the lines marked with darker green color in the Figure, using the *tie line*s (connecting lines). In the two-phase area, only one tie line passes through each point; the intersections of this cone with the single-phase–biphase boundary line give the exact compositions of the two phases in equilibrium. The ratio of the amounts of the two phases can be determined from the lever rule.

Experience shows that all tie lines pass through a common point (P), which is typically outside the triangle. An example of this is shown on Figure 13.3 for the case of one non-miscible liquid pair. The special point of the figure is the plait point (critical mixing point), K: this point does not have a pair with which it is in equilibrium. It is clear from the geometric interpretation of the figure that the straight line drawn from point K to P is the tangent of the boundary line separating the single-phase and the two-phase areas.

13.3 Practice procedures

During this laboratory practice, the three-component system of chloroform–acetic acid–water will be studied. Acetic acid is unlimitedly miscible with both chloroform and water, but chloroform and water are not.

Prepare mixtures of acetic acid and chloroform with a total volume of 20 cm^3 and a chloroform content of 15, 30, 50, 60, 70, 80, 85, 90 and 95 volume%, respectively.

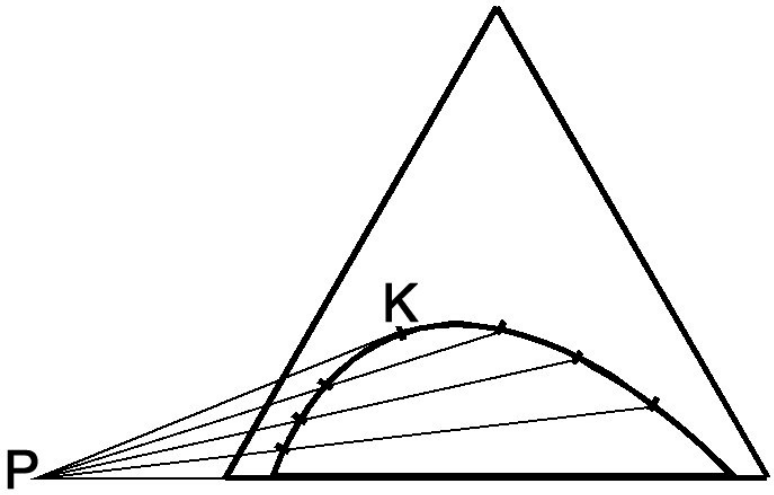

Figure 13.3: Determination of plait point

(Attention! Be careful! Pure acetic acid, *i.e.* glacial acetic acid is a bladder: if it drips on the skin, it leaves painful injuries for days!) Make a note of how the solutions were made (V_{CHCl_3} and V_{AcOH} volumes). Measure the components from an automatic burette into clean and dry Erlenmeyer flasks, mix the liquids and close the flask. Then, titrate the mixtures from an automatic burette carefully with distilled water until a slight cloudiness is observed (the system will then be biphasic). For each sample, write down the volume of water added (V_{water}). Thus, you will have nine measured points for drawing the line separating the single- and two-phase areas.

To determine the tie line needed to find the plait point, mix exactly 25.0 cm^3 distilled water, 25.0 cm^3 chloroform, and 5.0 cm^3 acetic acid in an Erlenmeyer flask. Shake the mixture thoroughly, transfer it to a separating funnel and separate the phases as accurately as possible. Take a 0.50 cm^3 sample from each phase, measure its exact mass, and titrate with a NaOH solution of 0.10 mol dm^{-3} concentration in the presence of phenolphthalein indicator. Write down the equivalence volumes ($V_{NaOH,\ aqueous}$ and $V_{NaOH,\ organic}$).

DO NOT pour the solutions containing chloroform into the sink. Dispoe them into the appropriate chlorform waste bottle that is found under the hood.

13.4 Evaluation

1. From the first set of experiments, calculate the exact solution concentrations in molar fractions (x) and in mass fraction (y). For the calculations, use the following density values: $\rho_{water} = 0.997$ g cm^{-3}, $\rho_{CHCl_3} = 1.478$ g cm^{-3} and $\rho_{AcOH} = 1.045$ g cm^{-3}. Summarize your data in the format of Table 13.1.

Table 13.1: Compositions valid for the boundary line between single and two-phase areas

experiment number	1	2	3	4	5	6	7	8	9
V_{CHCl_3} (cm^3)	...	...	...	...	...	...	...	...	...
V_{AcOH} (cm^3)									
V_{water} (cm^3)									
m_{CHCl_3} (g)									
m_{AcOH} (g)									
m_{water} (g)									
n_{CHCl_3} (mol)									
n_{AcOH} (mol)									
n_{water} (mol)									
$\sum m$ (g)									
$\sum n$ (mol)									
y_{CHCl_3}									
y_{AcOH}									
y_{water}									
x_{CHCl_3}									
x_{AcOH}									
x_{water}									

2. Prepare two triangle diagrams, one with molar fractions, and the second with mass fractions. For both, mark the nine points on the boundary between single- and two-phase systems. Based on these points, draw the continuous line that represents the boundary.

3. Determine the acetic acid content of the organic and aqueous phases in mass fraction from the titration results of the second measurement series.

4. Draw the straight line on the mass fraction phase diagram along which the mass fraction of acetic acid is the value calculated in the previous point for the organic phase and then find the analogous straight line with the result of the aqueous phase titration. The intersection of these with the boundary line gives the composition of two phases in equilibrium.

5. Draw a line through the two points defined in the previous step and determine its intersection with the chloroform-water axis. This will be point P in Figure 13.3.

6. Draw the tangent to the curve from point P. Touch point K is the plait point. Define the system composition at this point.

13.5 Advanced discussion points

1. How can one decide – without performing the experiment – which phase is on the top in the second series of measurements: the organic or the aqueous phase?

2. Why is it enough to construct a single tie line if the point P is the intersection of two tie lines?

3. What are the special properties of the plait point?

4. How could you estimate where the chloroform-water axis intersects boundary (for which all measured nine points are insie the triangle)?

5. Why do the points for a given mass fraction of acetic acid, but different amounts of the remaining two components fall on the same straight line?

6. On what basis would you be able to determine the plait point in the triangle diagram containing the molar fractions?

14 Determination of the composition of a complex by spectrophotometry

14.1 Check your previous studies

1. Thermodynamic description of chemical equilibria (lecture course)

2. Spectrophotometry and Beer's law (this book, Section B.)

14.2 Theoretical background

The formation of an ML_n complex can be described by the following equilibrium reaction:

$$M + nL \rightleftharpoons ML_n \tag{14.1}$$

As a consequence of the law off mass action, the equilibrium constant of the reaction is defined as follows:

$$K = \frac{[ML_n]}{[M][L]^n} \tag{14.2}$$

In this formula, K is the stability product of the complex, [M] is the equilibrium concentration of the free metal ion, [L] is the equilibrium concentration of the free ligand, [ML] is the equilibrium concentration of the complex, and n is the number of ligands coordinated to the metal ion.

A common approach to determine the composition of a complex is called Job's method: using solutions of the ligand and the metal that have the same concentrations, a series of samples is prepared in which the sum of these two analytical concentrations is constant, but the ratio varies. (For example, the final volume is always 10 cm^3, and a sample is prepared by mixing x cm^3 of the ligand solution with $(10 - x)$ cm^3 of the metal solution.) It can be proved easily that the sample with the highest concentration of the complex will be the one where the ratio of the ligand and metal ion analytical concentrations is the same as in the complex.

First, it is noted that the sum of the analytical concentrations of the ligand and the metal is a constant in all the samples:

$$c = c_L + c_M \tag{14.3}$$

Differentiating this equation with respect to c_L gives:

$$0 = 1 + \frac{dc_{\mathrm{M}}}{dc_{\mathrm{L}}} \tag{14.4}$$

Simply rearranging this equation gives the following formula for the derivative of c_{M} with respect to c_{L}:

$$\frac{dc_{\mathrm{M}}}{dc_{\mathrm{L}}} = -1 \tag{14.5}$$

Mass conservation for the metal ion gives:

$$[\mathrm{M}] = c_{\mathrm{M}} - [\mathrm{ML}_n] \tag{14.6}$$

The analogous mass conservation equation for the ligand takes the following form:

$$[\mathrm{L}] = c_{\mathrm{L}} - n[\mathrm{ML}_n] \tag{14.7}$$

Using these mass conservation equations, the equilibrium constant can be written as:

$$K = \frac{[\mathrm{ML}_n]}{(c_{\mathrm{M}} - [\mathrm{ML}_n])(c_{\mathrm{L}} - n[\mathrm{ML}_n])^n} \tag{14.8}$$

Differentiating this equation with respect to c_{L} gives:

$$\begin{aligned} 0 = K\tfrac{d[\mathrm{ML}_n]}{dc_{\mathrm{L}}} + \tfrac{-K}{(c_{\mathrm{M}}-[\mathrm{ML}_n])}\left(-1 - \tfrac{d[\mathrm{ML}_n]}{dc_{\mathrm{L}}}\right) \\ + \tfrac{-nK}{(c_{\mathrm{L}}-n[\mathrm{ML}_n])}\left(1 - n\tfrac{d[\mathrm{ML}_n]}{dc_{\mathrm{L}}}\right) \end{aligned} \tag{14.9}$$

At the maximum concentration of the ML_n complex, the derivative $d[\mathrm{ML}_n]/dc_{\mathrm{L}}$ is zero. In the previous equation, this leaves a very simple relationship:

$$0 = \frac{K}{(c_{\mathrm{M}} - [\mathrm{ML}_n])} + \frac{-nK}{(c_{\mathrm{L}} - n[\mathrm{ML}_n])} \tag{14.10}$$

This equation can be re-arranged further:

$$n(c_{\mathrm{M}} - [\mathrm{ML}_n]) = (c_{\mathrm{L}} - n[\mathrm{ML}_n]) \tag{14.11}$$

Finally, it is noted that the term $n[\mathrm{ML}_n]$ occurs on both sides, the ratio of the two analytical concentrations is obtained:

$$\frac{c_{\mathrm{L}}}{c_{\mathrm{M}}} = n \tag{14.12}$$

This line of thought proves that maximum concentration of ML_n will be reached in a solution where the ligand-to-metal concentration ratio is exactly n, i.e. the stoichiometric value.

If the complex is colored, the ratio at which maximum complex formation occurs can be determined easily and the composition of the complex can be deduced. According to Beer's law, the absorbance (A) of a solution at a given wavelength λ is given as:

$$A = \epsilon_\lambda c l \tag{14.13}$$

If all three components (M, L and ML_n) have absorptions, three terms need to be given in this equation:

$$A = (\epsilon_{\mathrm{M}}[\mathrm{M}] + \epsilon_{\mathrm{L}}[\mathrm{L}] + \epsilon_{\mathrm{ML}_n}[\mathrm{ML}_n])l \tag{14.14}$$

The molar absorbances of all species appear in this equation. In the absence of any complex formation, the expectation for the absorbance would be:

$$A' = \epsilon_{\mathrm{M}}(c - c_{\mathrm{L}})l + \epsilon_{\mathrm{L}}c_{\mathrm{L}}l \tag{14.15}$$

The difference between A and A' can be expressed taking the mass conservation equations into account:

$$\begin{aligned} A - A' &= \epsilon_{\mathrm{M}}(c - c_{\mathrm{L}} - [\mathrm{ML}_n])l + \epsilon_{\mathrm{L}}(c_{\mathrm{L}} - n[\mathrm{ML}_n])l + \epsilon_{\mathrm{ML}_n}[\mathrm{ML}_n]l \\ &-\epsilon_{\mathrm{M}}(c - c_{\mathrm{L}})l - \epsilon_{\mathrm{L}}c_{\mathrm{L}}l = \\ &(\epsilon_{\mathrm{ML}_n} - \epsilon_{\mathrm{M}} - n\epsilon_{\mathrm{L}})[\mathrm{ML}_n] \end{aligned} \tag{14.16}$$

Because of this direct proportionality, it is clear that $(A - A')$ will have an extremum exactly where $[ML_n]$ has. Therefore, the absorbance signal can be used for the determination of the composition of the complex.

14.3 Practice procedures

Ask your instructor which metal ion ligand pair you should do experiments on. Prepare 100 cm^3 20-fold dilutions of both of the stock solutions, then prepare the samples given in the following table:

Table 14.1: Compositions of individual experiments

sample number	V_M (cm^3)	V_L (cm^3)	Sample number	V_M (cm^3)	V_{water} (cm^3)
1	1.0	9.0	1'	1.0	9.0
2	2.0	8.0	2'	2.0	8.0
3	3.0	7.0	3'	3.0	7.0
4	4.0	6.0	4'	4.0	6.0
5	5.0	5.0	5'	5.0	5.0
6	6.0	4.0	6'	6.0	4.0
7	7.0	3.0	7'	7.0	3.0
8	8.0	2.0	8'	8.0	2.0
9	9.0	1.0	9'	9.0	1.0

Put the samples in the first series (1-9) on white paper and select the one that has the most intense color. Fill a 1.000 cm path length cuvette with this solution and record its spectrum in the visible range (370-650 nm) using water as a reference. Select the wavelength at which the absorbance is the highest (this is called the peak in the spectrum). Measure the absorbances of all other solutions at this wavelength.

Measure the absorbances of all samples in the second series (1'-9') at the same wavelength.

Finally, record the absorption spectrum of the metal ion solution using the original (undiluted) stock solution of the metal.

14.4 Evaluation

1. Draw the two absoprtion spectra (i.e. that of the complex and that of the metal ion). At the selected wavelength, give the measured absorbance values in a Table similar to Table 14.2.

Table 14.2: Summary of data for the Job plot

sample number	V_M (cm^3)	A	A'	$A - A'$
1 and 1'				
2 and 2'				
...				

2. Plot the $A - A'$ values as a function of the metal solution volume used (in cm^3), determine where the maximum occurs and deduce the composition of

the complex.

14.5 Advanced discussion points

1. What happens in Job's method if more than one complex is formed in the system simultaneously?

2. A possible coincidence is that the equation $\epsilon_{\mathrm{ML}_n} = \epsilon_{\mathrm{M}} + n\epsilon_{\mathrm{L}}$ holds for the molar absorbances in the system. What does this coincidence cause in the measured signal? Is it possible to complete the evaluation under such conditions?

3. Why are there no points with 0.0 cm^3 of M and L solutions in Table 14.1?

15 Investigating a clock reaction

15.1 Check your previous studies

1. Rate equations (lecture course)

2. van't Hoff method (initial rate method) to determine reaction orders (lecture course; this book, Chapter 5.)

15.2 Theoretical background

As seen during the investigation of the first order process (Chapter 5), 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 iodide ions react in a process (Dushman reaction) described by the following chemical equation:

$$\mathrm{IO_3^-} + 5\mathrm{I^-} + 6\mathrm{H^+} \longrightarrow 3\mathrm{I_2} + 3\mathrm{H_2O} \tag{15.1}$$

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:

$$r_0 = -\frac{\mathrm{d}[\mathrm{IO_3^-}]}{\mathrm{d}t} = k[\mathrm{IO_3^-}]^{\beta\mathrm{IO_3^-}}[\mathrm{I^-}]^{\beta\mathrm{I^-}}[\mathrm{H^+}]^{\beta\mathrm{H^+}} \tag{15.2}$$

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 reactants. This allows a low conversion for the reaction we wish to study, so the initial rate and other kinetic parameters can be determined relatively 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 change is sudden and time from the mixing to the ob-

servable change (Δt, clock time or Landolt time[26]) can be measured easily. Iodine and arsenous acid react as follows:

$$H_3AsO_3 + I_2 + H_2O \longrightarrow HAsO_4^{2-} + 2I^- + 4H^+ \tag{15.3}$$

The initial concentration of arsenous acid can also be used to control the time at which iodine appears, so this reaction is sometimes called a clock reaction[27].

The initial rate of the reactions can be estimated based on differences, using the stoichiometries of reactions 15.1 and 15.3:

$$-\frac{\mathrm{d}[IO_3^-]}{\mathrm{d}t} = \frac{1}{3}\frac{\mathrm{d}[I_2]}{\mathrm{d}t} = \frac{1}{3}\frac{\Delta[H_3AsO_3]}{\Delta t} \tag{15.4}$$

In this equation, $\Delta[H_3AsO_3]$ is the concentration of initially added arsenous acid and Δt is the clock time measured.

15.3 Practice procedures

Prepare the two buffer solutions as follows:

- Buffer A: Measure 100.0 cm^3 of 0.75 mol dm^{-3} $NaCH_3COO$ solution and 100.0 cm^3 of 0.20 mol dm^{-3} CH_3COOH solution into a 500.0 cm^3 volumetric flask. Fill up the flask to the mark. (This will give $[H^+] = 1 \cdot 10^{-5}$ mol dm^{-3}.)
- Buffer B: Measure 40.0 cm^3 of 0.75 mol dm^{-3} $NaCH_3COO$ solution and 80.0 cm^3 of 0.20 mol dm^{-3} CH_3COOH solution into a 200.0 cm^3 volumetric flask. Fill up the flask to the mark. (This will give $[H^+] = 2 \cdot 10^{-5}$ mol dm^{-3}.)

Prepare the sample solutions given in Table 15.1 in dry beakers except the KI solution, which should be measured into a separate beaker.

Write down the concentrations of all of the stock solutions (KI, KIO_3, H_3AsO_3) into your laboratory notebook.

Initiate the reaction by pouring the KI solution suddenly into the mixture of the other components and start the stopwatch. You can do the ten experiments relatively quickly if you prepare all the necessary solutions in 20 beakers and initiate the experiments in approximately half- or one-minute intervals. Record the time at which the blue color of the iodine starch complex suddenly appears for each

[26]Landolt time is not only the reaction time (clock time) measured in the Landolt reaction, but the time that elapses between the initiation of the reaction and a noticeable change in concentration at any other clock reaction.

[27]A class of chemical reaction systems. In case of these reactions, the change of concentration can be detected after a well-defined time lag (called Landolt time). This pehnomenon is originated from either stochiometric or kinetic constraint(s).

Table 15.1: Composition of individual samples for the determination of initial rates

experiment number	V_{KI} (cm^3)	V_{KIO_3} (cm^3)	$V_{H_3AsO_3}$ (cm^3)	V_{starch} (cm^3)	V_{H_2O} (cm^3)	$V_{Buffer\ A}$ (cm^3)	$V_{Buffer\ B}$ (cm^3)
1	6.0	2.0	0.5	1.0	7.5	33	0
2	6.0	3.0	0.5	1.0	6.5	33	0
3	6.0	4.0	0.5	1.0	5.5	33	0
4	6.0	5.0	0.5	1.0	4.5	33	0
5	8.0	2.0	0.5	1.0	5.5	33	0
6	10.0	2.0	0.5	1.0	3.5	33	0
7	12.5	2.0	0.5	1.0	1.0	33	0
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	0	33

experiment. Give the experimentally measured reaction times (Δt) in a format of Table 15.2.

After the kinetic measurements, prepare mixtures 1, 8, 9 and 10 but now, use deionized water instead of the KIO_3 solution. For these solutions, you can put every component (including KI) into the same beaker since there will be no reaction. So, you do not need to measure any reaction time for these samples. However, you should measure the pH of these solutions using a pH-meter calibrated with two buffers. This pH is the same as it would be with KIO_3 instead of water. Give the measured pH values in Table 15.2 (-pH = $\log_{10}[H^+]$). Calculate the hydrogen ion concentrations.

15.4 Evaluation

1. Calculate the initial rates of the experiments and give them in the format of Table 15.2:

Table 15.2: Reaction times (Δt (s)), initial rates (r_0 (mol dm^{-3} s^{-1})) and concentration ([X] (mol dm^{-3})) data for determining the reaction orders

experiment number	Δt	r_0	$\log_{10} r_0$	$[IO_3^-]$	$\log_{10}[IO_3^-]$	$[I^-]$	$\log_{10}[I^-]$	$[H^+]$	$\log_{10}[H^+]$
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 of the straight line. For example, for iodide ions:

$$\log_{10} r_0 = \log_{10} k' + \beta \mathrm{I}^- \log_{10}[\mathrm{I}^-] \tag{15.5}$$

The intercept of the fitted straight line is k', which contains the product of the orders of reactions and initial concentrations of the remaining components and the value of the rate constant (k) as well.

Plot $\log_{10} r_0$ as a function of the $\log_{10}$ of the appropriate concentration and determine the individual reaction orders ($\beta \mathrm{IO}_3^-$, $\beta \mathrm{I}^-$ and $\beta \mathrm{H}^+$ in eq. 15.2).

3. Use equation 15.2 to calculate the rate constant (k) for the reaction studied from all 10 experiments, using the reaction order values determined in the previous step. Give the average and the standard deviation of the ten data. Do not forget to give the unit also.

15.5 Advanced discussion points

1. What is the advantage of using initial rates instead of reaction rates at any other time in kinetics?

2. Why is it not necessary to thermostate the solutions?

3. If the kinetics of a reaction cannot be described by power law kinetics, how would a $\log_{10} r_0$ *versus* $\log_{10}[\mathrm{X}]$ plot look like?

4. What other clock reactions are known?

16 Investigating the kinetic salt effect

16.1 Check your previous studies

1. Activity of a solute, activity coefficient (lecture course)
2. Debye-Hückel theory of electrolytes (lecture course)
3. Reaction mechanisms, rate theories (lecture course)
4. Relationship between equilibrium constants given by activities and concentrations (this book, Section E.)
5. Investigating a clock reaction (this book, Chapter 15.)

16.2 Theoretical background

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.

The Debye-Hückel theory states that effect of an electrolyte is primarily exerted through the ionic strength (I) of the solution, which is defined as follows:

$$I = \frac{1}{2} \sum c_i z_i^2 \tag{16.1}$$

In this equation, z_i values are the ionic charges and c_i stands for the concentration of ion i. A combination of the the Eyring equation with Debye-Hückel theory gives the following equation:

$$\ln k = \ln k_0 - \frac{z_1 z_2 e^2}{k_\mathrm{B} T \epsilon a} + \frac{z_1 z_2 e^2}{k_\mathrm{B} T \epsilon (1 + Ia)} \tag{16.2}$$

Here ϵ is the dielectric constant of the medium, e is the charge of an electron, a is the smallest distance between two ions, and k_0 is the value of the rate constant in the ideal (reference) state. In ionic reactions, the reference state is $\epsilon \to \infty$ and $I \to 0$. In dilute aqueous solutions, the previous formula can be transformed into a somewhat simplified version:

$$\log_{10}\left(\frac{k}{k_0}\right) = 1.02 z_1 z_2 \sqrt{I} \tag{16.3}$$

Equation (16.3) is often referred to as the Brønsted equation in the literature of chemical kinetics. Note that equation (16.3) is a value equation: the ionic strength I can only be substituted in the units mol dm^{-3} into the formula.

During the calculation of the ionic strength, the contributions of all ionic species must be summed including reactants and non-reactive ions as well. According to equation (16.3), a plot of $\log_{10}k$ as a function of $\sqrt{I}$ 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 limited by the validity range of the extended Debye-Hückel theory, which means that deviations from linearity are expected at higher ionic strengths.

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

$$2\mathrm{I}^- + \mathrm{S_2O_8^{2-}} \longrightarrow \mathrm{I_2} + 2\mathrm{SO_4^{2-}} \tag{16.4}$$

The appearance 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 consumed. Therefore, if the initial thiosulfate ion concentration 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 reaction, the reduction of iodine with thiosulfate ions occurs at the same time as the studied reaction between iodide and peroxodisulfate ions progresses:

$$\mathrm{I_2} + 2\mathrm{S_2O_3^{2-}} \longrightarrow 2\mathrm{I}^- + \mathrm{S_4O_6^{2-}} \tag{16.5}$$

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. Thiosulfate 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 literature, the reaction between iodide and peroxodisulfate

ions is known to be first order with respect to both reagents:

$$r_0 = k[\mathrm{I}^-][\mathrm{S_2O_8^{2-}}] \tag{16.6}$$

In this equation, k is the second order rate constant of the reaction.

The initial rate of the reactions can be estimated based on differences, using the stoichiometries of reactions (16.4) and (16.5):

$$r_0 = -\frac{d[\mathrm{S_2O_8^{2-}}]}{\mathrm{d}t} \approx \frac{1}{2}\frac{\Delta[\mathrm{S_2O_3^{2-}}]}{\Delta t} \tag{16.7}$$

In this equation, $\Delta[\mathrm{S_2O_3^{2-}}]$ 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 experiment 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.

16.3 Practice procedures

Use the following stock solutions:

- 0.01 mol $\mathrm{dm^{-3}}$ KI solution
- 0.01 mol $\mathrm{dm^{-3}}$ $\mathrm{K_2S_2O_8}$ solution
- 0.001 mol $\mathrm{dm^{-3}}$ $\mathrm{Na_2S_2O_3}$ solution
- 0.25 mol $\mathrm{dm^{-3}}$ $\mathrm{KNO_3}$ solution
- Starch solution

Prepare the sample solutions given in Table 16.1 in dry beakers except the potassium peroxodisulfate solution, which should be measured into a separate beaker.

Initiate the reaction by pouring the potassium peroxodisulfate solution suddenly into the mixture of the other components and start the stopwatch. You can do the nine experiments relatively quickly if you prepare all the necessary solutions in 18 beakers and initiate the experiments in approximately half- or one-minute intervals. Record the time at which the blue color of the iodine starch complex suddenly appears for each experiment. Record all the reaction times.

16.4 Evaluation

1. Give the experimentally measured reaction times and the calculated initial rates in the form of Table 16.2:

Table 16.1: Composition of individual samples for investigating the kinetic salt effect in the iodine clock reaction

experiment number	$V_{K_2S_2O_8}$ (cm^3)	V_{KI} (cm^3)	$V_{Na_2S_2O_3}$ (cm^3)	V_{starch} (cm^3)	V_{KNO_3} (cm^3)	V_{water} (cm^3)
1	8.0	20.0	1.0	1.0	0	20.0
2	8.0	20.0	1.0	1.0	1.3	18.7
3	8.0	20.0	1.0	1.0	2.9	17.1
4	8.0	20.0	1.0	1.0	4.9	15.1
5	8.0	20.0	1.0	1.0	7.2	12.8
6	8.0	20.0	1.0	1.0	9.9	10.1
7	8.0	20.0	1.0	1.0	12.9	7.1
8	8.0	20.0	1.0	1.0	16.3	3.7
9	8.0	20.0	1.0	1.0	20.0	0.0

Table 16.2: Reaction times (Δt (s)), initial rates (r_0) and concentration ([X]) data in the iodine clock reaction

experiment number	Δt (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. Calculate the rate constants (k) and summarize them in the form of Table 16.3:

Table 16.3: Rate constants in the iodine clock reaction

experiment number	k (dm^3 mol^{-1} s^{-1})	$\log_{10}k$	ionic strength, I (mol dm^{-3})	$\sqrt{I}$ ($mol^{1/2}$ $dm^{-3/2}$)
1	...	...	...	...

3. Calculate the ionic strength values for the samples (I) and summarize them in the form of Table 16.3.

4. Plot $\log_{10}k$ as a function of $\sqrt{I}$. Fit a straight line to the points and determine the slope and the intercept of the straight line. From the intercept, give the value of the rate constant at 0 ionic strength (k_0).

5. Compare the slope of the straight line with the one expected from Equation (16.3).

16.5 Advanced discussion points

1. Which kinds of salts can be used in a reaction system to set the value of the ionic strength to the required value?

2. Why is a constant (and high) ionic strength used for most kinetic measurements?

3. Based on your measurements, what conclusion can you draw about the mechanism of the iodine clock reaction? Which of your data show this conclusion?

4. What kinds of reactions are not affected by the ionic strength of the solution?

5. Can you find the logic behind the series of solutions prepared for this experiment?

17 Electrochemical study of the catalytic oxidation of ascorbic acid

17.1 Check your previous studies

1. First order processes (lecture course)

2. Dynamic electrochemistry (lecture course)

17.2 Theoretical background

In this practice, you will use an electrochemical method, voltammetry to study the catalytic oxidation of ascorbic acid, which is an essential material for humans and is also called vitamin C. Its spontaneous oxidation is well known:

$$C_6H_8O_6 + 1/2O_2 = C_6H_6O_6 + H_2O \tag{17.1}$$

The reaction is catalyzed by multivalent metal ions. If there is excess oxygen, which is continuously replenished, the reaction becomes pseudo-first order. In this case, the measured rate constant is an *apparent rate constant*.

Consider a simple reaction as an example:

$$A + B = P \tag{17.2}$$

In this reaction, product P is formed from reactants A and B. Suppose that the following first-order rate equation is valid for the process:

$$r = -\frac{d[A]}{dt} = \frac{d[P]}{dt} = k[A] \tag{17.3}$$

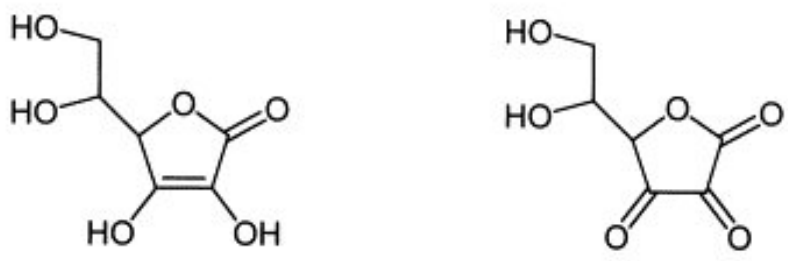

Figure 17.1: The structures of ascorbic acid (vitamin C, $C_6H_8O_6$) and dehydroascorbic acid ($C_6H_6O_6$)

To determine k, one can either measure the change in [A], [B] or [P] as a function of time t. Consider the change in [A]: with $[A]_0$ as the initial ($t = 0$) concentration, the differential equation 17.3 can be solved:

$$[A] = [A]_0 e^{-kt} \tag{17.4}$$

In a first order reaction, concentration changes exponentially in time. On the other hand, the logarithm of the concentration of the limiting reagent changes linearly as a function of time, which can be seen by taking the natural logarithms of both sides of equation 17.4:

$$\ln \frac{[A]}{[A]_0} = -kt \tag{17.5}$$

A traditional way of deciding whether a reaction is first order or not is to plot ln[A] as a function of time, and see if the points fit a straight line. If they do, the reaction is a first order process, and the slope is the rate constant k. However, at the time of the introduction of personal computers, this method (called linearization because it involves transforming the curve into a straight line) became obsolete. In modern science, an appropriate fitting software that uses a non-linear least squares algorithm is used instead of linearization.

The analytical method that you will use during the experiment to monitor the concentration of ascorbic acid is voltammetry. It is an electroanalytical technique, in which information about an analyte is obtained by measuring the current between two suitably chosen electrodes as the potential is varied. The analytical data for a voltammetric experiment comes in the form of a *voltammogram*, which plots the current produced by the analyte versus the potential difference between the electrodes. A representative voltammogram is shown in Figure 17.2. Generally, the potential values carry information on the identity of the components, whereas quantitative information can be extracted from the current.

17.3 Practice procedures

You will use voltammetry to determine the concentration of ascorbic acid at any time t. First, a calibration plot will be set up, then the oxidation of ascorbic acid will be monitored in real time by voltammetry. Start by preparing 25.0 cm^3 0.10 mol dm^{-3} stock solution ascorbic acid dissolved in deionized water.

(1) *Measuring ascorbic acid samples for the calibration plot:* Take a clean, small beaker and measure 10 cm^3 of 0.1 mol dm^{-3} NaCl solution into it. Place the beaker on a magnetic stirrer, and put a magnet into the beaker.

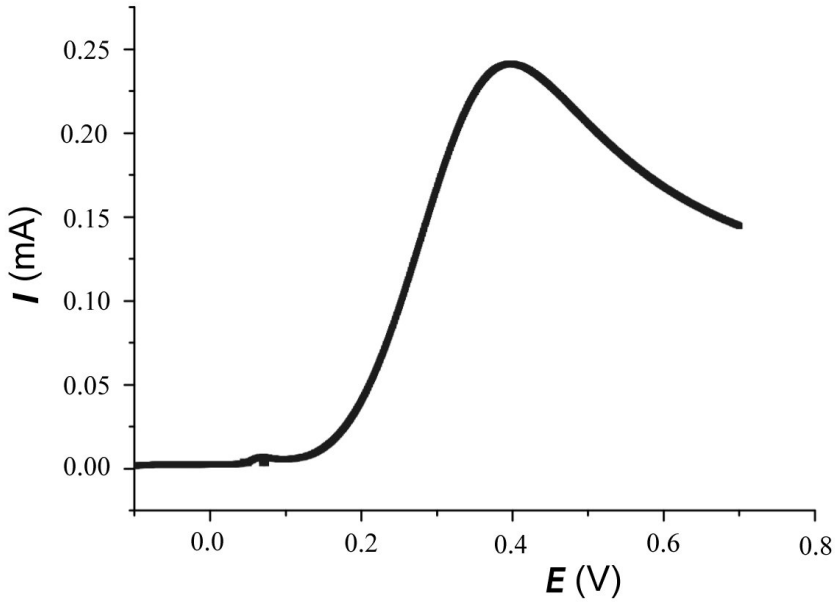

Figure 17.2: A typical voltammogram

Put the electrodes into the solution. You will use a glossy carbon working electrode, Ag/AgCl reference electrode, and a platinum auxiliary electrode. Polish the glossy carbon electrode before use!

Record a cyclic voltammogram between -0.2 and 0.8 V with a scan rate of 100 mV s^{-1}. Adjust the current range if necessary.

Start increasing the ascorbic acid concentration (first, it is of course zero) by adding small volumes (30 µl) from the stock solution. Record the voltammogram after every addition. Repeat it 10 times, so that you have 11 measurements. Now you have data for the calibration curve.

(2) *Monitoring the oxidation reaction of ascorbic acid by voltammetry:* The reakcion will be studied at room temperature. Write down the temperature of the laboratory into your laboratory notebook. Put 100 cm^3 of 0.1 mol dm^{-3} NaCl solution into a beaker. Add 200 µl of 0.1 mol dm^{-3} $CuCl_2$ solution. This will serve as the catalyst.

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.

Record the voltammogram of the sample (without ascorbic acid) in the same way you did in the calibration measurements.

Add 2.00 cm^3 of the ascorbic acid stock solution to the sample. Start a stopwatch

at the moment of addition. This is when the reaction starts.

At t = 5, 10, 15, 20, 25, 30, 35 and 40 minutes, record a voltammogram of the reaction mixture.

17.4 Evaluation

1. Prepare a calibration curve based on your calibration measurements. Calculate the concentrations of ascorbic acid for each of the solutions in your calibration series. Determine the anodic peak current (I_a) from each voltammogram: this is the difference at the peak potential between the current values of the samples containing ascorbic acid and the sample without ascorbic acid. Summarize your data in a form similar to Table 17.1.

Table 17.1: Experimental data for the voltammetric calibration

experiment number	$V_{\text{added solution}}$ (cm^3)	$c_{\text{ascorbic acid}}$ (mol dm^{-3})	I_a (μA)
1	...	...	...

Plot he anodic peak current as a function of ascorbic acid concentration. Observe the trend of the data points and fit an appropriate curve (straight line or polynomial) to them.

2. Record the anodic peak current (i.e. the difference at the peak potential between the current values of the samples containing ascorbic acid and the sample without ascorbic acid) in each of your voltammetric measurements done as a function of time, and calculate the corresponding ascorbic acid concentrations using the calibration curve. Summarize your data in a form similar to Table 17.2.

Table 17.2: Experimental data of the kinetic trace

reaction time (min)	I_a (μA)	$c_{\text{ascorbic acid}}$ (mol dm^{-3})
5	...	...
10	...	...
15	...	...
20	...	...
25	...	...
30	...	...
35	...	...
40	...	...

3. Plot the ascorbic acid concentrations as a function of time. Observe the trend of the data. Use non-linear least squares fitting to determine the value of the rate constant k.

4. As an alternative evaluation, plot the logarithms of the ascorbic acid concentrations as the function of time. Fit a straight line to your data points and determine the value of the rate constant k from the slope.

17.5 Advanced discussion points

1. Why is it enough to plot the logarithms of the concentration (ln[A]) instead of the logarithm of the ratio of the actual and initial concentrations (ln ($[A]/[A]_0$)) as written in equation 17.5?

2. Why is the non-linear least squares fitting method preferred to the linearization method today?

3. What could be the electrode reaction in the voltammetric measurement that gives a signal characteristic of ascorbic acid?

18 Kinetic investigation of sucrose inversion by polarimetry

18.1 Check your previous studies

1. First order and pseudo-first order processes (lecture course)
2. Half-life of a reaction (lecture course)
3. How to read a vernier scale (en.wikipedia.org/wiki/Vernier_scale)

18.2 Theoretical background

Sucrose (cane sugar) is a disaccharide which hydrolyzes under acidic conditions to produce D-glucose and D-fructose, according to Figure 18.1:

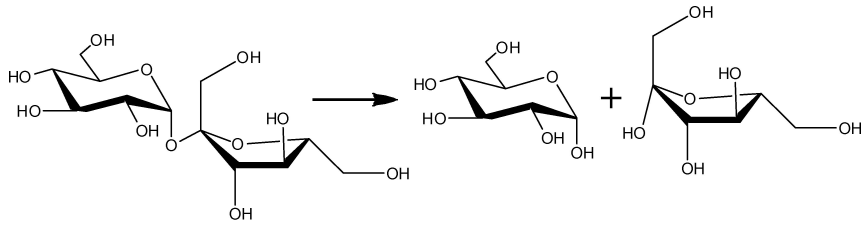

Figure 18.1: Acid catalyzed hydrolysis of sucrose

The progress of the process can be conveniently tracked by measuring optical rotation. In the system, both the starting material and the products are optically active: the solution of sucrose rotates the plane of linearly polarized light to the right (+), while the aqueous solution of hydrolysis products rotates left (−). The rotation of a solution (α) is similar to the absorbance: it depends not only on the chemical identity and wavelength, but also on the concentration of the solution and the path length. Thus, a value characteristic of the material, called specific rotation ($[\alpha]_\lambda$), can be obtained after dividing the rotation by the path length (l) and concentration (c):

$$[\alpha]_\lambda = \frac{\alpha}{cl} \tag{18.1}$$

In mixtures, each substance contributes linearly to the total rotation, in proportion to its concentration. The specific rotations of some carbohydrates are shown in Table 18.1.

It is clear from the literature that the process of sucrose conversion is first-order with respect to sucrose. This fact and the linear dependence of the rotation on the

Table 18.1: Specific rotations of some monosaccharides and disaccharides at the Na D line (589 nm)

substance	$[\alpha]_D$ ($^\circ$ dm^{-1} cm^3 g^{-1})
α-D-glucose	+112.0
D-glucose (α and β in equilibrium)	+52.7
β-D-fructose (an equilibrium mixture of furanose and pyranose)	-93.0
Saccharose	+66.5
Invert sugar (D-glucose and D-fructose in 1:1 ratio)	-20.2
Maltose (α and β in equilibrium)	+136.0
D-mannose (α and β in equilibrium)	+14.2
D-galaktose (α and β in equilibrium)	+80.5

concentration results in the following exponential formula for the time dependence of rotation:

$$\alpha_t = (\alpha_0 - \alpha_\infty)e^{-kt} + \alpha_\infty \tag{18.2}$$

In this formula, t is time, k is the pseudo-first order rate constant, and α_t is the optical rotation of the solution at time t. Linearization, which requires the knowledge of the final α_∞ values as well as logarithmization of the rate equation to determine the pseudo-first order rate constant, was used as a conventional procedure in evaluation. Since the spread of personal computers, however, this procedure has become obsolete.

Modern evaluation is based on the least squares method, and requires a lot of computation but is statistically sound. To do this, you should write the exponential function in a slightly different form:

$$g(t) = Xe^{-kt} + E \tag{18.3}$$

During the experiments, a total of N data points are measured to determine the $g_1, g_2, \ldots g_N$ values of the function at time values $t_1, t_2, \ldots t_N$. The best-fitting exponential curve is the one where the sum of the squares of the differences between this curve and the measured points (S) is minimal. S is a three-variable function because there are three parameters in the exponential formula:

$$S(X, E, k) = \sum_{i=1}^{N} \left(g_i - Xe^{-kt_i} - E\right)^2 \tag{18.4}$$

Note that due to squaring, each added term is non-negative in the above formula, so $S(X, E, k)$ cannot be negative, either. If its value is zero, the exponential function fits perfectly to the measured data: this never happens in a real system. The min-

imum of a three-variable function can be found where all three partial derivatives are zero:

$$\frac{\partial S(X,E,k)}{\partial X}=0 \qquad \frac{\partial S(X,E,k)}{\partial E}=0 \qquad \frac{\partial S(X,E,k)}{\partial k}=0 \tag{18.5}$$

The first two of these, X and E, are easy to derive, so the best-fitting value for these parameters can be determined if k is already known. Although the calculation is lengthy, the final result is relatively simple:

$$\begin{aligned} X &= \frac{N\sum_{i=1}^{N} g_i e^{-kt_i} - (\sum_{i=1}^{N} e^{-kt_i})(\sum_{i=1}^{N} g_i)}{N\sum_{i=1}^{N} e^{-2kt_i} - (\sum_{i=1}^{N} e^{-kt_i})^2} \\ E &= \frac{(\sum_{i=1}^{N} e^{-2kt_i})(\sum_{i=1}^{N} g_i) - (\sum_{i=1}^{N} e^{-kt_i})(\sum_{i=1}^{N} g_i e^{-kt_i})}{N\sum_{i=1}^{N} e^{-2kt_i} - (\sum_{i=1}^{N} e^{-kt_i})^2} \end{aligned} \tag{18.6}$$

Substituting these values into equation (18.4) and forming a partial derivative wiht respect to k, the resulting equation contains only k as unknown, and is theoretically possible to solve. However, this is a difficult task, so we usually make such adaptations with a proper computer program that does not require even the knowledge of the previous few equations.

In the present experiment, this method will be followed with a suitable spreadsheet program. First, a rough estimate of the value of k is obtained on the basis of the time scale of the process, and then equation (18.6) is used to calculate the optimal value for X and E. Then $S(X,E,k)$ is calculated by equation (18.4), and the optimal value of k that has the lowest $S(X,E,k)$ value is sought by systematic trial-and-error.

18.3 Practice procedures

Turn the polarimeter on. A polarimeter (Figure 18.2) is a device for measuring the optical rotation of solutions. The light beam from the light source passes through the lens, the filter, and the polarizer to become parallel and polarized. The light beam forms a triple field on a disk of wavelength $\pi/2$. The zero position can be adjusted by raising the position of the analyzer.

The cuvette, which is filled with optically active solution, is placed between the polarizers in the sample holder (e). The beam of light can be seen on the wavelength plate. By rotating the polarizer (f), the light beam is returned to its fully shaded position (Part B in Figure 18.3) and the rotation angle can be read from the scale (d).

Prepare 100.0 cm^3 of 30 m/m % sucrose solution.

To determine the initial rotation (α_0) of the sugar solution, mix in a beaker 10.0

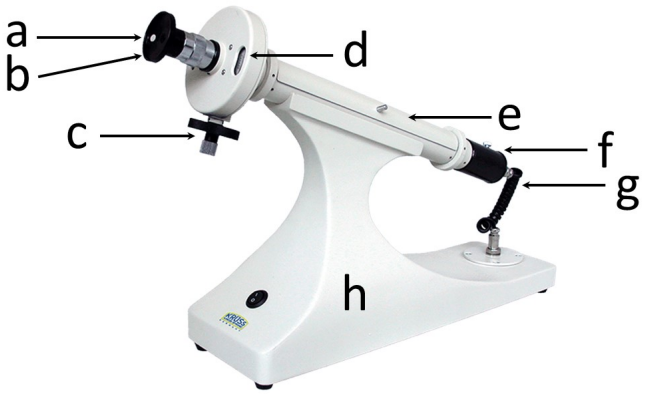

Figure 18.2: Parts of a polarimeter. a: magnifier lens; b: telescope eye piece; c: analyzer; d: scale and vernier scale; e: sample holder; f: polarizer; g: light source; h: polarimeter body

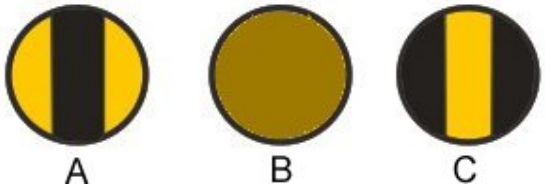

Figure 18.3: The images shown in the polarimeter. A: above or below optical zero; B: field at optical zero (this is what we want to find); C: below or above optical zero

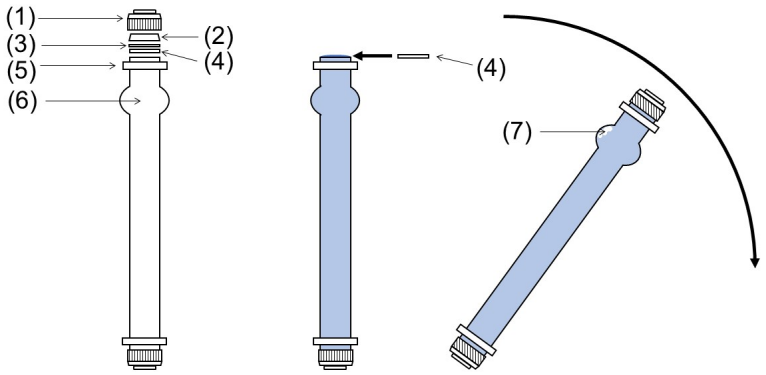

Figure 18.4: Parts of the polarimeter tube and the correct method of filling. (1) the top (outer cover) of the polarimeter tube; (2) inner cover; (3) sealing rubber; (4) glass window; (5) metal ring; (6) annular protrusion; (7) bubbles

cm^3 sugar solution and 10.0 cm^3 distilled water and fill the resulting solution into a clean, dry polarimeter tube. Write down the length of the polarimeter tube used in the experiment. The correct filling of the polarimeter tube consists of the following steps (follow the same steps for later measurements also):

1. Unscrew the top (outer cover) of the polarimeter tube (1).
2. Remove the inner cover (2), the glass window (4), and the sealing rubber (3).
3. Place the tube upright and fill it with the sample to be measured. Hold the metal ring (5) to prevent the sample in the polarimeter tube from heating up.
4. Fill the tube until the level of the liquid reaches the top of the glass tube (i.e. the tube should be filled to the brim with sample).
5. Slide the glass window (4) over the top of the tube, depressing the liquid surface. Avoid air bubbles in the polarimeter tube.
6. Replace the rubber seal (3) on the inner cover (2) and screw the outer cover (1) onto the glass window.
7. Collect any bubbles remaining in the sample (7) in the annular protrusion of the tube (6) by placing the tube in a horizontal position.

After filling the cuvette properly, place it in the polarimeter sample holder. Read the rotation of the solution to two decimal places (to do so, you will also need to use the vernier scale, which can be found at en.wikipedia.org/wiki/Vernier_scale).

Table 18.2: Composition of each sample for the kinetic study of sucrose inversion

sample number	$V_{\text{sugar solution}}$ (cm^3)	V_{HCl} (cm^3)	V_{water} (cm^3)
1	10.0	10,0	0
2	10.0	5,0	5.0
3	10.0	2,0	8.0

Table 18.3: Data of the kinetic traces. Sample number: ..., laboratory temperature = ...℃, $\alpha_0 = ...^\circ$, $\alpha_\infty = ...^\circ$

time (s)	$\alpha_t(^\circ)$
...	...

Pipette the required amounts (Table 18.2) of sugar solution and distilled water into a clean, dry beaker, then add the appropriate amount of hydrochloric acid solution. Prepare only one sample at a time. Start the stopwatch immediately after adding the hydrochloric acid. Stir the mixture well, then pour it into a clean polarimeter tube, close the plugs and place the cuvette in the polarimeter. Read the rotation of the solution to two decimals every minute until the rotation of the solution turns negative. If the rotation of the solution changes rapidly, read even more frequently (e.g. every half minute). Collect the measured data in a form similar to Table 18.3.

Because it takes hours for the reaction to reach completion, the α_∞ value belonging to t_∞ is obtained by re-assembling the original sugar-hydrochloric acid mixtures in Erlenmeyer flask and loosely plugging the flasks, then heat on a water bath (up to 50 ℃ to avoid caramelization) for 30-40 minutes to speed up the reaction. After cooling the samples back to the original temperature, measure the rotation of these solutions. Note that negative rotations are expected here (i.e. if the value read from the device is 176.26°, it is actually $176.26^\circ - 180^\circ = -3.74^\circ$). To speed up your work, these samples should be assembled and placed in the thermostat at 50 ℃ at the beginning of the laboratory practice, so you will have time to measure the kinetic curves of the same composition samples during the 30-40 minutes of heating and subsequent cooling.

Record the temperature of the laboratory (your kinetic measurements are also taken at this temperature).

18.4 Evaluation

1. Plot the measured rotation over time for each of the three experiments.

2. Determine the pseudo-first order rate constant in each of the three experi-

ments using the α_∞ values measured. To do this, the natural logarithm of the difference $\alpha_t - \alpha_\infty$ should be plotted against time. In this figure, the points give a straight line for a pseudo-first order process, and the pseudo-first order rate constant k is determined from the slope.

3. Also determine the k pseudo-first order rate constant with a spreadsheet computer program, using the least squares method described at the end of the Theoretical background subsection. Perform this determination for all three sets of data.

4. Plot the pseudo-first order rate constants measured in the three experiments as a function of hydrogen ion concentration. Use the plot to determine the reaction order with respect to hydrogen ion concentration.

5. Given the reaction order for the hydrogen ion (oxonium ion), give the actual (non-pseudo-first order) rate constant of the reaction at the temperature of the experiments.

18.5 Advanced discussion points

1. Which evaluation method do you consider more accurate? Why?

2. How do you know from your experiments that the reaction is first-order with respect to the concentration of the sugar?

3. Why did we only change the initial hydrogen ion concentration and not that of the sugar?

4. Does the hydrogen ion concentration change during the reaction?

5. Are your measured α_0 and α_∞ values in agreement with the data of Table 18.1? What could be the reason for the difference?