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Практическое руководство к лабораторным работам по физической химии

Laboratory Manual of Physical Chemistry

для студентов ИФМиБ

for IFMB students

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WORK #1. RATE OF SUCROSE INVERSION

Sucrose (S) is hydrolyzed to form D-glucose (G) and D-fructose (F):

$$\underset{}{C_{12}H_{22}O_{11}} + H_2O \rightarrow \underset{D\text{-}glucose}{C_6H_{12}O_6} + \underset{D\text{-}fructose}{C_6H_{12}O_6}$$

Without a catalyst this reaction goes too slow. It can be accelerated by adding acid (specific catalysis). The mechanism of catalysis can be represented as follows:

$$S + H^+ \leftrightarrow [SH]^+ \rightarrow G + F + H^+$$

The equilibrium at the first stage is achieved very rapidly, and the decomposition of $[SH]^+$ complex determines the rate of the process. The reaction is performed in aqueous solution with the initial sucrose concentration ≈10% (wt). Because of the large difference in the molecular weights of water (18) and sucrose (344), the molar concentration of sucrose is low. The reaction has the first order with respect to both sucrose and water, but the concentration of water doesn't change. The equation for the rate of reaction in this case can be written as:

$$w = k' \cdot C_s$$

where $k' = k \cdot C_{H2O}$. Then the pseudo-first order rate constant k' may be calculated according to equation (1).

$$k' = \frac{1}{t} \cdot ln\frac{Co}{Ct} \qquad (1)$$

Sucrose and products of its hydrolysis have asymmetric carbon atoms and are optically active. When linearly polarized light passes through the solutions of these substances, a rotation of the plane of polarization occurs.

The optical rotation for solutions (angle of rotation of the plane of polarization) α is directly proportional to the thickness of the solution layer *d* and the concentration of the active substance *C*,

$$\alpha = [\alpha]\cdot d\cdot C$$

where [α] - specific rotation (i.e. rotation at *d*= 1 dm and *C* = 1g/ml). The value [α] depends on the temperature, the wavelength of the polarized light and the nature of the solvent. At 20°C and at wavelength λ= 589.3 nm (D line of sodium spectrum) for the aqueous solutions of sucrose [α]= 66.5°; for glucose [α]=52.7°, for fructose [α]= –92°. Since fructose has a negative [α], the rotation angle decreases down to negative values during the hydrolysis process. Thus, the process is often called inversion. For a mixture of optically active substances, the rotation angle is equal to the algebraic sum of the angles of rotation for each of the optically active substances.

If α_0 is the angle of rotation at the beginning of the reaction, α_t — the rotation angle at the time *t*, α_∞ — the angle of rotation at the end of the reaction, equation (1) can be written as follows:

$$k = \frac{1}{t}\cdot \ln\frac{\alpha0 - \alpha\infty}{\alpha t - \alpha0} \qquad (2)$$

This work is an example of using polarimetry to study kinetics of chemical reactions. Measurement of rotation performed using a polarimeter (sugarmeter).

Experimental

Take a prepared 20% solution of sucrose. If the solution is turbid, it should be filtered. Then, using a pipette or graduated cylinder mix the sugar solution and HCl in a ratio told by the teacher into 50 ml flask. The mixture should be mixed thoroughly, and then half of it should poured into a polarimetric tube and placed in a polarimeter.

The remaining half of the reaction mixture is placed to a thermostat (60°C) for α_∞ assessment.

After that start the timer and immediately write down the initial value α_0. The frequency of measurements: it is recommended to make measurements every 2 minutes with total time of experiment of 30 minutes. After all measurements, the rotation corresponding to the end of reaction should be determined. A thermostatic reaction mixture should be cooled to room temperature and poured into the tube.

You should plot $ln(\alpha_t - \alpha_\infty)$ against t. The slope of the straight line taken with the opposite sign is the reaction rate constant *k*'.

The results of experiments and calculations should be presented as a Table 1, containing the following data.

Volume of sugar solution_________ml *Volume of catalyst solution_______ml*

Final rotation α_∞ __________ °

Table 1

Change of the rotation over time and the reaction rate constant of inversion of sugar

t	α_t	$\alpha_t - \alpha_\infty$	$ln(\alpha_t - \alpha_\infty)$	k', min^{-1}

The conclusions should contain comparison of the *k*' values obtained both graphically and analytically.

WORK #2. RATE OF OXIDATION OF HYDROIODIC ACID WITH HYDROGEN PEROXIDE

Oxidation of hydroiodic acid by hydrogen peroxide proceeds according to the equation:

$$HI + \frac{1}{2}H_2O_2 \rightarrow \frac{1}{2}I_2 + H_2O$$

When hydrogen peroxide is in significant excess the reaction is well described by the first order kinetic equation. In this case, the reaction rate constant can be calculated according to equation:

$$k = \frac{1}{t} \cdot ln\frac{Co}{Ct}$$

where k is reaction rate constant, t is time, C_0 is initial concentration, C_t is concentration at the time of measurement.

The conductivity of the reaction mixture depends on the concentration of hydroiodic acid which is strong electrolyte. As the reaction proceeds the conductivity will decrease proportionally to the concentration of electrolyte in solution. Because of the linear dependence (in dilute solutions) between concentration of strong electrolyte and conductivity the values of conductivity can be used instead of concentrations to calculate the first order rate constant, according to the following equation:

$$k = \frac{1}{t} \cdot ln\frac{\chi o}{\chi t} \qquad (1)$$

where χ_0 is the initial electrical conductivity of the solution, and χ_t — conductivity at time t.

Experimental

Measurements of the electrical conductivity is carried out by the calibrated Conductivity Meter. Before making measurements turn on the device and wait for 5 minutes for the instruments to warm up. Select measurement scale.

Place 10 ml of HI solution in a conductivity measurement flask. Place 0.1 ml of a 30% solution of hydrogen peroxide into measurement cylinder and add distilled water up to 15 ml. Add a solution of hydrogen peroxide to the hydroiodic acid solution and mix thoroughly. Lower the electrode into the mixture and start the timer, write the initial value χ_0. Further measurements should be carried out every minute. 20 minutes after the start of the experiment the measurement can be stopped.

Obtained data are plotted in coordinates **$\ln(\chi_t)$ against t**. The reaction rate constant k value is given by the slope of the approximating line. The reaction rate constant values at different times are also calculated using equation (1) and the average reaction rate constant is calculated. Experimental and calculated data are presented in Table 2.

Table 2

Changes in conductivity over time and the calculated rate constant values of the hydroiodic acid oxidation reaction

t, min	χ_t	$\ln \chi_t$	k, min^{-1}

The conclusions should contain comparison of the values obtained both graphically and analytically.

WORK #3. DECOMPOSITION RATE OF MANGANESE TRIOXALATE COMPLEX

Photometry can be used to study kinetics of chemical reactions that result in a change of color. One example of such reaction is the decomposition of the complex ion manganese trioxalate, which is brown-colored, while the reaction products are colorless.

$$Mn[(C_2O_4)_3]^{3-} \rightarrow Mn^{2+} + 2.5C_2O_4^{2-} + CO_2\uparrow$$

The reaction follows first order kinetics. The optical density of the solution depends on the concentration of manganese trioxalate. The optical density for solutions D is directly proportional to the thickness of the solution layer l and the concentration of the active substance C,

$$D = \varepsilon \cdot C \cdot l$$

where ε is molar extinction coefficient (i.e. optical density at $l = 1$ cm and $C = 1$ mol/L). The ε value depends on temperature, wavelength of the light and the nature of the solvent. The reaction rate constant can be calculated by modified equation:

$$k = \frac{1}{t} \cdot ln\frac{Do}{Dt}$$

where D_0 and D_t — the optical density of the solution at the initial time and at time t.

Spectrophotometer measures percentage of the transmitted light (N), from which the transmittance τ and the optical density of the solution D can be calculated:

$\tau = N / 100$

$D = -log_{10}(\tau)$

Experimental

Make sure that the light path on the sample compartment of the spectrophotometer is not blocked and the sample compartment lid is closed. Turn on the spectrophotometer using the power switch located on the rear panel. A beep sounds and the display will display the progress of the self-diagnosis procedure. Wait for at least 20 minutes for the instrument to warm up.

Place the first cuvette with distilled water into the sample compartment and press "Zero". The value "100" should be displayed on the screen.

The reaction mixture is prepared as follows: place 1ml of 0.1M solution of $MnSO_4$, 7ml of 0.1M solution of $H_2C_2O_4$ and 2 ml of 0.01M solution of $KMnO_4$ into a porcelain beaker and mix thoroughly. Fill the second cuvette with resulting mixture and place into the sample compartment of the device. Start the timer and write down the initial value of N.

Take measurements of the transmittance N every minute. Stop when values of the transmittance exceed 90 or after 20 minutes. Fill the Table 3.

After the measurements plot $ln(D_t)$ against t. The slope of the fitting line gives the value of the reaction rate constant.

Table 3

Changes in transmittance over time and calculated rate constant values of the decomposition reaction of manganese trioxalate

t, min	N	τ	D_t	$\ln D_t$	k, min^{-1}

The conclusions should contain comparison of the values obtained both graphically and analytically.

WORK #4. MEASUREMENT OF PH

The pH is a unit of the degree of acidity or alkalinity of a system (typically aqueous solution). It is used to make quantitative statements about the nature of solution, instead of subjective ones like “this solution is weakly acidic” or “orange juice is more sour than milk”. The concept of pH was originally defined in 1909 by the Danish chemist Søren Sørensen who used the formula:

$$pH = –\log_{10} a(H+)$$

where *a* is ion activity. For diluted solutions activity is nearly equal to the molar concentration, so we can write:

$$pH \approx –\log_{10} [H+]$$

Water is an electrically neutral molecule made of two hydrogen atoms and one oxygen atom (H2O). In the molecule, the electrons are not distributed evenly among the atoms, but are located closer to the oxygen atom than to the two hydrogen atoms. That is the reason why a water molecule can give off electrically charged particles (H+ ions, protons). This process produces two ions:

$$H_2O \leftrightarrow OH^– + H^+$$

The balance of this reaction is shifted greatly to the side of undissociated water. In reality, H^+ ions cannot exist in a solution because of extreme charge density (as H^+ is, in fact, an elementary particle), thus positively charge particles in water solutions are represented by complexes between H+ ion and water molecule, called hydronium H_3O^+. Because of hydrogen bonding species of compositions $(H_5O_2)^+$, $(H_7O_3)^+$ and so forth are also present.

At 22°C, only 10^{-7} mole of water per liter is dissociated. In aqueous systems, the following relationship exists between the activity of protons and the activity of hydroxyl ions:

$$K_w = [OH^–]\cdot[H^+] = 10^{-14}$$

If the activity of one type of ion is known, the activity of the other can be calculated. In practice, we usually only look at the proton concentration. It does not make sense to directly state the ionic activity because of the low concentration of these ions in water. By using the negative common logarithm, acidity scale is shifted to a more manageable numeric values. In other words, pH = 0 represents the activity of 1 mole/L of H^+ ions (e.g. in a hydrochloric acid solution of 1 mole/L). By contrast, pH = 14 shows an activity of 10^{-14} moles/L of H^+ ions (which is equivalent to 1 mole/L of OH- ions, e.g. to a sodium hydroxide solution of 1 mole/L). A pH of 7.0 defines a neutral aqueous solution. That means that the solution contains the same number of protons as hydroxyl ions.

pH < 7	acidic
pH = 7	neutral
pH > 7	basic

Raising the pH by a factor of 1 produces a ten-fold increase in the H^+ ion activity. The pH of alcohols and other "water-like" polar solvents can also be measured. These kinds of solutions can have extremely high pH values (up to pH = 29, which is equivalent to an extremely low proton activity of 10-29 moles/L). The neutral point of these (anhydrous) solvents is not around a pH of 7, but usually at much higher range (with the exception of anhydrous acids like acetic acid). The neutral point is the pH at which the activity of the protons is the same as the activity of the particles that have given off the proton (hydroxyl ions in an aqueous system). Correspondingly, substances that cannot give off protons very easily have a neutral point at much lower concentrations (and consequently at higher pHs) than in aqueous systems.

The following section will deal with aqueous systems as they represent the main applications for pH measurements. The most common way to determine pH is by electrochemical measurement. The instrument used for this is a pH meter equipped with an electrode suitably designed to measure the pH. A pH electrode (measuring electrode) generates a potential as a function of the pH of the surrounding solution. This potential is measured against that of a reference electrode, which provides a constant potential. The pH meter reads the potential difference of the two electrodes and converts it to pH units.

Accurate and reproducible measurements cannot be produced unless they are conducted under defined measuring conditions. It is particularly important that the temperature of the medium to be tested is kept constant and that it is homogeneous. In some samples, the time between sample collection and measurement plays a key role. For example, a number of alkaline samples with a low buffer capacity rapidly change their pH when they absorb CO_2 from the air.

Glass Electrode

The electrodes most commonly used to measure pH are glass membrane electrodes. This type of electrode features a glass membrane. When it is immersed in an aqueous solution, a hydrated layer (also referred to as a gel layer) forms on its surface. During this process, dissociation occurs at the junction site between glass and solution (in the older literature, this process is described as ion exchange). Alkali ions of the glass go into solution (dissociate) and are replaced by protons from the aqueous solution. This produces a thin layer containing abundant hydroxyl groups.

$$\equiv\text{Si-O-Na} + \text{H}^+ \rightarrow \equiv\text{Si-OH} + \text{Na}^+$$

Since this process does not lead to a stable potential on the glass surface until after approx. 72 hours, new or dried out electrodes have to first be formatted or regenerated by soaking them in an electrolyte solution. By contrast, newly purchased electrodes that contain a sufficient amount of fill solution and electrodes that have enough electrolyte in the wetting cap can be used right away.

In acidic to neutral solutions, a residue rich in silicic acid forms on the electrode surface over time; such corrosion products have to be constantly rinsed off and new hydrated layers are reproduced.

$$\equiv SiOH + HOSi\equiv \rightarrow \equiv Si\text{-}O\text{-}Si\equiv + H_2O$$

In basic solutions, by contrast, the silicic acid dissolves gradually. The dissolution rate of the outer layer is at a minimum at pH range = 3...5.

$$\equiv Si\text{-}O\text{-}Si\equiv + H_2O \rightarrow \equiv SiOH + HOSi\equiv$$

Depending on the pH of the sample, protons diffuse into the hydrated layer or out of it. This creates an electrochemical potential. The number of protons that can diffuse into this hydrated layer is limited by the number of solidly anchored hydroxyl and oxonium groups. On the inside of the membrane, the interior buffer ensures a constant potential. The potential at the glass membrane is measured against a reference electrode.

Silver Chloride Electrode

The reference electrode has a constant potential that is independent of the sample. It is comprised of a reference element that is immersed in a solution with a known, constant composition. The most well- established and widespread system uses silver/silver chloride (Ag/AgCl) that is immersed in a KCl solution, Fig. 1. Electrodes with "gel electrolyte" are extremely maintenance-free and suitable for many standard types of measurements. In this electrode, the KCl solution is thickened by adding viscosifiers to form a gel that is so thick that it cannot escape through the junction and therefore does not have to be refilled.

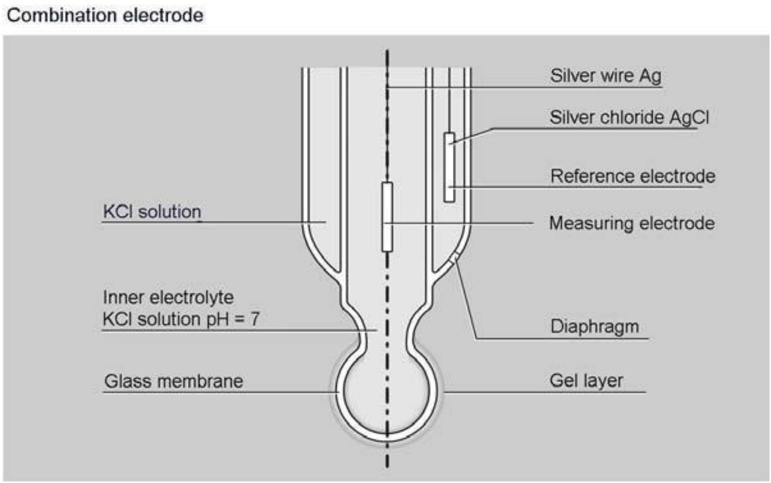


Figure 1. Ag/AgCl electrode

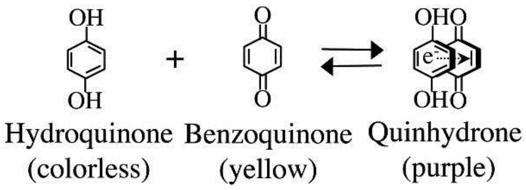
The electrical contact between the reference electrode and sample is generated at the junction site. This is an opening with a very small diameter which allows direct contact between the fluids but prevents them from becoming mixed together rapidly. In order to prevent the test solution from penetrating into the reference electrode, a slight overpressure in the reference electrode must be maintained to keep out the test solution. The escaping electrolyte solution forces back any test solution that is trying to diffuse into the opening. This is accomplished by filling the electrode in such a way that the level of electrolytes is approx. 2-3 cm higher than that of the fluid level of the sample. A highly concentrated KCl solution is used to avoid disturbances due to a diffusion potential at the junction site. In general, concentrations of 3 moles/L, 4 moles/L are common or a saturated KCl solution is used. The type of electrode filling is usually labeled on the body of the electrodes, thereby ensuring that the electrode filling is refilled to the right concentration.

Today, mostly electrodes are used in which the test and reference electrode are housed in one body (combination electrodes, see Figure 4). A number of combination electrodes additionally have a built-in temperature sensor, making it possible to capture all relevant parameters with just a single sensor. pH electrodes need to be kept moist at all times, if stored dry a complicated regeneration procedure is required before the next measurement can be performed. For storage, a plastic "wetting cap" is placed over the electrode. This cap contains a few milliliters of storage solution (usually KCl solution). pH electrodes can also be stored in a diluted buffer solution with a pH = 7.00 during work breaks.

Quinhydrone Electrode

The quinhydrone electrode is a type of redox electrode which can be used to measure the hydrogen ion concentration (pH) of a solution in a chemical experiment. It provides an alternative to the commonly used glass electrode in a pH-meter.

The quinhydrone electrode consists from a platinum dipped into a solution saturated with quinhydrone. Quinhydrone (QH) is a slightly soluble compound formed by the combination of one mole of benzoquinone (BQ) and one mole of hydroquinone (HQ). The electrode reaction is:



$$C_6H_4O_2 \quad + \quad 2H^+ \quad + 2e^- \quad = \quad C_6H_4(OH)_2$$

Benzoquinone (BQ) **Hydroquinone (HQ)**

Quinone is oxidant, and hydroquinone is reductant in this reaction. It very easy to prepare and handle. Pure solid quinhydrone is dissolved in the solution to be measured until the solution is saturated and an excess is present. A platinum wire is dipped into this solution. The electrode potential is given by:

$$E_{QH} = E_{QH,0} + (0.059/2)\cdot\log(a_{BQ}\cdot a^2_{H+}/a_{HQ})$$

$$E_{QH} = U + E_{AgCl}$$

Benzoquinone (BQ) and hydroquinone (HQ) are obtained by dissolving quinhydrone in solution, therefore:

$$a\mathrm{HQ} = a\mathrm{BQ}$$

Applying the following substitution, the equation can be simplified:

$$\boldsymbol{E_{\mathrm{QH}} = E_{\mathrm{QH,0}} - 0.059\cdot\mathrm{pH}}$$

The standard potential of the quinhydrone electrode is calculated according to equation:

$$\boldsymbol{E_{\mathrm{QH,0}} = 0.6994 - 7.36\cdot10^{-4}\cdot(t\text{-}25)}$$

where: t – is the temperature in degree Celsius.

Experimental

Glass Electrode

The fragile glass electrode must be handled with care, it should be rinsed carefully before and after the use. Between experiments, electrode should be kept in the storage solution. Do not forget to write down the laboratory temperature.

1. Turn on the pH-meter. Take the electrode from the storage solution (shift it vertically up without leaving the holder). Rinse it with distilled water.
2. Rinse the beaker with distilled water and then fill the beaker with measured solution.
3. Put the electrode back to the beaker and insert the electrode into the solution.
4. Read the pH from the display of pH-meter when the value is stable.
5. Write the pH value down.
6. Repeat the procedure for each solution.

Quinhydrone Electrode

1. Turn on the potentiometer. Take electrodes from the storage solution. Rinse them with distilled water, don´t dry it.
2. Fill the beaker with a measured solution. Approximate values of pH of solutions are written on the flasks. Measure the temperature of the solution (*t*) and write it down.
3. Take a little quinhydrone (black powder) using a spatula, and add it to the measured solution. Mix the solution carefully using a glass stick to obtain a saturated solution of quinhydrone.
4. Put the electrodes to the solution in the beaker.
5. Connect the quinhydrone electrode to the positive terminal, and the silver chloride electrode to the negative terminal.
6. Read the voltage (*E* in V or mV) from the display of potentiometer when the value is stable.
7. Write the *E* value down.
8. Repeat the procedure for each solution where the use of the quinhydrone electrode is possible. Clean both electrodes with distilled water. Calculate the standard potential of quinhydrone electrode at laboratory temperature. Calculate pH of the solution.

Obtained pH values should be written in the Table 4.

Table 4

pH measurements by different methods

Solution code number	pH from glass electrode	pH from QH electrode

Write the conclusion about the results of measurement by various methods.

WORK #5. POTENTIOMETRIC AND PH-METRIC TITRATION

Titration, also known as titrimetry, is a common laboratory method of quantitative chemical analysis that is used to determine the unknown concentration of an identified substance or mixture of substances. The key measurement which is used to determine the concentration is volume, so it is also known as volumetric analysis. A reagent, called “titrant” is prepared with a precisely known concentration. A known concentration and volume of titrant reacts with a solution of titrand (analyzed substance) to determine concentration. The volume of titrant reacted is called titration volume.

The titration is carried out by adding small amounts of titrant to the solution of titrand and taking sufficient measurements of solution properties (i.e. color, potential, conductivity). Titrant and titrand react, thus the amount of titrand slowly decreases. At certain point during the process the added amount of titrant would be enough for the titrand to be completely depleted. This means that added amount of titrant is in equivalence relation to the amount of titrand and the condition is called equivalence point. The precision of titrand concentration determination relies of the accuracy of equivalence point measurement.

The potentiometric titration uses measurement of the electrode potential to determine equivalence point. The titration curve of potentiometric titration is the dependence of potential in the analyzed solution on the volume of added titrant. At the equivalence point there usually is an inflection point on the titration curve. To find the position of equivalence point with higher precision, a first or second derivative of titration curve can be plotted.

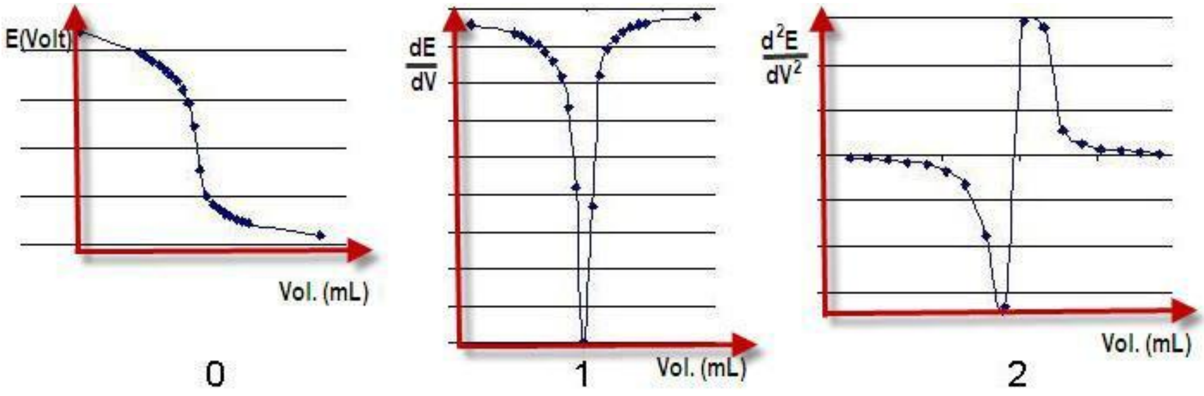


Figure 2. Typical curves of potentiometric titration: 0 – titration curve, 1 – first derivative of titration curve, 2 – second derivative of titration curve

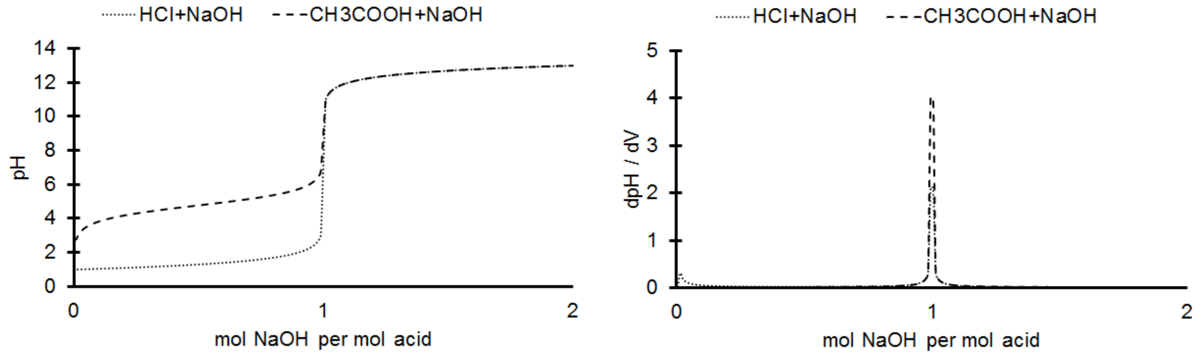


Figure 3. Typical curves of pH-metric titration: (left) *pH* vs. *V*; (right) $\Delta pH/\Delta V$ vs. *V*

To carry out potentiometric titration a galvanic cell must be used consisting of reference electrode (its potential does not depend on the composition of mixture) and indicator electrode. Different types of titrations including acid-base, redox, metal-ion titration can be carried out with a sufficient indicator electrode.

For acid-base titration a glass electrode with a membrane sensitive to the hydrogen-ion activity is used. The electrode consists of small glass vessel with a bubble on the tip which is covered by a thin glass membrane. A caution must be taken so that the membrane is not accidentally broken. Silver chloride electrode is used as reference.

Experimental

Turn on the pH-meter. Burette must be filled with titrant (0.1M NaOH). Take notice of the level of the solution before starting titration. Glass, magnetic rod for the stirrer and a sensor of the pH-meter must be washed thoroughly with distilled water.

10 ml of the solution of hydrochloric acid (HCl) must be placed in a clean glass from burette along with a stirring rod. Acid solution must be diluted so that the volume of the liquid in a glass is enough to submerge sensor of the pH-meter.

After everything is in place stirrer must be turned on and sufficient stirring speed must be set, the reading of potential shown by pH-meter should settle to a constant value. This is the initial value of potential for our experiment, write it down. Once the value is constant 1 ml of NaOH solution is added to the glass, after which a new potential reading is taken, write it down. This operation repeated until 20 ml of NaOH is added to the solution.

Next the experiment must be repeated with 10 ml of the solution of acetic acid (CH_3COOH) and with the mixture of hydrochloric and acetic acids. In case of the mixture titrant must be added with 0.5 ml increments throughout the entire titration.

Fill the table:

Table 5

Titration data

V_{NaOH}	E or pH	$\Delta E/\Delta V$ or $\Delta pH/\Delta V$
0		–
1		
…		
20		

For potentiometric titration, the plots of electrode potential vs added titrant volume as well as first derivative ($\Delta E/\Delta V$ vs V) of the graph must be drawn. For pH-metric titration, the plots of pH vs added titrant volume must be drawn, as well as first derivative ($\Delta pH/\Delta V$ vs V).

Determine equivalence points using those graphs. When equivalence points are found, corresponding concentrations of acids can be calculated by an equation

$$V_{\text{e.p.}} \cdot C_{\text{NaOH}} = V_{\text{a}} \cdot C_{\text{a}},$$

where $V_{\text{e.p.}}$ – the volume of added titrant at equivalence point, C_{NaOH} – concentration of the titrant, V_{a} – volume of acid, C_{a} – concentration of acid.

Write the conclusion about concentrations obtained.

WORK #6. CONDUCTOMETRIC TITRATION

Titration, also known as titrimetry, is a common laboratory method of quantitative chemical analysis that is used to determine the unknown concentration of an identified substance or mixture of substances. The key measurement which is used to determine the concentration is volume, so it is also known as volumetric analysis. A reagent, called “titrant” is prepared with a precisely known concentration. A known concentration and volume of titrant reacts with a solution of titrand (analyzed substance) to determine concentration. The volume of titrant reacted is called titration volume.

The titration is carried out by adding small amounts of titrant to the solution of titrand and taking sufficient measurements of solution properties (i.e. color, potential, conductivity). Titrant and titrand react, thus the amount of titrand slowly decreases. At certain point during the process the added amount of titrant would be enough for the titrand to be completely depleted. This means that added amount of titrant is in equivalence relation to the amount of titrand and the condition is called equivalence point. The precision of titrand concentration determination relies of the accuracy of equivalence point measurement.

The conductometric titration uses measurement of the conductivity (χ) to determine equivalence point. The titration curve of conductometric titration is the dependence of conductivity of the analyzed solution on the volume of added titrant. At the equivalence point there usually is a corner on the conductometric titration curve.

Conductometric titration can be applied to the diluted electrolyte solutions if during the reaction between titrand and titrant weakly dissociating compounds (such as water) or ions with low- mobility are formed or if highly mobile ions are substituted with lowly mobile ones. Conductometric titration is especially useful when used for colored or cloudy solutions where usual titration which uses indicator color change cannot be used. Conductometric titration can also be relatively easily automated, i.e.

the process of titrant addition and titration curve registration can be controlled by a computer.

Conductometric titration is possible because the specific and total conductivity of the diluted electrolyte solutions are almost linearly dependent on electrolyte concentration. The examples of the titration curves of conductometric titration are presented on the picture below:

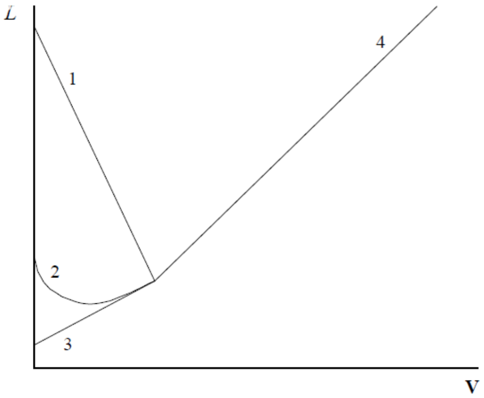


Figure 4. Typical conductometric acid-base titration curves: (1+4) strong acid (or base) with strong base (or acid), (2+4) – medium strength acid or base, (3+4) weak acid or base

Let's look in a greater detail into the nature of processes which cause the particular shape of the titration curve. In case of titration of strong acid HA with strong base NaOH, the acid is neutralized and a salt is formed. Because of this the amount of highly mobile H^+ ions decreases and the same amount of Na^+ ions appears. However, due to the lower mobility of Na^+ as compared with H^+, the conductivity of the solution decreases. After the equivalence point, addition of base does not cause the decrease in the concentration of any of the ions, highly mobile OH^- ions are appearing in the solution instead (as they are not consumed in the neutralization reaction anymore). Thus after passing equivalence point the conductivity of the solution rises.

In case of weak acid, the conductivity of the solution will rise upon the addition of the strong base even before the equivalence point, because weakly dissociating electrolyte which is acid is replaced with its salt, which fully dissociates. However, after passing equivalence point the conductivity of the solution will grow faster, as addition of strong base increases the amount of highly mobile OH^- ions.

Medium strength acid represents an intermediate situation and the determination of the equivalence point might appear tricky. Additives which inhibit dissociation (such as organic solvents) can be added to the solution so that the acid behaves more like weak one and the determination of equivalence point is more straightforward.

The mixture of strong and weak acids will produce two corners on the titration curve. The first corner corresponds to a stronger acid. If dissociation constants of polybasic acids are sufficiently different, then multiple corners on the titration curve can also be observed.

Experimental

Turn on the conductometer. Burette must be filled with titrant (0.1M NaOH). Take notice of the level of the solution before starting titration. Glass, magnetic rod for the stirrer and a sensor of the conductometer must be washed thoroughly with distilled water.

10 ml of the solution of hydrochloric acid (HCl) must be placed in a clean glass from burette along with a stirring rod. Acid solution must be diluted so that the volume of the liquid in a glass is enough to submerge sensor of the conductometer to the level of the mark.

After everything is in place stirrer must be turned on and sufficient stirring speed must be set, the reading of conductivity shown by conductometer should settle to a constant value. This is the initial value of conductivity for our experiment, write it down. Once the value is constant 1 ml of NaOH solution is added to the glass, after which a new conductivity reading is taken, write it down. This operation repeated until

20 ml of NaOH is added to the solution. When 20 ml of titrant is added to the solution the experiment is stopped. Glass, stirring rod and the sensor must be washed thoroughly with distilled water.

Next the experiment must be repeated with 10 ml of the solution of acetic acid (CH_3COOH) and with the mixture of hydrochloric and acetic acids. In case of the mixture titrant must be added with 0.5 ml increments throughout the entire titration.

Fill the **Table 6** with data obtained: V_{NaOH} and corresponding χ values. The graphs of conductivity vs added titrant volume must be drawn. Determine equivalence points using those graphs. When equivalence points are found, corresponding concentrations of acids can be calculated by an equation

$$V_{\mathrm{e.p.}} \cdot C_{\mathrm{NaOH}} = V_{\mathrm{a}} \cdot C_{\mathrm{a}},$$

where $V_{\mathrm{e.p.}}$ – the volume of added titrant at equivalence point, C_{NaOH} – concentration of the titrant, V_{a} – volume of acid, C_{a} – concentration of acid.

Write the conclusion about concentrations obtained.

WORK #7. DETERMINATION OF SOLUBILITY OF A POORLY SOLUBLE SALT

The concentration of even saturated solution of poorly soluble salt is extremely low, thus its equivalent conductivity approaches limiting molar conductivity λ_0. Therefore, the concentration of salt can be calculated based on Kohlrausch law using the following equation:

$$Cn = \frac{\chi s - \chi w}{1000 \cdot (\lambda^{+} + \lambda^{-})}$$

where Cn is equivalent concentration (g-eq/l), χs — conductivity of the solution, χw — conductivity of water, λ^{+} and λ^{-} are limiting molar ionic conductivities for cation and anion, respectively.

Molar concentration cm can be calculated from equivalent concentration taking ion charges into account, i.e. for salt $M_x^{z+}A_y^{z-}$, the molar concentration can be calculated as:

$$Cm = \frac{Cn}{x \cdot z^{+}} = \frac{Cn}{y \cdot z^{-}}$$

For saturated solution the determined molar concentration is equal to the solubility (s) of corresponding salt. Another common measure of solubility of ionic compounds is solubility product K_S. For salt M_xA_y, solubility product will be calculated from the ionic concentrations:

$$K_S = [M^{z+}]^x \cdot [A^{z-}]^y$$

Experimental

The specific conductivity of distilled water must be measured. In order to do this, glass beaker must be thoroughly washed with distilled water, then measurements of χ_w must be taken. Measurement must be repeated few times to ensure correct result.

After measurement of specific conductivity of distilled water, small amount of poorly soluble salt must be grounded in pestle and mortar and transferred into flat bottomed flask. Then it should be washed two or three times with distilled water. 70-80 ml of distilled water should be added to the washed salt and the flask should be kept at constant temperature for 10 to 15 minutes under stirring. Then about 50 ml of clear solution must be transferred (using pipette or measuring cylinder) to the beaker and conductivity of this solution (χ_s) must be measured.

The solution above the salt in the flask must be dispensed, and again 70-80 ml of distilled water must be added to the flask. After this same measurement procedure must be repeated and new measurement of conductivity must be performed.

This procedure must be repeated a few times before measured conductivity values converge. Flask and measuring beaker must be washed with distilled water thoroughly after the experiment.

Using measured values of χ_s and χ_w as well as values of λ from the table 7.1, solubility Cn and Cm, as well as K_s must be calculated and presented in the Table 7.

Table 7

Solubility of the studied salts

Salt	Corrected conductivity $\chi_s - \chi_w$	Limiting molar conductivity $\lambda_0 = \lambda^+ + \lambda^-$	Cn	Cm	K_s

Find the literature data for solubility of salts studied and compare it with your results. Write the conclusion about the results obtained.

Necessary data:

Table 7.1

Limiting ionic conductivities

cation	λ^+, m²/Ohm·g-eq	anion	λ^-, m²/Ohm·g-eq
Ba^{2+}	127	SO_4^{2-}	160
Ca^{2+}	119	CO_3^{2-}	139
Zn^{2+}	108	Cl^-	76.4
Cd^{2+}	108	Br^-	78.1
Ag^+	61.9	I^-	76.8

WORK #8. GALVANIC POTENTIALS

An electrode in an electrochemical cell is referred to as either an anode or a cathode. The anode is now defined as the electrode at which electrons leave the cell and oxidation occurs (indicated by a minus symbol, "−"), and the cathode as the electrode at which electrons enter the cell and reduction occurs (indicated by a plus symbol, "+"). Each electrode may become either the anode or the cathode depending on the direction of current through the cell.

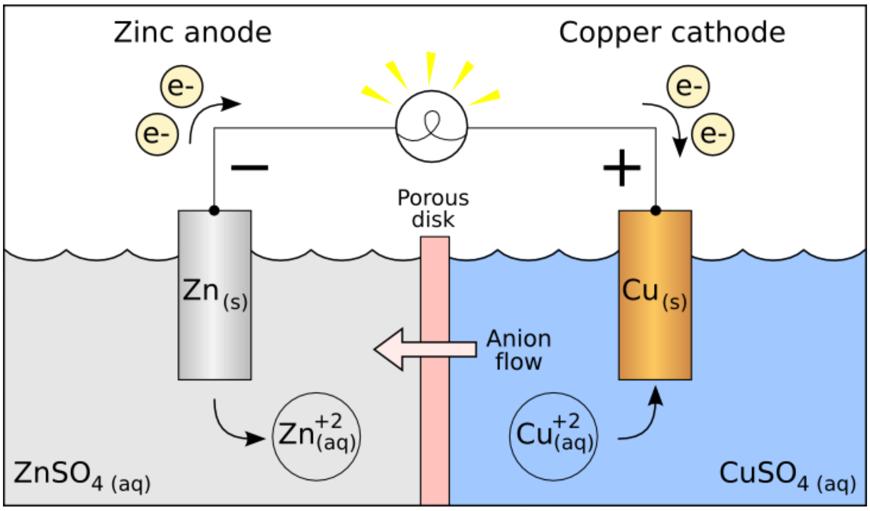


Figure 5. Zinc-Copper galvanic system

In electrochemistry, the Nernst equation is an equation that relates the reduction potential of an electrochemical reaction (half-cell or full cell reaction) to the standard electrode potential E_0, number of electrons of electrode reaction n, temperature T, and activities a (often approximated by concentrations C) of the chemical species undergoing reduction and oxidation. It is the most important equation in the field of electrochemistry.

$$E = E_0 + \frac{RT}{nF}\ln(\frac{a_{ox}}{a_{red}}) \qquad (1)$$

$$E = E_0 + \frac{0.059}{n}\lg(C_{Me}) \qquad (2)$$

$$U = E_{cat} - E_{an} \qquad (3)$$

In this work, *four* solutions of metal sulphates will be given for you: two solution of Metal 1 (with concentrations 0.1 and 1M) and two solution of Metal 2 (also with concentrations 0.1 and 1M). You should measure 4 voltages: 4 measurements between Metal 1 and Metal 2 with different concentrations combination and 4 measurements between metal salt solution and standard AgCl electrode (E_0 = 0.222 V). Calculate potentials for each of four metal electrodes E (Eq. 2), voltages for all pairs *Ucalc* (Eq. 3) and fill the Table 8 for the report. Write the conclusion.

Table 8

Experimental measurement of galvanic voltages

Electrodes	***Uexp***	***Ucalc***	***error, %***
Metal 1 (0.1M) - Metal 2 (0.1M)			
Metal 1 (0.1M) - Metal 2 (1M)			
Metal 1 (1M) - Metal 2 (0.1M)			
Metal 1 (1M) - Metal 2 (1M)			
Metal 1 (0.1M) - AgCl			
Metal 1 (1M) - AgCl			
Metal 2 (0.1M) - AgCl			
Metal 2 (1M) - AgCl			

$$error(\%) = \frac{|\,Uexp - Ucalc\,|}{U\ calc} \cdot 100\%$$

Table 8.1

Standard electrode potentials E_0

Metal	**Cation**	**E_0, V**	**Metal**	**Cation**	**E_0, V**
Li	Li^+	–3.04	Fe	Fe^{3+}	–0.425
Rb	Rb^+	–2.98	Cd	Cd^{2+}	–0.404
K	K^+	–2.931	Ni	Ni^{2+}	–0.234
Ba	Ba^{2+}	–2.905	Sn	Sn^{2+}	–0.141
Sr	Sr^{2+}	–2.899	Pb	Pb^{2+}	–0.126
Ca	Ca^{2+}	–2.868	H_2	H^+	0
Na	Na^+	–2.71	Cu	Cu^{2+}	+0.338
Mg	Mg^{2+}	–2.372	Hg	Hg^+	+0.797
Al	Al^{3+}	–1.7	Pb	Pb^{4+}	+0.8
Mn	Mn^{2+}	–1.185	Ag	Ag^+	+0.799
Zn	Zn^{2+}	–0.763	Hg	Hg^{2+}	+0.851
Cr	Cr^{3+}	–0.74	Pt	Pt^{2+}	+0.963
Fe	Fe^{2+}	–0.441	Au	Au^{3+}	+1.498

RECOMMENDED LITERATURE

1. Upadhyay S. K., Chemical Kinetics and Reaction Dynamics, Anamaya Publishers, 2006.

2. Soustelle M., An Introduction to Chemical Kinetics, ISTE, 2011.

3. Bard A. J., Faulkner L. R., Electrochemical Methods: Fundamentals and Applications, John Wiley & Sons, Inc., 2001.

4. Eliaz N., Gileadi E., Physical Electrochemistry: Fundamentals, Techniques, and Applications, Wiley-VCH, 2019.

5. Holze R., Experimental Electrochemistry: A Laboratory Textbook, Wiley-VCH, 2019.

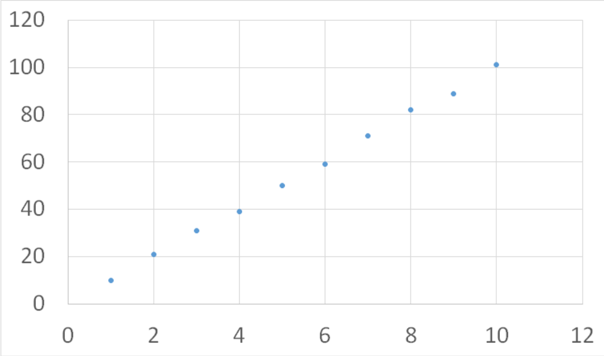
SUPPLEMENTARY. HOW TO PLOT GRAPHIC AND TO FIND SLOPE OF APPROXIMATING LINE USING MICROSOFT EXCEL® OR ALTERNATIVE SOFTWARE

Initially, all data should be input to a spreadsheet. For example:

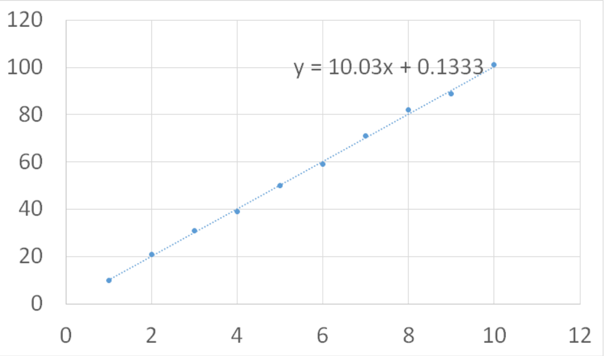
t	*Y*
1	10
2	21
3	31
4	39
5	50
6	59
7	71
8	82
9	89
10	101

As one can see, some *Y* values are approximately **10** times higher than corresponding *t* time.

Select the cells with your data and add a scatter plot. Select scatter without any lines, dots only. You will get a graphic like (2). Right-click on any dot of the plot and add a trend line. In a trend line format window check a box «Show equation». You will get a graphic like (3).



(2)



(3)

As one can see, the equation of trend line obtained is:

$$y = 10.03x + 0.1333$$

So, the slope coefficient is 10.03, what can be rounded to **10** mentioned above.