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***LABORATORY SESSION 4***

***Study of the effect of temperature on the reaction rate***

OBJECTIVES:

1. To analyze how temperature affects the reaction rate.
2. To relate rate constants and partial reaction times.
3. To determine the activation energy of the reaction.
4. To determine the experimental rate law for the oxidation reaction of hydroiodic acid by hydrogen peroxide in acidic medium (pseudo-order of reaction and apparent rate constant).

***LABORATORY SESSION 5***

***Kinetic study of the reaction between iodine and acetone catalyzed by acid***

OBJECTIVES:

1. To sequentially determine the kinetic parameters: partial orders, apparent rate constants and absolute rate constants.
2. To apply the Ostwald isolation method.
3. To verify the coherence between the rate law and the reaction mechanism.

***LABORATORY SESSION 6***

***Phase diagram: Boiling temperature-composition for a binary liquid mixture***

OBJECTIVES:

1. To construct the temperature-composition phase diagram for the methanol-chloroform mixture.
2. To determine the composition of the vapor phase (mole fraction) using the refractive index.
3. To determine the boiling temperature of binary mixtures.
4. To characterize the azeotropic point (azeotropic composition) of the binary mixture.
5. To determine the activity coefficients of the pure components and binary mixtures in the liquid and vapor phases.

# ***THE LABORATORY DIARY***

A laboratory diary is a complete record of the practical work a researcher has conducted in the laboratory. It is an essential component of any work in Chemistry. Containing detailed information to enable other researchers to reproduce the same experiments in exactly the same way, it includes all the operations the author has conducted as well as the facts they have observed and the conclusions they have drawn.

## ***Content and format of the laboratory diary***

**1.** The diary will comprise A4 sheets permanently attached and numbered. Loose sheets will not be used since they can easily get lost.

**2.** The language employed should be plain and simple, indicating what has been done (not what was supposed to have been done), preferably using impersonal forms, and including sufficient detail to make the experiment reproducible.

**3.** The laboratory diary is a working instrument in constant use. Its use is mandatory during the laboratory session.

**4.** The work expressed in the diary should be the author's own. When experiments are conducted in pairs, the data will be common to both authors but the wording will be different.

**5. Before beginning a laboratory experiment**, it is good practice to include in the diary all the information that is needed to perform the experiment correctly. This information includes:

- The title of the experiment
- The date of completion
- The laboratory conditions, i.e. pressure and temperature
- The aims of the experiment, including a brief description of why the work will be useful and what the intended conclusions will be.
- The formulation of the reactions involved (balanced).
- Relevant information about the starting materials, e.g. molecular masses, densities, precautions, dangers, etc.
- The amounts of the starting compounds, e.g. masses, volumes, etc., with their units and expressed in tabulated form.

- A summary or scheme (diagram) of the experimental procedure. This does not mean reproducing the guide but writing a brief description to enable you to easily interpret all the steps that must be taken.

**6. After beginning the experiment:** suitable notes must to be taken to enable the experiment to be reproduced under the same conditions. Information about the facts or observed data should also be recorded. This normally includes:

- The quantities actually used (examples), e.g. masses, volumes, etc., with their units and expressed in tabulated form.
- The procedure followed, including the laboratory equipment used, e.g. pipettes, burettes, scales, etc. Any modifications to the initially planned procedure must be discussed. Any errors made must also be discussed and how these errors were corrected must be explained.
- The data obtained, which must be tabulated with their units, e.g. times, volumes and absorbances (spectroscopic data), etc.

**7. After completing the experiment:** The calculations needed to satisfy the initial objectives must be shown. These calculations should:

- clearly explain what has been done (they should provide further explanations, i.e. they should not be limited to the use of formulas), and
- use the proper units to express the results correctly.

Presentation of results:

- Tables: whenever possible, indicate in each table what the data represent.
- Graphs: indicate what each graph represents, including the magnitudes and their units on the axes.

Discussion of results:

Discuss whether the results are in line with what was expected or explain possible causes of error.

**Note:** If you make an error while performing the experiment, erase it (in a way that is legible) and amend it appropriately.

***<u>The REPORT must have the following structure:</u>***

- The title of the practice session, the author, the group and name of the professor.

- An index with pages numbered accordingly.

- The aims and implementation method (10–20 lines).

- The theoretical background. The theoretical concepts used in the experiment should be explained briefly but rigorously.

- The experimental procedure. This should include materials, apparatus and assemblies, prior calculations, preparation of solutions, and detailed experimental procedure.

- Results. This should include the primary data collected in the laboratory and the results obtained from the calculations. The results should be presented in tables and graphs whenever possible. Treatment of the experimental data should be included in accordance with the questions raised in the script.

- Analysis and discussion of results. The results should be analyzed and discussed in relation to the knowledge and skills acquired. When bibliographic data are available, the results should be compared with those in the bibliography.

- Conclusions. These will emerge from the experiment conducted.

- Bibliography. All sources consulted must be cited.

# LABORATORY SESSION 1

## Conductometric determination of the ionization constant of a weak electrolyte (acetic acid)

| **Material** | |
|---|---|
| 1 x 1000 mL volumetric flask, shared | 1 glass rod / 1 funnel / 1 weighing boat / 1 Pasteur pipette |
| 2 x 250 mL volumetric flasks | 1 dropping pipette and 1 washing bottle |
| 1 x 100 mL volumetric flask | 1 x 50 mL burette |
| 2 x 250 mL Erlenmeyer flasks with caps | 1 conductivity instrument with its conductivity cell |
| 1 x 250 mL tall beaker | |
| 3 x 100 mL beakers | **Products** |
| 1 x 50mL tall beaker | Sodium hydroxide |
| 4 x 100 mL Erlenmeyer flasks with caps | Phenolphthalein |
| 1 x 10 mL graduated pipette | KCl standard solution 0.01M |
| 1 x 2 mL graduated pipette | Acetic acid |
| 1 x 25 mL graduated pipette | Potassium phthalate acid |

## Objectives

1. To relate the ionization constant of acetic acid with the dissociation degree and activity coefficients.
2. To determine the specific conductivity and molar conductivity of the acetic acid solutions.
3. To determine the ionization degree as a function of the concentration and molar conductivity.
4. To determine the ionic strength and average ionic activity coefficient.
5. To determine the ionization/dissociation constant for the acetic acid.

## Theoretical background

### 1. Acid-base equilibrium of the acetic acid

The objective of many studies has been to measure a chemical magnitude related to the dissociation constant of a weak acid. As a result, numerous methods have been developed to obtain a precise measurement of this magnitude. In this laboratory session we describe a procedure based on measuring the conductivity of electrolyte dilute solutions.

For weak type 1:1 electrolytes the equilibrium between the ionized and non-ionized forms of the solute can be written as:

$$HAc + H_2O \xleftrightarrow{K_a} Ac^- + H_3O^+ \qquad (1)$$

and the acidity constant as a function of the activities is:

$$K_a = \frac{a_{Ac^-} a_{H^+}}{a_{HAc}} \qquad (2)$$

where the activity is defined as:

$$a_i = \gamma_i [c]_i \qquad (3)$$

By substituting (3) in (2) and reorganizing, the equilibrium constant $K_a$ can be written as:

$$K_a = \frac{\gamma_- \gamma_+}{\gamma_{HAc}} \frac{[Ac^-][H^+]}{[HAc]} \qquad (4a)$$

or: $K_a = \gamma_{\pm}^2 \; K'_a$ (4b)

where $\gamma_{\pm}$ is the ionic average activity coefficient ($\gamma_{\pm}^2 = \gamma_+ \gamma_-$) and $K'_a$ is the equilibrium apparent constant in function of the concentrations (remember that $\gamma_{HAc}$ = 1). To determine $K_a$, therefore, $K'_a$ and $\gamma_{\pm}$ should be known.

Also, since HAc is a weak electrolyte it will be partially dissociated according to:

$$HAc + H_2O \xleftrightarrow{K'_a} Ac^- + H_3O^+$$

| | | | | |
|---|---|---|---|---|
| i) | $c_0$ | | | |
| eq) | $c_0 - x$ | | $x$ | $x$ |

If the dissociation degree, $\alpha$, is defined as: $\alpha = \frac{x}{c_0}$ (5)

the apparent equilibrium constant will be:

$$K'_a = \frac{[Ac^-][H^+]}{[HAc]} = \frac{c_0 \alpha^2}{1-\alpha} \quad (6)$$

**2. Degree of dissociation and conductivity: determination of K'$_a$**

Conductivity is the capacity of the ions of an electrolytic solution to carry or move the electricity (electrons or charges) through the solution. In electrolytic conduction, matter transport also takes place. Conductivity depends on several factors, including the size and charge of the electrolyte (the chemical nature of the electrolyte), the speed of the ions, the number of ions (concentration), the solution viscosity and the temperature.

Specific conductivity (the conductivity measured by electrical conductivity meters) is defined as:

$$\kappa = k \; L \quad (7)$$

where k is the cell constant and L is the conductance. The units of $\kappa$ in the International System of Units (S.I.) are S.m$^{-1}$ (though they are usually expressed as S.cm$^{-1}$). As this is an additive magnitude, total solution conductivity is the conductivity for the dissolvent plus the conductivity for the solute.

The molar conductivity, $\Lambda$, is defined as:

$$\Lambda = 1000 \frac{\kappa}{c_0} \quad (8)$$

where $c_o$ is the molar concentration and 1000 is a conversion (between L and cm$^3$).

The relationship between molar conductivity, concentration and dissociation degree is given by Kohlrausch's equation (obtained for diluted solutions of strong electrolytes):

$$\Lambda_e = \Lambda^0 - B\sqrt{c_0 \alpha} \quad (9)$$

where $\Lambda_e$ is the equivalent molar conductivity a weak electrolyte would have if it were fully dissociated, $\Lambda^0$ is molar conductivity at infinite dilution (when the solute concentration tends to zero), and B is Onsager's limit coefficient, whose value is: $B = a + b \; \Lambda^0$ (10)

For diluted water solutions of type 1:1 electrolytes and at 25 ºC, the coefficients are: a= 60.2 S $cm^2$ $mol^{-1}$ $M^{-1/2}$ and b = 0.229 $M^{-1/2}$, while the value of $\Lambda^0$ for HAc is: $\Lambda^0 = \lambda_+^0 + \lambda_-^0 = 390{,}51\ \ Scm^2mol^{-1}$. Substituting these values in equations (9) and (10), Kohlrausch's equation for HAc can be written as follows:

$$\Lambda_e = 390{,}51 - 149{,}63\sqrt{c_0\alpha} \qquad (11)$$

To calculate the dissociation degree using conductivity measurements, as a first step we will use the Arrhenius equation for the molar conductivity (though this equation is not fully accurate):

$$\alpha = \frac{\Lambda}{\Lambda^0} \qquad (12)$$

This equation was subsequently improved as follows:

$$\alpha = \frac{\Lambda}{\Lambda_e} \qquad (13)$$

Finally, substituting equation (11) into (13) we obtain the expression for calculating $\alpha$:

$$\alpha = \frac{\Lambda}{\Lambda^0 - 149{,}63\sqrt{c_0\alpha}} \qquad (14)$$

To solve this irrational equation we need an iterative process. Using the value of $\alpha$ for each concentration and equation (6), we can obtain the equilibrium apparent constants K'a.

### 3. Debye-Hückel limiting law: determination of $\gamma_\pm$

To fulfil the objective, the $\gamma_\pm$ coefficient should be calculated for each concentration using the Debye-Hückel limiting law:

$$\log\gamma_\pm = Az_+z_-\sqrt{I} \qquad (15)$$

where I is the ionic strength of the medium: $I = \frac{1}{2}\sum_i m_i|z_i|^2$ and $z_+ = 1$ $z_- = -1$ are the charges of the $H_3O^+$ and $Ac^-$ ions, respectively. The relationship between the molality and the molarity is $c_i = \rho_1 m_i$ and the water density is $\rho_1 = 1\ g/mL$. As $c_i = c_0\alpha$, then $I = \frac{1}{2}(c_0\alpha + c_0\alpha) = c_0\alpha$. Finally equation (15) can be expressed as:

$$\log\gamma_\pm = -A\sqrt{c_0\alpha} \qquad (16)$$

where "A" is the Debye-Hückel constant, whose theoretical value can be calculated from:

$$A = \frac{\sqrt{2\pi N_A\rho_1}}{2{,}303}\sqrt{\left(\frac{e^2}{4\pi\varepsilon k_B T}\right)^3} \qquad (17)$$

where $N_A$ is Avogadro's number, e is the electron charge, $\varepsilon$ is the medium dielectric permittivity ($\varepsilon = \varepsilon_r . \varepsilon_0$), $k_B$ is Boltzman's constant, and T is the absolute temperature.

Finally, for each concentration, $\alpha$ will be calculated from equation (14), $K'_a$ will be calculated from equation (6), $\gamma_\pm$ will be calculated from equation (16), and the acidity constant $K_a$ will be calculated from equation (4b).

## Solutions

1. 250 mL of acetic acid approximately 0.1 M from the commercial acid (in the glass cabinet).
2. 250 mL of sodium hydroxide approximately 0.1 M from the solid form.

## Experimental procedure

1. Connect the conductivity meter.
2. Prepare the acetic acid and sodium hydroxide solutions.
3. Titrate the NaOH solution using the potassium phthalate acid and phenolphthalein solution as indicator (at least three times).
4. Titrate the acetic acid solution using the NaOH and phenolphthalein solution as indicator (at least three times).
5. Also titrate the acetic acid solution by conductivity.
6. From the 0.1M acetic acid solution, prepare by dilution 100 mL of any of the following HAc solutions: 0.001, 0.005, 0.01, 0.02 or 0.05 M.
7. Calibrate the conductivity meter using a standard solution of KCl 0.01M (from the instructions in the manual, specific conductivity $\kappa_{KCl}$ = 1,41 mS/cm at 25 C). Write down the cell constant.

**Conductivity measurements:** Before measuring any solution, clean the cell first with deionized water and then with the problem solution. All conductivity measurements must be taken at a constant temperature of 25 ºC by adjusting the temperature sounding line of the conductivity meter. It is suggested that the measurements should be taken in increasing order of concentration (for the first measurement, clean the cell first with deionized water and then with the problem solution; for later measurements, clean the cell only with the problem solution).

8. Measure the solvent conductivity, $\kappa_{H20}$, and note down the measurement.
9. Transfer the prepared AcH solutions to a 100 mL Erlenmeyer flask with a cap or to a tall 50 mL beaker, measure the conductivities, and write down the measurements.

   **Note:** Remember that containers are available for discarding the residues after each experiment.

## Experimental results: data presentation

1. Tabulate the data (mass and volume) needed (both real and calculated) to prepare solutions 1 and 2.
2. Tabulate the results of the titration of sodium hydroxide with potassium phthalate acid and the titration of acetic acid with NaOH. For the conductometry, conductivity must be shown as a function of the volume of NaOH.
3. Tabulate the volumes to be taken from the mother solution of acetic acid to prepare the five solutions.
4. Tabulate the specific conductivities measured for the solvent and the five acetic acid solutions.

## Processing and discussion of results

1. Calculate the real concentration of NaOH and its accidental error.
2. Calculate the real concentration of HAc and its accidental error.
3. Recalculate the concentrations of all HAc solutions and their significant figures.
4. Create a new table containing:
   - the real concentrations of the acid solutions
   - the specific conductivity of each solution ($\kappa_{HAc} = \kappa_i - \kappa_{H2O}$)
   - the molar conductivity for each concentration
   - the ionization degree** (see point 5 below to calculate this)
   - the $K'_a$
   - the $\gamma_\pm$
   - the $c_0\alpha$ product
5. ** To calculate the ionization degree, use the following procedure: for each $c_0$, obtain the testing value of $\alpha$ using equation (12), which will be then used in equation (14) in an iterative process until a constant value is reached (usually three iterations are required).

$$\alpha_0 = \frac{\Lambda}{\Lambda^0} \rightarrow \alpha_1 = \frac{\Lambda}{\Lambda^0 - B\sqrt{c_0\alpha_0}} \rightarrow \alpha_2 = \frac{\Lambda}{\Lambda^0 - B\sqrt{c_0\alpha_1}} \rightarrow \alpha_3 = \frac{\Lambda}{\Lambda^0 - B\sqrt{c_0\alpha_2}}$$

   To make the iterative process easier, create a new table containing the concentration and the various values of $\alpha$ obtained. Transfer the final value of $\alpha$ to the general table in point 4.
6. Calculate Debye-Huckel's A constant using equation (17), expressing all magnitudes in S.I. units. To do so, find the values of e, $k_B$ , $\varepsilon_0$, $\varepsilon_r$, $\rho_1$ (at 25 ºC) in a data base (http://chemnetbase.com).
7. Determine the acidity constant $K_a$ using equation (4b), showing its average value and accidental error. Find the value of $K_{a(HAc)}$ at 25 ºC in the literature and compare it with the experimental value.
8. Graphically represent how $\kappa_{soluto}$, $\Lambda_m$, $\alpha$ and $\gamma_\pm$ vary with concentration graphically and discuss the dependences.

9. Determine the concentration of acetic acid from the conductometric titration. To do so, represent the specific conductivity of the solution as a function of the volume of NaOH added, linearly adjust the points, and obtain the volume of NaOH at the point of equivalence from the point of intersection of the two straight lines. Compare this result with that obtained in point 2.

# LABORATORY SESSION 2

## Spectrophotometric determination of the pK of an indicator

**Material**

2 x 500 mL volumetric flasks
2 x 25 mL volumetric flasks
3 x 250 mL Erlenmeyer flasks
2 x 100 mL beakers
1 x 25 mL graduated pipette
1 x 10 mL volumetric pipette
1 x 10 mL graduated pipette
1 x 2 mL graduated pipette
1 x 50 mL burette
1 spectrophotometer
1 glass rod / 1 weight funnel / 1 dropper / 1 funnel
2 spectrophotometer cuvettes
1 dropping pipette /1 wash-bottle

**Products**

Sodium hydroxide
Sodium hydroxide solution, 2M
Methyl orange solution, 0.002%
Hydrochloric acid
Formic acid
Phenolphthalein indicator

## Objectives

1. To obtain the absorption spectrum of methyl orange at different pHs.
2. To locate the isosbestic point.
3. To use the spectrophotometer to measure absorbances and relate them to the concentration.
4. To prepare buffer solutions from formic acid and NaOH and obtain their pHs.
5. To determine the $pK_a$ of methyl orange from the absorbance measurements.

## Theoretical basics

In general, acid-base indicators can be considered compounds (**weak** acids or bases) whose acidic form (protonated) in solution has a different color from its basic form (deprotonated). The change in structure, which causes the change in color, takes place in a small pH range (1–2 units of pK around the pK of the indicator), which is called the "*pH turning range*". In this interval, both forms of the indicator (acidic and basic) are simultaneously present.

The ionization balance of an indicator can be expressed by the equation:

$$HIn + H_2O \xleftrightarrow{K_{HIn}} In^- + H_3O^+ \qquad (1)$$

where HIn represents the acidic form of the indicator molecule and $In^-$ represents its basic form. The apparent ionization constant (as a function of concentration) is expressed as:

$$K_{HIn} = \frac{[H_3O^+][In^-]}{[HIn]} \qquad (2)$$

The solutions are assumed to be sufficiently diluted that all the activity coefficients are very close to unity. Under these conditions, the **Henderson-Hasselbalch** equation is applicable. Using logarithms in equation 2:

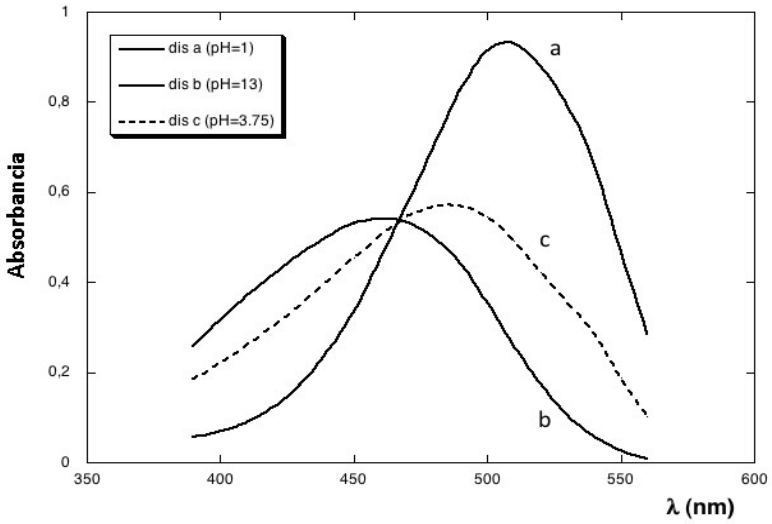
$$pH = pK_{HIn} + \log\frac{[In^-]}{[HIn]} \qquad (3)$$

If we know the [In -] / [HIn] ratio for a given pH, we can determine the pK of the indicator.

In our case, i.e. determination of the pK of methyl orange, the concentration quotient is calculated from the absorbances obtained by recording the electronic absorption spectrum of a series of solutions, i.e.:

- **a)** a solution exclusively containing the indicator in its red acidic form, HIn, for which the pH of the solution must be very low, i.e. pH≈1.
- **b)** a solution exclusively containing the indicator in its yellow basic form, $In^-$, for which the pH of the solution must be very basic, i.e. pH≈13.
- **c)** solutions simultaneously containing both forms of the indicator, which is achieved with buffer solutions whose pH lies in the interval 3.2-4.4, where the color of the methyl orange indicator changes.

The figure below shows an example of the recorded spectra for these solutions.




Using Beer-Lambert's law, we can express the ratio of concentrations in equation 3 in terms of the methyl orange absorbance for each solution. For the same wavelength, λ:

pH = 1 $$A_{HIn} = \varepsilon_{HIn} \cdot l \cdot c_0 \quad (4)$$

pH = 13 $$A_{In^-} = \varepsilon_{In^-} \cdot l \cdot c_0 \quad (5)$$

pH = 3.8 $$A = \varepsilon_{HIn} \cdot l \cdot [HIn] + \varepsilon_{In^-} \cdot l \cdot [In^-] \quad (6)$$

where $A_{HIn}$ and $A_{In-}$ represent, respectively, the absorbance of a solution in which only one form of the indicator (acidic or basic) is present; "A" is the absorbance of the solution in which both forms of the indicator coexist (in the buffer solution); $\varepsilon_{HIn}$ and $\varepsilon_{In-}$ represent the molar absorption coefficients of the acidic and basic forms of the indicator, respectively; and l is the optical path (width of the cuvette). Also, in the buffer solutions it is true that $c_0 = [In^-] + [HIn]$.

Finally, from equations (4) to (6) we can deduce:

$$pH = pK_{HIn} + \log\left(\frac{A_{HIn} - A}{A - A_{In^-}}\right) \quad (7)$$

## Solutions

1. 500 mL of 0.1 M formic acid solution, from the commercial product (in fume hoods).
2. 500 mL of 0.1 M NaOH solution, from solid NaOH.

## Experimental procedure

1) Connect the spectrophotometer as soon as the session begins, or at least 15 minutes before measuring.

2) Prepare the formic acid and sodium hydroxide solutions.

3) Titrate 25 mL of 0.1 M formic acid solution with NaOH 0.1 M, using phenolphthalein as the indicator. Repeat the titration at least three times.

4) After preparing each sample as described below, record the absorption spectra of the solutions. How is this done? Insert the cuvette covered with white into the position through which the light passes and press BASELINE. Insert the cuvette covered with the sample and press SCAN. Follow the instructions on the spectrophotometer. Measure the absorbance of the problem solution every 5 nm in the wavelength range of 250 to 640 nm.

**Be careful!** The spectrophotometer cell must be clean: do not touch its walls with your fingers. Also, fill it to ¾ of its capacity only (do not fill it to the brim).

The spectra of at least seven different solutions are recorded in the following order:

### 4.1. **Absorption spectra of the acidic form of the indicator.**

Prepare:

a) **Blank**: pipette 10 mL of water into the 25 mL volumetric flask, add 4 drops of concentrated HCl and fill the flask with water up to the etched line. Use this solution to clean and fill the spectrophotometer cuvette.

b) **Problem** methyl orange solution: pipette 10 mL of 0.002 % methyl orange solution into the 25 mL volumetric flask, add 4 drops of concentrated HCl and fill the flask with water up to the etched line. Use this solution to clean and fill the spectrophotometer cuvette.

### 4.2. **Absorption spectra of the basic form of the indicator.**

Prepare:

a) **Blank**: pipette 10 mL of water into the 25 mL volumetric flask, add 24 drops of NaOH 2 M and fill the flask with water up to the etched line. Use this solution to clean and fill the spectrophotometer cuvette.

b) **Problem** methyl orange solution: pipette 10 mL of 0.002 % methyl orange solution into the 25 mL volumetric flask, add 24 drops of NaOH 2 M and fill the flask with water up to the etched line. Use this solution to clean and fill the spectrophotometer cuvette.

### 4.3. **Absorption spectra of solutions with both forms of the indicator.**

Before beginning this part of the experiment, prepare five buffer solutions of different pHs. These will be used to dilute the indicator solution and fix the pH.

#### 4.3.1. **Buffer solution 1** (pH=3.382)

To prepare the buffer solution: insert 25 mL of 0.1 M formic acid solution into an Erlenmeyer flask and add **30 %** of the volume of 0.1 M NaOH used at the equivalence point for the titration of the formic acid. The resulting pH will be 3.382. (Note: this value must later be calculated from the $pK_a$ of the formic acid). When you have prepared buffer 1, use it to prepare:

a) **Blank**: pipette 10 mL of water into the 25 mL volumetric flask and fill the flask with buffer 1 solution. With this solution clean and fill the spectrophotometer cuvette.

b) Indicator **problem** solution: pipette 10 mL of methyl orange 0.002 % solution into the 25 mL volumetric flask and fill the flask with the buffer 1 solution. Use this solution to clean and fill the spectrophotometer cuvette.

#### 4.3.2. **Buffer solution 2** (pH=3.574)

To prepare the buffer solution: insert 25 mL of 0.1 M formic acid solution into an Erlenmeyer flask and add **40 %** of the volume of 0.1 M NaOH used at the equivalence point for the titration of the formic acid. The resulting pH will be 3.574. (Note: this value must later be calculated from the $pK_a$ of the formic acid). When you have prepared buffer 2, use it to prepare:

a) **Blank**: pipette 10 mL of water into the 25 mL volumetric flask and fill the flask with buffer 2 solution. Use this solution to clean and fill the spectrophotometer cuvette.

b) Indicator **problem** solution: pipette 10 mL of methyl orange 0.002 % solution into the 25 mL volumetric flask and fill the flask with the buffer 2 solution. Use this solution to clean and fill the spectrophotometer cuvette.

#### 4.3.3. **Buffer solution 3** (pH=3.574)

To prepare the buffer solution: insert 25 mL of 0.1 M formic acid solution into an Erlenmeyer flask and add **50 %** of the volume of 0.1 M NaOH used at the equivalence point for the titration of the formic acid. The resulting pH will be 3.574. (Note: this value must later be calculated from the $pK_a$ of the formic acid). After you have prepared buffer 3, use it to prepare:

a) **Blank**: pipette 10 mL of water into the 25 mL volumetric flask and fill the flask with buffer 3 solution. Use this solution to clean and fill the spectrophotometer cuvette.

b) Indicator **problem** solution: pipette 10 mL of methyl orange 0.002 % solution into the 25 mL volumetric flask and fill the flask with the buffer 3 solution. Use this solution to clean and fill the spectrophotometer cuvette.

4.3.4. **Buffer solution 4** (pH=3.926)

To prepare the buffer solution: insert 25 mL of 0.1 M formic acid solution into an Erlenmeyer flask and add **60 %** of the volume of 0.1 M NaOH used at the equivalence point for the titration of the formic acid. The resulting pH will be 3.926. (Note: this value must later be calculated from the $pK_a$ of the formic acid). After you have prepared buffer 4, use it to prepare:

a) **Blank**: pipette 10 mL of water into the 25 mL volumetric flask and fill the flask with buffer 4 solution. Use this solution to clean and fill the spectrophotometer cuvette.

b) Indicator **problem** solution: pipette 10 mL of methyl orange 0.002 % solution into the 25 mL volumetric flask and fill the flask with the buffer 4 solution. Use this solution to clean and fill the spectrophotometer cuvette.

4.3.5. **Buffer solution 5** (pH=4.118)

To prepare the buffer solution: insert 25 mL of 0.1 M formic acid solution into an Erlenmeyer flask and add **70 %** of the volume of 0.1 M NaOH used at the equivalence point for the titration of the formic acid. The resulting pH will be 4.118. (Note: this value must later be calculated from the $pK_a$ of the formic acid). After you have prepared buffer 5, use it to prepare:

a) **Blank**: pipette 10 mL of water into the 25 mL volumetric flask and fill the flask with buffer 5 solution. Use this solution to clean and fill the spectrophotometer cuvette.

b) Indicator **problem** solution: pipette 10 mL of methyl orange 0.002 % solution into the 25 mL volumetric flask and fill the flask with the buffer 5 solution. Use this solution to clean and fill the spectrophotometer cuvette.

## OPTIONAL

1. **Buffer solution 6**

To prepare the buffer solution: insert 25 mL of 0.1 M formic acid solution into an Erlenmeyer flask and add **90 %** of the volume of 0.1 M NaOH used at the equivalence point for the titration of the formic acid. (Note: The resulting pH must be calculated later from the pKa of formic acid). After you have prepared buffer 6, use it to prepare:

a) **Blank**: pipette 10 mL of water into the 25 mL volumetric flask and fill the flask with buffer 6 solution. Use this solution to clean and fill the spectrophotometer cuvette.

b) Indicator **problem** solution: pipette 10 mL of methyl orange 0.002 % solution into the 25 mL volumetric flask and fill the flask with the buffer 6 solution. Use this solution to clean and fill the spectrophotometer cuvette.

### 2. Measure the pH of the buffer solutions

**Note:** Remember that containers are available to dispose of waste after the experiment.

## Experimental results: presentation of data

1. Tabulate the data (masses or volumes) needed to prepare solutions 1 and 2 (both the calculated and the actual amounts).
2. In another table tabulate the results of the titration of formic acid with sodium hydroxide (volume of NaOH). Also calculate its mean value (together with its random error) as well as the figures for 40, 50 and 60 % of that value.
3. Create tables that schematically list the volumes that were used to prepare the buffers and the five problem solutions together with their five corresponding blanks.
4. In another Table, show the absorbances measured at each wavelength for the five indicator solutions.

## Treatment and discussion of results

1. Draw all the recorded spectra on the same graph.
2. Indicate the wavelength of the isosbestic point and show that, at that point, the molar absorption coefficients of both the acidic and basic forms of the indicator have the same value.
3. Calculate the pK of the indicator at different wavelengths, $\lambda$. For each $\lambda$ use the absorbances of the three buffer solutions, i.e. obtain three pK values for each wavelength, and find the average. Suggestion: compare the pKs obtained at $\lambda$ close to the maximum absorbance of the acidic solution with those obtained at others areas of the spectrum, e.g. near the isosbestic point. Discuss your results.
4. Calculate the pHs of the buffer solutions (1, 2 and 3) and check that they match those indicated in the text. In the literature find the value of the formic acid $pK_a$ at 25 ºC.
5. What conditions must be met in order for equation (3) to be applicable? Indicate your approach when making your deductions.
6. Prove equation (7).

# LABORATORY SESSION 3

## Kinetic study of the decolorization of phenolphthalein in alkaline solution

**Material**

1 spectrometer
2 spectrometer cuvettes
1 x 5 mL volumetric pipette
1 x 10 mL volumetric pipette
1 x 20 mL volumetric pipette
1 x 25 mL volumetric pipette
1 x 200 mL volumetric flask
1 x 500 mL volumetric flask
3 x 250 mL Erlenmeyer flasks
1 50 mL burette
3 x 100 mL beakers
1 x 250 mL beaker
1 glass rod / 1 dropper / 1 weighing bottle
1 wash-bottle / 1 funnel / 1 dropping pipette
1 chronometer

**Chemicals**

Sodium chloride
Sodium hydroxide
8% phenolphthalein alcoholic solution
Potassium hydrogen phthalate

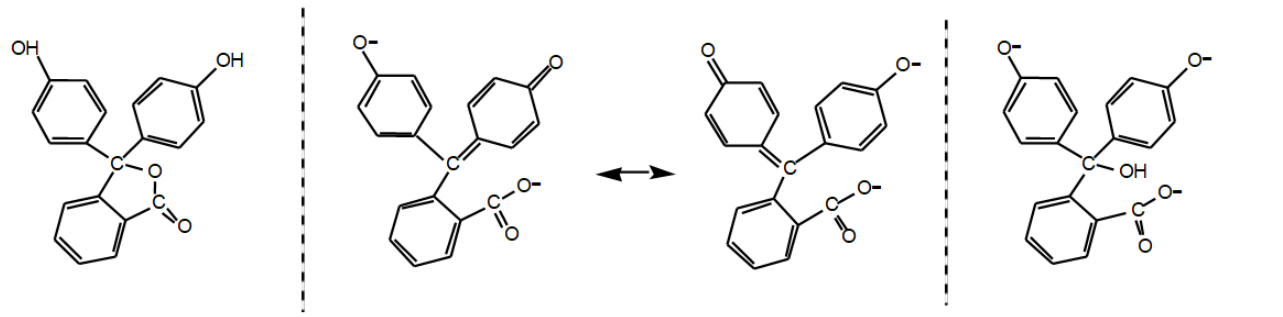
## Objectives

1. To determine the rate equation of the phenolphthalein decolorization reaction in alkaline solution by absorption spectroscopy under irreversibility and reversibility conditions.
2. To determine the kinetic parameters: partial orders, apparent constants, and absolute velocity constants.
3. To apply the Ostwald isolation method.
4. To analyze how concentration affects the reaction rate.
5. To use a spectrophotometer to measure absorbances and relate them to concentration.

## Theory

Phenolphthalein is used as an acid-base indicator to determine the endpoint in a volumetric titration, where it changes from a colorless to a pinkish-red solution. However, if there is excess base at the endpoint, the pink color of the phenolphthalein disappears over time. This is not due to the titration procedure and can be used as a good example of a pseudo-first-order reaction.

Phenolphthalein is not a simple indicator with a conjugated acid-base pair $HIn/In^-$ but has complex structures. The structures of the most important forms of phenolphthalein are:



**1** **2** **3**

**pH < 8 (colorless)** **8 < pH < 10 (pink-red)** **pH > 10 (colorless)**

**$H_2P$** **$P^{-2}$** **$POH^{3-}$**

Phenolphthalein is colorless at pH below 8 and has structure 1 ($H_2P$). When the pH is between 8 and 10, the phenolic protons are removed and the lactone ring opens, producing the familiar pink-red shape with structure 2 ($P^{2-}$). At a higher pH, the pink color slowly fades and structure 3 ($POH^{3-}$) appears. All color changes are reversible. Also, while the conversion of $H_2P$ to $P^{2-}$ is fast and complete, the conversion of $P^{2-}$ to $POH^{3-}$ at a higher pH is quite slow, so the reaction rate can be easily measured.

The phenolphthalein decolorization reaction in alkali solution is:

$$P^{2-} + OH^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} POH^{3-} \qquad (1)$$

and the rate law has the form:

$$v = k_1[P^{2-}]^n\,[OH^-]^m - k_{-1}[POH^{3-}]^p \qquad (2)$$

where the reaction rate is first-order for the phenolphthalein in the direct and reverse reaction (n=p=1):

$$v = k_1[P^{2-}]\,[OH^-]^m - k_{-1}[POH^{3-}] \qquad (3)$$

If the initial mixture of the reaction is a strongly basic solution, the concentration of $OH^-$ is much higher than that of phenolphthalein ($[OH^-]/[P^{2-}]>10^4$) and we can consider that the concentration of $OH^-$ remains constant throughout the measurements ($[OH^-]_0 = [OH^-] = ct$). The rate law can therefore be expressed as:

$$v = k_{ap}[P^{2-}] - k_{-1}[POH^{3-}] \qquad (4)$$

where $k_{ap}$ is an apparent reaction rate constant:

$$k_{ap} = k_1[OH^-]_0^m \qquad (5)$$

Since the $P^{2-}$ form has an intense color, the conversion from $P^{2-}$ to $POH^{3-}$ can be followed by measuring changes in the absorbance of the solution. This magnitude is related to the concentration by means of **Lambert-Beer's law**:

$$A = \varepsilon\,\ell\,[c] = cte\,[P^{2-}] \qquad (6)$$

where $\varepsilon$ is the molar absorption coefficient (an intrinsic property of the substance that is constant at a given wavelength, $\lambda$); $\ell$ is the pathlength (or internal width of the cuvette), and [c] is the molar concentration of the solution.

The experiment can be performed under two conditions:

a) **Irreversible treatment**: in the first stages of the reaction.

b) **Reversible treatment**: when the reaction reaches equilibrium.

**a) Irreversible treatment**

When the concentrations of the reagents and products are far from their equilibrium values, we can consider that the inverse reaction rate is negligible compared to the direct reaction rate, so equation (4) is:

$$v = -\frac{d[P^{2-}]}{dt} = k_{ap}[P^{2-}] \qquad (7)$$

which is first order with respect to phenolphthalein. By integrating equation (7) between t=0 and t=t, and rearranging, we have:

$$\ln[P^{2-}]_t = \ln[P^{2-}]_0 - k_{ap}t \qquad (8)$$

Finally, by introducing Lambert-Beer's law (eq (6)), we have:

$$\ln A_t = \ln A_0 - k_{ap}t \qquad (9)$$

where $A_t$ is the phenolphthalein absorbance at the time t. The graphical representation of $\ln(A_t)$ over time must therefore be a straight line (if the reaction is pseudo-first-order) whose slope is equal to $-k_{ap}$. This will enable us to determine the apparent reaction rate constant.

If we have $k_{ap}$ values at different $[OH^-]_0$, we can obtain the partial order with respect to $OH^-$ (m) and the absolute rate constant ($k_1$) by linearizing eq (5) simply by taking logarithms on both sides:

$$\ln k_{ap} = \ln k_1 + m \ln [OH^-]_o \qquad (10)$$

Another way to determine constant $k_1$ is to obtain it for each experiment and calculate its average from:

$$k_{1,i(irrev)} = \frac{k_{ap,i}}{[OH^-]_o} \qquad (11)$$

while assuming m=1.

**b) Reversible treatment**

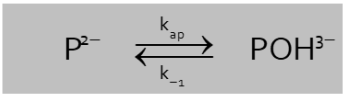
When the reaction is close to equilibrium, the reverse reaction cannot be underestimated. We will therefore now propose a simple first-order reversible reaction with a single reagent of the type:

| | $A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}}$ | B |
|---|---|---|
| $t = o)$ | $[A]_o$ | |
| $t = t)$ | $[A]_o - x$ | $x$ |
| $t = \infty)$ | $[A]_o - x_e$ | $x_e$ |

where $[A]_0$ and $x_e$ are known. At any instant and at equilibrium, the reagent concentrations are therefore, respectively: $[A]_t = [A]_0 - x$ and $[A]_e = [A]_0 - x_e$. The corresponding integrated equation is:

$$\ln \frac{x_e}{x_e - x} = \ln \frac{[A]_o - [A]_e}{[A]_t - [A]_e} = (k_1 + k_{-1})t \qquad (12)$$

In our case, the first-order reversible reaction with respect to phenolphthalein is:



The reaction rate will be given by eq (4) and the integrated rate equation (see eq (12)) will be:

$$\ln \frac{[P^{2-}]_o - [P^{2-}]_e}{[P^{2-}]_t - [P^{2-}]_e} = (k_{ap} + k_{-1})t \qquad (13a)$$

where

$$k_{-1} = k_{ap} \frac{[P^{2-}]_e}{[P^{2-}]_o - [P^{2-}]_e} \qquad (13b)$$

By using Lambert-Beer's law, eq (13a) is:

$$\ln (A_t - A_e) = \ln (A_o - A_e) - (k_{ap} + k_{-1})t \qquad (14a)$$

Or by substituting eq (13b) into eq (14a), finally we have:

$$\ln (A_t - A_e) = \ln (A_o - A_e) - k_{ap}\left(\frac{A_o}{A_o - A_e}\right)t \qquad (14b)$$

where $\mathbf{A_e}$ is the absorbance at an infinite time when the reaction reaches equilibrium. Since the value of $\mathbf{A_e}$ is known, $\mathbf{\ln(A_t - A_e)}$ can be plotted against time to obtain $k_{ap}$ and $k_{-1}$ from the linear fitting because, if we compare equations (14a) and (14b), we have:

$$k_{-1} = k_{ap}\left(\frac{A_e}{A_o - A_e}\right) \qquad (15)$$

Finally, the absolute constant of the direct reaction is obtained by applying eq (5) to reversible conditions and assuming the order m=1:

$$k_{1(rev)} = \frac{k_{ap(rev)}}{[OH^-]_o} \qquad (16)$$

## Solutions

1. 500 mL of 0.3 M NaOH solution, from solid NaOH.
2. 200 mL of 0.3 M NaCl solution, from a NaCl solid (after titration of the NaOH solution).

## Experimental procedure

To study the kinetics of the reaction, the absorbance of phenolphthalein in strongly alkaline solutions is registered as a function of time. The reaction is followed in four solutions with different NaOH concentrations to provide four different series of absorbance.

**We will work at a wavelength of 550 nm.**

For a given NaOH concentration, the decolorization rate increases as the ionic strength increases. To keep the ionic strength constant, NaOH and NaCl solutions of the same concentration (0.30 M) are prepared. To prepare the most diluted NaOH solutions, solution 1 must be diluted with solution 2, i.e. to try to keep the ionic strength constant, the NaCl solution will be used as a solvent instead of water.

1. Connect the spectrometer 15-20 minutes before taking the measurement and adjust the wavelength to 550 nm.
2. Prepare the 0.3 M NaOH solution.
3. Titrate roughly 20 mL of 0.3 M NaOH solution with potassium hydrogen phthalate using phenolphthalein as an indicator. Repeat at least 3 times.
4. Prepare the NaCl solution with the same concentration as the titrated NaOH solution.
5. Measure the absorbance of each series as a function of time at $\lambda$=550 nm.

**Note**: **(1)** you must wash the cell in the spectrophotometer with the appropriate blank solution and keep it clean; you should fill the cuvette to roughly ¾ of its capacity and not touch it with your fingers; **(2)** the initial absorbance of the problem solutions must be between 0.8 and 1.0. Therefore, when the absorbance of the sample is ≈ 0.8, the chronometer will start (t = 0).

Four sets of measurements should be taken. We recommend beginning with the series with the highest concentration of NaOH.

**SERIES 1: 0.3 M NaOH solution**

a) Prepare the blank. In this case, it is the same 0.3 M NaOH solution. Transfer part of this solution to a cuvette.

b) Use the blank to adjust the absorbance to 0.

c) Remove the cuvette from the spectrometer and add 1 or 2 drops of phenolphthalein. Then invert the cuvette to homogenize the mixture. This will be problem solution 1.

d) Measure the absorbance (without removing the cuvette) every 30 seconds for 5 minutes.

**SERIES 2: 0.2 M NaOH solution**

a) Prepare the blank (20 mL of 0.3 M NaOH and 10 ml of 0.3 M NaCl) in a beaker. Transfer part of this solution to a cuvette.

b) Use the blank to adjust the absorbance to 0.

c) Remove the cuvette from the spectrometer and add 1 or 2 drops of phenolphthalein. Then invert the cuvette to homogenize the mixture. This will be problem solution 2.

d) Measure the absorbance (without removing the cuvette) every 30 minutes for 5 minutes.

**SERIES 3: 0.1 M NaOH solution**

a) Prepare the blank (10 mL of 0.3 M NaOH and 20 mL of 0.3 M NaCl) in a beaker. Transfer part of this solution to a cuvette.

b) Use the blank to adjust the absorbance to 0.

c) Remove the cuvette from the spectrometer and add 1 or 2 drops of phenolphthalein. Then invert the cuvette to homogenize the mixture. This will be problem solution 3.

d) Measure the absorbance (without removing the cuvette) every 1 minute for 10 minutes.

**SERIES 4: 0.05 M NaOH solution**

a) Prepare the blank (5 mL of 0.3 M NaOH and 25 mL of 0.3 M NaCl) in a beaker. Transfer part of this solution to a cuvette.

b) Use the blank to adjust the absorbance to 0.

c) Remove the cuvette from the spectrometer and add 1 or 2 drops of phenolphthalein. Then invert the cuvette to homogenize the mixture. This will be problem solution 4.

d) Measure the absorbance every 1 minute for 15 minutes and then every 5 minutes until one hour has elapsed. (In this series, after 20 minutes the reverse reaction becomes important and, to perform appropriate reversible treatment, it is necessary to reach equilibrium, which occurs roughly two hours after the beginning of the reaction).

**Note**: Remember that containers are available for waste disposal after you finish the experiment.

## Experimental results: data presentation

1. Tabulate the data (both calculated and real) for preparing the solutions.
2. Tabulate the results of the NaOH titration.
3. In another table, present the absorbances measured in each series as a function of time in minutes (it is also a good idea to include the times as read on the chronometer).

## Treatment and discussion of results

1. Recalculate the real NaOH concentration from the titration together with its random error. Do the same for NaCl and the solutions.

**2. Irreversible treatment:**

2.1 Draw, on the same graph, the values of $\ln(A_t)$ over time for the four series (for series 4 only up to minute 15), and check that the reaction is of pseudo-first-order with respect to phenolphthalein (eq 9).

2.2 From the slope of the fittings, obtain the apparent reaction rate constants for each series.

2.3 Represent eq (10) and, from the slope of the fitting, obtain the order of reaction with respect to the $OH^-$ (m).

2.4 Calculate the absolute rate constant ($k_{1(irrev)}$) with its random error (eq 11).

**3. Reversible treatment (only for series 4):**

3.1 Determine the value of $k_{ap}$ for series 4, representing eq (14b) and the value of $k_{-1}$ (eq 15). Obtain $k_{1(rev)}$ from eq (16) and the $OH^-$ concentration of series 4. Compare this value with that obtained from the irreversible treatment (section 2.4).

3.2 Compare the values of $k_{ap,4(rev)}$ with those of $k_{ap,4(irrev)}$, and discuss.

3.3 Compare the values of $k_1$ and $k_{-1}$, and discuss.

4. Calculate the ionic strength of each series.

# LABORATORY SESSION 4

## Study of the effect of temperature on the reaction rate

| **Material** | 1 shared methacrylate bucket, thermostat and refrigeration unit |
|---|---|
| 1 x 500 mL volumetric flask | 1 solids carrier for weighing / 1 stirring rod / 1 eyedropper/ 1 funnel |
| 1 x 250 mL volumetric flask | 1 x 250 mL amber bottle (for $Na_2S_2O_3$) |
| 1 x 100 mL volumetric flask | 1 washing bottle |
| 1 x 25 mL volumetric flask | 1 magnetic stirrer with magnet |
| 1 x 1000 mL Erlenmeyer flask | |
| 4 x 100 mL beakers | **Products** |
| 1 x 100 mL graduated cylinder | Potassium iodide |
| 1 x 5 mL graduated pipette | Sodium thiosulfate pentahydrate |
| 1 x 2 mL graduated pipette | Hydrogen peroxide of 110 vol. |
| 1 micropipette, 1 dropping pipette | Starch indicator 1% |
| 1 chronometer | Sulfuric acid |

## Objectives

1. To analyze how temperature affects the reaction rate.
2. To relate rate constants and partial reaction times.
3. To determine the activation energy of the reaction.
4. To determine the experimental rate law for the oxidation reaction of hydroiodic acid by hydrogen peroxide in acidic medium (pseudo-order of reaction and apparent rate constant).

## Theoretical foundations

The rate of almost every chemical reaction generally increases with temperature (doubling or trebling with every 10ºC increase). One of the most common equations to represent how the rate constant changes with temperature is the empirical Arrhenius equation:

$$k = Ae^{-E_a/RT} \qquad (1)$$

where A is the frequency factor and $E_a$ is the **activation energy**. Using logarithms in equation (1), we have:

$$\ln k = \ln A - \frac{E_a}{R}\frac{1}{T} \qquad (2)$$

When applied at two temperatures ($T_1$ and $T_2$) and when both temperatures are divided, this becomes:

$$\ln \frac{k_2}{k_1} = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \qquad (3)$$

This is a valid equation if we assume that A and $E_a$ are constant in the studied temperature range. The activation energy of the reaction can therefore be determined from the relationship between the rate constants at two temperatures.

In this experiment we determine the relationship between the rate constants, and therefore the value of the activation energy, by:

a) determining the partial reaction time, and

b) using the integrated rate equations.

**(a)** The **partial reaction time**, $t_p$, is defined as the time required to consume a given amount of reagent under certain initial reaction conditions.

At two temperatures ($T_1$ and $T_2$), provided the initial concentration ($[A]_0$ at t=0) and instantaneous concentration ($[A]_t$ at t=t) of all the reagents are the same at both temperatures, the rate constants are inversely proportional to the partial reaction times $t_{p1}$ and $t_{p2}$:

$$\frac{k_1}{k_2} = \frac{t_{p_2}}{t_{p_1}} \qquad (4)$$

The chosen **reaction** is the oxidation of the iodide ion by hydrogen peroxide in an acidic (sulfuric) medium:

$$\mathbf{H_2O_2 + 2I^- + 2H^+ \rightarrow I_2 + 2\,H_2O}$$

$$H_2O_2 + 2\,KI + H_2SO_4 \rightarrow I_2 + 2\,H_2O + K_2SO_4 \qquad (5)$$

with a **rate equation** that can be expressed as:

$$v = k\,[I^-]^a\,[H_2O_2]^b\,[H^+]^c \qquad (6)$$

where k is the absolute rate constant and *a*, *b* and *c* are the partial reaction orders with respect to $I^-$, $H_2O_2$ and $H^+$, respectively.

The rate equation is simplified because the acidic medium remains approximately constant (excess $H^+$ with respect to the other components) and the experimental design enables the concentration of $I^-$ to remain constant throughout the reaction (as we will see). Then:

$$v = k_{ap}\,[H_2O_2]^b \quad \text{where} \quad k_{ap} = k\,[I^-]^a\,[H^+]^c \cong cte \qquad (7)$$

The amount of iodine produced (and therefore the amount of hydrogen peroxide that is reacted) is determined by adding to the reaction medium a predetermined amount of sodium thiosulfate, which, depending on the reaction, reduces the iodine as it is produced:

$$I_2 + 2Na_2S_2O_3 \rightarrow Na_2S_4O_6 + 2NaI \qquad (8)$$

Consequently, the number of moles (and the concentration) of $I^-$ will remain roughly constant.

$$2NaI + 2H_2SO_4 \rightarrow 2HI + 2NaHSO_4 \qquad (9)$$

and the number of moles (and the concentration) of HI will also remain roughly constant.

According to the stoichiometry of the reaction (5), the moles of $I_2$ produced are equal to those of $H_2O_2$ consumed and, since $I_2$ reacts immediately with thiosulfate, we can determine the amount of hydrogen peroxide that has reacted from the amount of thiosulfate that is added to the reaction medium. The time needed to consume an added and prefixed amount of sodium thiosulfate for the iodine produced will be a measure of the partial reaction time. The presence of iodine is easily detected by adding a few drops of starch (due to the blue complex iodine forms with the starch).

**(b)** The rate constants can also be obtained from the slopes of the graph of the corresponding integrated equation, for which the order of the reaction must be determined in advance.

Given equations (5) and (7), the integrated equation of order one (b=1) is:

$$\ln[H_2O_2] = \ln[H_2O_2]_0 - k_{ap}t \qquad (10)$$

and that of order two is:

$$\frac{1}{[H_2O_2]} = \frac{1}{[H_2O_2]_0} + k_{ap}t \qquad (11)$$

The $k_{ap}$ at each temperature ($k_{ap1}$ and $k_{ap2}$) will be obtained from the slope of the best fit. Their quotient, according to equation (7) and since the starting concentrations of $I^-$ and $H^+$ in each series are equal, is:

$$\frac{k_{ap1}}{k_{ap2}} = \frac{k_1}{k_2} \qquad (12)$$

Using this relationship and equation (3), we can determine the activation energy.

**Note:** To deduce equation (4) it is taken into account that the integrated rate equation, in simple mechanism reactions, can always be written as:

$$f([A],[A]_0) = kt \qquad (a)$$

where $[A]_0$ and $[A]$ are the concentrations of reagent A at t=0 and at time t, respectively. This equation is valid for any temperature provided there are no changes in the mechanism. Therefore, at two temperatures ($T_1$ and $T_2$):

$$f([A],[A]_0) = k_1 t_1 \quad \text{and} \quad f([A],[A]_0) = k_2 t_2 \qquad (b)$$

If f ($[A]_0$, $[A]$) is the same at both temperatures, then: $k_1 t_1 = k_2 t_2$ (c)

Also, if the reaction times correspond to the partial times in which a certain fraction of reagent has been consumed, the above equality leads us to equation (4).

## Solutions

1. 250 mL of 0.1 M $Na_2S_2O_3$ solution (to be stored in a topaz-colored bottle or light shelter).
2. 100 mL of hydrogen peroxide ($H_2O_2$) of 2 volumes, by dilution of that of 110 vol. (in the fume cupboard)

   For **each series** (temperature), the following must be prepared:
3. 500 mL of KI of 0.12% by weight (0.6 g in 500 mL of water).

4. **10 mL of concentrated sulfuric acid** (in the fume cupboard). The **procedure** is as follows: add the prepared KI dissolution (500 mL) to a 1000 mL Erlenmeyer flask; then (**in the fume cupboard!!!**) add 10 mL of concentrated sulfuric acid **VERY SLOWLY** to the Erlenmeyer flask using the dispenser (or pipette).

## Experimental procedure

The study is performed at two temperatures (two series), which must be noted down:

Series 1 is performed at a temperature of 10°C in a thermostatic bath with cryostat.

Series 2 is performed at a temperature of 22°C in a thermostatic bath (if necessary, use the cryostat).

For **each series** the procedure is as follows:

1. In the bath and on the magnetic stirrer (so that they reach the experimental temperature), place:
   - the 1000 mL Erlenmeyer flask with the KI solution, the 10 mL sulfuric acid (prepared in the fume cupboard) and the magnet. The agitator starts and must not be stopped throughout the experiment.
   - an Erlenmeyer flask covered with 25 mL of the $H_2O_2$ solution.
2. When the thermal equilibrium has been reached (after roughly 10 minutes), add 1 mL of starch indicator (measured with a pipette) to the reaction flask. Then add the 25 mL of $H_2O_2$ to the reaction Erlenmeyer flask and start the timer **(t=0).**
3. When the solution changes color, immediately add 3 mL of sodium thiosulfate solution using the micropipette. The blue color will disappear (because of the complex that forms between the iodine that is produced and the starch indicator). When the color reappears (which indicates that the thiosulfate is no longer in the solution), record the time without stopping the timer and add another 3 mL aliquot of sodium thiosulfate.
4. Repeat step 3 until you complete a 12-part time series. **Note**: The time it takes for the blue color to appear is the time it takes for the added thiosulfate to be consumed and will be the partial reaction time.
5. Prepare solutions 3 and 4 again, making sure that the mass of KI is as close as possible to that of series 1.
6. Repeat the experiment at a temperature of 22°C but now adding 20 aliquots of thiosulphate, and write down 20 part-time values.

**Note:** Remember that containers are available to dispose of waste after you finish the experiment.

## Experimental results: presentation of the data

1. Tabulate the calculated theoretical masses or volumes, the masses or volumes actually used, and the concentrations of thiosulfate and hydrogen peroxide solutions actually used.
2. In another table present the experimental data: for both temperatures, the volume of thiosulphate added and the times at which each aliquot was consumed.

## Treatment and discussion of results

1. Determine the concentration of hydrogen peroxide based on the volume of thiosulfate added and record it in Table 2 (use the actual thiosulfate and hydrogen peroxide concentrations).

2. Determine the partial reaction times for both series and complete Table 2.

3. Discuss the values and trends for $t_p$ at each temperature and their possible relationship to the reaction order.

4. Use equation (4) to calculate the average value of $k_1/k_2$ from the part-time quotients. Also calculate the random error.

5. Use equation (3) to calculate the activation energy with the appropriate number of significant figures.

6. Construct Table 3 with $[H_2O_2]$, $\ln[H_2O_2]$ and $1/[H_2O_2]$ as a function of time for both temperatures.

7. Plot the integrated rate equations for orders one and two (plot the data for both temperatures on each graph). Determine the order of reaction with respect to hydrogen peroxide.

8. Use the slope of the lines in the above graph to determine the apparent rate constants at each temperature and the activation energy using the Arrhenius equation. Compare the activation energy with the value obtained from the partial reaction times.

# LABORATORY SESSION 5

## Kinetic study of the reaction between iodine and acetone catalyzed by acid

| **Material** | |
|---|---|
| 1 x 500 mL volumetric flask | 1 x 100 mL test tube |
| 1 x 100 mL volumetric flask | 1 thermostatic bath with thermometer |
| 1 x 250 mL volumetric flask (shared) | 1 x 1 L topaz bottle |
| 1 x 250 mL volumetric flask | 1 stirrer / 1 magnet / 1 weighting glass |
| 7 x 100 mL Erlenmeyer flasks | 1 chronometer |
| 1 x 3 mL volumetric pipette | **Products** |
| 1 x 5 mL volumetric pipette | Sodium thiosulfate pentahydrate |
| 1 x 10 mL volumetric pipette | Acetone |
| 1 x 15 mL volumetric pipette | Hydrochloric acid |
| 1 x 10 mL graduated pipette | Sodium acetate trihydrate |
| 1 x 50 mL burette | Sodium hydroxide 1M |
| 1 x 250 mL Erlenmeyer flask | Phenolphthalein |
| 2 x 100 mL beakers | Starch indicator |
| 1 x 50 mL beaker | Iodine 0.06 M |

## Objectives

1. To sequentially determine the kinetic parameters: partial orders, apparent rate constants and absolute rate constants.
2. To apply the Ostwald isolation method.
3. To verify the coherence between the rate law and the reaction mechanism.

## Theoretical background

In water solution, the acetone iodation reaction is slow but can be accelerated when catalyzed in acid medium:

$$CH_3 - CO - CH_3 + I_2 \xrightarrow{H^+} CH_3 - CO - CH_2I + HI$$

This reaction occurs via a three-step mechanism: the first (1) and second steps (2) are the keto-enol equilibrium in acid medium, while the third step (3) is the reaction between the enol and the iodine. From a kinetic point of view, steps (1) and (3) are fast but step (2) is slow. Step (2) is therefore the determining step in the mechanism.

$$CH_3 - CO - CH_3 + H^+ \xleftarrow{(1)} CH_3 - COH^+ - CH_3 \xleftarrow{(2)} CH_3 - COH = CH_2 + H^+$$

$$CH_3 - COH = CH_2 + I_2 \xrightarrow{(3)} CH_3 - CO - CH_2I + HI$$

The reaction rate can be expressed as:

$$v = -\frac{d[I_2]}{dt} = k[Acet]^a[H^+]^b[I_2]^c \qquad (1)$$

where "k" is the absolute rate constant, and "a", "b" and "c" are the partial orders with respect to acetone (Acet), protons and iodine, respectively.

In this experimental set up, as the concentration of acetone and acid will remain constant during the reaction, the kinetic can be followed with respect to the iodine (the test reagent or indicator). We will therefore be using the Ostwald isolation method. To do so, we use a very high initial concentration of acetone and, since HCl is the catalyzer (the number of moles at any given moment is practically equal to the initial number), the concentrations will remain constant throughout the reaction:

$$\left([H^+]_0, [Acet]_0 \cong [H^+], [Acet] \cong cts\right)$$

Bearing this in mind, the reaction will be of pseudo-order "c" and the rate expression can be simplified as:

$$v = k_{ap}\,[I_2]^c \qquad (2)$$

where the apparent constant is:

$$k_{ap} = k[Acet]_o^a[H^+]_o^b \qquad (3)$$

Given that iodine is not involved in the determining step, the rate will not depend on the concentration of iodine, i.e. the rate will be of zero order with respect to iodine (c=0), and:

$$v = k_{ap} \qquad (4)$$

To follow the evolution of iodine concentration, sample aliquots will be extracted from the reaction. The reaction will then be stopped in each aliquot and the iodine concentration will be determined by titration with sodium thiosulfate, in accordance with the following reaction:

$$I_2 + 2Na_2S_2O_3 \rightarrow Na_2S_4O_6 + 2NaI$$

Since the reaction is catalyzed by acid, the reaction will stop when the catalyzer is removed by adding a base or basic salt. By conducting several experiments in which only the concentration of one of the excess reagents (acetone or acid) is varied, we can measure how these reagents affect the rate reaction and so calculate their partial orders of reaction.

## Solutions

1. Iodine 0.06 M ($I_2$) (already prepared).
2. NaOH 1 M standardized (already prepared).
3. Sodium thiosulfate ($Na_2S_2O_3$) 0.005 M, 500 mL. To avoid exposure to light, the solution must be transferred to a topaz bottle after preparation.
4. HCl 1.2 M, 250 mL (to be shared with all your classmates at the table), from the commercial HCl solution (in the laboratory fume cupboard).

5. Sodium acetate (AcNa) 2.5 % in weight, 250 mL. (**Warning**: sodium acetate is trihydrate).

## Experimental procedure

1. Connect the thermostatic bath at 25 ºC.
2. Prepare solutions 3 (shared) and 4.
3. Titrate the HCl solution (solution 4; take a 10 mL sample) with NaOH 1M (solution 2). Each pair will perform one titration and share their results.
4. Three series of experiments are carried out where, compared two by two, the concentration of one of the reagents, acid or acetone, is varied and that of the other is kept constant. As described below.

### Series 1: acetone 5 mL and hydrochloric acid 5 mL 1.2 M

5. In a 100 mL volumetric flask, prepare the mixture for the reaction in the following order: water 50 mL + HCl 5 mL + acetone 5 mL. Adjust the volume with water.
6. Transfer this solution to an Erlenmeyer flask with a magnetic stirrer and insert the flask into the thermostatic bath onto the stirrer.
7. Prepare 7 Erlenmeyer flasks with 10 mL of sodium acetate 2.5 %.
8. Fill the burette with sodium thiosulfate and adjust the volume.
9. When thermal equilibrium is reached (after roughly 5 minutes), add 10 mL of $I_2$ (solution 1) to the Erlenmeyer flask. Start the chronometer (**t = 0**) when the pipette is half empty.
10. Two or three minutes later, take a sample aliquot of 10 mL, $V_{aliq}$, and drop it into an Erlenmeyer flask with sodium acetate 2.5 %. Record the time at which the volume in the pipette is halved (t = length of time at which the reaction is stopped).
11. Titrate the sample with $Na_2S_2O_3$ 0.005 M until the color fades. Warning! Before the titration ends, add the starch indicator.
12. Take sample aliquots of 10 mL every **eight minutes** and titrate as indicated in point 11 until all samples (seven) are taken.

### Series 2: acetone 15 mL and hydrochloric acid 3 mL

Repeat the experiment as indicated for Series 1, taking sample aliquots every **6 minutes**.

### Series 3: acetone 15 mL and hydrochloric 5 mL

Repeat the experiment as indicated for Series 1, taking sample aliquots every **4 minutes**.

**Note:** Remember that all residues must be disposed of in suitable containers when you finish the experiments.

## Experimental results: data presentation

1. Clearly show the calculations you performed to prepare the various solutions. Indicate the theoretical masses or volumes and the real masses or volumes and recalculate all concentrations (Table 1).
2. Present the titration data for the hydrochloric acid solution with NaOH and calculate the concentration of HCl with its random error (Table 2).
3. Tabulate the results of each series, i.e. the times of the reaction and the volume of thiosulfate consumed (Table 3).

## Data treatment and discussion

**WARNING!!! Very important: show the UNITS for all magnitudes**

1. Verify that the reaction is of zero order with respect to iodine (c=0). To do so, the integrated rate law of zero order must be represented, where the iodine concentration changes linearly over time, according to:

$$[I_2]_t = [I_2]_o - k_{ap} t \qquad (5)$$

Instead of this equation, we will show an equivalent equation based on the volume of thiosulfate consumed in the titration of the aliquot sample ($V_{tios}$), since the stoichiometric ratio between the number of moles of iodine and the number of moles of thiosulfate is $n_{I_2} = 1/2\, n_{tios}$. The iodine concentration at a given instant t, $[I_2]_t$, is therefore directly proportional to the volume of thiosulfate, according to:

$$[I_2]_t = \frac{1}{2}\frac{[S_2O_3^{2-}]V_{tios\,(t)}}{V_{I_2}} = A\, V_{tios\,(t)} \qquad (6)$$

where A is a constant whose value is $A = \frac{1}{2}[S_2O_3^{2-}]/V_{I_2}$. Replacing expression (6) in (5) we obtain:

$$V_{tios\,(t)} = V_{tios\,(o)} - k'_{ap}\, t \qquad (7)$$

where

$$k'_{ap} = \frac{k_{ap}}{A} \qquad (8)$$

and $V_{tios(0)}$ is the volume of thiosulfate that would be consumed in order to titrate an aliquot when the reaction begins, i.e. t = 0.

If the volume of thiosulfate is represented over time for each series and the points have a linear fit, it is verified that the reaction is of zero order with respect to iodine. All series must be represented on the same graph.

2. Calculate the apparent rate constants.

   From the linear fit in point 1 above (equation 7), $\mathbf{k'_{ap,i}}$ will be obtained from the slope and, with the value of constant A, finally we will obtain the apparent rate constants for each series: $\mathbf{k_{ap,i}}$.

3. Calculate the initial concentrations for acetone and acid for each series.

4. Calculate the partial orders with respect to acetone (a) and acid (protons) (b).

   To do so, apply equation (3) to the series taken in pairs so that the concentration of one reagent is the same.

   4.1. [HCl] equal in series 1 and 3:

$$\frac{series\ 1}{series\ 3} \Rightarrow \frac{k_{ap,1}}{k_{ap,3}} = \left(\frac{[Acet]_{o,1}}{[Acet]_{o,3}}\right)^a \text{, take logarithms: } \ln\left(\frac{k_{ap,1}}{k_{ap,3}}\right) = a\ln\left(\frac{[Acet]_{o,1}}{[Acet]_{o,3}}\right) \text{ and isolate:}$$

$$a = \frac{\ln k_{ap,1} - \ln k_{ap,3}}{\ln [Acet]_{o,1} - \ln [Acet]_{o,3}} \qquad (9)$$

   4.2. [Acet] equal in series 2 and 3:

$$\frac{series\ 2}{series\ 3} \Rightarrow \frac{k_{ap,2}}{k_{ap,3}} = \left(\frac{[HCl]_{o,2}}{[HCl]_{o,3}}\right)^b \text{, take logarithms: } \ln\left(\frac{k_{ap,2}}{k_{ap,3}}\right) = b\ln\left(\frac{[HCl]_{o,2}}{[HCl]_{o,3}}\right) \text{ and isolate:}$$

$$b = \frac{\ln k_{ap,2} - \ln k_{ap,3}}{\ln [HCl]_{o,2} - \ln [HCl]_{o,3}} \qquad (10)$$

5. Calculate the absolute rate constant with its random error. With the values of a and b (a=b=1), apply equation (3) for each series and obtain the following expression:

$$k_i = \frac{k_{ap,i}}{[Acet]_{o,i}\,[H^+]_{o,i}} \qquad (11)$$

   Calculate the mean value $\overline{k}$ with the three $k_i$ and the random error.

6. Deduce and discuss, from the volume-time graphs and the apparent rate constants obtained for each series, the effect of acetone and HCl on the reaction rate.

7. Confirm that the proposed mechanism is in agreement with the experimental rate law obtained experimentally.

**LABORATORY SESSION 6**

**Phase diagram: Boiling temperature/composition of a binary liquid mixture**

| **Material** | **products** |
|---|---|
| 2 vials | Methanol |
| 2 spherical flasks with two 50 mL mouths | Chloroform |
| 3 rubber stoppers | Acetone for cleaning |
| 2 cork bases | |
| 4 droppers | |
| 1 refractometer | |
| 2 methanol and chloroform dispensers | |
| glass beads for boiling / 2 magnets | |
| 1 distillation assembly / 1 heated magnetic stirrer / 1 NiCr-Ni thermocouple / 1 computer | |

## Objectives

1. To construct the phase diagram of the boiling temperature/composition of the methanol-chloroform mixture.
2. To determine the composition of the vapor phase (mole fraction) using the refractive index.
3. To determine the boiling temperature of binary mixtures.
4. To characterize the azeotropic point (azeotropic composition) of the binary mixture.
5. To determine the activity coefficients of the pure components and binary mixtures in the liquid and vapor phases.

## Theoretical background

### a) Concepts:

Since we are to construct a phase diagram, we will begin by defining the concept of **phase**, i.e. the homogeneous part of a system, whose macroscopic intensive thermodynamic variables (P, T, density, concentration, etc.) have the same value throughout the region, i.e. they are constant (do not change). A heterogeneous system is therefore one made up of two or more phases of the same component (a pure substance) or more than one component (a mixture).

A **phase diagram** is therefore a graphic representation that tells us which phase or phases a component or several components are in under certain conditions (P, T, etc.). Such diagrams can represent pressure-temperature values (one component) or be pressure-composition at T = const. or Temperature-composition at P = const. for mixtures of two or more components (binary, ternary, etc.).

A particular type of mixture is a **solution**, i.e. a homogeneous mixture of two or more substances (components). Solutions can be classified in many ways. However, from the thermodynamic perspective and taking into account the interactions between their components, solutions can be ideal or real (not ideal).

In this practice session, we will focus on liquid binary solutions (two components: A and B) in the study of liquid-vapor balance (two phases).

### b) Ideal solutions: laws, L–V equilibrium, diagrams.

A solution is ideal when the molecules of the various species are so similar to each other that the molecules of one component can replace those of the other without changing the spatial structure of the solution or the energy of the intermolecular interactions. In other words, A–A, B–B and A–B interactions are all of the same intensity.

Thermodynamically speaking, when the pure components form an ideal solution, the value of the mixing variables will be equal to the difference between the magnitude in the solution and the magnitude of the pure components. Therefore:

$\Delta V_M = 0$ there is no change in volume when the solution is formed since the spatial structure does not change.

$\Delta U_M = 0$ the energy of the interactions does not change as the solution forms.

$\Delta H_M = 0$ there is no mixing heat at constant P, i.e. heat is neither absorbed nor released.

$\Delta S_M > 0$ disorder increases.

$\Delta G_M < 0$ the formation of the solution is a spontaneous process.

An ideal solution is one that follows **Raoult's law**:

$$P_i = P_i^0 x_i^L \qquad (1)$$

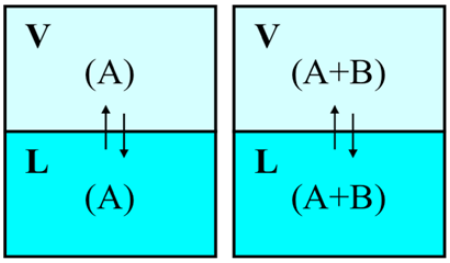
where i = A, B. Raoult's law provides the vapor pressure of a component i (partial pressure, $P_i$) in the solution as a function of the vapor pressure of the pure component ($P^o_i$) and the mole fraction of the component in the solution ( $x_i^L$ ) (at $T_b$ = constant).

**Dalton's law** for ideal gas mixtures, on the other hand, provides the partial pressure of each gas component ($P_i$) in the gas mixture as a function of the mole fraction of the component in the gas or vapor mixture ( $x_i^V$ ) and total gas pressure ($P_T$):

$$P_i = x_i^V P_T \qquad (2)$$

By combining equations (1) and (2), we can determine the composition of the vapor from the composition of the liquid, or vice versa, since the two compositions are not necessarily the same.

**liquid-vapor equilibrium** (L–V) can be represented for a pure substance and a binary liquid solution (in a closed system) as:




In this case, the boiling temperature/composition ($T_b$ – x) **phase diagram** of a binary liquid mixture (at constant P) shows the compositions of the liquid and vapor phases of the mixture as a function of its boiling

temperature. These diagrams are needed when the aim is to separate the two liquids by fractional distillation. Figure 1 shows the phase diagram for an ideal solution. In a distillation experiment with constant pressure, the solution is heated and steam is extracted and condensed. The condensed liquid is richer in the more volatile component than in the original liquid. Fractional distillation repeats the boiling and condensation cycle several times until the pure component is obtained.

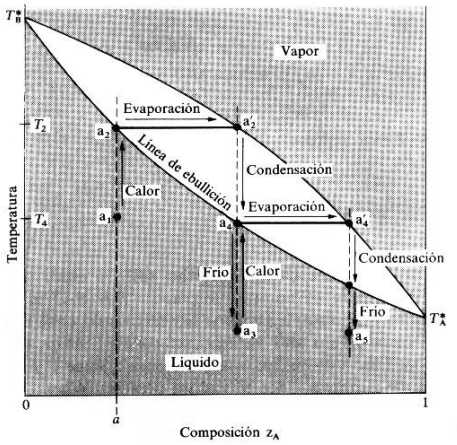



**Figure 1**. Temperature versus composition phase diagram (liquid-vapor) for an ideal mixture in which A is more volatile than B.

**c) Real solutions:** laws, L–V equilibrium, diagrams.

A real solution is one that does not obey ideal behavior, i.e. it does not comply with Raoult's law but deviates from it positively or negatively because the interactions between its components are not of the same intensity but are favorable or unfavorable.

In these cases, Raoult's law must be modified with an **activity coefficient** ($\gamma_i$) that accounts for the interactions:

$$P_i = P_i^O a_i = P_i^O x_i^L \gamma_i \qquad (3)$$

By combining equations (2) and (3), we obtain the expression for the activity coefficient:

$$\gamma_i = \frac{P_i}{P_i^O x_i^L} = \frac{P_T x_i^V}{P_i^O x_i^L} \qquad (4)$$

Real solutions can show:

**c.1) positive deviation from Raoult's law:**

$\gamma_A > 1 \Rightarrow$ $P_A$ (real) > $P_A$ (ideal) $\Rightarrow \Delta G^{exc} > 0$ $\Rightarrow$ Unfavorable liquid A–B interactions.

In other words, the mixing process is not spontaneous. As A-B interactions are less intense than A-A or B-B interactions, the molecules escape more easily from the solution to the vapor phase and their partial pressures are higher than with ideal solutions (Raoult law). Also, $\Delta H_M > 0$ and $\Delta V_M > 0$.

**c.2) negative deviation from Raoult's law**

$\gamma_A < 1 \Rightarrow$ $P_A$ (real) $< P_A$ (ideal) $\Rightarrow \Delta G^{exc} < 0$ $\Rightarrow$ Favorable A–B interactions in the liquid.

In other words, the mixing process is spontaneous, so the liquid solution is stable. A-B interactions are more intense than A-A or B-B interactions. Also, $\Delta H_M < 0$ and $\Delta V_M < 0$.

In this case, since the solution is real and has a positive deviation, the phase diagrams show a maximum on curve P versus x on the pressure-composition phase diagram at constant temperature (fig. 2 (a)) or a minimum on the T – x phase diagram at constant pressure (fig. 2 (b)). Conversely, a negative deviation from Raoult's law produces a maximum on the T – x diagram.

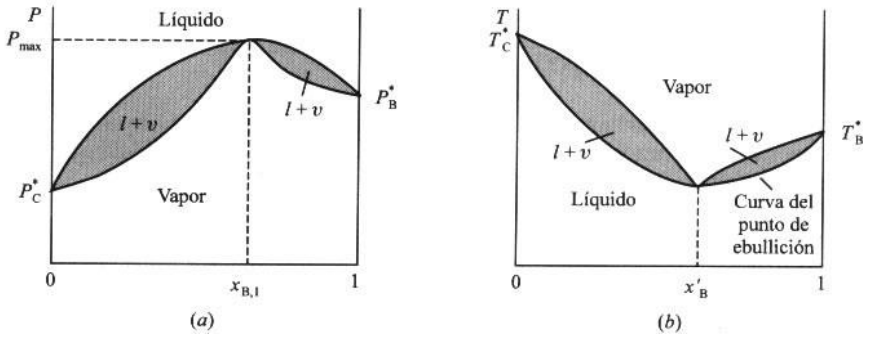



**Figure 2**. (a) Liquid-vapor phase diagram of pressure versus composition with a maximum. (b) Liquid-vapor phase diagram of temperature versus composition with a minimum.

The fractional distillation of these solutions produces a mixture whose composition corresponds to the maximum or minimum of the curve, where evaporation takes place without a change in composition. This mixture is called **azeotrope** (from the Greek "boiling without change"). Once the azeotropic composition is reached, the distillation cannot separate the two pure liquids and only pure azeotropic A or pure azeotropic B is obtained. At the azeotropic point, the following is true: $x_i^L = x_i^V$. An example is ethanol-water (96% v / v ethanol).

**d) Determination of the composition:** from a physical property.

To determine the composition of our solutions for constructing the phase diagram, we will measure a physical magnitude of the solution, i.e. the refractive index, n. The **refractive index** (n = c / c ') is defined as the relationship between the speed of light in vacuum (c = constant) and the speed of light in the medium or solution (c'), which depends on the composition of the medium.

## Experimental procedure

Before beginning the experiment connect the refractometer and the thermostatic bath at 20° C , the water pump for cooling the columns, and the Cobra equipment (computer and potentiometer).

**Do not use** water at any time during the experiment.

**PRECAUTIONS WHEN HANDLING THE REFRACTOMETER**

**The surface of the refractometer must be cleaned and dried before each measurement.**

**Do not use aggressive substances or objects since they can scratch the surface of the refractometer.**

**No bubbles should appear inside the prism.**

1. Record the atmospheric pressure (from the laboratory).

2. Measure the refractive index of a pure substance.

   Use a dropper to place a few drops of pure methanol onto the surface of the refractometer prism and note its refractive index.

3. Determine the boiling temperature of a pure component and calibrate the temperature unit.

   Insert 20 mL of pure methanol into a 50 mL round flask with 6 or 7 boiling pearls and the magnet and proceed as follows:

   3.1. Place the flask in the reflux assembly with the temperature probe. Set the hot plate and stirrer to position 1 **(moderate stirring level and with the magnet not touching the thermocouple)**. Click on the "Measure" icon and then on the first button from the left in the row above  . Then click on "continue" and on "start the measurement". A temperature point will appear on the screen every second.

   3.2. When the temperature remains constant for at least one quadrant, it is calibrated as follows:

   Click on "finish the measurement", begin a new measurement using  , press on "calibrate" **(down)**, enter the boiling temperature of pure methanol (see Data) and press the "calibrate" button **(right box)** and OK. Begin a new measurement and check the boiling temperature of the methanol.

   Remove the round-bottom flask from the distillation apparatus, remove the temperature probe, and cool the flask in the bath with the rubber stoppers on. When it is not hot, pour the contents into the waste container and collect the pearls and the magnet.

4. Construct the boiling temperature/composition diagram

   The methanol-chloroform solutions shown in the Table below are to be prepared successively in the two-neck flask (with boiling beads and magnet):

| V Methanol (mL) | 20 | 19 | 18 | 16 | 14 | 12 | 10 | 8 | 6 | 4 | 2 | 1 | 0.5 | 0 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| V Chloroform (mL) | 0 | 1 | 2 | 4 | 6 | 8 | 10 | 12 | 14 | 16 | 18 | 19 | 19.5 | 20 |

With each solution, proceed as follows:

4.1. Measure the refractive index of the solution ($n_L$).

4.2. Place the flask into the reflux assembly with the temperature probe. Put the hot plate and stirrer into position 1. Click on the "Measure" icon, on the button , on "continue" and on "start the measurement". A temperature point will appear on the screen every second.

4.3. When the temperature remains constant for at least one quadrant (record this temperature), close the Teflon tap and extract a few drops of the condensate with the syringe and without removing the needle, collect them in a vial and cool them in the bath. Reopen the Teflon tap.

4.4. Measure the refractive index of the condensate ($n_V$).

4.5. Press "finish measurement". A rescaled graph will appear on the screen, T = f(t). Click on the cross-shaped button, , which is the fourth from the right on the top bar and, with the mouse, drag it across the constant temperature zone. Press the third button from the left on the bar below, , and the average temperature of the indicated area will appear. Record this temperature.

4.6. Remove the round-bottom flask from the assembly, remove the stopper with the temperature probe, fit another stopper and refrigerate the flask in the bath. When the flask is not hot, pour the solution into the waste container.

5. Measure the refractive index and boiling temperature of pure chloroform.

## Treatment and discussion of results

1. Calculate the mole fractions of each component in the liquid mixtures.

   Data:

| | Methanol | Chloroform |
|---|---|---|
| $d^{20}$ ($g.cm^{-3}$) | 0.7914 | 1.4832 |
| $n^{20}$ | 1.3288 | 1.4459 |
| $M_r$ ($g.mol^{-1}$) | 32.04 | 119.32 |
| $T_b$ (ºC) | 64.6 | 61.2 |

2. Build the composition calibration curve as a function of the refractive index, $x^L_{Metanol} = f(n^L)$ of the methanol-chloroform solutions. Include the points that correspond to the pure components.

3. Determine the mole fractions of the components in the gas phase from the above calibration curve. Include these results in the Table.

4. Draw the boiling temperature/composition diagram.

5. Characterize the azeotropic point. At that point, the two phases have the same composition, $\boxed{x_i^L = x_i^V}$.

   Therefore, if we plot the mole fraction of one of the phases against the mole fraction of the other, the azeotropic point must be located on the line that joins the points of equal composition in both phases. This graph is constructed for one of the components, e.g. methanol. The azeotrope point will be the point at which the curve obtained intersects the line that joins the points of equal composition in both phases.

   Search in the bibliography (www.chemnetbase.com) for the T and x (methanol) of the azeotrope and compare these values with the experimental results.

6. Determine the activity coefficients of methanol, chloroform and their mixtures from equation (4).

   Take the atmospheric pressure of the laboratory as the value of total pressure. We also need to know the vapor pressure of a pure component as a function of temperature, which is given by Antoine's equation:

$$\log P_i^o = A - \frac{B}{C+T} \qquad (5)$$

   where $P_i^o$ is expressed in hPa units, T is the temperature expressed in Celsius, and A, B and C are constants that are characteristic of each component:

| | A | B | C |
|---|---|---|---|
| Chloroform | 7.07959 | 1170,966 | 226,232 |
| Methanol | 8.20591 | 1582,271 | 239,726 |