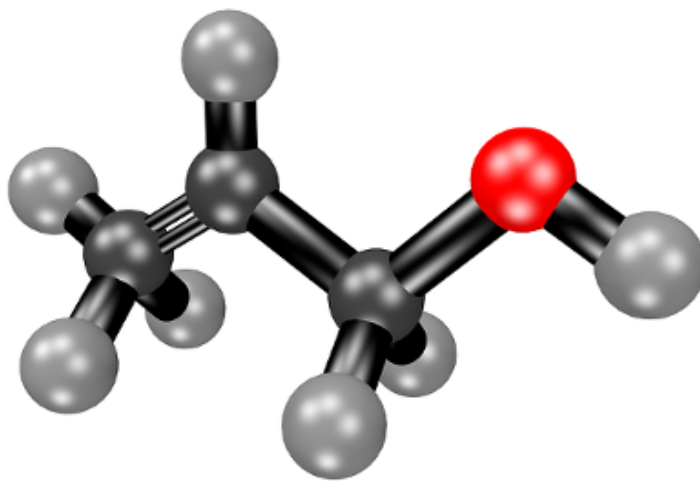# *Experiments in College Chemistry*

AN OPENTEXTBOOK

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**Science Department**
**B.M.C.C.**
**The City University of New York**

THIS BOOK NEEDS TO BE SPIRAL BOUNDED + PRINTED DOUBLESIDED

# Contents

**1 Isomers**

<div align="center">

EXPERIMENT

# Geometric isomers

</div>

## Goal

The goal of this experiment is to understand the concept of **isomerism**. During this practice, the student will identify two different molecules based on their properties. Later, a simple reaction will be carried out in an attempt to transform each molecule into its corresponding isomer. The student should be able to identify the new products based on the first observations (i.e. the properties of each molecule) and to validate the success of the transformation. The experiment will also familiarize the students with the separation technique known as suction filtration.

## Materials

- ☐ 4 small test tubes, with 2 suitable test tube stoppers
- ☐ 2 test tube holders
- ☐ Bunsen burner
- ☐ 250 mL Erlenmeyer
- ☐ Ring stand, Iron ring, Wire gauze, Clamps and Büchner funnel
- ☐ Rubber tubing

- ☐ Suction flask
- ☐ Round filter paper
- ☐ plastic funnel
- ☐ stirring rod
- ☐ Fumaric Acid, and Maleic Acid,
- ☐ 12 M Hydrochloric Acid
- ☐ Ice

## Background

Consider a set of Lego® blocks with different sizes and colors. We can combine them in numerous ways to construct many different structures. Similarly, if those blocks were atoms, we would obtain different molecules from the same set of atoms. Isomers are molecules with the same number and nature of atoms, and therefore the same molecular formula, but with different structures. Diverse structures arise from variations in the bonds between atoms and lead to new molecules, with different names and properties.

*Geometric isomers* are a subclass of isomers where not only the number and nature of the atoms are the same, but also the bonds. In this case, it is the spatial distribution or 3D structure that differs. This little change can lead to considerable differences in basic properties such as melting points and solubilities. In molecules with four ligands distributed around a central atom or a double bond, the isomerism can arise from the distribution of those four ligands around the molecule, leading to *cis-* and *trans-* isomers. This is the case in the proposed experiment.

The process of **isomerization** is the transformation from one molecule into its corresponding isomer. This transformation does not take place spontaneously but typically requires external energy and, in some cases, specific conditions. Energy is necessary to break certain bonds to allow the molecule to restructure into the corresponding isomer.

## Procedure

### Part A. Identify the products by their melting point.

☐ *Step 1:* – Obtain the two unknowns. One unknown should be fumaric acid (*white powder*), and the other maleic acid (*white powder*). If both unknowns show the same properties in the following experiment, be prepared to select a different unknown.

☐ *Step 2:* – Label two small test tubes as A and B.

☐ *Step 3:* – Put a pea-size amount of one product in test tube A, and a similar amount of the other product in test tube B.

☐ *Step 4:* – Using a striker, light the Bunsen burner. Using a test tube holder for each sample, hold test tubes closely together, in the same hand. The samples must be heated in similar conditions. Make sure you never heat a test tube with a tube stopper on as they will explode.

☐ *Step 5:* – Write your results in the Results section, characterizing the melting point of each unknown by comparison as low or high.

> **Good Lab Practice**
>
> ✍ The burner should stand stable with no additional support. Coil the tubing at each end to stabilize the burner.
>
> ✍ Work safely and avoid burns.
>
> ✍ Always ensure easy access to the gas valve. Remove any items around the valve, and do not set the flame on your way.
>
> ✍ Never leave the flame unattended. In case of accident or any risk, close the gas immediately.

☐ *Step 6:* – Start a timer. Swing the test tubes over the flame. Stop as soon as one of the two powders melts. Pay attention to the test tubes' label. Was it test tube A or test tube B? Write down the time it took to melt the isomer on the Results table.

☐ *Step 7:* – Refer to the known properties of maleic acid and fumaric acid (from the prelab) to determine which product is unknown A and which is unknown B.

☐ *Step 8:* – Allow the test tubes to cool down. Discard the contents in the indicated waste containers. Clean the test tubes.

### Part B. Identify the products by their solubility in water.

☐ *Step 1:* – Label two small test tubes as A and B.

☐ *Step 2:* – Put a pea-size amount of one product in test tube A, and a similar amount of the other product in test tube B.

☐ *Step 3:* – Add similar amounts of distilled water to each test tube. Approximately 2 mL of water should be enough.

☐ *Step 4:* – Cover the tube using the stoppers and shake them until one of the 2 powders dissolves completely in the liquid.

☐ *Step 5:* – Refer to the known properties of maleic acid and fumaric acid (from the prelab) to determine which product is unknown A and which is unknown B.

☐ *Step 6:* – Your result should be consistent with Part A. If not, first repeat part B to double-check if the labeling was correct. If the mistake was not in part B, then repeat part A.

☐ *Step 7:* – Write your results in the Results section, characterizing the solubility of each unknown by comparison as low or high.

## Part C. Isomerization reaction. Preparing the setup

☐ *Step 1:* – Obtain **about** 1.0 grams of the most soluble sample in Part B, using the scale and a weighing boat.

☐ *Step 2:* – Transfer the powder into a 250 mL Erlenmeyer flask and add **around** 10 mL of distilled water.

☐ *Step 3:* – Now, we will prepare a setup to boil the solution that will remove the vapors from the reaction.

☐ *Step 4:* – Set up a ring stand and the iron ring with the wire gauze on top. Do not put the Erlenmeyer with the solution yet. Make sure that the height of the platform is appropriate for the size of the flame.

☐ *Step 5:* – Use a second, smaller ring above the platform as protection.

☐ *Step 6:* – To remove the vapors improvise a little hood using a plastic funnel. Connect the funnel to the vacuum line using the rubber tubing and set it with a clamp, upside down, at a certain distance over the platform.

☐ *Step 7:* – Start the ventilation.

☐ *Step 8:* – Show the setup to your instructor, who will make sure it is sturdy enough. In particular, the instructor will sure all vapor is removed with the funnel, if not, adjust the setup right away. You want to avoid the release of any vapor into the air.

☐ *Step 9:* – Place the maleic acid solution in the Erlenmeyer, and light the burner to gently warming up the solution.

> ⚠ CAUTION!
>
> ⚠ Wear goggles at all times.
>
> ⚠ Handle concentrated acid with care to avoid chemical burns.
>
> ⚠ Use latex gloves when handling concentrated acid.
>
> ⚠ Ensure that the mouth of the test tube is pointed away from you and any other persons around you, including those on the opposite side of the bench.

## Part C. Isomerization reaction. Adding the concentrated acid

☐ *Step 1:* – Make sure you wear some protective latex gloves.

☐ *Step 2:* – While the solution warms up obtain 10 mL (approx.) of concentrated hydrochloric acid, HCl, in a 25 mL graduated cylinder. Use a plastic dropper to transfer the acid from its container into the cylinder. Mind this is a very concentrated acid that can hurt you.

☐ *Step 3:* – Keep the cylinder all the time in the hood to minimize the release of acidic vapors.

☐ *Step 4:* – When the solution starts to boil, bring the acid from the hood, and add *carefully* the acid into the solution using a plastic dropper.

☐ *Step 5:* – There should be no acid left over. If so, get rid of the leftover acid right away.

☐ *Step 6:* – Wait until the boiling is re-established, and make sure no vapor scapes the ventilation system.

☐ *Step 7:* – Let the reaction boil for 1 minute and then turn off the gas. Continue preparing the next steps.

## Part C. Isomerization reaction. Filtration

☐ *Step 1:* – Put 40 mL of distilled water in a clean 50 mL beaker. Cool down this water using an ice bath. Get ice in a large enough beaker and dip the 50 mL beaker in the ice.

☐ *Step 2:* – Go back to the Erlenmeyer with the solid dissolved and the acid. Allow the Erlenmeyer to cool down for 10 minutes. In the meantime, obtain ice in a 600 mL beaker and add some water to the ice.

☐ *Step 3:* – After the 10 minutes of cooling down, transfer the Erlenmeyer carefully and safely into the large ice bath.

☐ *Step 4:* – Get the suction filtration setup ready. Connect the suction flask to the vacuum and put the Büchner funnel on top.

☐ *Step 5:* – Obtain a flat, round filter paper with a diameter slightly smaller than the bottom of the funnel. Start the vacuum and add some distilled water with a wash bottle to test the suction.

☐ *Step 6:* – Filter the solution. Stir the mixture to help the precipitate to suspend and add the liquid carefully over the filter paper. Use the cold distilled water in the 50 mL beaker to remove any solid left in the Erlenmeyer and to wash the filtrate.

☐ *Step 7:* – Keep the suction on for another 5 minutes. This will help remove all the water and partially dry the filter.

☐ *Step 8:* – Turn off the vacuum and remove the filter from the funnel carefully.

☐ *Step 9:* – Keep the solid product until the end of the experiment.

## Part C. Isomerization reaction. Testing the product

☐ *Step 1:* – Identify your product following the steps in Part B.

☐ *Step 2:* – Write your results in the Results section, characterizing the solubility of the isomerization product by comparison as low or high.

**Pre-lab Questions**

# Geometric isomers

1. Complete the table for the molecules Fumaric Acid and Maleic Acid

|  | Fumaric Acid | Maleic Acid |
| --- | --- | --- |
| Molecular formula | | |
| Draw the structure | | |
| Solubility in water | | |
| Melting point | | |
| What is it used for? | | |
| Where is it found? | | |

2. Draw the setup for suction filtration (Büchner funnel, suction flask, tubing...)

3. What are the dangers of an improper installation of the ventilation system in this experiment?What chemical in this experiment can be dangerous?

4. Define:

   (a) Isomers

(b) Geometric Isomers

(c) Isomerization

(d) Suction filtration

(e) Filtrate

5. When you mix hydrocloric acid and water, what do you add first the acid or water?

**Results**
**EXPERIMENT**

# Geometric isomers

This experiment is qualitative, which means that the results are based on observations. Record your observations for each sample during and after each part of the activity.

| | Before isomerization | | After isomerization |
|---|---|---|---|
| | Sample A | Sample B | |
| Part A. Time to melt (secs) | | | |
| Part A. Melting point (lower/higher) | | | |
| Part B. Solubility in water (smaller/larger) | | | |
| Isomer name (fumaric/maleic) | | | |
| Part C. Selected for isomerization? (yes/no) | | | |

**STUDENT INFO**

Name:                                    Date:

**Post-lab Questions**

# Geometric isomers

1. A Similar amount of both unknowns are used for their characterization in Parts A and B. Why is it important to use similar amounts? What would change if the amounts used were very different?

2. How can you prove that the isomerization process was successful?

3. Why did you cool down the solution after the isomerization?

4. What would happen if hot water was used to wash the filtrate?

EXPERIMENT

# Conductivity of electrolyte solutions

## Goal

The terms of **conductivity** and **electrolytes** will be introduced and related to the concept of dissociation. The use of the conductivity meter, very similar to the pH meter, will help to differentiate between strong and weak electrolytes. In the last part of the experiment, the presence of chemical reactions will be identified by measuring changes in conductivity.

## Materials

- ☐ jumbo test tubes
- ☐ conductivity meter
- ☐ 6M solution of $NH_3$
- ☐ 6M solution of $CH_3COOH$
- ☐ Ethyl alcohol

- ☐ 0.1M solutions of $KNO_3$, KCl, KOH, HCl, and $Ca(NO_3)_2$
- ☐ an unknown solution
- ☐ 5mL, 10mL, 25mL pipets (preferred Mohr's)
- ☐ 250mL and 50mL beakers
- ☐ rinsing water bottle

## Background

Playing with water near electrical appliances can be risky. Surprisingly, however, water does not conduct electricity. For electricity to propagate through media there must be free charges that move along the electric field. Pure water does not contain a significant number of charges and does not conduct electricity. However, when there is something dissolved in the water, therefore making an aqueous solution, it can be conductive.

### Conductivity and aqueous solutions

Whether the aqueous solution is conductive or not depends on the nature of the solute. If the solute dissociates into ions when dissolved in water, the ions will conduct electricity. These types of chemicals are called electrolytes. If the solute dissolves as a molecule without dissociation, the solution will not conduct electricity and the solute will be called nonelectrolyte.

### Conductivity units

The unit for conductivity is Siemens per centimeter, $S \cdot cm^{-1}$. Pay attention to the units during this experiment because the tool will often display prefixes like milliSiemens or microSiemens per centimeter. Temperature affects conductivity and must be recorded during the measurement of this property.

### Types of electrolytes and factors affecting their conductivity.

Salt and sugar are soluble in water. When sugar dissolves in water its molecules remain intact because water can not break apart the strong covalent bonds between their atoms. As a neutral molecule, sugar in solution will not conduct electricity and it is an example of a **nonelectrolyte**. Salt, sodium chloride or NaCl, is an ionic compound that gives place to two ions, $Na^+$ and $Cl^-$ when dissolved in water. These ions are responsible for the solution's conductivity. The number or more specifically

the concentration, and the mobility of these ions will determine how conductive the solution is. Based on these principles we can classify substances as:

- × **Non-electrolytes**. When the aqueous solution of that substance does not conduct electricity. In general terms, these electrolytes present low conductivities, lower than $10 \mu S \cdot cm^{-1}$.

- × **Weak electrolyte**. When the aqueous solution of that substance conducts electricity poorly. In general terms, these electrolytes present medium conductivities, between $10\text{-}1000 \mu S \cdot cm^{-1}$.

- × **Strong electrolyte**. When the conductivity of the aqueous solution of that substance is high. In general terms, these electrolytes present large conductivities, larger than $1000 \mu S \cdot cm^{-1}$.

The **mobility** of the ions is related to their size. Small ions move fast which enhances conductivity, while large ions encounter more resistance to move and show lower conductivities. The table below displays a series of mobility values for positive and negative ions at infinite dilution and 298K and 1 atm.

| Ion | $H_3O^+$ | $Li^+$ | $Na^+$ | $Mg^{2+}$ | $OH^-$ | $Cl^-$ | $Br^-$ | $NO_3{}^-$ |
|---|---|---|---|---|---|---|---|---|
| movility, $u^\infty$ $(10^5 cm^2 \cdot V^{-1} \cdot s^{-1})$ | 363 | 41 | 52 | 55 | 206 | 80 | 81 | 74 |

The effect of ions′ mobility is easily appreciated in isomolar solutions, which are solutions with the same molarity. The more ions in the solution, the higher the conductivity will be. For the same substance, the number of ions is determined by the **concentration**; more concentration means more ions and more conductivity. It is important to recall that only ions contribute to conductivity. While some molecules dissociate completely, others dissociate only partially. The latter are weak electrolytes. Interestingly, when two solutions containing ions are mixed, the conductivity of the resulting solution will be equal to the sum of the two separate solutions with the same concentration as in the mixture. This is called the **additivity rule** and will hold as long as the ions do not react with each other. When two electrolytes undergo a chemical reaction, new products will form and the additivity rule will not apply. A large deviation from the sum of separate conductivities is an indication of a chemical reaction.

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### Example

*The conductivity of a 0.050 M solutions of $HNO_3$ is measure to be 19.6 mS/cm. That of a 0.050 M solution of KCl is 9.6 mS/cm. A new solution is prepared mixing 10 mL of $HNO_3$ 0.10 M and 10 mL of KCl 0.10 M. The conductivity of the resulting mixture is measure to be 29.6 mS/cm. Calculate the concentration of each spices in the mixture and determine if their compounds have reacted or not.*

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**Answer**: To calculate the new concentration use the formula for dilutions:

$$V_1 \times M_1 = V_2 \times M_2$$

where $V_1$ and $M_1$ are the initial volume and concentration and $V_2$ and $M_2$ are the values after the dilution.
We look for $M_2$, therefore

$$M_2 = V_1 \times \frac{M_1}{V_2}$$

for $HNO_3$,

$$M_2 = \frac{10 \, mL \times 0.10 \, M}{(10 \, mL + 10 \, mL)} = 0.05 \, M$$

The same values apply for KCl.
We can see that the addition of the separate conductivities ($\kappa$) is very close to the total conductivity of the mixture with the same concentrations for each electrolyte.

$$\kappa(HNO_3 \ 0.05 \ M) + \kappa(KCl \ 0.05 \ M) = 19.6 \ mS/cm + 9.6 \ mS/cm = 29.2 \ mS/cm$$
$$\kappa(HNO_3 \ 0.05M + KCl \ 0.05M) = 29.6 \ mS/cm$$

The additivity rules applies, meaning that there is no reaction between $HNO_3$ and KCl.

## Procedure

### Part A. Getting started: standardize the conductimeter

☐ *Step 1:* – Install the conductivity meter. The probe of the instrument is immersed in a clean solution that must be kept aside until the end of the experiment. Mind the probe needs to be hydrated at all times.

☐ *Step 2:* – To calibrate the conductivity meter, place 40mL of standard conductivity solution in a 50mL beaker while placing the probe in it.

☐ *Step 3:* – Make sure the conductivity cell is fully submerged in the liquid.

☐ *Step 4:* – Now press Setup (top right menu). Normal setups are: cell constant of 1.0, standard recognition with manual selected, reference temperature 25 degrees, temperature coefficient of 2.1%, and alarm limits off.

☐ *Step 5:* – Now press Standardize (top right menu) and input 1.000 mS/cm (or 1000 $\mu$S/cm) in the keypad and press confirm (this should be the conductivity value of the standard). Finally, press Confirm (top right menu) to save the standard value. Now you are ready to measure.

### Part A. Getting started: measuring conductivity

☐ *Step 1:* – It is very important to follow some cleaning steps before you measure the conductivity of any solution. You will need a 100 mL beaker labeled as waste, a wash bottle, and a 250 mL beaker with distilled water.

1. Rinse the probe using the wash bottle over the waste beaker.
2. Dip the probe 3-4 times into the 250 mL beaker with clean distilled water.
3. Dip the probe into the solution to be measured. Use a 50 mL beaker (or a jumbo test tube) with at least 25 mL of solution. Use the same volume for all conductivity measurements.
4. Repeat cleaning steps 1 and 2.

☐ *Step 2:* – It is critical to properly read the conductivity units from the conductimeter. Every solution would give a different conductivity value and sometimes a different unit. The conductivity units are written next to the measurement in the conductivity. It is critical you copy the measurement with the unit given by the tool.

> **Good Lab Practice**
>
> ✐ To ensure the probe is well cleaned and the water in the 250 mL beaker remains clean, the conductivity meter should display a value close to that of the distilled water during the cleaning.
>
> ✐ If the conductivity value of the cleaning water differs from the one of distilled water, replace the water in the 250 mL beaker with fresh distilled water, and thoroughly clean the probe.

### Part B. Pure substances.

☐ *Step 1:* – Following the procedure outlined above, measure the conductivity of distilled water. Record the value in the Results section.

☐ *Step 2:* – Following the procedure outlined above, measure the conductivity of tap water. Record the value in the Results section.

☐ *Step 3:* – Following the procedure outlined above, measure the conductivity of Ethyl alcohol ($C_2H_5OH$). Record the value in the Results section.

☐ *Step 4:* – Classify the substance as strong, weak, or nonelectrolyte.

## Part C. Series of electrolytes.

☐ *Step 5:* – In a clean 50 mL beaker, add 20 mL of 0.10 M HCl and 20 mL of distilled water (this is a $\frac{1}{2}$ dilution). Use a Mohrs pipet to transfer the liquids, making sure you rinse with distilled water between transfers. Mix well and measure the conductivity. Recalculate the concentration after the dilution and write it down in the Results section.

☐ *Step 6:* – In a clean 50 mL beaker, add 20 mL of 0.10 M KOH and 20 mL of distilled water (this is a $\frac{1}{2}$ dilution). Use a Mohrs pipet to transfer the liquids, making sure you rinse with distilled water between transfers. Mix well and measure the conductivity. Recalculate the concentration after the dilution and write it down in the Results section.

☐ *Step 7:* – In a clean 50 mL beaker, add 20 mL of 0.10 M KCl and 20 mL of distilled water (this is a $\frac{1}{2}$ dilution). Use a Mohrs pipet to transfer the liquids, making sure you rinse with distilled water between transfers. Mix well and measure the conductivity. Recalculate the concentration after the dilution and write it down in the Results section.

☐ *Step 8:* – In a clean 50 mL beaker, add 20 mL of 0.10 M $KNO_3$ and 20 mL of distilled water (this is a $\frac{1}{2}$ dilution). Use a Mohrs pipet to transfer the liquids, making sure you rinse with distilled water between transfers. Mix well and measure the conductivity. Recalculate the concentration after the dilution and write it down in the Results section.

☐ *Step 9:* – In a clean 50 mL beaker, add 20 mL of 0.10 M $Ca(NO_3)_2$ and 20 mL of distilled water (this is a $\frac{1}{2}$ dilution). Use a Mohrs pipet to transfer the liquids, making sure you rinse with distilled water between transfers. Mix well and measure the conductivity. Recalculate the concentration after the dilution and write it down in the Results section.

☐ *Step 10:* – Find an unknown solution. In a clean 50 mL beaker, add 20 mL of the unknown solution and 20 mL of distilled water (this is a $\frac{1}{2}$ dilution). Use a Mohrs pipet to transfer the liquids, making sure you rinse with distilled water between transfers. Mix well and measure the conductivity.

☐ *Step 11:* – Classify all substances as strong, weak, or nonelectrolytes and identify the unknown compound based on the conductivity values. Know that the unknown can also be water.

## Part D. Series of Dilutions.

☐ *Step 12:* – Obtained the conductivity of a 0.1 M solution of HCl from previous section. Write down the result in the Results section.

☐ *Step 13:* – Now you are going to prepare two dilutions. Starting from the concentrated 0.1 M solution of HCl, you are going to prepare 40mL volumes of the following dilutions: 0.050 M and 0.020 M. The first is a $\frac{1}{2}$ dilution, that is 20ml of acid needs to be mixed with 20ml of water to get 40mL of 0.050M solution, whereas the second is a $\frac{1}{5}$ dilution, that is 8ml of acid needs to be mixed with 32ml of water. Use a Mohrs pipet to transfer the liquids, making sure you rinse with distilled water between transfers.

☐ *Step 14:* – Measure the conductivity of the two diluted HCl solutions (0.050 M, and 0.020 M) and record the values.

## Part E. Mixtures of HCl and $KNO_3$.

☐ *Step 15:* – Write down the conductivity of the 0.050 M solution of HCl from the previous section in the Results section.

☐ *Step 16:* – Write down the conductivity of the solution of $KNO_3$ from the previous section in the Results section.

☐ *Step 17:* – In a clean 50 mL beaker, add 20 mL of 0.10 M HCl and 20 mL of 0.10 M $KNO_3$. Use a Mohrs pipet to transfer the liquids, making sure you rinse with distilled water between transfers. Mix well and measure the conductivity. Recalculate the concentration after the dilution and write it down in the Results section, minding that both solutions have now the same concentration and therefore only one number needs to be listed.

## Part F. Mixtures of NH$_3$ and HC$_2$H$_3$O$_2$.

☐ *Step 18:* – Prepare the following dilutions: 100mL of acetic acid (HC$_2$H$_3$O$_2$) 0.12 M from 6M (add 2mL of concentrated solution and fill up with water until 100mL) and 40mL of ammonia (NH$_3$) 0.12 M from 6M (add 2mL of concentrated solution and fill up with water until 100mL). Carefully read the concentration of the initial concentrated solutions indicated in the labels. Work in the hood when handling highly concentrated solutions.

☐ *Step 19:* – In a clean 50 mL beaker, add 20 mL of the 0.12 M NH$_3$ dilution and 20 mL of distilled water (this is a $\frac{1}{2}$ dilution). Use a Mohrs pipet to transfer the liquids, making sure you rinse with distilled water between transfers. Mix well and measure the conductivity. Recalculate the concentration after the dilution and write it down in the Results section. Work in the hood when handling highly concentrated solutions.

☐ *Step 20:* – In a clean 50 mL beaker, add 20 mL of 0.12 M HC$_2$H$_3$O$_2$ and 20 mL of distilled water (this is a $\frac{1}{2}$ dilution). Use a Mohrs pipet to transfer the liquids, making sure you rinse with distilled water between transfers. Mix well and measure the conductivity. Recalculate the concentration after the dilution and write it down in the Results section.

☐ *Step 21:* – In a clean 50 mL beaker, add 20 mL of 0.12 M NH$_3$ and 20 mL of 0.12 M HC$_2$H$_3$O$_2$. Use a Mohrs pipet to transfer the liquids, making sure you rinse with distilled water between transfers. Mix well and measure the conductivity. Recalculate the concentration after the dilution and write it down in the Results section, minding that both solutions have now the same concentration and therefore only one number needs to be listed.

⚠CAUTION!

⚠ Handle concentrated acid or bases with care to avoid chemical burns.

⚠ Are you wearing your goggles? Do you know where the eye-washer is?

**Pre-lab Questions**

# Conductivity of electrolyte solutions

1. Starting with a 6 M solution of NaCl, calculate the volume of solution and the volume of water necessary to prepare 10 mL of a 3 M solution of NaCl.

2. How can you dilute a 3 M solution to form a 1.5 M solution? (e.g. I would pick up X mL of the solution and YmL of distilled water.)

3. How can you prepare 40mL of acetic acid ($HC_2H_3O_2$) 0.12 M from 6M.

4. How can you prepare 40mL of ammonia ($NH_3$) 0.12 M from 6M.

5. Given the data below, classify the following electrolytes as strong, weak, or nonelectrolytes:

| | Concentration (M) | Conductivity | Units | Type of electrolyte |
|---|---|---|---|---|
| $CuSO_4$ | 0.05M | 4000 | $\mu S \cdot cm^{-1}$ | _____ |
| $FeCl_3$ | 0.05M | 10000 | $\mu S \cdot cm^{-1}$ | _____ |
| $C_6H_{12}O_6$ | 0.05M | 9 | $\mu S \cdot cm^{-1}$ | _____ |
| $CH_3COOH$ | 0.05M | 320 | $\mu S \cdot cm^{-1}$ | _____ |

**Results**
**EXPERIMENT**

# Conductivity of electrolyte solutions

Part B: Substances

|  | Conductivity | Units | Electrolyte type |
|---|---|---|---|
| Distilled water | —————— | ——— | ——— |
| Tap water | —————— | ——— | ——— |
| $C_2H_5OH$ | —————— | ——— | ——— |

Part C: Electrolytes

|  | Concentration (M) | Conductivity | Units | Electrolyte type |
|---|---|---|---|---|
| HCl | —————— | —————— | ——— | ——— |
| KOH | —————— | —————— | ——— | ——— |
| KCl | —————— | —————— | ——— | ——— |
| $KNO_3$ | —————— | —————— | ——— | ——— |
| $Ca(NO_3)_2$ | —————— | —————— | ——— | ——— |
| Unknown | | —————— | ——— | |

| Unknown # | —————— | Unknown identity | ——— |
|---|---|---|---|

## Part D: Concentration effect

|  | Concentration (M) | Conductivity | Units |
|---|---|---|---|
| HCl | —————— | ————— | ——— |
| HCl | —————— | ————— | ——— |
| HCl | —————— | ————— | ——— |

## Part E: HCl+KNO$_3$ mixture

|  | Concentration (M) | Conductivity | Units |
|---|---|---|---|
| HCl | —————— | ————— | ——— |
| KNO$_3$ | —————— | ————— | ——— |
| HCl+KNO$_3$ | —————— | ————— | ——— |

## Part F: HC$_2$H$_3$O$_2$+NH$_3$ mixture

|  | Concentration (M) | Conductivity | Units |
|---|---|---|---|
| HC$_2$H$_3$O$_2$ | —————— | ————— | ——— |
| NH$_3$ | —————— | ————— | ——— |
| HC$_2$H$_3$O$_2$+NH$_3$ | —————— | ————— | ——— |

**Post-lab Questions**

# Conductivity of electrolyte solutions

1. Based on your results on Part B, which conductivity was higher, the one for distilled water or for tap water? Why?

2. Based on your results on Part C, specifically the conductivity values of KCl and KOH, how does ion mobility affect conductivity (see table in the Background section)? Use your data to illustrate your answer.

3. Based on your results on Part D, how does concentration affect conductivity? Use your data to illustrate your answer.

4. Based on your results in Part E, determine if their compounds have reacted or not. Does the additivity rule hold for this case?

5. Based on your results in Part F, determine if their compounds have reacted or not. Does the additivity rule hold for this case?

**3**   Softening of hard water

<div align="center">

EXPERIMENT

# Softening of hard water

</div>

## Goal

The goal of this experiment is to understand the concepts of hard and soft water and their implications in daily life. The student will also experiment with the *dissociation of ionic compounds* in water, from which the **hydrogen-donor** nature of the acids and the notion of *pH* are emphasized. Other principles, such as equilibrium and ion exchange, are also presented.

## Materials

- □ 250mL and 50mL beakers
- □ cation-exchange resin
- □ 6M HCl
- □ distilled water (not tab water)
- □ Litmus paper
- □ 50mL graduated cylinder
- □ 125mL Erlenmeyer

- □ $NH_3/NH_4Cl$ buffer
- □ 0.01M $Na_2H_2$(EDTA
- □ indicator (Eriochrome black mixed with NaCl)
- □ dropper solutions (0.10 M $Ca(NO_3)_2$, 0.10 M $Na_2CO_3$, and 0.10 M $Mg(NO_3)_2$)
- □ 0.10 M$NaHCO_3$ solution
- □ solid $CaCO_3$

## Background

The term **"hard water"** refers to the concentration of certain minerals in the water. This topic concerns **aqueous solutions** in which water is the solvent and minerals are the solutes. These minerals are ionic compounds that dissociate in aqueous solutions producing ions. The hardness of water is an indication of the concentration of $Ca^{2+}$ and $Mg^{2+}$ ions.

### Dissolving the insoluble

$Ca^{2+}$ and $Mg^{2+}$ ions originate in limestone ($CaCO_3$, the material of the pyramids) and chalk ($MgCO_3$, used to write on the chalkboard) deposits. However, chalk will not dissolve in water and neither the pyramids dissolve in the rain. How is dissolving these carbonates possible?

### The answer is in the air

Water in contact with the air absorbs $CO_2$ in the atmosphere according to the equation:

$$CO_2\,(g) + H_2O\,(l) \longrightarrow H_2CO_3\,(aq)$$
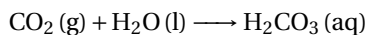
Where $H_2CO_3$ is carbonic acid, which reacts with the carbonate to form hydrogen bicarbonate. For the case of $CaCO_3$

$$CaCO_3\,(s) + H_2CO_3\,(aq) \longrightarrow Ca(HCO_3)_2\,(aq)$$
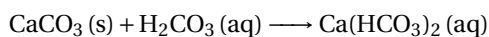
Calcium hydrogen carbonate is also called calcium bicarbonate. Bicarbonates are soluble in water (baking soda is sodium bicarbonate, $NaCO_3$) and, as ionic compounds, they are dissociated into its ions;

$$Ca(HCO_3)_2 \, (aq) \longrightarrow Ca^{2+} + 2\,HCO_3^{\,-}$$
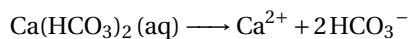
The overall reaction is the 3 previous equations added together:

$$CaCO_3 \, (s) + CO_2 \, (g) + H_2O \, (l) \longrightarrow Ca^{2+} + 2\,HCO_3^{\,-}$$
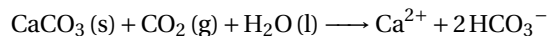
and this is how carbonates dissolve in water.

Sodium hydrogen carbonate can decompose under different conditions. On one hand, in acidic conditions, it produces carbonic acid that quickly decomposes to give carbon dioxide:

$$NaHCO_{3\,(aq)} \xrightarrow{H^+} Na^+ + CO_{2\,(g)} + H_2O_{(l)}$$
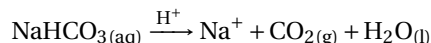
On the other side, when heated it produces: $2\,NaHCO_{3\,(aq)} \xrightarrow{\Delta} Na_2CO_3 + CO_{2\,(g)} + H_2O_{(l)}$

## Implications in daily life

The presence of these ions in water has several implications for routine actions in our lives. The problem arises when the latter reaction takes place in the opposite direction, releasing $CO_2$ gas in the process and depositing solid carbonate. This direction is favored when water is heated and explains the white residue in bathrooms and kettles. This is especially a problem for boilers, that suffer from scaling when operating hard water.

## The experiment

The experiment consists of four parts: preparing the ion exchange resin, measuring the hardness of a sample of water, reducing the hardness also called softening, of the sample, and testing the hardness of the softened sample. Additionally, a series of simple reactions will be done to test the reactivity of $Ca^{2+}$ and $Mg^{2+}$ ions.

## Measuring the hardness of the sample

The concentration of $Ca^{2+}$ ions, or any other metallic cation, is usually measured by titration of the aqueous sample using a sodium salt as the titrant, a solution of known concentration added to the sample. First, an indicator will be added to the sample which will color the solution pink. The indicator chosen is Eriochrome Black T, which will turn blue when the $Ca^{2+}$ ion is removed from the cation-indicator complex:

$$\underset{indicator\,complex\,(pink)}{Ca(In)^{2+}_{(aq)}} \longrightarrow Ca^{2+}_{(aq)} + \underset{indicator\,(blue)}{In_{(aq)}}$$
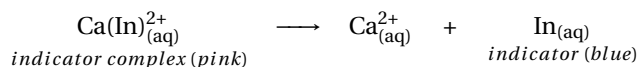
To achieve the color change $H_2EDTA^{2-}$ will be used. $H_2EDTA^{2-}$ (dihydrogen ethylenediaminetetraacetate) is an anion with a stronger affinity for the $Ca^{2+}$ cations than the indicator. As $H_2EDTA^{2-}$ is added to the solution it will replace the indicator forming a new complex, leaving the indicator alone, which in turn will become blue.

$$H_2EDTA^{2-}_{(aq)} + \underset{(pink)}{Ca(In)^{2+}_{(aq)}} \longleftrightarrow Ca(EDTA)^{2+}_{(aq)} + \underset{(blue)}{In_{(aq)}} + 2\,H^+_{(aq)}$$
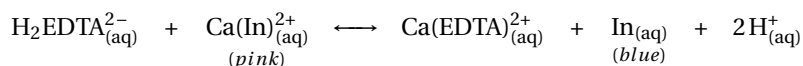
Even when the example described above refers to calcium ions, the same chemistry applies to magnesium ions. It is important to note down the exact number of drops required to achieve the endpoint of the titration.

## Softening the hard water

After measuring the hardness of the water sample, the next step is to soften the water. *Softening* is the process where ions, particularly calcium and magnesium ions, are removed from the water. When a hard water sample is softened we can refer to it as *softened water*. A cation-exchange resin will be used to soften the water. This resin contains many sulfonic groups, $(-SO_3H)$. Every two hydrogens in these acidic groups will be replaced by a metallic cation, $Ca^{2+}$ and $Mg^{2+}$, in a mechanism called *cation exchange*. Finally, it is necessary to evaluate whether the water sample has been softened. As such the titration performed in Part A will be repeated, but this time with the softened sample. The most relevant parameter is the amount of EDTA added to achieve the endpoint of the titration, to compare this result to the previous titration. This experiment aims to be a qualitative analysis of the water treatment. For that reason, and to simplify the process, the titration will be done using droppers instead of the more precise burette typically used in titrations.

# Procedure

## Part A. Preparing the resin.

☐ *Step 1:* – Obtain around 5g of the dry, ion exchange resin in a 250 mL beaker. Remember that this resin can be recycled. Do not discard it at the end of the experiment.

☐ *Step 2:* – Add enough 6 M HCl to cover the resin. By adding the acid, the resin is cleaned of metallic cations. To use the ion exchange resin, it must be clean, also known as "in $H^+$ form".

> ⚠CAUTION!
>
> ⚠  Handle concentrated acid with care to avoid chemical burns.
>
> ⚠  Are you wearing your goggles? Do you know where the eye-washer is?

☐ *Step 3:* – Now you are going to wash the acid away. After 2 minutes, add 200 mL of distilled water to the resin-acid mixture. Allow the resin to settle in the bottom of the beaker.

☐ *Step 4:* – Carefully, pour the liquid off (decant) into another beaker. This liquid is an HCl solution and should be handled and discarded as such.

☐ *Step 5:* – To ensure that all the acid is gone, wash again the resin with 200 mL of distilled water. Allow the resin to settle in the bottom of the beaker and pour the liquid into another beaker.

☐ *Step 6:* – Before you discard the liquid you can test the pH. Dip the tip of a glass stirring rod in the liquid and poke the wet end of the rod into a piece of Blue Litmus paper. If the Litmus paper turns pink, there is still acid, repeat steps 5 and 6. If it does not turn pink, the resin is clean and ready to be used. Reserve the resin for Part B.

## Part B. Measure the hardness of a sample of softened water

☐ *Step 1:* – Obtain a little bit more than 150 mL of hard water in a beaker. Hard water is already prepared in the lab.

☐ *Step 2:* – Using a graduated cylinder, add 20.0 mL of hard water to a 125 mL Erlenmeyer. Reserve this water for Part C. Use the rest of the water for this part of the experiment.

☐ *Step 3:* – Transfer the remaining hard water to the beaker with the resin and let it stand for 25 minutes. In the meantime, proceed with Parts C and D.

☐ *Step 4:* – Pour off about 40 mL of the water sample that has been in contact with the resin into a clean beaker. This sample would be referred to as the softened water.

☐ *Step 5:* – Using a graduated cylinder, add 20.0 mL of the softened water to a 125 mL Erlenmeyer.

☐ *Step 6:* – Add 5 mL of an $NH_3/NH_4Cl$ buffer solution (not to be confused with $Na_2H_2(EDTA)$) to the Erlenmeyer and the tip of a spatula (less than a pea-sized amount) of the indicator (a solid mixture of eriochrome black T and sodium chloride). Adding too many indicators will ruin the experiment. The solution color will be rose pink after the addition of the indicator.

☐ *Step 7:* – Now, we are going to titrate the water sample. Obtain about 20 mL of 0.01 M $Na_2H_2(EDTA)$ (the full name is Ethylenediaminetetraacetic acid) in a 50 mL beaker and a medicine dropper (or a plastic Pasteur pipette). Add the $Na_2H_2(EDTA)$ drop by drop to the mixture while stirring. As the endpoint is approached the solution color will become lavender. Count the drops needed for the analyte to turn blue. When the addition of one drop turns the solution blue, all $Ca_2^+$ and $Mg_2^+$ ions have been removed from the sample

☐ *Step 8:* – Clean the resin as described in Part A, and return the resin to the instructor–there is a large beaker ready to collect wet resin.

## Part C. Measure the hardness of a water sample

☐ *Step 1:* – While Part B takes place, and the water becomes softer, add 5 mL of a $NH_3/NH_4Cl$ buffer solution (not to be confused with $Na_2H_2(EDTA)$) to the Erlenmeyer, and the tip of a spatula (less than a pea-sized amount) of the indicator. Rememer that the indicator is just a solid mixture of eriochrome black T and sodium chloride. Adding too many indicators will ruin the experiment. The solution color will be rose pink after the addition of the indicator.

☐ *Step 2:* – Now, we are going to titrate the water sample. Obtain about 20 mL of 0.01 M $Na_2H_2(EDTA)$ in a 50 mL beaker and a medicine dropper (or a plastic Pasteur pipette). Add the $Na_2H_2(EDTA)$ drop by drop to the mixture while stirring. As the endpoint is approached the solution color will become lavender. Count the drops needed for the analyte to turn blue. When the addition of one drop turns the solution blue, all $Ca_2^+$ and $Mg_2^+$ ions have been removed from the sample

## Part D. Observing reactions with $Ca^{2+}$ and $Mg^{2+}$ ions

☐ *Step 1:* – Obtain 4 test tubes and locate the following solutions: 0.10 M $Ca(NO_3)_2$, 0.10 M $Na_2CO_3$, 0.10 M$NaHCO_3$, and 0.10 M $Mg(NO_3)_2$.

☐ *Step 2:* – In test tube 1, add 10 drops of **$Ca(NO_3)_2$**. Add 10 drops of $Na_2CO_3$ and write down your observations.

☐ *Step 3:* – In test tube 2, add 10 drops of **$Ca(NO_3)_2$**. Add 2 drops of HCl and write down your observations.

☐ *Step 4:* – In test tube 3, add 10 drops of **$Ca(NO_3)_2$**. Add 10 drops of 0.1 M $NaHCO_3$ and write down your observations.

☐ *Step 5:* – Now, Heat test tube 3 in the flame of a Bunsen burner. Write down your observations.

☐ *Step 6:* – Now, cool down test tube 3. Add 2 drops of 6M HCl and write down your observations.

☐ *Step 7:* – In test tube 4, add a pea-sized amount of solid $CaCO_3$. Add 2 drops of 6M HCl and write down your observations.

☐ *Step 8:* – Now, repeat the steps above using **$Mg(NO_3)_2$** instead of **$Ca(NO_3)_2$**.

☐ *Step 9:* – At this point, complete the remaining steps of Part B.

**Pre-lab Questions**

# Softening of hard water

1. A student needs 10 drops of EDTA to reach the equivalency point when titrating a sample of hard water. After the students soften the water with the resin, it requires 12 drops of EDTA to reach the equivalency. Are these results correct? Explain.

2. Find the definition of the following concepts:

    (a) Titration

    (b) Titrant

    (c) Litmus paper

    (d) Ion exchange resin

3. Where is the term **hard water** derived from?

4. Compare the sizes used in the experiment. Circle the bigger size:

    (a) Pea-size

    (b) Tip of a spatula

5. In the experiment, find the chemical name of EDTA.

**STUDENT INFO**

Name:                              Date:

**Results**
**EXPERIMENT**

# Softening of hard water

## Parts B and C: Comparing titrations

Indicate how many drops you used to achieve the endpoint for:

Hard water sample (Part C): _____         drops of $Na_2H_2$(EDTA)

Softened water sample (Part B): _____         drops of $Na_2H_2$(EDTA)

## Part D: Observing reactions with $Ca^{2+}$ and $Mg^{2+}$ ions

Write down your observations such as gas evolution, the appearance of precipitate, dissolving of precipitate, and no observation.

|  | $Ca(NO_3)_2$ | $Mg(NO_3)_2$ |
|---|---|---|
| $Na_2CO_3$ |  |  |
| HCl |  |  |
| $NaHCO_3$ |  |  |
| $NaHCO_3$+heat |  |  |
| $NaHCO_3$+heat+HCl |  |  |
| Solid $CaCO_3$+HCl |  |  |

**Post-lab Questions**

# Softening of hard water

1. Based on your measurements. Did the ion exchange resin soften the hard water sample? Explain.

2. Write the balanced equations for the chemical reactions below. Mind that calcium carbonate is an insoluble compound.
.

$$Na_2CO_{3(aq)} \quad + \quad Ca(NO_3)_{2(aq)} \quad \longrightarrow$$

$$Ca(NO_3)_{2(aq)} \quad \xrightarrow{H^+}$$

$$NaHCO_{3(aq)} \quad + \quad Ca(NO_3)_{2(aq)} \quad \longrightarrow$$

$$NaHCO_{3(aq)} \quad + \quad Ca(NO_3)_{2(aq)} \quad \xrightarrow{\Delta}$$

$$NaHCO_{3(aq)} \quad + \quad Ca(NO_3)_{2(aq)} \quad \xrightarrow{H^+}$$

$$CaCO_{3(s)} \quad \xrightarrow{H^+}$$
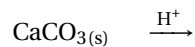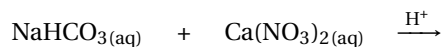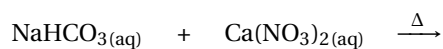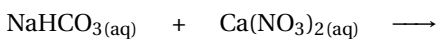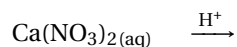
3. Write the balanced equations for the chemical reactions below. Mind that magnesium carbonate is an insoluble compound.

$$Na_2CO_{3(aq)} \quad + \quad Mg(NO_3)_{2(aq)} \quad \longrightarrow$$

$$Mg(NO_3)_{2(aq)} \quad \xrightarrow{H^+}$$

$$NaHCO_{3(aq)} \quad + \quad Mg(NO_3)_{2(aq)} \quad \longrightarrow$$

$$NaHCO_{3(aq)} \quad + \quad Mg(NO_3)_{2(aq)} \quad \xrightarrow{\Delta}$$

$$NaHCO_{3(aq)} \quad + \quad Mg(NO_3)_{2(aq)} \quad \xrightarrow{H^+}$$
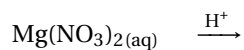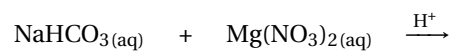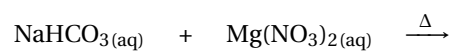
4. Using the equivalency between drops and mL (1mL=15drops), calculate the number of mL of $Na_2H_2(EDTA)$ needed for the titration of the soft and hard water samples.

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EXPERIMENT

# Freezing point depression

## Goal

The goal of this laboratory is to put into practice the theory seen for *properties of solutions* and to experimentally see the *freezing point depression* effect. The added value is to play detective by relating the nature of *colligative properties* to the molar mass, to identify the unknown powder.

## Materials

- ☐ A ring stand and two iron rings with a wire gauze
- ☐ two or three jumbo text tubes with stoppers
- ☐ A series of 50mL, 100mL, 250mL and 600mL beaker
- ☐ Cyclohexane

- ☐ 20mL pipet
- ☐ Ice
- ☐ Perforated stoppers with stirring wire and thermometer

## Background

During winter, salt is poured over the street to melt the ice on the floor. General knowledge says that the salt melts the ice, while some venture to claim that the salt lowers the freezing temperature of the water. Both assertions might be in the right direction but are, if not false, at least incorrect. When salt is mixed with water, there is no water or salt anymore. Instead, there is a *solution* of salt in water. Since the freezing point of the solution is lower than that of the pure water, the solution is no longer solid at outdoor temperatures. Notice that there is no need to state the nature of the solution or the solute because it is irrelevant. The depression of the freezing point is not a property specific to the salt, (i.e. the sodium chloride, NaCl), but rather a general effect of any solute. Salt is used because it is widely available, dissolves fast, and is inexpensive.

### Freezing point depression

The formula governing the change ($\Delta$) in the freezing point ($T_f$) is given by:

$$\Delta T_f = - K_f m$$

where $m$ is the concentration in terms of *molality* and $K_f$ is the *molal freezing-point depression constant*. $K_f$ is characteristic of the solvent being experimentally determined. Remember that molality $m$ refers to the moles of solute concerning the kilograms of solvent. $\Delta T_f$ is the difference between the freezing point of the pure solvent ($T_f^{solvent}$) and that of the solution ($T_f^{solution}$). The solvent used in this experiment will be *cyclohexane*, a very *volatile* organic solvent. Special precautions must be taken to avoid evaporation of the solvent. $K_f$ for cylohexane is 20.1 °C/m. The solute will be an unknown compound. Hence you will not know its molar mass and therefore the molarity will not be explicitly known here.

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**Example**

*The freezing point of pure benzene is 5.50 °C. A solution is prepared by dissolving 0.450 g of an unknown substance in 27.3 g of benzene. The new freezing point is determined to be 4.18 °C. What is the molar mass of the unknown substance? The freezing point constant, $K_f$, for benzene is 5.12 °C/m.*

**Answer**: calculate the concentration first:

$$\Delta T_f = K_f \times m \qquad\qquad m = \frac{\Delta T_f}{K_f} \qquad\qquad m = \frac{5.50°C - 4.18°C}{5.12°C \frac{kg}{mol}} = 0.258 \frac{mol}{kg}$$

then, calculate the molar mass:

$$0.258 \frac{mol}{kg} \times 27.3g \times \frac{1kg}{1000g} = 7.04 \times 10^{-3} mol \qquad\qquad \text{molar mass} = \frac{0.450g}{7.04 \times 10^{-3} mol} = 63.9 \frac{g}{mol}$$

## The experiment

The experiment today is divided into the following parts: finding the freezing point of the pure solvent, finding the freezing point of the solution, finding the freezing point after increasing the concentration, and solving the molar mass of the solute.

## Cooling plots

During a phase change, all the energy transferred is used to reorganize the molecules and none is used to change the temperature of the substance. A liquid at a higher temperature than its surroundings gives up the heat and its temperature falls until it reaches the freezing point. The liquid continues to give up heat to the surroundings, but its temperature remains constant. Only when all the liquid is frozen will the temperature start to fall again.

   If one plots temperature vs. time for the freezing of the pure liquid, a negative slope line will represent the cooling down, while the flat horizontal line (plateau) corresponds to the freezing process. These types of plots are called cooling plots. Notice that the transition from the cooling line to the horizontal line is not sharp. For that reason, the best way to determine the freezing point is to draw a straight line fitting most of the cooling points and another straight line fitting most of the cooling points, while finding the crossing point between two lines. You can measure the freezing point as the temperature measurement of this crossing point. For a pure solvent, the freezing point should be near the temperature corresponding to the plateau. This is the graphical method to find freezing points. In the case of a solution, this constant-temperature plateau does not exist anymore. In contrast, when a solution freezes its temperature decreases with time. However, the same graphical method can be used to obtain the freezing point of a solution. Mixing the solution well is critical to obtaining a good cooling plot. If you do not mix the solution well you will obtain a series of steps when the solution freezes that will not allow you to measure an accurate freezing point.

## Finding the freezing point of the pure solvent.

In this part of the experiment, you will obtain the cooling plot of the pure solvent, cyclohexane. Using the graphical method you will obtain the freezing point as an average between two replications. You must plot the results carefully to obtain accurate results.
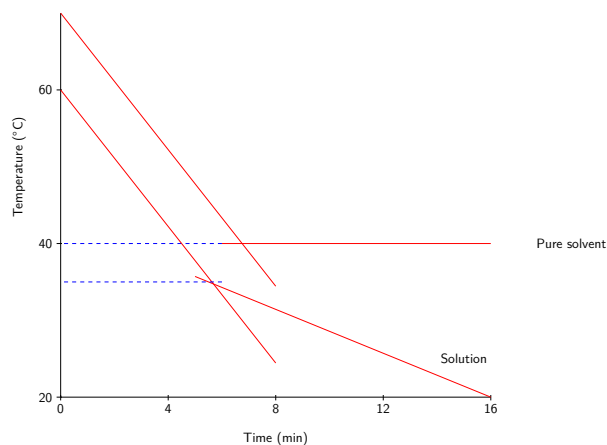


## Finding the freezing point of a solution.

In this part of the experiment, you will obtain the cooling plot of a solution made of cyclohexane and an unknown solute. Using the graphical method you will obtain the freezing point. You will work with two different concentrations and will carry

out one replication per concentration. This part aims to calculate the molar mass of the solute.

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### Example

*Use the date replorted below to graph a cooling plot, and use the graphical method to calculate the freezing point of the substance. Is this a pure substance or a solution?*

| t (min) | T (°C) | t (min) | T (°C) |
|---------|--------|---------|--------|
| 1 | 65.6 | 9 | 40 |
| 2 | 61.6 | 10 | 40 |
| 3 | 56.7 | 11 | 40 |
| 4 | 52.2 | 12 | 40 |
| 5 | 47.8 | 13 | 40 |
| 6 | 43.3 | 14 | 40 |
| 7 | 38.9 | 15 | 40 |
| 8 | 40 | 16 | 40 |

**Answer**: Based on the plot below, we have that at early times the liquid is being cooled down and its temperature decreases with time. At late times, the liquiz freezes and its temperature reaches a plateau. The graphical method to obtain freezing points consist on ploting a line for early times and another line for late times. These two lines intersect in a point, and the temperature for this point is the freezing point. As the temperature reaches a platea, we are dealing here with a pure substance.
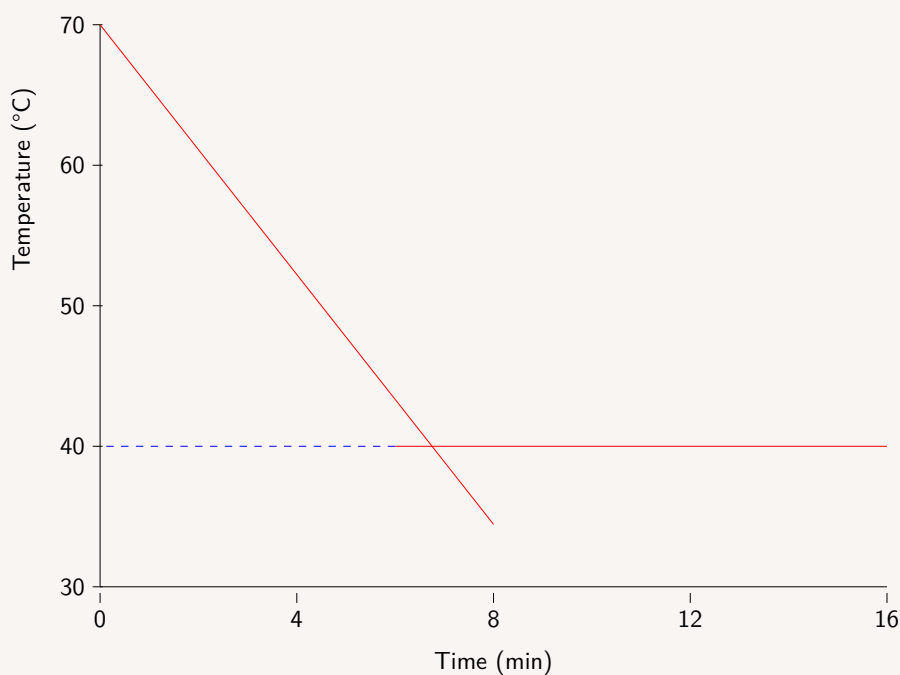
## Procedure

### Preparing the setup.

☐ *Step 1:* – Prepare the set-up to cool down the solution. Set up a ring stand and an iron ring with wire gauze on top. The height of the platform will normally be very low.

☐ *Step 2:* – Use a second, larger ring above the platform as protection. Attach a small clamp above the second iron ring.

☐ *Step 3:* – Put ice with some water in a 500 mL beaker and set it on the platform. This will be your cool bath. Water helps create a homogeneous bath.

> **Good Lab Practice**
>
> ✍ Never add the liquid or solid to be weighed to the container while on the scale. Take the container *off* the scale prior to adding the product. A spill on the scale will ruin both your measurement and the scale.

### Preparing a cyclohexane sample.

☐ *Step 1:* – Find 100mL and 50mL beakers and a 20 mL pipet.

☐ *Step 2:* – Obtain a large test tube that is clean and dry, a suitable rubber stopper, and a 100 mL beaker. The beaker will be used to hold the test tube vertically. Get the mass of the test tube with stopper and the beaker in the scale and write it down in the Results section.

☐ *Step 3:* – Pour no more than 25 mL of cyclohexane into the 50 mL beaker. Using the pipet, transfer exactly 20.0 mL of cyclohexane from the 50 mL beaker to the test tube and close it with the stopper immediately. Mind that as the liquid is volatile the measured volume will not be accurate. Using the scale get the mass of the test tube with the cyclohexane, the stopper, and the beaker. Make sure you do not weigh the thermometer or the stirring system.

☐ *Step 4:* – Get the mass of the filled-test tube with stopper and the beaker in the scale and write it down in the Results section.

### Part A. Freezing point of the pure solvent.

☐ *Step 1:* – Insert the test tube into the ice and hold it vertically using the clamp. Make sure all liquid is fully submerged in the cool bath. Find the perforated stoppers with the stirring wire and the thermometer. The round wire end must encircle the thermometer probe. Exchange the stopper on the test tube with this gadget.

☐ *Step 2:* – As soon as the temperature is 15°C (or lower) start stirring the solvent with the wire and record the temperature every 15 seconds. Use all the digits given by the thermometer down to the tenth of the degree Celsius.

☐ *Step 3:* – Start plotting the results on the graph. Plotting temperature (in °C) in the vertical axis and time in the horizontal axis.

☐ *Step 4:* – Stop the experiment when the temperature starts dropping after several minutes of having a constant temperature. Do not stop until the temperature reaches at least 7°C.

☐ *Step 5:* – Now you will repeat the measurement one more time.

☐ *Step 6:* – Lift the test tube with the clamp above the ice and allow the cyclohexane to melt. Avoid using your hands to accelerate the process. Before the cyclohexane gets to 15°C get a second measurement by repeating the step above.

Good Lab Practice

✎ Stirr, and do not shake. It is very important to stir the cyclohexane constantly and gently until it is completely frozen.

✎ Make sure the wire stays around the thermometer and that the latter is centered in the test tube.

✎ The thermometer should not touch the walls of the test tube.

✎ A bad stirring method will lead to a partial freezing and the graph will not show straight lines.

## Part B. Freezing point of the less concentrated solution.

☐ *Step 1:* – Pick up an unknown solute. You have to carry out Parts B and C at the same time.

☐ *Step 2:* – The same cyclohexane can be used in Part B. However, if you work in teams you can prepare another cyclohexane sample and carry out work in parallel.

☐ *Step 3:* – If you use the sample from part A, lift the test tube with the clamp above the ice and allow the cyclohexane to melt. Avoid using your hands to accelerate the process. During the next steps be careful to avoid the cyclohexane's temperature from getting above 15°C.

☐ *Step 4:* – If you prepare a new cyclohexane sample, see the steps above.

☐ *Step 5:* – Tare the scale with the weighing boat and obtain between 0.10 g and 0.11 g of the unknown solute. Remove the boat with the solute, tare the empty scale, and record the mass of the weighing boat together with the solute. Use the balance of maximum precision.

☐ *Step 6:* – Carefully add the solute into the test tube with the pure solvent. Make sure no solute is spilled. There is no need to add all the solute from the weighing boat, the amount added will be calculated by difference.

☐ *Step 7:* – Weight the weighing boat with the solute leftovers. Record the mass on the results page.

☐ *Step 8:* – Mix the solution well and insert the test tube in the ice while holding it vertically using the clamp.

☐ *Step 9:* – Start stirring the solution with the wire and record the temperature every 15 seconds. This time the temperature should not reach constant. Stop the experiment when the temperature reaches 1°C.

## Part C. Freezing point of the more concentrated solution.

☐ *Step 1:* – Lift the test tube with the clamp above the ice and allow the cyclohexane to melt. Avoid using your hands to accelerate the process. During the next steps be careful to avoid the cyclohexane getting above 15°C.

☐ *Step 2:* – The same boat can be reused without cleaning. Tare the scale with the boat inside. Obtain between 0.24 g and 0.25 g of the unknown solute and record the mass of the weighing boat together with the solute using maximum precision.

☐ *Step 3:* – Add carefully the solute into the test tube with a fresh new 20mL sample of the pure solvent. Make sure no solute is spilled. There is no need to add all the solute from the weighing boat, the amount added will be calculated by difference.

☐ *Step 4:* – Weight the weighing boat with the solute leftovers. Record the mass on the results page.

☐ *Step 5:* – Mix the solution well and insert the test tube in the ice while holding it vertically using the clamp.

☐ *Step 6:* – Start stirring the solution with the wire and record the temperature every 15 seconds. This time the temperature should not reach a constant. Stop the experiment when the temperature reaches 0.5°C.

## Calculations

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( 1 ) This is the mass of the empty test tube with a cork and placed in a beaker.

( 2 ) This is the mass of the test tube filled with cyclohexane, with a cork, and placed in a beaker.

( 3 ) This is the mass of solvent, $m_{liquid}$:

$$m_{solvent} = \boxed{2} - \boxed{1}$$

( 4 ) This is the volume of cyclohexane added, where $d$ is the density of cyclohexane:

$$v_{solvent} = \frac{m_{liquid}}{d} = \frac{\boxed{3}}{0.779}$$

( 5 ) These are two replicates for the freezing point of the solvent obtained through the graphical method.

( 6 ) This is the freezing point of the solvent.

( 7 ) This is the mass of the weighing boat with solute before adding the solute to the solvent.

( 8 ) This is the mass of the weighing boat with solute after adding the solute to the solvent.

( 9 ) This is the mass of solute:

$$m_{solute} = \boxed{7} - \boxed{8}$$

( 10 ) These are the freezing points of two solutions.

( 11 ) These are the values of the freezing points depression:

$$\Delta T_f = \boxed{10} - \boxed{6}$$

( 12 ) These is the molar mass of the solute:

$$\text{MW} = -\frac{K_f \cdot m_{solute}}{\Delta T_f \cdot m_{solvent}} \times 1000 = -\frac{20.1 \cdot \boxed{9}}{\boxed{11} \cdot \boxed{3}} \times 1000$$

**Pre-lab Questions**

# Freezing point depression

1. What does volatile mean?

2. What are the colligative properties?

3. What is molality? What are the units?

4. Why is molality used in this experiment instead of Molarity?

5. Use the date reported below to graph a cooling plot and use the graphical method to calculate the freezing point of the substance. Is this a pure substance or a solution?

| t (min) | T (°C) | t (min) | T (°C) |
|---------|--------|---------|--------|
| 1       | 55.6   | 9       | 30     |
| 2       | 51.1   | 10      | 28.6   |
| 3       | 46.7   | 11      | 27.1   |
| 4       | 42.2   | 12      | 25.7   |
| 5       | 37.8   | 13      | 24.3   |
| 6       | 33.3   | 14      | 22.86  |
| 7       | 28.9   | 15      | 21.6   |
| 8       | 31.4   | 16      | 20     |

(the question continues on the back)
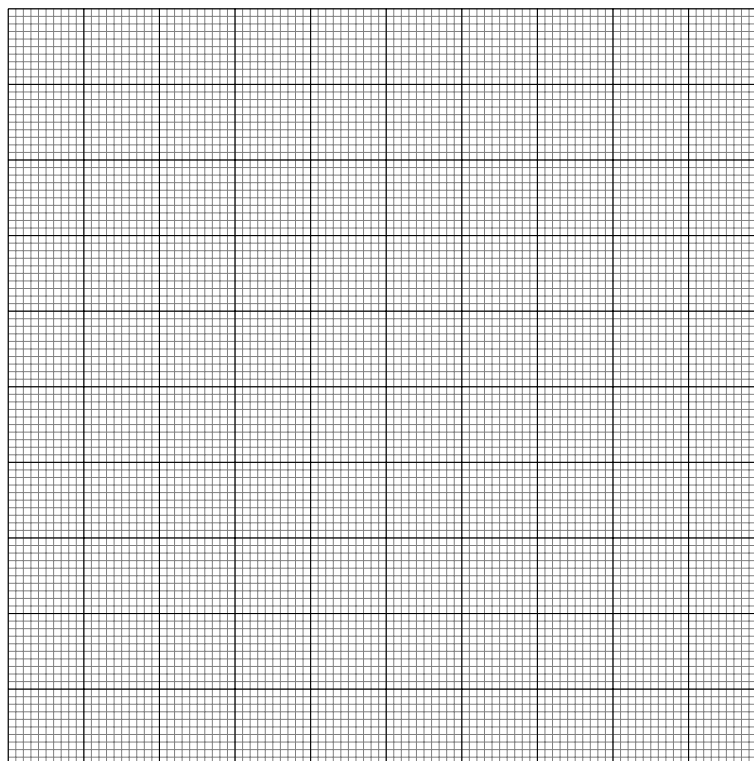
6. What is the freezing point you calculated in the previous question?

Results
EXPERIMENT

# Freezing point depression

**Parts A. Freezing point of the pure solvent.**

①     Mass of the empty test tube with cork and beaker:    _____ g

②     Mass of the filled test tube with cork and beaker:    _____ g

③     Mass of the cyclohexane:    _____ g

④     Volume of the cyclohexane used:    _____ mL

| Trial 1 | | | | Trial 2 | | | |
|---|---|---|---|---|---|---|---|
| Time (sec) | Temp. (°C) | Time (sec) | Temp. (°C) | Time (sec) | Temp. (°C) | Time (sec) | Temp. (°C) |
| \_\_\_\_ | \_\_\_\_ | \_\_\_\_ | \_\_\_\_ | \_\_\_\_ | \_\_\_\_ | \_\_\_\_ | \_\_\_\_ |
| \_\_\_\_ | \_\_\_\_ | \_\_\_\_ | \_\_\_\_ | \_\_\_\_ | \_\_\_\_ | \_\_\_\_ | \_\_\_\_ |
| \_\_\_\_ | \_\_\_\_ | \_\_\_\_ | \_\_\_\_ | \_\_\_\_ | \_\_\_\_ | \_\_\_\_ | \_\_\_\_ |
| \_\_\_\_ | \_\_\_\_ | \_\_\_\_ | \_\_\_\_ | \_\_\_\_ | \_\_\_\_ | \_\_\_\_ | \_\_\_\_ |
| \_\_\_\_ | \_\_\_\_ | \_\_\_\_ | \_\_\_\_ | \_\_\_\_ | \_\_\_\_ | \_\_\_\_ | \_\_\_\_ |
| \_\_\_\_ | \_\_\_\_ | \_\_\_\_ | \_\_\_\_ | \_\_\_\_ | \_\_\_\_ | \_\_\_\_ | \_\_\_\_ |

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(5) Freezing point of the pure cyclohexane.   Trial 1: _____ °C      Trial 2: _____ °C

(6)  Mean: _____ °C

## Parts B and C. Freezing point of solutions.

(1)    Mass of the empty test tube with cork and beaker:    ————— g

(2)    Mass of the filled test tube with cork and beaker:    ————— g

(3)    Mass of the cyclohexane:    ————— g

| Low concentration | High concentration |
|---|---|

Unkown #:   —————

(7)   Mass of boat:   ————— g         Mass of boat:   ————— g

(8)   Mass of boat (after adding):   ————— g     Mass of boat (after adding):   ————— g

(9)   Mass of solute:   ————— g         Mass of solute:   ————— g

| Time (sec) | Temp. (°C) | Time (sec) | Temp. (°C) | Time (sec) | Temp. (°C) | Time (sec) | Temp. (°C) |
|---|---|---|---|---|---|---|---|
| ————— | ————— | ————— | ————— | ————— | ————— | ————— | ————— |
| ————— | ————— | ————— | ————— | ————— | ————— | ————— | ————— |
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| Low concentration | | High concentration | |
| --- | --- | --- | --- |
| (10) | Freezing point: _____ °C | Freezing point: _____ °C |
| (11) | $\Delta T_f$: _____ °C | $\Delta T_f$: _____ °C |
| (12) | Molar mass: _____ g/mol | Molar mass: _____ g/mol |

Mean molar mass: _____ g/mol
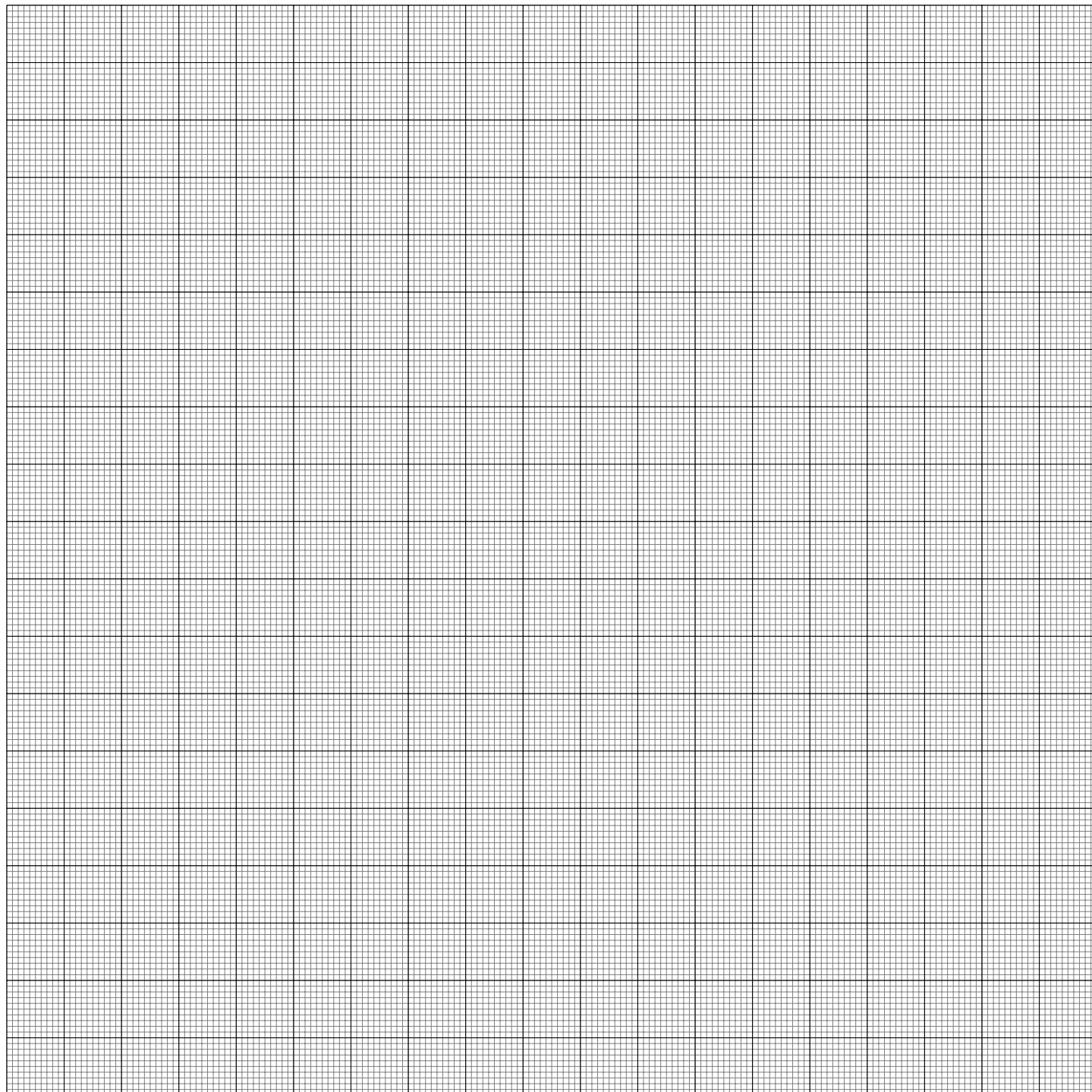
Figure 1: Temperature (Y axis) vs. time (X axis)
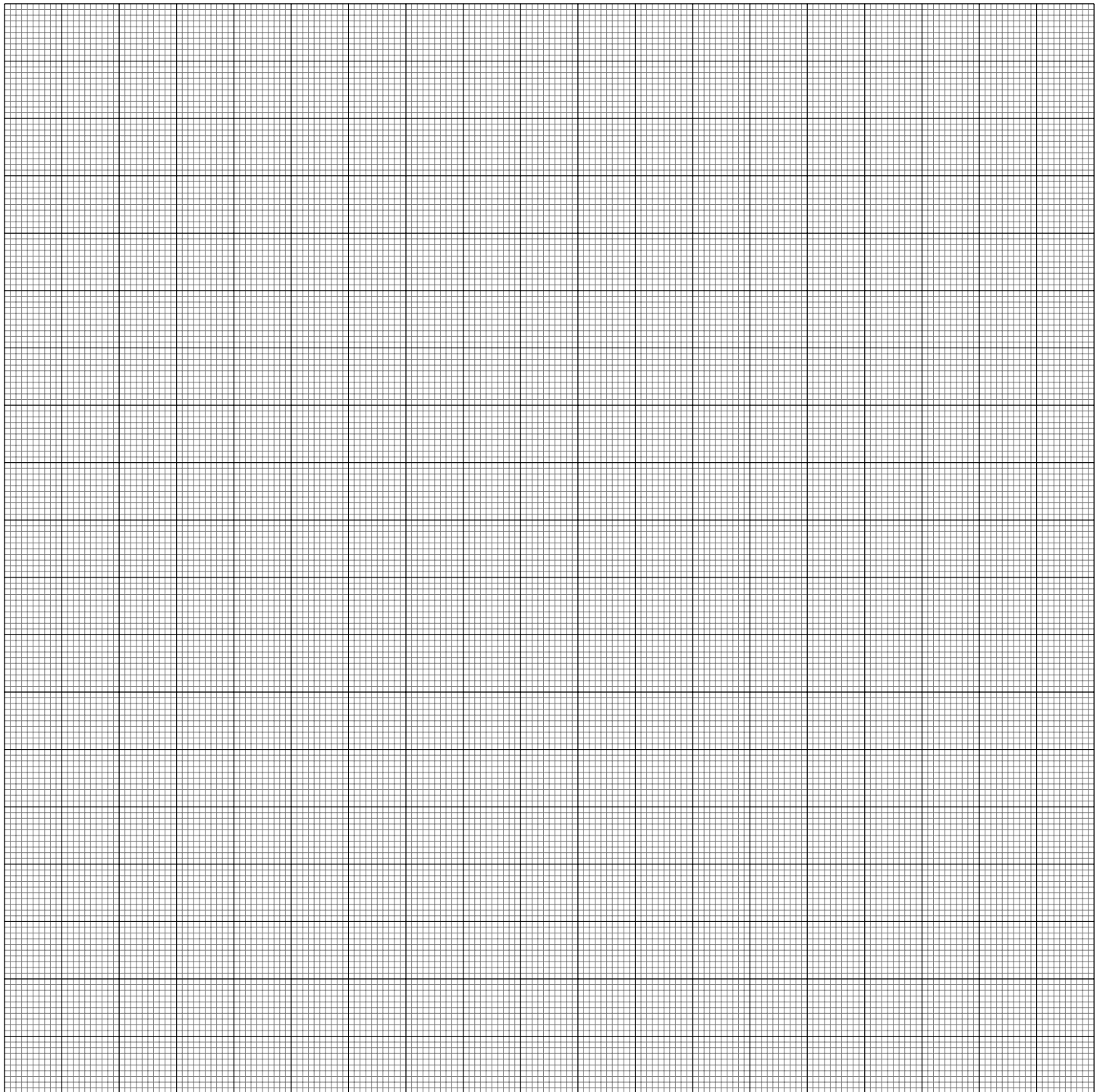
Figure 2: Temperature (Y axis) vs. time (X axis)
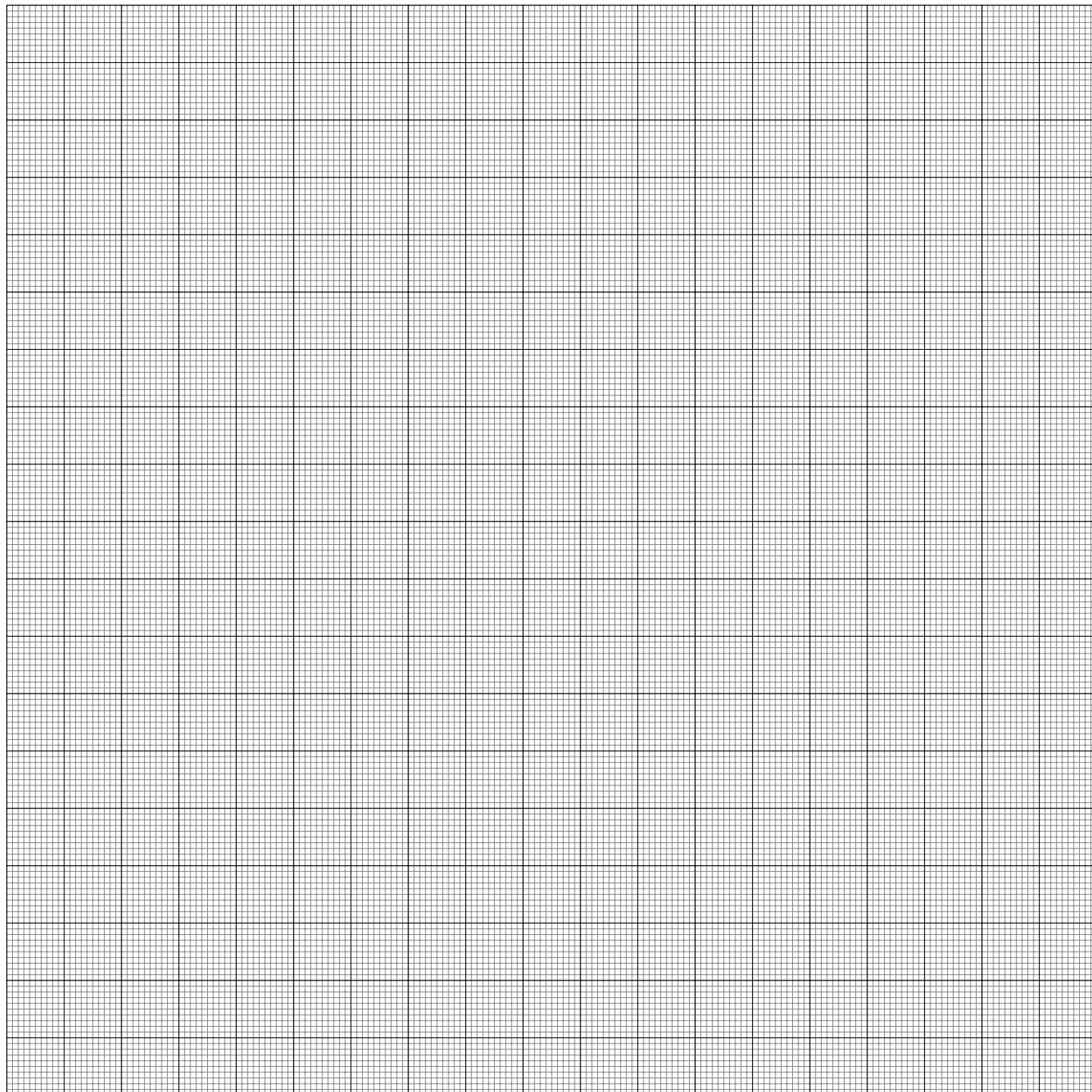
Figure 3: Temperature (Y axis) vs. time (X axis)
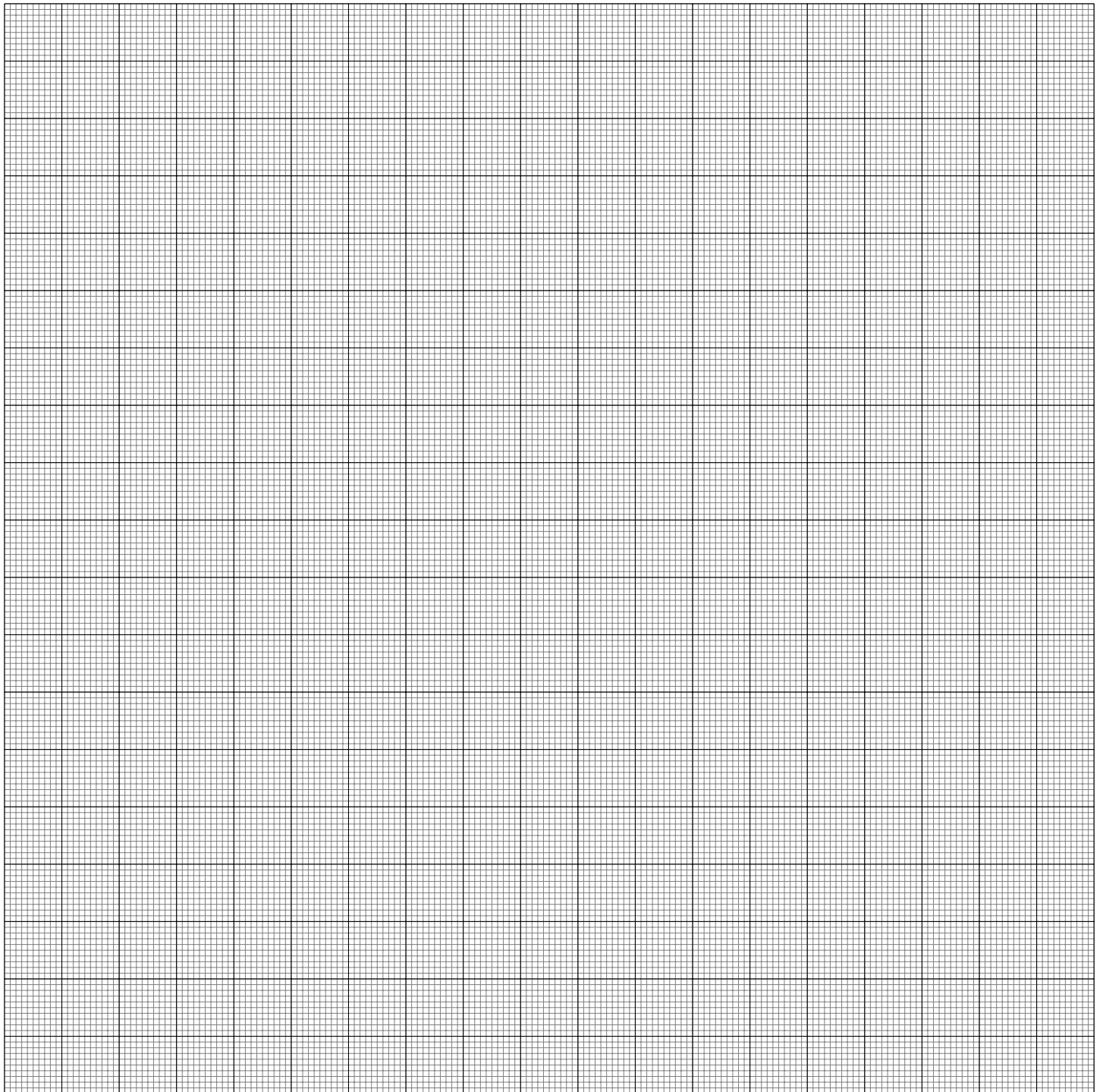
Figure 4: Temperature (Y axis) vs. time (X axis)

**Post-lab Questions**

# Freezing point depression

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1. If the empirical formula of the solute used in this experiment is $C_3H_2Cl$, what is the molecular formula?

2. What would be the effect on the molar mass in the following situations? Explain why.

   (a) A decrease in the mass measured for the solute.

   (b) An increase in the mass measured for the solute.

   (c) Dirt (soluble) from the stopper was added to the solution.

   (d) A loss of cyclohexane.

3. How much would the molar mass change if 1.000 g of the cyclohexane evaporates during part B? What would be the induced error?

EXPERIMENT

# The iodine clock

## Goal

The goal of this laboratory is to use the **method of initial rates** to calculate the rate of a chemical reaction. On top of that, the student will also visualize experimentally the effect of **temperature** and of a **catalyst** on the rate of a chemical reaction.

## Background

The rate law expresses the progress of a chemical reaction in function of the concentration of the reactant

$$\text{Rate} = k[\text{A}]^a[\text{B}]^b,$$

where $k$ is the proportionality constant called the **rate constant**, [A] and [B] are the respective concentrations for reactants A and B, and the exponents are the **orders of the reactants**, a way to establish their corresponding relevance in the reaction rate.

### Initial rates method

The initial rates method is used to measure the rate for a chemical reaction and to find out the rate constant $k$ and the order of the reactions. This method is based on the assumption that at the beginning of a chemical reaction, there is no reverse reaction, i.e. forming reactants from the products, can take place, and therefore the rate is solely affected by the reactants concentrations. The time for the reactant concentrations to change by the same amount is measured. Several experiments are carried out using all the same starting concentrations but for one reactant. The beauty of this experiment is the method used to make the reactant's concentration change by the same amount for all the experiments. This is probably the most often misunderstood part of this laboratory and it is key to understand it thoroughly.

### The Iodine Clock

A watch system is a method used in the Navy to schedule regular periods aboard. A ship's bell is used to indicate the end of each period, allowing the crew to know when it is time to switch their task, take breaks, or have lunch.

A **chemical clock** is a chemical reaction with a sudden change in one of its properties, the tempo of which can be adjusted by adjusting the concentrations. The **iodine clock** is a chemical clock marked by a sudden, almost magical, color change. For the present experiment, the iodine clock will be connected to the reaction being studied and will indicate the moment our reaction reaches the change in concentration desired. It is very important to understand the mechanism of the two competing reactions involved in this experiment to fully understand this activity.

The reaction setting the time is:

$$\text{I}_2(aq) + 2\,\text{S}_2\text{O}_3{}^{2-}(aq) \longrightarrow \text{S}_4\text{O}_6{}^{2-}(aq) + 2\,\text{I}^-(aq)$$
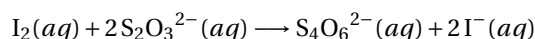
This reaction consumes iodine, $\text{I}_2$. Iodine reacts with starch turning the solution dark. The starch will be used in this experiment in a way similar to the indicator used in titration.

$$\underset{\text{black-dark blue}}{\overset{\text{starch with iodine}}{\textbf{starch} + \textbf{I}_2(aq)}} + 2\,\text{S}_2\text{O}_3{}^{2-}(aq) \longrightarrow \text{S}_4\text{O}_6{}^{2-}(aq) + 2\,\text{I}^-(aq) + \underset{\text{transparent}}{\overset{\text{starch , no I}_2}{\text{starch}}}$$
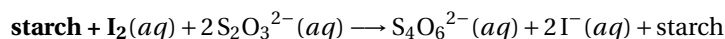
The iodine clock reaction will be running in parallel with another reaction that produces iodine. In the presence of starch, iodine becomes dark blue, almost black. Therefore, as long as there is thiosulfate ($S_2O_3^{2-}$) in the beaker the iodine will react with the latter and keep the solution transparent. We could say that the timer is adjusted by the concentration of thiosulfate ($S_2O_3^{2-}$).

## The reaction to be studied

In this experiment, the student will determine the reaction rate of the reduction of potassium persulfate ($K_2S_2O_8$) with sodium iodide (NaI).

$$K_2S_2O_8(aq) + 2\,NaI(aq) \longrightarrow 2\,Na_2SO_4(aq) + I_2(aq)$$
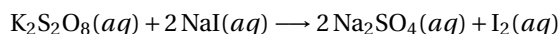
As ionic compounds dissociate in aqueous solutions it is more accurate to write the **net ionic equation**. These are the ionic net equations for the two reactions, the reduction of potassium persulfate with sodium iodide and the iodine clock:

$$S_2O_8^{2-}(aq) + 2\,I^-(aq) \longrightarrow 2\,SO_4^{2-}(aq) + \textbf{I}_2\textbf{(aq)} \qquad \leftarrow \textit{rate to be measured}$$
$$\Downarrow$$
$$\textit{iodine clock} \rightarrow \qquad \textbf{I}_2\textbf{(aq)} + 2\,S_2O_3^{2-}(aq) \longrightarrow S_4O_6^{2-}(aq) + 2\,I^-(aq)$$
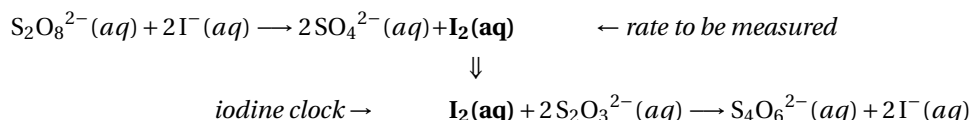
To summarize: The first reaction will be running producing $I_2$, which would turn dark blue in the presence of starch. However, the second reaction will avoid the color change by reducing the iodine into iodide. The solution will remain transparent as long as there is thiosulfate ($S_2O_3^{2-}$) available. Once the thiosulfate is finished, iodine will finally remain in the solution turning it dark blue. Since the amount of thiosulfate will be constant for all the experiments to be performed, the amount of iodine produced in the first reaction, and therefore the reactant's concentration change, will be the same each time the solution turns dark. The iodine clock is being used to schedule a constant change in the reactant's concentrations.

# The experiment

The experiment today is divided into the following parts: obtaining the reaction rate constant, evaluating the influence of the temperature on the reaction rate, and evaluating the influence of a catalyst on the reaction rate.

## Part A. Obtaining the reaction rate constant.

The reaction to be studied and its rate law are:

$$K_2S_2O_8{}_{(aq)} + 2\,NaI_{(aq)} \longrightarrow 2\,Na_2SO_4{}_{(aq)} + I_2{}_{(s)} \qquad\qquad r = k\,[S_2O_8^{2-}]^a\,[I^-]^b$$

Using the **initial rates method** the reactants orders, $a$ and $b$, can be solved. Find the suitable combinations of experiments where only one initial concentration of $S_2O_8^{2-}$ or $I^-$ changes and compare the rates using a fraction. The initial concentrations must be recalculated using the volumes and their original concentrations. Once the reactant orders are known and the initial concentrations of $S_2O_8^{2-}$ and $I^-$ for each reaction have been recalculated, the reaction constant, $k$, can be solved. See the example for more details:

| | Volume | | | | | ⏱ |
|---|---|---|---|---|---|---|
| | NaI | NaCl | $Na_2S_2O_3$ | Starch | $K_2SO_4$ | $K_2S_2O_8$ |
| | 0.2M | 0.2M | 0.01M | 2% | 0.2M | 0.2M |
| Exp. 1 | 2.0 | 2.0 | 2.0 | 1.0 | 2.0 | 2.0 |
| Exp. 2 | 2.0 | 2.0 | 2.0 | 1.0 | 0 | 4.0 |
| Exp. 3 | 4.0 | 0 | 2.0 | 1.0 | 2.0 | 2.0 |

## Example

*The reaction starts from a solution containing A (1 M) and B (0.5) M and D (1 M). There are two reactions occurring in the solution. A slow reaction were C is produced and a fast reaction where C is reduced to E ions by D:*

$$A + B \longrightarrow 2\,C$$
$$C + D \longrightarrow E$$
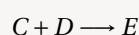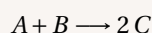
*An indicator is added, such that the solution will turn dark in the presence of substance C.*
*Three experiments are performed using different initial volumes and the following times for the solution to turn dark are measured;*

| | Volumes (mL) | | | | time |
|---|---|---|---|---|---|
| | *A* | *B* | *D* | *Water* | *(s)* |
| *Exp. 1* | *4.0* | *2.0* | *2.0* | *2.0* | *20* |
| *Exp. 2* | *4.0* | *1.0* | *2.0* | *2.0* | *40* |
| *Exp. 3* | *2.0* | *1.0* | *2.0* | *4.0* | *160* |

*Calculate the reactant orders and the reaction rate constant.*

**Answer**: First write the reaction rate expression: Rate = $k[A]^a[B]^b$
Recalculate the concentrations for each reactant. Use the formula for dilutions $M_1V_1 = M_2V_2$, where $V_2$ is the total volume $V_A + V_B + V_D + V_{water}$.
For example, to calculate the concentration of A in Experiment 1:

$$M_1V_1 = M_2V_2 \qquad M_2 = \frac{M_1V_1}{V_2} \qquad M_2 = \frac{1M4mL}{10mL} = 0.4M$$

| | [A] | [B] | [D] | rate (Ms$^{-1}$) |
|---|---|---|---|---|
| Exp. 1 | 0.4 M | 0.2 M | 0.2 M | $5 \cdot 10^{-3}$ |
| Exp. 2 | 0.4 M | 0.1 M | 0.2 M | $2.5 \cdot 10^{-3}$ |
| Exp. 3 | 0.2 M | 0.1 M | 0.2 M | $6.25 \cdot 10^{-4}$ |

The reaction rate is the change in concentration per unit time. The change in concentration is determined by the second reaction (the clock). For the first experiment it takes 20 seconds to turn black. In those 20 seconds all of D has reacted, i.e. 0.2 M in 20 seconds.
Following the stoichiometry of the reaction, if 1 mole of D reacts with 1 mole of C and every 2 moles of C are produced when 1 mole of A reacts. The relation between D and A is 2:1.

$$1 \text{ mole of A} = 1 \text{ mole A} \frac{2 \text{ moles C}}{1 \text{ moles A}} \frac{1 \text{ mole D}}{1 \text{ mole C}} = 2 \text{ moles of D}$$

Therefore, 0.2 M of D corresponds to 0.1 M of A reacting in 20 s. The rate for experiment 1 is $5 \cdot 10^{-3}$ M/s.

The order of the reactants are calculated by comparing the rate laws. Each time, choose two experiments were only one parameter is different.

$$\frac{\text{Rate } 2}{\text{Rate } 3} = \frac{k \, [A]^a [B]^b}{k [A]^a [B]^b} = \frac{k \, 0.4^a 0.1^b}{k \, 0.2^a 0.1^b} = \frac{2.5 \cdot 10^{-3}}{6.25 \cdot 10^{-4}}$$

$$2^a = 4 \qquad a = 2$$

Similarly, using rate 2 over rate 1, b=1 is obtained.

The reactant order can be used to obtain the reaction rate.

$$Rate = k[A]^a[B]^b \qquad k = \frac{Rate}{[A]^a[B]^b} = \frac{5 \cdot 10^{-3} M s^{-1}}{(0.4M)^2 (0.1M)^1} = 0.15625 M^{-2} s^{-1}$$

Since experimentally it is more likely to obtain one slightly different $k$ for each experiment, an average should be calculated.

## Parts B. Evaluating the influence of the temperature on the reaction rate.

According to **Arrhenius equation**, the rate constant is affected by the temperature following the equation:

$$k = Ae^{-E_a/RT}$$

where $A$ is a constant, $E_a$ is the activation energy, $R$ is the universal gas constant, and $T$ is the temperature. A higher temperature would make the negative exponent smaller, and therefore the $k$ would be greater. In other words, an increase in the temperature should accelerate the reaction. It is possible to calculate the activation energy by measuring the reaction rates at two different temperatures. After calculating the respective rate constants these are compared in their logarithmic forms:

$$\ln(k) = -\frac{E_a}{RT} + \ln(A)$$

After subtracting the expression above for both temperatures, $T_1$ and $T_2$, the following equation is generated:

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

The values of $k_1$ and $k_2$ obtained respectively at $T_1$ and $T_2$ are used to calculate $E_a$. The temperatures should be given in Kelvins since $R = 8.3145$ J/K mol.

## Part C. Evaluating the influence of a catalyst on the reaction rate.

A catalyst is a substance that without being consumed, accelerates the reaction. The catalyst generates a new reaction path with a lower activation energy. Looking at the Arrhenius equation, the effect of lowering the activation energy works in the same way as an increase in temperature. The catalyst used in this experiment will be copper sulfate ($CuSO_4$). The Cu(II) cations are responsible for the catalytic effect.

# Procedure

## Part A. Obtaining the rate law. Preparing the mixtures

☐ *Step 1:* – Obtain three large test tubes with their corresponding stoppers, a suitable grid or rack, a Mohr pipet, and a thermometer.

☐ *Step 2:* – Label the test tubes with numbers 1, 2 and 3.

☐ *Step 3:* – Read the Good Lab Practice box

> ### Good Lab Practice
>
> ✍ Pipettes are always used together with a suction bulb or a syringe. **Never** such a chemical using the mouth!
>
> ✍ **Never** leave a pipette laying on the table **while connected to the syringe**. Remaining liquid can leak into the syringe. The syringe will be damage and the liquid will return contaminated to the pipette.
>
> ✍ Always wash pipettes with distilled water and rinse them using the same product to be measured. Such a small volume, disconnect the syringe and move the liquid about displacing the distilled water. Discard the rinsing liquid as waste. Rinse twice.

☐ *Step 4:* – Obtain about 25 mL **0.20 M NaI** in a small beaker.

☐ *Step 5:* – Clean and rinse the pipette with NaI. Pipette 2.0 mL in test tube 1, 2.0 mL in test tube 2 and 4.0 mL in test tube 3. Refer to the table below (Table of quantities) for the reagent quantities to add.

☐ *Step 6:* – Obtain no more than 20 mL **0.20 M NaCl** in a small beaker.

☐ *Step 7:* – Clean and rinse the pipette with NaCl. Pipette 2.0 mL in test tube 1 and 2.0 mL in test tube 2. Nothing in test tube 3. Refer to the table below (Table of quantities) for the reagent quantities to add.

☐ *Step 8:* – Obtain no more than 20 mL **0.010 M Na$_2$S$_2$O$_3$** in a small beaker.

☐ *Step 9:* – Clean and rinse the pipette with Na$_2$S$_2$O$_3$. Pipette 2.0 mL in each test tube. Refer to the table below (Table of quantities) for the reagent quantities to add.

☐ *Step 10:* – Obtain aproximately 10 mL **2% starch solution** in a small beaker.

☐ *Step 11:* – Clean and rinse the pipette with starch. Pipette 1.0 mL in each test tube. Refer to the table below (Table of quantities) for the reagent quantities to add.

☐ *Step 12:* – Obtain no more than 20 mL **0.20 M K$_2$SO$_4$** in a small beaker.

☐ *Step 13:* – Clean and rinse the pipette with K$_2$SO$_4$. Pipette 2.0 mL in test tube 1, nothing in test tube 2 and 2.0 mL in test tube 3. Refer to the table below (Table of quantities) for the reagent quantities to add.

☐ *Step 14:* – Check that the volumes in the 3 test tubes make sense with the following table. Test tubes 1 and 3 should have the same volume. Test tube 2 should have slightly less volume.

☐ *Step 15:* – Using the thermometer, record the room temperature in Kelvins.

| Table of quantities | | | | | | |
|---|---|---|---|---|---|---|
| | Volume (mL) | | | | | ⏱ |
| | NaI 0.2M | NaCl 0.2M | Na$_2$S$_2$O$_3$ 0.01M | Starch 2% | K$_2$SO$_4$ 0.2M | K$_2$S$_2$O$_8$ 0.2M |
| Exp. 1 | 2.0 | 2.0 | 2.0 | 1.0 | 2.0 | 2.0 |
| Exp. 2 | 2.0 | 2.0 | 2.0 | 1.0 | 0 | 4.0 |
| Exp. 3 | 4.0 | 0 | 2.0 | 1.0 | 2.0 | 2.0 |

## Part A. Obtaining the rate law. Mixing the test tubes

☐ *Step 1:* – Now you are about to start up the reaction. It is critical to follow the steps below.

☐ *Step 2:* – Every reaction should be done in **the same way** to be comparable. The same steps, in the same order and at the same pace should be followed.

☐ *Step 3:* – You will be adding $K_2S_2O_8$. After adding the $K_2S_2O_8$, the test tube should be closed with the stopper, and the content should be mixed by inverting the test tube 16 times. Do not rush, turn the test tube *Mississippily.* Do the same for the following reactions.

> ⚠ CAUTION!
>
> ⚠ The stopper should always be placed before inverting the test tube.
>
> ⚠ Failure to place the stopper will cause the spill of the reaction.
>
> ⚠ There is a story behind every Caution Box.

## Part A. Obtaining the rate law. Starting the reaction

☐ *Step 1:* – Obtain about 25 mL **0.20 M $K_2S_2O_8$** in a small beaker. Make sure you do not contaminate the bottle of reagent by always retrying out of the bottle into a beaker and never pipetting directly from the bottle. Clean and rinse the pipette with $K_2S_2O_8$.

☐ *Step 2:* – Get test tube 1 and a stopper. Set the time to zero.

☐ *Step 3:* – Start the stopwatch as you pipette 2.0 mL of $K_2S_2O_8$ in test tube 1. Time should start to be measured as soon as you add the first drop of $K_2S_2O_8$ in a test tube. Mix the reaction as explained above.

☐ *Step 4:* – Stop the stopwatch when the solution turns dark. The color will appear suddenly. If more than 5 minutes elapse without the solution turning dark, start doubting about what have you mixed.

☐ *Step 5:* – Repeat the previous steps now for test tube 2 and pipetting this time 4.0 mL of $K_2S_2O_8$ into the test tube. .

☐ *Step 6:* – Repeat one more time the previous steps now for test tube 3 and pipetting this time 2.0 mL of $K_2S_2O_8$ into the test tube.

☐ *Step 7:* – Now you need to repeat all steps above (mixture preparation and reaction) to do a second trial for the three test tubes.

☐ *Step 8:* – Discard the solutions in the indicated waste container and clean the test tubes.

## Part B. Evaluating the influence of the temperature on the reaction rate.

☐ *Step 1:* – Label three large test tubes with the letters "**T**", "**C**"' and "**K**"'. "T" stands for "Temperature", "C" for "Catalyst" and "K" for "$K_2S_2O_8$".

☐ *Step 2:* – Add to test tubes "T" and "C" the same volumes of NaI, NaCl, $Na_2S_2O_3$, Starch and $K_2SO_4$ as for test tube 1. Do not add the $K_2S_2O_8$ yet. Reserve test tube "C" in the rack for Part C.

☐ *Step 3:* – Add about 5 mL of $K_2S_2O_8$ to test tube "K".

☐ *Step 4:* – Obtain a 600 mL beaker and, with the help of the thermometer, add hot and cold water until you have about 400 mL of water between 40 and 45 degrees Celsius.

☐ *Step 5:* – Place the test tubes "T" and "K" in the hot water bath and allow them to temper for at least 5 minutes. Part C can be done during those 5 minutes. .

☐ *Step 6:* – Measure the temperature of the water after the tempering time. Write down this temperature in the results table. Start the reaction by pipetting 2 mL of $K_2S_2O_8$ from test tube "K" into test tube "T". After the 16-Mississippi mixing, return the test tube to the bath and wait to record the time it takes for the solution to turn dark.

## Part C. Evaluating the influence of a catalyst on the reaction rate.

☐ *Step 1:* – Add **one drop** of **0.2 M CuSO$_4$** to test tube "C". Shake the test tube to mix the solution.

☐ *Step 2:* – Start the stopwatch as you pipette 2.0 mL of $K_2S_2O_8$ in the test tube. Mix the reaction as explained above.

☐ *Step 3:* – Record the time it takes for the solution to turn dark.

# Calculations

(0) This is lab temperature. You will use this value for Part B as well.

(1) This is the volume of iodine added in each experiment.

(2) This is the volume of thiosulfate added in each experiment.

(3) This is the volume of peroxydisulfate added in each experiment.

(4) This is the total volume $v_{total}$ of the reacting mixture.

(5) This is the peroxy disulfate concentration in the mixture:

$$[S_2O_8{}^{-2}] = \frac{v_{S_2O_8{}^{-2}} \cdot c_{S_2O_8{}^{-2}}}{v_{total}} = \frac{(3) \cdot 0.2}{(4)}$$

(6) This is the iodine concentration in the mixture:

$$[I^-] = \frac{v_{I^-} \cdot c_{I^-}}{v_{total}} = \frac{(1) \cdot 0.2}{(4)}$$

(7) This is the change in thiosulfate concentration during the reaction:

$$\Delta[S_2O_3{}^{-2}] = \frac{v_{S_2O_3{}^{-2}} \cdot c_{S_2O_3{}^{-2}}}{v_{total}} = \frac{(2) \cdot 0.01}{(4)}$$

(8) This is the average time $\Delta t$ for each experiment.

(9) This is the reaction rate:

$$r = \frac{\Delta[S_2O_3{}^{-2}]}{2 \cdot \Delta t} = \frac{(7)}{2 \cdot (8)}$$

(10) This is the peroxy disulfate order in the rate law:

$$a = \frac{\ln\left(\frac{r_{Exp1}}{r_{Exp2}}\right)}{\ln\left(\frac{[S_2O_8^{-2}]_{Exp1}}{[S_2O_8^{-2}]_{Exp2}}\right)} = \frac{\ln\left(\textcircled{9}_{Exp1} \div \textcircled{9}_{Exp2}\right)}{\ln\left(\textcircled{5}_{Exp1} \div \textcircled{5}_{Exp2}\right)}$$

⑪ This is the iodide order in the rate law:

$$b = \frac{\ln\left(\frac{r_{Exp1}}{r_{Exp3}}\right)}{\ln\left(\frac{[I^-]_{Exp1}}{[I^-]_{Exp3}}\right)} = \frac{\ln\left(\textcircled{9}_{Exp1} \div \textcircled{9}_{Exp3}\right)}{\ln\left(\textcircled{6}_{Exp1} \div \textcircled{6}_{Exp3}\right)}$$

⑫ The are the rate constant calculated for each experiment:

$$k = \frac{r}{[S_2O_8^{-2}] \cdot [I^-]} = \frac{\textcircled{9}}{\textcircled{5} \cdot \textcircled{6}}$$

⑬ This is the average rate constant.

⑭ The data on this row should be the same as in the first row in the Results table of Part B.

⑮ This is the activation energy. You need to use the two different reaction constants at different temperatures. R is 3.184 J/K·mol:

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

**Pre-lab Questions**

# The iodine clock

1. What is the difference between a test tube and a jumbo test tube?.

2. For the reaction $2A + 3B \rightarrow C$ what is the mathematical expression that relates the rate of A ($r_a$) and the rate of B ($r_b$)?

3. Explain the Iodine clock reaction used in this experiment.

4. What is starch and where can you find it in nature?

5. Low-quality boiled ham often contains potatoes to make it cheaper. How could you test if one piece of ham is pure meat or it contains potatoes?

6. Find out the difference between a **Mohr pipette** and a **transfer pipette**.

Name: _____ Date: _____

**Results**
**EXPERIMENT**

# The iodine clock

(0) Laboratory Temperature _____ K

| Trial | Exp. | $c_{NaI}$ (1) | $c_{NaCl}$ | $c_{Na_2S_2O_3}$ (2) | $c_{Starch}$ | $c_{K_2SO_4}$ | $c_{K_2S_2O_8}$ (3) | $v_{Total}$ (4) | time | $[S_2O_8^{-2}]$ (5) | $[I^-]$ (6) | $\Delta[S_2O_3^{-2}]$ (7) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 0.2M | 0.2M | 0.01M | 2% | 0.2M | 0.2M | (mL) | (s) | (M) | (M) | (M) |
| 1 | 1 | 2mL | 2mL | 2mL | 1mL | 2mL | 2mL | 11mL | —— | —— | —— | —— |
| 1 | 2 | 2mL | 2mL | 2mL | 1mL | 0mL | 4mL | 11mL | —— | —— | —— | —— |
| 1 | 3 | 4mL | 0mL | 2mL | 1mL | 2mL | 2mL | 11mL | —— | —— | —— | —— |
| 2 | 1 | 2mL | 2mL | 2mL | 1mL | 2mL | 2mL | 11mL | —— | —— | —— | —— |
| 2 | 2 | 2mL | 2mL | 2mL | 1mL | 0mL | 4mL | 11mL | —— | —— | —— | —— |
| 2 | 3 | 4mL | 0mL | 2mL | 1mL | 2mL | 2mL | 11mL | —— | —— | —— | —— |

(8) Average time $\Delta t(s)$

1 ——

2 ——

3 ——

## Part A. Obtaining the rate law.

| | Exp. | $\Delta[S_2O_3{}^{-2}]$ (M) ⑦ | $\Delta t$ (s) ⑧ | r (M/s) ⑨ | $[S_2O_8{}^{-2}]$ (M) ⑤ | $[I^-]$ (M) ⑥ | k ⑫ |
|---|---|---|---|---|---|---|---|
| ⑭ | 1 | _____ | _____ | _____ | _____ | _____ | _____ |
| | 2 | _____ | _____ | _____ | _____ | _____ | _____ |
| | 3 | _____ | _____ | _____ | _____ | _____ | _____ |

$$r = k\,[S_2O_8{}^{2-}]^a\,[I^-]^b$$

⑩  a= _____          ⑪  b= _____          ⑬  Average k (write down units)= _____

## Parts B and C. Evaluating the influence of the temperature on the reaction rate and a catalyst

| | Exp. | Temperature (K) | $\Delta[S_2O_3{}^{-2}]$ (M) ⑦ | $\Delta t$ (s) ⑧ | r (M/s) ⑨ | $[S_2O_8{}^{-2}]$ (M) ⑤ | $[I^-]$ (M) ⑥ | k ⑫ |
|---|---|---|---|---|---|---|---|---|
| ⑭ | 1 | _____ | _____ | _____ | _____ | _____ | _____ | _____ |
| | 1 | _____ | _____ | _____ | _____ | _____ | _____ | _____ |

(Results on the first row of Table A and Table B should be the same)

| Catalyst | 1 | _____ | | _____ | |
|---|---|---|---|---|---|

⑮  $E_a$= _____          J/K·mol

**Post-lab Questions**

# The iodine clock

1. Explain the effect of adding a catalyst to the reaction rate.

2. Using collision theory, explain how the concentration of the reactants affect the rate of the reaction.

**6** Le Châtelier's Principle

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<div align="center">

EXPERIMENT

# Le Châtelier's Principle

</div>

## Goal

The goal of this laboratory is to see the shift in the **equilibrium position** and to connect the observations to **Le Châtelier's Principle**, which states that:

> Any change in status quo prompts an opposing reaction in the responding system.

## Background

A double arrow in a chemical reaction indicates that the reaction can proceed in both directions. Products can react with each other to generate the original reactant.

$$A + B \rightleftharpoons C + D$$

Since the speed of most reactions depends on the concentration of the combining species, the forward reaction rate will decrease when products are formed, and the reverse reaction rate will increase. The latter will replenish the concentration of reactants which in turn will accelerate the forward reaction. Eventually, forward and backward reaction rates will equal each other and the concentrations of reactants and product will remain constant; at this point, the equilibrium has been reached.

## The experiment

The experiment today is divided into the following parts: colored complexed ions ($FeSCN^{2+}$), colored complexed ions ($Ni(NH_3)_6^{2+}$), the effect of pH on an indicator, effect of pH on solubility, and heat as a product.

### Part A. Colored complexed ions; $FeSCN^{2+}$.

Many metals form colored complex ions with several ligands, such as iron (III) ion $Fe^{3+}$ with thiocyanate SCN:

$$Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons FeSCN^{2+}(aq)$$
$$\text{yellow} \qquad\qquad\qquad \text{red}$$

The Iron (III) solution is yellow, the thiocyanate is transparent and the Iron (III) thiocyanate is red. The final color of the solution will be determined by the concentrations in the final equilibrium position.

### Part B. Colored complexed ions; $Ni(NH_3)_6^{2+}$

.

In the case of Hexaaminenickel (II), you will also study the change in equilibrium position when adding an acid. The ligand will act as a base reacting with the acid and detaching from the metal.

$$\text{green} \qquad\qquad\qquad \text{blue}$$
$$\text{Ni}^{2+}(aq) + 6\,\text{NH}_3(aq) \rightleftharpoons \textbf{Ni(NH}_3\textbf{)}_6{}^{2+}\textbf{ (aq)}$$
$$\Downarrow$$
$$\textbf{Ni(NH}_3\textbf{)}_6{}^{2+}\textbf{ (aq)} + 6\,\text{HCl}(aq) \rightleftharpoons \text{NiCl}_2(aq) + 6\,\text{NH}_4\text{Cl}(aq)$$
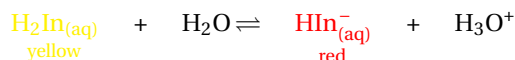$$\text{blue} \qquad\qquad\qquad \text{green}$$
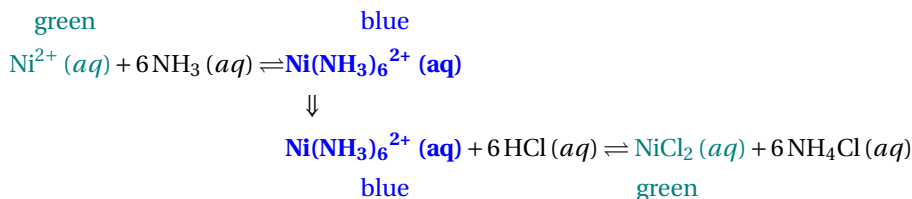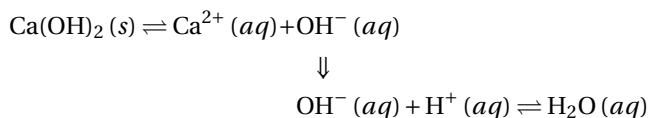
## Part C. Effect of pH on an indicator.

pH indicators are substances that change color depending on the medium pH. Typically they are weak bases or acids. As such, they dissociate slightly in water forming ions. Those ions might be colored species. The general expression for the dissociation of a divalent weak acid indicator (H2In) is:

$$\underset{\text{yellow}}{\text{H}_2\text{In}_{(aq)}} \quad + \quad \text{H}_2\text{O} \rightleftharpoons \quad \underset{\text{red}}{\text{HIn}^-_{(aq)}} \quad + \quad \text{H}_3\text{O}^+$$

In the case of Methyl orange, the protonated form is red, while the conjugated base is yellow. Notice that hydronium is a product in this equilibrium. How will adding an acid affect this equilibrium?
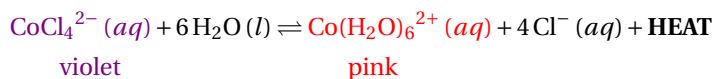
## Part D. Effect of pH on solubility.

Hydroxide salts of Group II elements (Ca, Sr, and Ba) are slightly soluble. Adding acid will neutralize the hydroxides in the solution while adding more hydroxide will increase the ion product. In both cases, the amount of precipitate will be affected.

$$\text{Ca(OH)}_2(s) \rightleftharpoons \text{Ca}^{2+}(aq) + \text{OH}^-(aq)$$
$$\Downarrow$$
$$\text{OH}^-(aq) + \text{H}^+(aq) \rightleftharpoons \text{H}_2\text{O}(aq)$$

## Part E. Heat as a product

Lastly, you will experience Le Châtelier's Principle in an exothermic reaction, where the heat can be viewed as a product of the reaction.

$$\underset{\text{violet}}{\text{CoCl}_4{}^{2-}(aq)} + 6\,\text{H}_2\text{O}(l) \rightleftharpoons \underset{\text{pink}}{\text{Co(H}_2\text{O)}_6{}^{2+}(aq)} + 4\,\text{Cl}^-(aq) + \textbf{HEAT}$$

---

**Example**

*The following endothermic reaction is allowed to reach equilibrium:*

$$\underset{\text{blue}}{A(aq)} + B(aq) + HEAT \rightleftharpoons C(aq) + D(aq)$$

*Where A, the only colored compound, is blue. How will the following changes affect the color/equilibrium: (a) Adding more B reactant, (b) Adding more C product, (c) Heating the mixture.*

- - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - -

**Answer**: (a) less blue/equilibrium shifts to the right. (b) more blue/ equilibrium shifts left. (c) Heat is a reactant; less blue/equilibrium shifts to the right.

# Procedure

## Part A. Colored complexed ions: FeSCN$^{2+}$

☐ *Step 1:* – Find 3 test tubes and a 100 mL beaker, clean them, and mark the test tubes with letters A, B, and R.

☐ *Step 2:* – Read the Good Lab Practice box

> ### Good Lab Practice
>
> ✍ Concentrated solutions of ammonia, sodium hydroxide and hydrochloric acid should be handled with care.
>
> ✍ Do not shake open test tubes. Do not use your fingers as stoppers, even if you wear gloves.

☐ *Step 3:* – Add about 20 mL of distilled water to the beaker, 20 drops of 0.1 M Fe(NO$_3$)$_3$ and 20 drops of 0.1 M KSCN. Mixed the solution until the color is homogeneous.

☐ *Step 4:* – Use a 10 mL graduated cylinder to add 3 mL of the mixture to each of the test tubes.

☐ *Step 5:* – Add 20 drops of 0.1 M Fe(NO$_3$)$_3$ to test tube A. Put a stopper and mix the solution.

☐ *Step 6:* – Add 20 drops of 0.1 M KSCN to test tube B. Put a stopper and mix the solution.

☐ *Step 7:* – Add 20 drops of distilled water to test tube R. Put a stopper and mix the solution.

☐ *Step 8:* – Compare the color of the test tubes A and B to R and write down your observations.

## Part B. Colored complexed ions: Ni(NH$_3$)$_6$$^{2+}$.

☐ *Step 1:* – Obtain 1 test tube and clean it.

☐ *Step 2:* – Add 10 drops of 0.1 M Ni(NO$_3$)$_2$. Indicate the color on the results page.

☐ *Step 3:* – Add drops of 6 M NH$_3$ until the color changes.

☐ *Step 4:* – Add drops of 6 M HCl until the color changes.

## Part C. Effect of PH on an indicator.

☐ *Step 1:* – Obtain two 50 mL beakers, clean them, and mark them with letters A (for Acid) and B (for Base). Find and clean a test tube.

☐ *Step 2:* – Add 10 mL of distilled water to each beaker and 1 mL of distilled water to a test tube.

☐ *Step 3:* – Add 4 drops of 6 M HCl to beaker A and stir it (this is the diluted acid).

☐ *Step 4:* – Add 4 drops of 6 M NH$_3$ to beaker B and stir it (this is the diluted base).

☐ *Step 5:* – Add 4 drops of the indicator (methyl orange) to the test tube.

☐ *Step 6:* – Add 2 drops from the diluted acid in beaker A to the test tube. Mix gently the solution. Record the color on the results page.

☐ *Step 7:* – Drop by drop, add the diluted ammonia solution from beaker B until the color changes. Homogenize the solution from time to time. Write down the number of drops.

☐ *Step 8:* – Attempt one more time for another color change by adding drop-by-drop diluted acid solution. Warite down the number of drops.

## Part D. Effect of pH on solubility.

☐ *Step 1:* – Add 5 mL of 6 M NaOH to a 50mL beaker using the graduated cylinder.

☐ *Step 2:* – Rinse a 10mL cylinder with water 3 times. Then, use it to add 5 mL of 1 M $Ca(NO_3)_2$ to the beaker.

☐ *Step 3:* – Stir the mixture.

☐ *Step 4:* – Make a cone with filter paper and place it in a funnel, on top of the Erlenmeyer. Filter the solution with the precipitate. Carry out a couple of washings with distilled water to make sure you collect all solids. Transfer with a spatula the white solid to a small clean beaker.

☐ *Step 5:* – Add 10 mL of distilled water to the beaker with the white solid. Stir the mixture. Do not expect the solid to completely dissolve. The solution is saturated.

☐ *Step 6:* – Add drops of 6 M HCl until a change is observed. Record your results.

☐ *Step 7:* – Add drops of 6 M NaOH until a change is observed. Record your results.

## Part E. Heat as a product.

☐ *Step 1:* – Obtain a Bunsen burner, a stand, two iron rings, a wire gauze, two 250 mL beakers, and a test tube.

☐ *Step 2:* – Prepare the setup for the bunsen burner, using the second iron ring to protect the beaker from falling. Put about 100 mL of distilled water in the beaker and bring the water to a boil.

☐ *Step 3:* – Add 5 drops of 0.1 M $Co(NO_3)_2$ to the test tube.

☐ *Step 4:* – Record the color of the liquid solution after each step.

☐ *Step 5:* – Add drops of 12 M HCl until the color of the solution changes. You might need to stir the test tube to help mix the reagents.

☐ *Step 6:* – Add 5 drops of distilled water and mix.

☐ *Step 7:* – Place the test tube in the boiling water and wait for another color change.

☐ *Step 8:* – Attempt to reverse the reaction by placing the test tube in a beaker with ice or cold water.

**Pre-lab Questions**

# Le Châtelier's Principle

1. Write the equilibrium constant expressions for all reactions involved in this experiment.

2. How does pH affect the solubility of $Ca(OH)_2$?

3. Is heat being consumed (reactants) or produced (product) in an endothermic reaction?

4. Is heat being consumed (reactants) or produced (product) in an exothermic reaction?
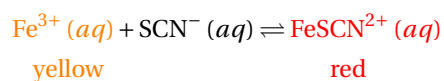
**Results**
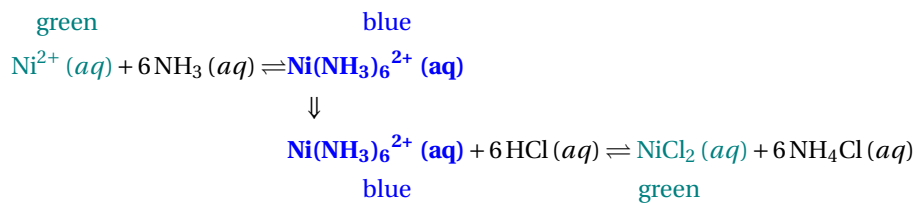**EXPERIMENT**

# Le Châtelier's Principle

## Part A. Colored complexed ions: FeSCN$^{2+}$

$$Fe^{3+}\,(aq) + SCN^-\,(aq) \rightleftharpoons FeSCN^{2+}\,(aq)$$
yellow                          red

| After step # | | | Before color | After color |
|---|---|---|---|---|
| 5 | Add Fe$^{3+}$ | Solution in test tube A | _____ | _____ |
| 6 | Add SCN$^-$ | Solution in test tube B | _____ | _____ |
| 7 | Add H$_2$O | Solution in test tube R | _____ | _____ |

## Part B. Colored complexed ions: Ni(NH$_3$)$_6$$^{2+}$.

green                          blue
$$Ni^{2+}\,(aq) + 6\,NH_3\,(aq) \rightleftharpoons Ni(NH_3)_6{}^{2+}\,(aq)$$
$$\Downarrow$$
$$Ni(NH_3)_6{}^{2+}\,(aq) + 6\,HCl\,(aq) \rightleftharpoons NiCl_2\,(aq) + 6\,NH_4Cl\,(aq)$$
blue                          green

| After step # | Color | | |
|---|---|---|---|
| 2 | Add Ni$^{2+}$ | _____ | |
| 3 | Add NH$_3$ | _____ | # drops added _____ |
| 4 | Add HCl | _____ | # drops added _____ |

## Part C. Effect of pH on an indicator.

$$H_2In_{(aq)} \quad + \quad H_2O \longrightarrow \quad HIn^-_{(aq)} \quad + \quad H_3O^+$$
$$\text{yellow} \qquad\qquad\qquad\qquad \text{red}$$
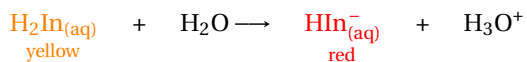
| After step # | | Before color | After color | |
|---|---|---|---|---|
| 5 | Add indicator | _____ | _____ | |
| 6 | Add diluted acid | _____ | _____ | |
| 7 | Add diluted base | _____ | _____ | # drops added ___ |
| 8 | Add diluted acid | _____ | _____ | # drops added ___ |

## Part D. Effect of pH on solubility.

$$Ca(OH)_2\,(s) \rightleftharpoons Ca^{2+}\,(aq) + OH^-\,(aq)$$
$$\Downarrow$$
$$OH^-\,(aq) + H^+\,(aq) \rightleftharpoons H_2O\,(aq)$$
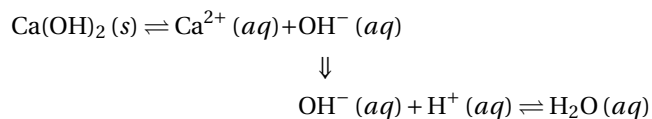
| After step # | | Indicate # drops added |
|---|---|---|
| 6 | Add acid | ___ |
| 7 | Add base | ___ |

## Part E. Heat as a product.

$$CoCl_4{}^{2-}\,(aq) + 6\,H_2O\,(l) \rightleftharpoons Co(H_2O)_6{}^{2+}\,(aq) + 4\,Cl^-\,(aq) + \textbf{HEAT}$$
$$\text{violet} \qquad\qquad\qquad \text{pink}$$
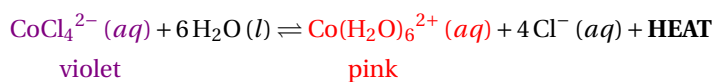
| After step # | | color | |
|---|---|---|---|
| 3 | Add $Co^{2+}$ | _____ | |
| 5 | Add acid | _____ | # drops added ___ |
| 6 | Add $H_2O$ | _____ | |
| 7 | Heat | _____ | |
| 8 | Cool | _____ | |

**Post-lab Questions**

# Le Châtelier's Principle

1. In part A. Explain the different colors based on the equilibrium reaction and Le Châtelier's Principle.

2. In part A. Given that water is not involved in the equilibrium, explain the color change you observed after adding water to the mixture.

3. In part B. What did you observe after adding the acid and after adding the base? Explain the different colors based on the equilibrium reaction and Le Châtelier's Principle.

4. In Part C. What did you observe after adding the acid and after adding the base? Explain the changes based on the equilibrium reaction and Le Châtelier's Principle.

5. In Part D. What did you observe after adding the acid and after adding the base? Explain the changes based on the equilibrium reaction and Le Châtelier's Principle?

6. In Part E. What did you observe after heating and after cooling? Explain the changes based on the equilibrium reaction and Le Châtelier's Principle.

**7**  Equilibrium constant

<div align="center">

EXPERIMENT

# Equilibrium constant

</div>

## Goal

The goal of this laboratory is to determine *the equilibrium constant* of a chemical reaction by using the *Lambert-Beer's law* to measure the concentration of the species in solution.

## Background

Most chemical reactions do not proceed to completion, proceeding only to the point where both reactants and products have constant concentration. This is because most reactions are reversible and they can run in both forward and reverse directions. The concentrations of the species involved in the equilibrium will achieve an *equilibrium state* when the reaction rates in both directions equalize. For a certain chemical reaction:

$$aA \quad + \quad bB \quad \rightleftharpoons \quad cC \quad + \quad dD$$
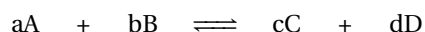
The equilibrium can be characterized by the expression:

$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

where $K_c$ (capital letter) is the equilibrium constant in terms of molarity, the brackets represent the concentrations of the respective species and the exponents are their corresponding stoichiometric coefficients.

### Spectrophotometry

*Spectrophotometry* is a technique that measures the amount of light absorbed by a chemical substance, typically in solution, using the use of a *spectrophotometer*. Spectrophotometers display the absorbance, the amount of light absorbed by a sample. To properly measure the absorbance of a chemical in a water-based solution you need to set the blank by using a sample containing only the solvent without a solute. The blank establishes the baseline of the measurement, eliminating any absorbance caused by the solvent.

The spectrometer allows the measurement of absorbance at a single wavelength. Interestingly, for each substance, there is a wavelength of *maximum absorbance*, which allows us to differentiate among chemical substances with different maximum absorbances. For example, in the current experiment, you will analyze mixtures containing $Fe^{3+}_{(aq)}$, $SCN^-_{(aq)}$, and $Fe(SCN)^{2+}_{(aq)}$. However, only $Fe(SCN)^{2+}_{(aq)}$ will absorb radiation at $\lambda$=450 nm, and hence we can track the absorbance of this chemical only in the mixture.

### Lambert-Beer's law

Liquids *attenuated* the intensity of light passing through a colored solution. The effect can be comparable to a dirty window that attenuates the light passing through. The dirtier the window (higher concentration of dirt), the less one can see through it (because more light is absorbed, reflected, or refracted by the dirt). Lambert-Beer's law establishes the relationship between absorbance and concentration:

$$A = k_\lambda c$$

In this formula, $A$ stands for the *absorbance* (light absorbed by the liquid), $k_\lambda$ (lower case, not to be confused with the equilibrium constant, $K$) is a **proportionality constant**, which is specific to each compound and at the wavelength ($\lambda$) specified by the subindex, and $c$ is the solution concentration. Lambert-Beer's law is a linear function of the form $y = mx + b$.

When graphing the absorbance ($y$-axes) versus the concentration ($x$-axes), the slope of the line corresponds to Lambert-Beer's proportionality constant. This line should cross the origin as there should be no absorbance when the concentration is null.

## The experiment

The experiment today is divided into 2 parts: determining Lambert-Beer's constant $k$ and determining the equilibrium constant $K$.

### Part A. Determining Lambert-Beer's constant $k$.

This experiment studies the reaction between iron(III) and thiocyanate to give an iron-thiocyanate complex:

$$Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons Fe(SCN)^{2+}(aq)$$
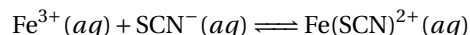
Interestingly, $Fe^{3+}$ in solution is yellow and becomes red when reacting with thiocyanate to produce the $(FeSCN)^{2+}$ complex. This intense red coloration allows us to use spectrophotometry to measure the $(FeSCN)^{2+}$ concentration and hence, of all the species in equilibrium.

The first part of this experiment requires the determination of Lambert-Beer's constant, $k_\lambda$. However, here we deal with a chemical reaction. According to the equilibrium, $Fe(SCN)^{2+}$ in solution will follow the reverse reaction forming iron(III) and thiocyanate ions. The shift due to the equilibrium makes the concentration of $Fe(SCN)^{2+}$ unknown.

To solve this problem $Fe^{3+}$ ion will be added in excess (0.0025 M) while adding only small amounts of $SCN^-$ ($10^{-4}$ M). This trick will displace the equilibrium to the right: according to Le Châtelier's, the equilibrium shifts to the products when one reactant is added. Hence, if one of the reactants is added in overwhelming excess, the other reactant will be consumed almost to exhaustion forming the product. Therefore, the $FeSCN^{2+}$ concentration can be calculated using the concentration of $SCN^-$.

In this part, a set of solutions will be added to a clean cuvette, and absorbance at $\lambda$=450 nm will be measured using the spectrophotometer. With the 5 points obtained and the origin of the coordinates, a graph will be plotted to calculate the slope of the line. Notice again that in this linear representation, the line must pass through the origin by definition, since at concentration=0, absorbance must be 0.

### Parts B. Determining the equilibrium constant $K_c$.

Using the absorbance measured and the value of $k_{450nm}$, in this second part of the experiment you will calculate the concentration in equilibrium of all species involved in the equilibrium. First, the concentration of the product will depend on the absorbance, and will be given by the formula below:

$$A = k_{450nm}[Fe(SCN)^{2+}] \qquad [Fe(SCN)^{2+}] = \frac{A}{k_{450nm}}$$

An ICE chart given below will be used to calculate the equilibrium concentration of reactants, where ③ is calculated from the absorbance, and ② and ① are recalculated from the initial concentrations:

|  | $[Fe(NO_3)_3]$ | $[KSCN]$ | $[Fe(SCN)^{2+}]$ |
|---|---|---|---|
| Initial | ① | ② | 0 M |
| Change | $-$③ | $-$③ | $+$③ |
| Equilibrium | ① $-$ ③ | ② $-$ ③ | ③ |

## Procedure

### Preparing a diluted KSCN solution

☐ *Step 1:* – Clean 5 large test tubes and the matching stoppers and set them upside down on a rack. Number the test tubes from 1 to 5.

☐ *Step 2:* – Obtain a 100.0 mL volumetric flask and a Mohr pipette.

☐ *Step 3:* – Obtain about 15 mL of 0.0025 M KSCN in a 50 mL beaker. Rinse the Mohr pipette a couple of times with a small amount of this solution. Always discard the rinsing liquid. Then, transfer 4.00 mL into the volumetric flask.

☐ *Step 4:* – In a clean 100 mL beaker, obtain about 100 mL of distilled water. Carefully add water to the volumetric flask directly from the beaker and stop adding before you reach the 100.0 mL mark. Use a plastic dropper to level the water to the mark, drop by drop. This is the diluted KSCN solution.

☐ *Step 5:* – Rinse the Mohr pipette with the diluted solution of KSCN again.

### Good Lab Practice

✐ Pipettes are always used together with a suction bulb or a syringe. **Never** suck a chemical using the mouth!

✐ **Never** leave a pipette lying on the table **while connected to the syringe**. Remaining liquid can leak into the syringe. The syringe will be damaged and the liquid will return to the pipette contaminated.

✐ Always wash pipettes with distilled water and rinse them using the same product to be measured. Suck a small volume, disconnect the syringe and move the liquid about, displacing the distilled water. Discard the rinsing liquid as waste. Rinse twice.

## Part A. Determining Lambert-Beer's constant $k$. Preparing the mixtures

☐ *Step 1:* – Following the Table in the description of Part A, add 1.00 mL of the diluted KSCN solution to jumbo test tube 1, 2.00 mL to test tube 2, 3.00 mL to test tube 3, 4.00 mL to test tube 4 and 5.00 mL to test tube 5. You will use jumbo test tubes throughout the experiment.

☐ *Step 2:* – Rinse the pipet with distilled water. Obtain about 50 mL of 0.25 M $Fe(NO_3)_3$ in a 100 mL beaker. Rinse the pipette with the solution of $Fe(NO_3)_3$ from the beaker.

☐ *Step 3:* – Add 5.0 mL of 0.25 M $Fe(NO_3)_3$ in each test tube.

☐ *Step 4:* – Rinse the pipette with distilled water. Obtain about 40 mL of 0.1 M $HNO_3$ in a 50 mL beaker. Rinse the pipette with the solution of $HNO_3$ from the beaker.

☐ *Step 5:* – Following the Table below, add 4.00 mL of the $HNO_3$ solution to test tube 1; 3.00 mL to test tube 2, 2.00 mL to test tube 3, and 1.00 mL to test tube 4.

☐ *Step 6:* – At this point, all your test tubes should have the same volume of liquid. If not, repeat the ones that diverge.

☐ *Step 7:* – Put the stoppers in the test tubes and mix the solutions.

| Part A | $Fe(NO_3)_3$ | KSCN | $HNO_3$ | $v_{total}$ |
|---|---|---|---|---|
| | 0.25 M | 0.0025 M | 0.1 M | |
| Test Tube 1 | 5.0 mL | 1.0 mL | 4.0 mL | 10.0 mL |
| Test Tube 2 | 5.0 mL | 2.0 mL | 3.0 mL | 10.0 mL |
| Test Tube 3 | 5.0 mL | 3.0 mL | 2.0 mL | 10.0 mL |
| Test Tube 4 | 5.0 mL | 4.0 mL | 1.0 mL | 10.0 mL |
| Test Tube 5 | 5.0 mL | 5.0 mL | 0.0 mL | 10.0 mL |

## Part A. Determining Lambert-Beer's constant $k$. Measuring absorbance

☐ *Step 1:* – Start the spectrophotometer. The bulb needs time to heat up to a stable temperature.

☐ *Step 2:* – Get a 250 mL beaker for waste. Refill the 100 mL beaker with distilled water.

☐ *Step 3:* – Using the plastic dropper, fill the cuvette 3/4 full with distilled water.

☐ *Step 4:* – Insert the cuvette into the spectrophotometer, set the wavelength to 450 nm, and press "blank" or "zero".

☐ *Step 5:* – Use a new cuvette. Fill the cuvette 3/4 full with the solution from test tube 1.

☐ *Step 6:* – Insert the cuvette into the spectrophotometer to measure the absorbance. Record the result.

☐ *Step 7:* – Repeat for test tubes 2, 3, 4, and 5, always using new cuvettes for each measurement.

☐ *Step 8:* – Plot absorbance (7) vs. concentration (6) in order to obtain the Lambert-Beer's constant $k$.

☐ *Step 9:* – Measure the absorbance of an unknown solution and use the linear regression ($A/k$) to obtain its concentration.

☐ *Step 10:* – Do not proceed unless you show the instructor your graph.

**Good Lab Practice**

✍ For best results, use the same cuvette, with the same orientation, for all the measurements.

✍ Keep the outer walls of the cuvette clean. Do not touch them. Wipe them with a piece of optical paper.

✍ Rinse the cuvette at the same time as you rinse the pipette.

## Part B. Determining the equilibrium constant $K$. Preparing a different set of mixtures

☐ *Step 1:* – Prepare a new set of mixtures based on the proportions reported in the Table below.

☐ *Step 2:* – Make sure you use the 0.0025 M $Fe(NO_3)_3$ solution and not the 0.25M.

☐ *Step 3:* – The 0.0025 M KSCN solution to be used has already been prepared at the lab.

☐ *Step 4:* – Measure the absorbance for the new set of mixtures.

| Part B | $Fe(NO_3)_3$ 0.0025 M | KSCN 0.0025 M | $HNO_3$ 0.1 M | $v_{total}$ |
|---|---|---|---|---|
| Test Tube 6 | 1.0 mL | 5.0 mL | 1.0 mL | 7mL |
| Test Tube 7 | 1.0 mL | 4.5 mL | 1.5 mL | 7mL |
| Test Tube 8 | 1.0 mL | 4.0 mL | 2.0 mL | 7mL |
| Test Tube 9 | 1.0 mL | 3.5 mL | 2.5 mL | 7mL |
| Test Tube 10 | 1.0 mL | 3.0 mL | 3.0 mL | 7mL |
| Test Tube 11 | 2.0 mL | 4.0 mL | 1.0 mL | 7mL |
| Test Tube 12 | 2.0 mL | 3.5 mL | 1.5 mL | 7mL |
| Test Tube 13 | 2.0 mL | 3.0 mL | 2.0 mL | 7mL |
| Test Tube 14 | 2.0 mL | 2.5 mL | 2.5 mL | 7mL |
| Test Tube 15 | 2.0 mL | 2.0 mL | 3.0 mL | 7mL |

## Calculations

(1) This is the volume of Fe(NO$_3$)$_3$ added.

(2) This is the volume of KSCN added.

(3) This is the total volume of the mixtures.

(4) This is the initial Iron(III) concentration in the mixtures:

$$[Fe^{+3}]_0 = \frac{v_{Fe^{+3}} \cdot c_{Fe^{+3}}}{v_{total}} = \frac{\boxed{1} \cdot 0.25}{\boxed{3}}$$

(5) This is the initial thiocyanide concentration in the mixtures:

$$[SCN^-]_0 = \frac{v_{SCN^-} \cdot c_{SCN^-}}{v_{total}} = \frac{\boxed{2} \cdot 0.0025}{\boxed{3}}$$

(6) This is the concentration of Fe(SCN)$^{+2}$ in the mixture:

$$[Fe(SCN)^{+2}] = [SCN^-] = \boxed{5}$$

(7) This is the measured absorbance of the mixture.

(8) This step is needed to calculate numerically the Lambert-Beer's constant $k$:

$$[Fe(SCN)^{+2}] \cdot A = \boxed{6} \cdot \boxed{7}$$

(9) This step is needed to calculate numerically the Lambert-Beer's constant $k$:

$$[Fe(SCN)^{+2}]^2 = \boxed{6}^2$$

(10) This step is needed to calculate numerically Lambert-Beer's constant $k$, and results from adding all values of $\boxed{8}$ .

(11) This step is needed to calculate numerically Lambert-Beer's constant $k$, and results from adding all values of $\boxed{9}$ .

(12) This step the Lambert-Beer's constant $k$:

$$k = \frac{\sum [Fe(SCN)^{+2}] \cdot A}{\sum [Fe(SCN)^{+2}]^2} = \frac{\boxed{10}}{\boxed{11}}$$

(13) This is the volume of Fe(NO$_3$)$_3$ added.

(14) This is the volume of KSCN added.

(15) This is the total volume of the mixtures.

(16) This is the initial Iron(III) concentration in the mixtures:

$$[Fe^{+3}]_0 = \frac{v_{Fe^{+3}} \cdot c_{Fe^{+3}}}{v_{total}} = \frac{\boxed{13} \cdot 0.0025}{\boxed{15}}$$

⑰ This is the initial thiocyanide concentration in the mixtures:

$$[SCN^-]_0 = \frac{v_{SCN^-} \cdot c_{SCN^-}}{v_{total}} = \frac{\boxed{14} \cdot 0.0025}{\boxed{15}}$$

⑱ This is the measured absorbance of the mixture.

⑲ This is the concentration of $Fe(SCN)^{+2}$ in equilibrium:

$$[Fe(SCN)^{+2}]_{eq} = \frac{A}{k} = \frac{\boxed{18}}{\boxed{12}}$$

⑳ This is the concentration of $Fe^{+3}$ in equilibrium:

$$[Fe^{+3}]_{eq} = [Fe^{+3}]_0 - [Fe(SCN)^{+2}]_{eq} = \boxed{16} - \boxed{19}$$

㉑ This is the concentration of $SCN^-$ in equilibrium:

$$[SCN^-]_{eq} = [SCN^-]_0 - [Fe(SCN)^{+2}]_{eq} = \boxed{17} - \boxed{19}$$

㉒ This is the equilibrium constant:

$$K = \frac{[Fe(SCN)^{+2}]_{eq}}{[Fe^{+3}]_{eq} \cdot [SCN^-]_{eq}} = \frac{\boxed{19}}{\boxed{20} \cdot \boxed{21}}$$

**Pre-lab Questions**

# Equilibrium constant

1. You prepare a solution by following the procedure described next. You first obtain about 15 mL of 0.0025 M KSCN in a 50 mL beaker. Then you transfer 4.00 mL into the volumetric flask. In a clean 100 mL beaker, you obtain about 100 mL of distilled water, and carefully add water to the volumetric flask directly from the beaker stopping before reaching the 100.0 mL mark. Finally, you use a plastic dropper to level the water to the mark, drop by drop. Calculate the molarity of the solution you prepared.

2. You mix 1mL of $Fe(NO_3)_3$ 0.25 M with 5mL of KSCN $10^{-4}$ M and 1mL of $HNO_3$ 0.1 M into a volumetric flask. Sketch a volumentric flask and calculate the initial concentration of $Fe^{3+}$ in the mixture.

3. Write down the formula for the equilibrium constant in terms of concentration for the equilibrium below:

$$Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons Fe(SCN)^{2+}(aq)$$

4. A set of absorbances, $A$, for different concentrations, $c$, are given below.

(a) Plot $A$ vs. $c$ in the graph below.

(b) Compute the slope of the graph by using the formula:

$$k = \frac{\sum c \cdot A}{\sum c^2}$$

| $c$ (M) | $A$ | $c \cdot A$ (M) | $c^2$ ($M^2$) |
|---------|-----|-----------------|---------------|
| 0.0120 | 0.681 | | |
| 0.00960 | 0.540 | | |
| 0.00720 | 0.389 | | |
| 0.00480 | 0.270 | | |
| 0.00240 | 0.133 | | |
| Sum | | | |
| $k$ ($M^{-1}$) | | | |
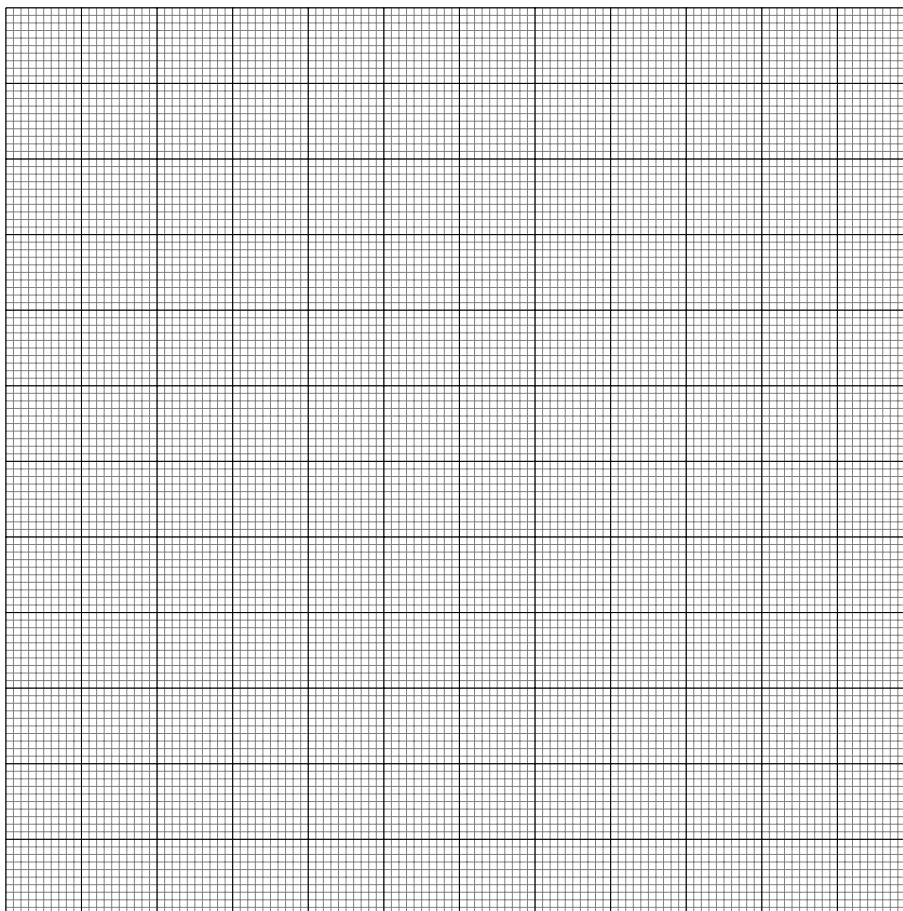


(c) After calculating $k$, now write down the formula for absorbance in the form: $A = k \cdot c$

# Equilibrium constant

**STUDENT INFO**

Name:      Date:

**Parts A. Determining Lambert-Beer's constant $k$.**

| | $Fe(NO_3)_3$ 0.25M | KSCN 0.0025M | $HNO_3$ 0.1M | $v_{tot}$ | $[Fe^{+3}]_0$ | $[SCN^-]_0$ | $[FeSCN^{+2}]$ | A | $[FeSCN^{+2}] \cdot A$ | $[FeSCN^{+2}]^2$ |
|---|---|---|---|---|---|---|---|---|---|---|
| | ① | ② | | ③ | ④ | ⑤ | ⑥ | ⑦ | ⑧ | ⑨ |
| Test Tube 1 | 5mL | 1mL | 4mL | 10mL | —— | —— | —— | —— | —— | —— |
| Test Tube 2 | 5mL | 2mL | 3mL | 10mL | —— | —— | —— | —— | —— | —— |
| Test Tube 3 | 5mL | 3mL | 2mL | 10mL | —— | —— | —— | —— | —— | —— |
| Test Tube 4 | 5mL | 4mL | 1mL | 10mL | —— | —— | —— | —— | —— | —— |
| Test Tube 5 | 5mL | 5mL | 0mL | 10mL | —— | —— | —— | —— | —— | —— |
| Origin | | | | | | | 0 | 0 | 0 | 0 |

Sum=    ⑩ ——    ⑪ ——

⑫ $k =$ _____

—— ——

Unknown

## Parts B. Determining the equilibrium constant $K$.

| Test Tube | Fe(NO$_3$)$_3$ 0.0025M ⑬ | KSCN 0.0025M ⑭ | HNO$_3$ 0.1M | $v_{tot}$ ⑮ | $[Fe^{3+}]_0$ ⑯ | $[SCN^-]_0$ ⑰ | A ⑱ | $[Fe(SCN)^{2+}]_{eq}$ ⑲ | $[Fe^{3+}]_{eq}$ ⑳ | $[SCN^-]_{eq}$ ㉑ | K ㉒ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 6 | 1mL | 5.0mL | 1.0mL | 7.0mL | —— | —— | —— | —— | —— | —— | —— |
| 7 | 1mL | 4.5mL | 1.5mL | 7.0mL | —— | —— | —— | —— | —— | —— | —— |
| 8 | 1mL | 4.0mL | 2.0mL | 7.0mL | —— | —— | —— | —— | —— | —— | —— |
| 9 | 1mL | 3.5mL | 2.5mL | 7.0mL | —— | —— | —— | —— | —— | —— | —— |
| 10 | 1mL | 3.0mL | 3.0mL | 7.0mL | —— | —— | —— | —— | —— | —— | —— |
| 11 | 2mL | 4.0mL | 1.0mL | 7.0mL | —— | —— | —— | —— | —— | —— | —— |
| 12 | 2mL | 3.5mL | 1.5mL | 7.0mL | —— | —— | —— | —— | —— | —— | —— |
| 13 | 2mL | 3.0mL | 2.0mL | 7.0mL | —— | —— | —— | —— | —— | —— | —— |
| 14 | 2mL | 2.5mL | 2.5mL | 7.0mL | —— | —— | —— | —— | —— | —— | —— |
| 15 | 2mL | 2.0mL | 3.0mL | 7.0mL | —— | —— | —— | —— | —— | —— | —— |

Average $K=$ ——

Figure 5: Column 6 [Fe(SCN)$^{+2}$] (X axis) vs. A Column 7 (Y axis)

**Post-lab Questions**

# Equilibrium constant

1. The absorbance of a colored substance in a colorless liquid is measured at each of a series of wavelengths, and the data is given below:

| $\lambda$(nm) | 325 | 350 | 375 | 400 | 425 | 450 | 475 | 500 | 525 |
|---|---|---|---|---|---|---|---|---|---|
| $A$ | 0.016 | 0.144 | 0.341 | 0.578 | 0.681 | 0.558 | 0.281 | 0.092 | 0.031 |

(a) Plot $A$ vs. $\lambda$ in the graph below.

(b) Calculate the $\lambda$ value that gives a maximum $A$.
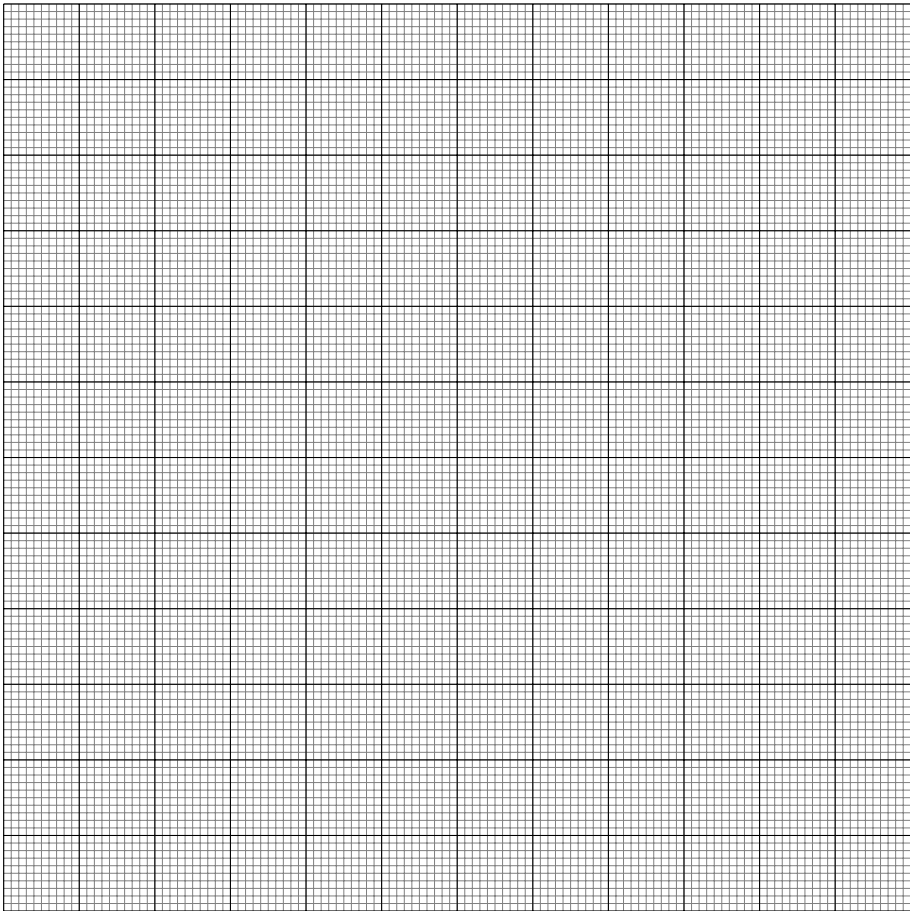
$\lambda(A_{max})$  =_____

2. In parts A and B you use different iron and thiocyanate solutions: in part, A you use a 0.25M-$Fe(NO_3)_2$ solution and a 0.0025M-KSCN solution, whereas on part B you use a 0.0025M-$Fe(NO_3)_2$ solution and a 0.0025M-KSCN solution. Explain why you do this.

3. You mix 5mL of $Fe(NO_3)_3$ 0.25 M with 2mL of KSCN 0.0025 M and 3mL of $HNO_3$ 0.1 M. Calculate the initial concentration of $SCN^-$ in the mixture.

4. You mix 5mL of $Fe(NO_3)_3$ 0.25 M with 4mL of KSCN 0.0025 M and 1mL of $HNO_3$ 0.1 M. Calculate the concentration of $FeSCN^{2+}$ in the mixture.

EXPERIMENT

# Titration Curve

## Goal

The goal of this laboratory is to graph a titration curve and to use this curve to standardize an acid solution while determining the acidity constant of the acid.

## Background

Titrations were used in previous experiments to analyze the concentration of a solution, the so-called *analyte*. Using the *titrant*, a reactant of known concentration, it is possible to determine the concentration of the analyte if the volumes are measured carefully. The titrant is added from a buret until the solution changes color due to the presence of an indicator. The indicator denotes the moment when the *equivalence point* is achieved. The equivalence point is the moment at which equivalent molar amounts of both reactants have been added.

In an acid-base reaction, the acid reacts with the base, forming salt and water. This process is called *neutralization*; the protons released by the acid are neutralized by the hydroxide ions formed in the presence of the base. For strong acids and strong bases that dissociate completely in water, the equivalence point occurs at pH=7 and, therefore, an indicator with a color transition at pH=7 is used.

However, not all acids have the same strength. Weak acids do not release as many protons as strong acids do. The strength of a weak acid, and the consequent number of protons released, depend on its dissociation constant, $K_a$. Because of the partial dissociation of these species, the equivalence point in a weak acid titration does not occur at pH=7. The moment at which equivalent amounts of a weak acid and a strong base (titrant) have been added will take place at pH>7 (due to the non-complete dissociation). Determining the equivalence point is necessary to know the correct indicator to be used for titrations of weak acids.

### The titration curve

During the neutralization process of an acid, the pH of the solution starts at a low value - lower than 7 since it is an acid - and increases with the addition of the base. If one plots the pH versus the volume of base added, the result is not a straight line, but an S-shape curve. This shape shows that the pH changes slowly at the beginning and the end of the process, but there is a region in the graph where the pH increases rapidly with small additions of the base. When that abrupt pH change takes place depends on the acid and the base used.

For the titration of a weak acid (analyte) using a strong base (titrant), the endpoint will be achieved at a pH higher than 7. For the titration of a weak base (analyte) using a strong acid (titrant), the endpoint will be achieved at a pH lower than 7. The titration curve for every base or acid is unique and it is useful for determining the dissociation constant ($K_a$ or $K_b$) of the analyte.

### The acid dissociation constant

The acid dissociation constant for a weak acid is a ratio of the amounts of products and reactants at the equilibrium position. The ratio is constant for a fixed temperature. The concentration of $H^+$ will always be among the products for the dissociation of an acid. Recalling that the concentration of $H^+$ defines the pH, the latter can be solved as follows:

$$HA(aq) \quad \rightleftharpoons \quad H^+(aq) + A^-(aq)$$

$$K_a = \frac{[\mathbf{H^+}][A^-]}{[HA]} \qquad [\mathbf{H^+}] = K_a \frac{[HA]}{[A^-]} \quad ; \qquad pH = pK_a + log\frac{[A^-]}{[HA]}$$

This expression is known as the *Henderson-Hasselbalch equation*, where [HA] is the concentration of the weak acid, and [A$^-$] is the concentration of its conjugated base. It is possible to visualize the $pK_a$ from the titration curve by using the Henderson-Hasselbalch equation.

First, notice that at the equivalence point, the same amounts of acid and base have reacted and there will be no acid; [HA] = 0. But *halfway* to that point, when half of the acid has been converted to the same amount of its conjugated base, the concentrations of the two will be equal, [A$^-$]=[HA]. The fraction in the previous expression becomes equal to 1 and, since log 1 = 0, then pH = pK$_a$.

$$pH = pK_a + log\frac{[A^-]}{[HA]} \quad ; \qquad pH = pK_a + log1 \quad ; \qquad pH = pK_a$$

The equivalence point would correspond to the inflection point of the titration curve. By reading the volume of base added at that point, it is possible to calculate the volume needed to reach the halfway point ($V_{eq}/2$). The pH when that volume of base was added is taken from the the titration curve and corresponds to the weak acid's $pK_a$.

The location of the equivalence point can be estimated by fitting two straight lines to the straight sections of the curve, as depicted in Figure 1, and a third line equidistant to the previous two. The point at which the third line and the titration curve intersect is the equivalence point.

## The experiment

The experimental part consists of the titration only. The data will be used later to plot the curve. From the plotted curve the equivalence point and the acid $pK_a$ should be calculated.

The weak acid studied in this experiment is potassium hydrogen phthalate, $KHC_8H_4O_4$ (KHP). The base used as a titrant is sodium hydroxide (NaOH), a strong base. It is very important to obtain precise measurements of the volumes and masses used during this experiment.

The analyte (KHP) will be dissolved in a beaker. The titrant (NaOH) will be added from a buret. A pH meter will be used to monitor the pH and magnetic stirring will be used during the measurement to homogenize the solution pH.

**Example**

*A solution of hydrogen cyanide (HCN), a weak acid, is titrated using NaOH, a strong base. The pH is monitored during the titration using a pH-meter. The following plot is obtained:*
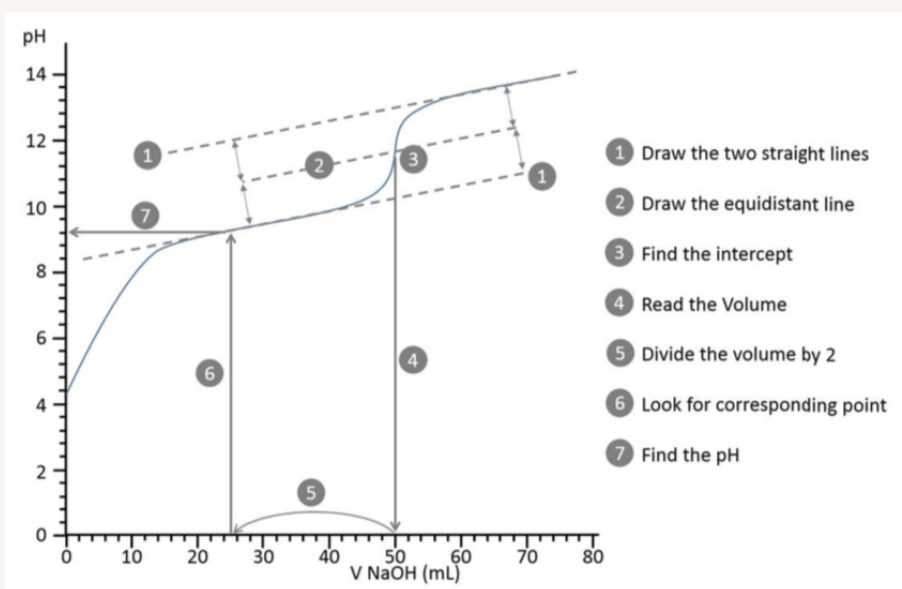


Figure 6: Titration curve of a HCN solution using NaOH. The numbers indicates the steps to follow as indicated in the answer.

*Use the graphical method to identify the equivalence point for the titration, the volume of base added at the equivalence point, the midpoint, and the HCN $K_a$.*

**Answer**: The equivalence point is obtained from the graph. (1) Draw the lines for the 2 straight sectors. (2) Draw the equidistant line. (3) Identify the equivalence point were the equidistant line intercepts the curve. (4) Draw a vertical line to find the volume; 50.0 mL. (5) The half-way point would be: 50.0 mL/2 = 25.0 mL. (6) Draw a vertical line up to the curve. (7) From the curve draw an horizontal line to find the pH; 9.21. The $pK_a$ = 9.21 (7), and therefore $K_a = 10^{-9.21} = 6.2 \times 10^{-10}$

# Procedure

## Preparing the setup

☐ *Step 1:* – Obtain a 50 mL buret, rinse it with distilled water, and verify that it operates correctly (you should be able to add drops but also larger quantities).

☐ *Step 2:* – Obtain a hot plate with magnetic stirring, a magnetic stirring rod, a stand, two 200 mL beakers, and a pH meter.

☐ *Step 3:* – Arrange the setup so that the beaker is on the hot plate, the pH meter is to its left, with the probe inserted in one of the beakers, and the tip of the buret is also slightly inserted into the beaker. The number markings on the buret should be facing you, and the valve should be accessible and operative.

☐ *Step 4:* – Rinse the buret with a small amount of 0.1 M NaOH solution. Discard the rinsing liquid. Fill the buret with fresh NaOH solution. Your instructor will either give you an unknown or instruct you to use the already prepared NaOH solution. Discard the first 3-4 mL (the volume of solution in the tip of the buret used for the rinsing).

> **Good Lab Practice**
>
> ✍ Burets are read from top to bottom.
>
> ✍ The volume added is calculated by difference. It is not necessary to start from 0 mL.
>
> ✍ Use a funnel to fill the buret but remove it always before the first reading. Drops from the funnel will affect the measurements.
>
> ✍ Do **never** refill the buret with the Erlenmeyer/beaker of the analyte below it. A spill would ruin the titration.

## Preparing the KHP solutions

☐ *Step 1:* – Put one of the beakers on the scale and set it to zero (T/O). The beaker must be dry. Remove the beaker from the scale to add a small amount of KHP. You need an amount between 0.45 and 0.55 grams. Record the value with all the decimals.

☐ *Step 2:* – Obtain 50.0 mL of distilled water in a graduated cylinder.

☐ *Step 3:* – Carefully add the 50.0 mL of distilled water from the graduated cylinder into the beaker containing the KHP.

☐ *Step 4:* – Repeat the procedire to prepare a second solution on a second beaker.

## Measuring

☐ *Step 1:* – Add the magnetic stirrer to one of the beakers, put the beaker on the hotplate, and set a gentle stirring speed. Do not start the heat on the plate!

☐ *Step 2:* – Clean the pH-meter probe before immersing it in the KHP solution.

☐ *Step 3:* – Either you are given an unknown or you will use the NaOH already prepared from the lab. Read and record the initial pH before adding any NaOH.

☐ *Step 4:* – Start adding the titrant (the base). After every addition (see next step) record the **buret reading** (not the volume added) and the corresponding pH measurement.

☐ *Step 5:* – NaOH should be added initially in 1 mL increments, but at a certain moment, additions should be reduced to 0.2 mL portions. Mind that the pH will change very slowly at the beginning and the end of the titration. However, around the equivalence point, the pH will change extremely fast with small additions of the titrant.

☐ *Step 6:* – Read the buret and record the volume with all the digits given by the buret plus the estimated digit.

☐ *Step 7:* – Add the titrant in 1 mL portions making sure the buret readings are precise.

☐ *Step 8:* – After every addition, estimate how much the pH changed from the previous pH measurement. If the pH has changed by less than 0.3 pH units, add 1 mL of titrant in the next step. If the pH has changed by 0.3 pH-units or more, begin adding the titrant in 0.2 mL portions.

☐ *Step 9:* – When adding 0.2 mL portions, if the pH change starts to slow down and increases by less than 0.3 pH-units between measurements **for at least 3 measurements in a row**, then you can start adding 1 mL portions again.

☐ *Step 10:* – Stop the titration when the pH exceeds 11.5.

☐ *Step 11:* – Do a second titration trial. Clean and reuse the magnetic stirred; in the results section, plot by hand the titration plot.

## Calculations

⓪ This is the molarity of the base solution, written on the label.

① This is the mass of your sample.

② These are the moles on your sample:

$$n_{KHP} = \frac{①}{204.22}$$

③ These are the molarity on your acid sample:

$$c_a = \frac{②}{50} \times 10^3$$

④ This is the burette reading in mL.

⑤ This is the PH as given by the OH meter.

⑥ This is the cumulative volume of base added.

**STUDENT INFO**

Name:                                Date:

**Pre-lab Questions**

# Titration Curve

1. The data below represents the titration of a weak base with a strong acid. Use the data below to answer the following questions:

| $V_{HCl}^{Added}$ mL | PH | $V_{HCl}^{Added}$ mL | PH | $V_{HCl}^{Added}$ mL | PH | $V_{HCl}^{Added}$ mL | PH |
|---|---|---|---|---|---|---|---|
| 0 | 11.12 | 45.01 | 8.3 | 49.97 | 6.1 | 50.32 | 3.5 |
| 0.71 | 10.9 | 45.95 | 8.2 | 49.98 | 5.9 | 50.4 | 3.4 |
| 1.48 | 10.7 | 47.89 | 7.9 | 49.99 | 5.7 | 50.63 | 3.2 |
| 1.96 | 10.6 | 48.31 | 7.8 | 50.00 | 5.4 | 50.8 | 3.1 |
| 4.03 | 10.3 | 48.65 | 7.7 | 50.01 | 5 | 51.01 | 3 |
| 6.18 | 10.1 | 49.31 | 7.4 | 50.02 | 4.7 | 51.27 | 2.9 |
| 11.06 | 9.8 | 49.45 | 7.3 | 50.03 | 4.5 | 51.61 | 2.8 |
| 13.18 | 9.7 | 49.56 | 7.2 | 50.04 | 4.4 | 52.04 | 2.7 |
| 18.12 | 9.5 | 49.72 | 7.0 | 50.06 | 4.2 | 52.58 | 2.6 |
| 20.85 | 9.4 | 49.78 | 6.9 | 50.08 | 4.1 | 53.27 | 2.5 |
| 26.58 | 9.2 | 49.83 | 6.8 | 50.1 | 4 | 54.15 | 2.4 |
| 29.41 | 9.1 | 49.89 | 6.6 | 50.13 | 3.9 | 55.28 | 2.3 |
| 37.02 | 8.8 | 49.91 | 6.5 | 50.16 | 3.8 | 56.73 | 2.2 |
| 40.94 | 8.6 | 49.93 | 6.4 | 50.2 | 3.7 | 58.63 | 2.1 |
| 42.53 | 8.5 | 49.95 | 6.3 | 50.25 | 3.6 | 61.11 | 2 |

    1.1. Plot PH (vertical axis) vs. volume of titrant added (horizontal axis), identifying the initial, mid, and endpoints.
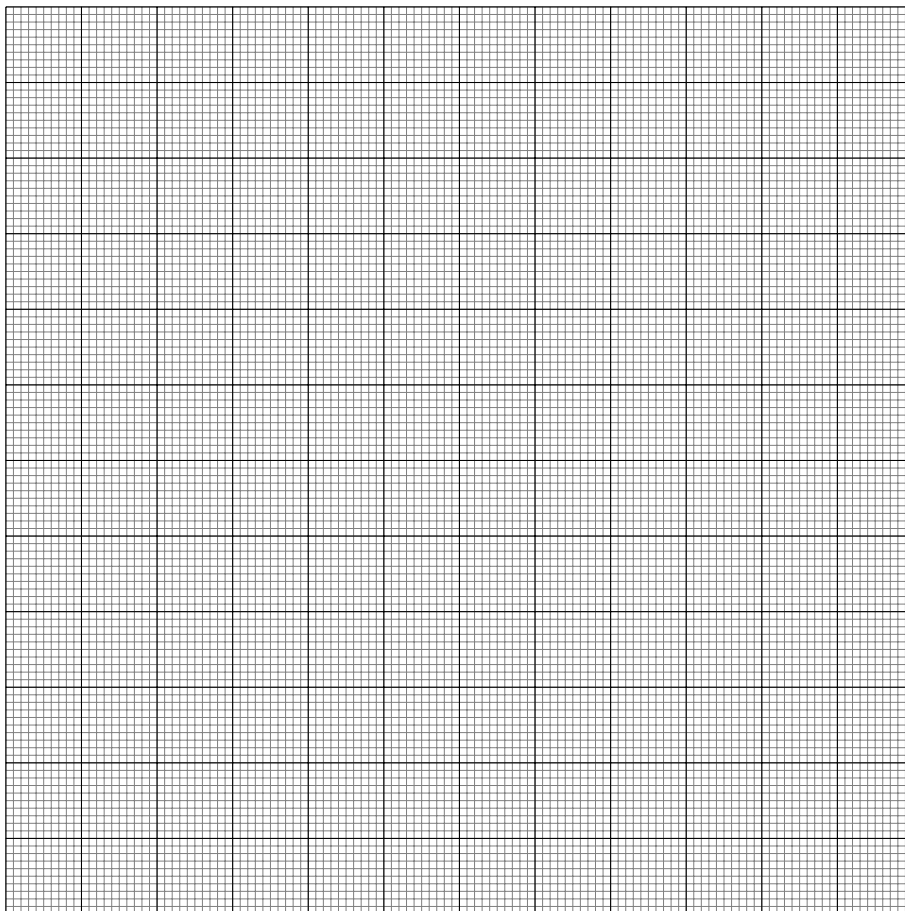
1.2. Fill the table below based on the plot above:

| Experimental Data | | | | | | |
|---|---|---|---|---|---|---|
| | Initial Point | | Midpoint | | Endpoint | |
| | $V_{HCl}^{Added}$ | PH | $V_{HCl}^{Added}$ | PH | $V_{HCl}^{Added}$ | PH |
| | 0 | | | | | |

1.3. Use the midpoint to compute the basicity constant of the titrate given that at that point $PH = PK_b$. Write down the $K_b$ value under the graph.

2. Calculate the PH of a 0.5M solution of an acid with $K_a = 1.4 \times 10^{-5}$.

**Results**
**EXPERIMENT**

# Titration Curve

$(0)$  $c_{\text{NaOH}}$ (M) = _____

| Trial 1 | | |
|---|---|---|
| KHP mass (g)  $(1)$ | | _____ |
| moles of KHP  $(2)$ | | _____ |
| $c_{KHP}$  $(3)$ | | _____ |

| Buret reading  $(4)$ | pH  $(5)$ | $V_{\text{NaOH}}^{Added}$ (mL)  $(6)$ |
|---|---|---|
| _____ | _____ | 0 |
| _____ | _____ | _____ |
| _____ | _____ | _____ |
| _____ | _____ | _____ |
| _____ | _____ | _____ |
| _____ | _____ | _____ |
| _____ | _____ | _____ |
| _____ | _____ | _____ |
| _____ | _____ | _____ |

| Trial 2 | | |
|---|---|---|
| KHP mass (g) | | _____ |
| moles of KHP | | _____ |
| $c_{KHP}$ | | _____ |

| Buret reading  $(4)$ | pH  $(5)$ | $V_{\text{NaOH}}^{Added}$ (mL)  $(6)$ |
|---|---|---|
| _____ | _____ | 0 |
| _____ | _____ | _____ |
| _____ | _____ | _____ |
| _____ | _____ | _____ |
| _____ | _____ | _____ |
| _____ | _____ | _____ |
| _____ | _____ | _____ |
| _____ | _____ | _____ |
| _____ | _____ | _____ |

| Buret reading | pH | $V_{\text{NaOH}}^{Added}$ (mL) | Buret reading | pH | $V_{\text{NaOH}}^{Added}$ (mL) |
|---|---|---|---|---|---|
| _____ | _____ | _____ | _____ | _____ | _____ |
| _____ | _____ | _____ | _____ | _____ | _____ |
| _____ | _____ | _____ | _____ | _____ | _____ |
| _____ | _____ | _____ | _____ | _____ | _____ |
| _____ | _____ | _____ | _____ | _____ | _____ |
| _____ | _____ | _____ | _____ | _____ | _____ |
| _____ | _____ | _____ | _____ | _____ | _____ |
| _____ | _____ | _____ | _____ | _____ | _____ |
| _____ | _____ | _____ | _____ | _____ | _____ |
| _____ | _____ | _____ | _____ | _____ | _____ |
| _____ | _____ | _____ | _____ | _____ | _____ |
| _____ | _____ | _____ | _____ | _____ | _____ |
| _____ | _____ | _____ | _____ | _____ | _____ |
| _____ | _____ | _____ | _____ | _____ | _____ |
| _____ | _____ | _____ | _____ | _____ | _____ |
| _____ | _____ | _____ | _____ | _____ | _____ |
| _____ | _____ | _____ | _____ | _____ | _____ |

| Buret reading | pH | $V_{\text{NaOH}}^{Added}$ (mL) | | Buret reading | pH | $V_{\text{NaOH}}^{Added}$ (mL) |
|---|---|---|---|---|---|---|
| _____ | _____ | _____ | | _____ | _____ | _____ |
| _____ | _____ | _____ | | _____ | _____ | _____ |
| _____ | _____ | _____ | | _____ | _____ | _____ |
| _____ | _____ | _____ | | _____ | _____ | _____ |
| _____ | _____ | _____ | | _____ | _____ | _____ |
| _____ | _____ | _____ | | _____ | _____ | _____ |
| _____ | _____ | _____ | | _____ | _____ | _____ |
| _____ | _____ | _____ | | _____ | _____ | _____ |
| _____ | _____ | _____ | | _____ | _____ | _____ |
| _____ | _____ | _____ | | _____ | _____ | _____ |
| _____ | _____ | _____ | | _____ | _____ | _____ |
| _____ | _____ | _____ | | _____ | _____ | _____ |
| _____ | _____ | _____ | | _____ | _____ | _____ |
| _____ | _____ | _____ | | _____ | _____ | _____ |
| _____ | _____ | _____ | | _____ | _____ | _____ |
| _____ | _____ | _____ | | _____ | _____ | _____ |
| _____ | _____ | _____ | | _____ | _____ | _____ |

| Buret reading | pH | $V_{NaOH}^{Added}$ (mL) | Buret reading | pH | $V_{NaOH}^{Added}$ (mL) |
|---|---|---|---|---|---|
| _____ | _____ | _____ | _____ | _____ | _____ |
| _____ | _____ | _____ | _____ | _____ | _____ |
| _____ | _____ | _____ | _____ | _____ | _____ |
| _____ | _____ | _____ | _____ | _____ | _____ |
| _____ | _____ | _____ | _____ | _____ | _____ |
| _____ | _____ | _____ | _____ | _____ | _____ |
| _____ | _____ | _____ | _____ | _____ | _____ |
| _____ | _____ | _____ | _____ | _____ | _____ |
| _____ | _____ | _____ | _____ | _____ | _____ |
| _____ | _____ | _____ | _____ | _____ | _____ |
| _____ | _____ | _____ | _____ | _____ | _____ |
| _____ | _____ | _____ | _____ | _____ | _____ |
| _____ | _____ | _____ | _____ | _____ | _____ |
| _____ | _____ | _____ | _____ | _____ | _____ |
| _____ | _____ | _____ | _____ | _____ | _____ |
| _____ | _____ | _____ | _____ | _____ | _____ |
| _____ | _____ | _____ | _____ | _____ | _____ |

| | Initial Point | | Midpoint | | Endpoint | |
|---|---|---|---|---|---|---|
| Experimental Data | | | | | | |
| | $V_{\text{NaOH}}^{Added}$ | PH | $V_{\text{NaOH}}^{Added}$ | PH | $V_{\text{NaOH}}^{Added}$ | PH |
| Trial 1 | 0 | | | | | |



Figure 7: PH (Y axis) vs. $V_{\text{NaOH}}^{Added}$ (X axis)

| | Initial Point | | Midpoint | | Endpoint | |
|---|---|---|---|---|---|---|
| | $V_{\text{NaOH}}^{Added}$ | PH | $V_{\text{NaOH}}^{Added}$ | PH | $V_{\text{NaOH}}^{Added}$ | PH |
| Trial 2 | 0 | | | | | |

*Experimental Data* (header spanning the table)
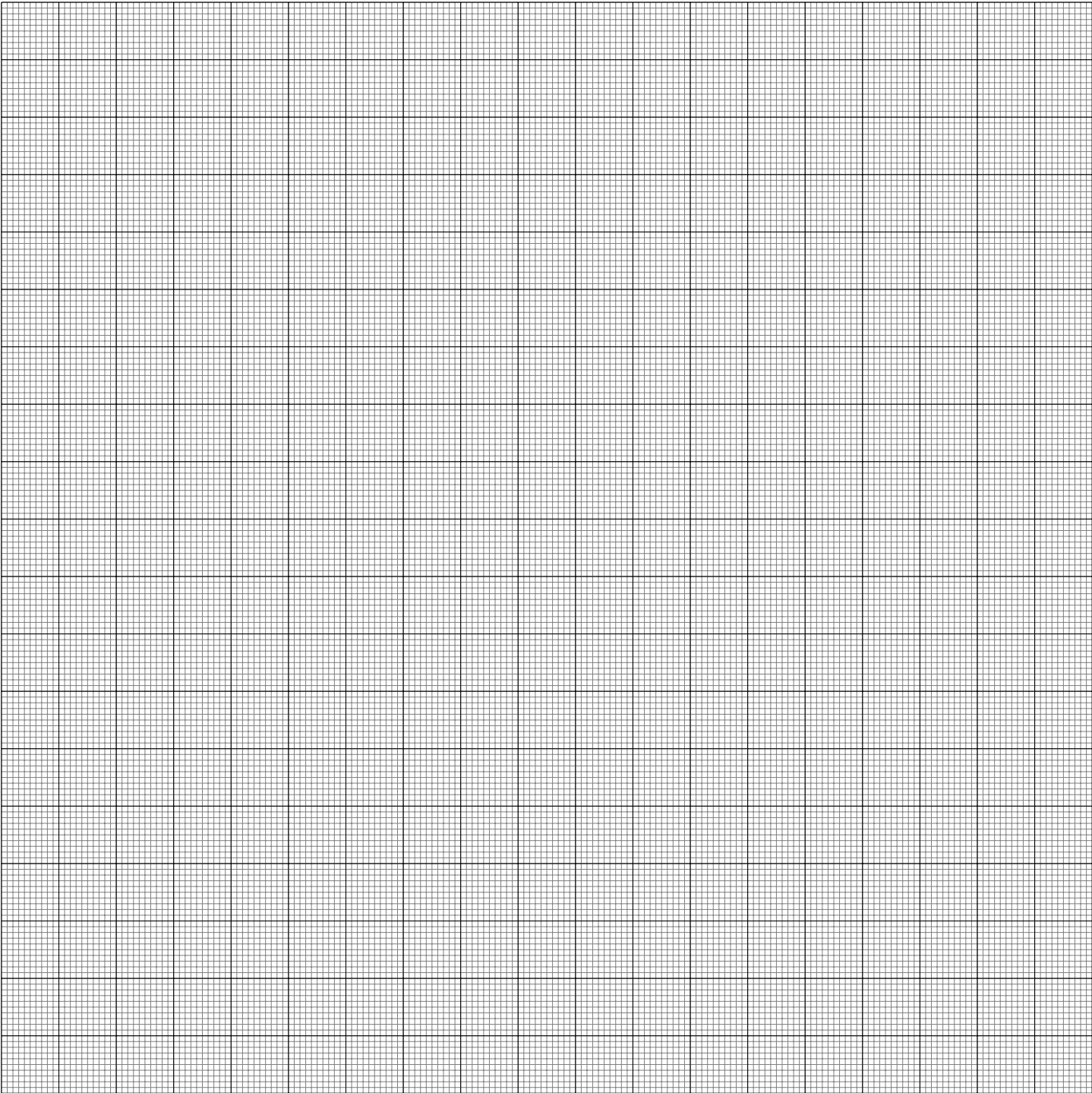
Figure 8: PH (Y axis) vs. $V_{\text{NaOH}}^{Added}$ (X axis)

**Post-lab Questions**

# Titration Curve

1. Preparing a NaOH solution, starting from a solid NaOH sample, is difficult because NaOH is very hygroscopic (absorbs water from the air). This affects the mass measured and therefore the real concentration expected. The NaOH solution used was estimated to be 0.10 M but it might not be correct. Using the information from the titration (mass of the phthalate), and knowing that the acid and the base react 1:1, calculate the real concentration from each trial, and the mean value.

|  | Trial 1 | Trial 2 |
|---|---|---|
| KHP mass | _____ | _____ |
| KHP moles | _____ | _____ |
| $V_{NaOH}$ @ equiv. | _____ | _____ |
| Real $c_b$, [NaOH] | _____ | _____ |
| Mean $c_b$, [NaOH] | _____ | |

2. Calculate the volume of NaOH for the halfway point (half of the volume added at the equivalence point) and locate in the graph the pH for the solution after that volume was added. Use the value of the pH to calculate the KHP $pK_a$.

|  | | |
|---|---|---|
| $V_{NaOH}$ @ halfway | _____ | _____ |
| pH @ halfway | _____ | _____ |
| $pK_a$ | _____ | _____ |
| Mean $pK_a$ | _____ | |

3. Using the $pK_a$ mean value, calculate KHP's $K_a$. Write the whole expression for $K_a$.

4. Using the KHP's $K_a$ and its initial concentration, calculate the theoretical pH before any NaOH was added, and compare the calculated values to the pHs measured experimentally.

|  | Trial 1 | Trial 2 |
| --- | --- | --- |
| KHP moles | _____ | _____ |
| $c_a$, [KHP] | _____ | _____ |
| Theoretical pH | _____ | _____ |
| Experimental pH | _____ | _____ |

5. Using the $K_a$ for KHP, calculate $K_b$ for its conjugated base, $C_8H_4O_4{}^{2-}$, given that $K_w = K_a \times K_b$.

**9**  Bleach Strength

<div style="text-align: center">EXPERIMENT</div>

# Strength of Laundry Bleach

## Goal

The goal of this laboratory is to perform an **oxidation-reduction titration** to determine the concentration of sodium hypochlorite (NaOCl) in commercial bleach samples.

## Materials

- ☐ A buret, a stad and a clamp
- ☐ 100mL, 50mL beakers
- ☐ 125mL Erlenmeyer
- ☐ 0.025M $Na_2S_2O_3$ solution
- ☐ solid KI

- ☐ 10% diluted bleach
- ☐ 10mL transfer pipet
- ☐ 2M HCl solution
- ☐ 0.2% starch solution

## Background

The properties of chlorine for bleaching fabrics were discovered in the 18th century by the French scientist Claude Berthollet. He was able to make an aqueous solution of sodium hypochlorite which was named after the quarter in Paris where it was produced, Javel. *Eau de Javel* (Javel water) is still used in French to name bleach.

At the beginning of the 18th century, the pharmacist Antoine Germain Labarraque discovered the disinfecting ability of another hypochlorite solution, this time calcium hypochlorite. The so-called "Eau de Labarraque" was employed in the disinfection of animal guts to make musical instrument strings. Hypochlorite was the first antiseptic product, helping to treat gangrene and putrescent wounds in people in the 1820s, and ending with the propagation of "cadaveric particles" in morgues.

Nowadays bleach is a common product at home, used to whiten clothes, remove stains, and as a disinfectant. Because of its strong bactericidal properties, hypochlorite is also used for disinfecting and to prevent the proliferation of algae in swimming pools. Bleach can be consumed. The CDC recommends adding eight drops of bleach per gallon of clear water. For cloudy water, the bleach quantity should be doubled to 16 drops per gallon. Bleach can be found in powder form as well, in the form of Bleaching powder. This is indeed, a solid combination of chlorine and slaked lime, introduced in 1799 by Scottish chemist Charles Tennant.

### Chlorine

Chlorine forms four different polyatomic anions with oxygen:

$ClO^-$ (hypochlorite)     $ClO_2^-$ (chlorite)     $ClO_3^-$ (chlorate)     $ClO_4^-$ (perchlorate)

These are called **oxoanions** and illustrate 4 possible oxidation states of chlorine atoms; +1, +3, +5, and +7 respectively. When the oxidation state of the chlorine decreases, for instance going from $ClO_4^-$ to $ClO_3^-$ (+7 → +5), it reduces. For reduction to happen another species must be oxidized. Chlorine is then acting as the **oxidizing agent**. Perchlorate it is the strongest oxidizing agent of the 4 oxoanions, but even $ClO^-$ can still be reduced to Cl- (Cl oxidation state -1).

## The first oxidation

To determine the concentration of $ClO^-$, two consecutive oxidation-reduction reactions will be performed. In the first reaction, all the $ClO^-$ present in the sample will be oxidized into $Cl^-$. The **oxidizing agent** will be $I^-$, which will be in turn reduced into $I_2$. The reaction, carried out in an acidic medium, will read as:

$$H^+_{(aq)} \quad + \quad ClO^-_{(aq)} \quad + \quad I^-_{(aq)} \quad \longrightarrow \quad I_{2\,(s)} \quad + \quad Cl^-_{(aq)} \quad + \quad H_2O_{(l)} \qquad \triangle \quad \text{(unbalanced)}$$
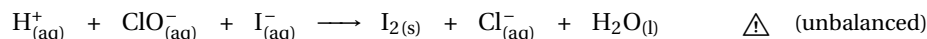
The reaction above is not balanced. You can determine the number of electrons being transferred using the oxidation states to help you balance the reaction. An excess amount of $I^-$ will be used to ensure that all the $ClO^-$ is oxidized. The iodine ($I_2$) formed in this reaction will be therefore limited by the amount of hypochlorite present in the sample. Keep in mind that the amount of hypochlorite is what we want to determine, and it can be stoichiometrically calculated from the amount of iodine produced. In the following step, the amount of $I_2$ will be determined using an oxidation-reduction titration. The solution might turn slightly brownish due to the presence of a Lewis complex between iodine and water.

## The oxidation-reduction titration

The titration to be performed accounts for the following redox reaction:

$$I_{2\,(s)} \quad + \quad S_2O_3{}^{2-}{}_{(aq)} \quad \longrightarrow \quad I^-_{(aq)} \quad + \quad S_4O_6{}^{2-}{}_{(aq)} \qquad \triangle \quad \text{(unbalanced)}$$
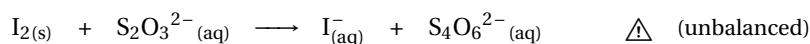
Again, this reaction is not balanced. Iodine ($I_2$) is reduced back to iodide $I^-$. Thiosulfate $S_2O_3{}^{2-}$ is the reducing agent, being itself oxidized into tetrathionate ions ($S_4O_6{}^{2-}$). The titration endpoint will be determined by adding starch as an indicator at the beginning of the reaction. Remember from previous experiments that starch and $I_2$ react turning the solution into a dark blue color, therefore, the titration should be stopped when all the iodine has been reduced and the solution becomes transparent.

## Redox reactions

Redox reaction are different than acid-base or precipitation reaction. They contain the same chemical element in two different states resulting from the loss or win of electrons. For example:

$$2\,Al_{(s)} \quad + \quad 3\,Cu^{2+}_{(aq)} \quad \longrightarrow \quad 2\,Al^{3+}_{(aq)} \quad + \quad 3\,Cu_{(s)} \text{ (redox reaction)}$$
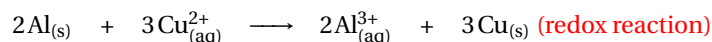
We have that neither $Al_{(s)}$ or $Cu^{2+}_{(aq)}$ are an acid or a base. Also there is no product precipitate. Hence, this reaction is not an acid-base reaction or a precipitation reaction. This is a redox reaction, as we have Al in two different states: as metallic $Al_{(s)}$ and as ionic $Al^{3+}_{(aq)}$, which result from the loss of an electron. In redox reaction there is always elements in the chemicals that lose electrons and chemicals winning electrons. The redox number, also called oxidation number or oxidation state helps compare elements that have lost (or gained) different charge. When comparing two elements with different redox numbers, the larger this number the more electrons the element has lost. Similarly, the smaller this number the smaller this number the more electrons the element has won.

We indicate redox numbers with roman number on top of the element. For example the redox number of manganese in this compound is +7: $\underline{Mn^{VII}}O_4{}^-$. The redox number can be a non integer number. There is five rules to identify the redox number of an element.

- ☞ **Rule 1** Single atoms or elements have zero redox number. Examples are Na or $H_2$, both with redox zero.

- ☞ **Rule 2** Monoatomic ions have redox number equal to their charge. Examples are $Na^+$ or $Cl^-$ with redox +1 and −1, respectively.

- ☞ **Rule 3** The redox number of fluorine is −1

- ☞ **Rule 4** The redox number of hydrogen on its covalent (e.g. $H_2O$) compounds is +1.

- ☞ **Rule 5** The redox number of oxygen in normal oxides (e.g. MgO) is normally −2, with the exception of peroxides (e.g. $H_2O_2$) in which is −1.

How do we calculate the redox number for example of manganese in this chemical: $\underline{Mn}O_4{}^-$, permanganate. In order to do this, we need to set up a formula so that the redox numbers of all elements in the molecule–taking into account the number of atoms in the molecule–equals to the charge. In the case of permanganate, let us call $x$ to the redox number of manganese. We know the redox of oxygen is −2 and we have four oxygens in the molecule. We also know the charge of the ion is −1. Therefore we have:

$$x + 4 \cdot (-2) = -1$$

If we solve for $x$ we obtain a redox number of manganese of VII.

**Example**

*Calculate the redox number of the elements underlined in the following molecules: (a) $K_2\underline{C}O_3$ and (b) $H_2\underline{C}O$.*

- - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - -

**Answer**: Let us set up the redox equation for the first compound, knowing that the redox of oxygen is $-2$ and potassium $+1$. The unknown variable $x$ represents the redox number of the underlined element. We have:

$$2 \cdot (+1) + x + 3 \cdot (-2) = 0$$

Mind we have two potassium and three oxygens hence we need to time the redox of K by two and the redox of O by three. If we solve for $x$ we obtain a redox number for carbon of IV. The redox equation for the second example is:

$$2 \cdot (+1) + x + (-2) = 0$$

Mind that according to the redox rules, the redox number of oxygen is $+1$. Solving for $x$ we have a redox number of zero.

By comparing the redox number of the same element in two different compounds we can figure out in what compound the element has lost or gained electrons. Look for example the case of $\underline{Cr}^{VI}_2O_7{}^{2-}$ and $\underline{Cr}^{III}_2O_3$. The same element in two different molecules has two different redox numbers. In the case of dichromate, the redox of Cr is VI, whereas in the case of chromium(III) oxide the redox of Cr is III. The larger the redox number the more oxidized is an element, and that means the element has lost electrons. The smaller the redox number the more reduced is the element and that means it has gained electrons. If we compare both case, we have that Cr in dichromate is oxidized–it lost electrons–and Cr in chromium(III) oxide is reduced–it gained electrons. The goal is to identify the element that undergoes oxidation and reduction in a chemical reaction. We can reach this goal by using the half-reaction method. Every redox reaction is composed of two process, a reduction and the oxidation. These two processes can be separated into two half-reactions so that the combination of both half-reactions lead to the balanced redox. Let us work on a simple unbalanced redox reaction:

$$\text{Al}_{(s)} + \text{Cu}_{(aq)}{}^{+2} \longrightarrow \text{Al}_{(aq)}{}^{+3} + \text{Cu}_{(s)}$$
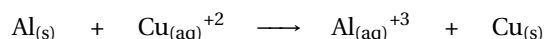
Solid $\text{Al}_{(s)}$ on the reactant side has zero redox number, whereas ionic $\text{Al}_{(aq)}{}^{+3}$ on the product side has redox number equal to III. Al has undergone oxidation as its redox number increases from zero to three. Al has lost three electrons. We can write the oxidation half-reaction:
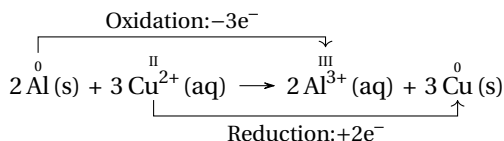
$$\text{Al}_{(s)} \longrightarrow \text{Al}_{(aq)}{}^{+3} + 3\,\text{e}^- \text{ (oxidation)}$$
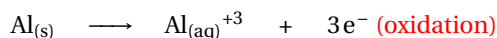
Mind that electrons have negative charge and we add electrons to compensate the charge of $\text{Al}_{(aq)}{}^{+3}$. Now let us compare the redox number of Cu. In the reactant side we have $\text{Cu}_{(aq)}{}^{+2}$ with redox of II. In the product side we have $\text{Cu}_{(s)}$ with zero redox number. Cu has undergone reduction as its redox number has decreases. This means it has gained electrons, in particular two electrons:

$$\text{Cu}_{(aq)}{}^{+2} + 2\,\text{e}^- \longrightarrow \text{Cu}_{(s)} \text{ (reduction)}$$
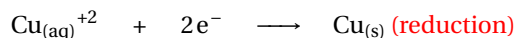
The goal here is to balance a redox chemical reaction by combining two half-reactions. In the example above the oxidation and reaction involve different number of electrons. Hence in order to be able to add both redox we need to time each half-reaction by a number so that the number of electrons cancel out. As the first reaction involved three electrons and the second two, we will do:

$$2 \cdot \left( \text{Al}_{(s)} \longrightarrow \text{Al}_{(aq)}{}^{+3} + 3\,\text{e}^- \right) \qquad \text{(oxidation)}$$
$$3 \cdot \left( \text{Cu}_{(aq)}{}^{+2} + 2\,\text{e}^- \longrightarrow \text{Cu}_{(s)} \right) \qquad \text{(reduction)}$$
$$\overline{2\,\text{Al}_{(s)} + 3\,\text{Cu}_{(aq)}{}^{+2} + \cancel{6\,\text{e}^-} \longrightarrow 2\,\text{Al}_{(aq)}{}^{+3} + 3\,\text{Cu}_{(s)} + \cancel{6\,\text{e}^-}} \text{ +} \qquad \text{(redox)}$$
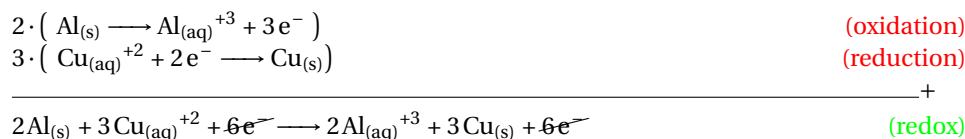
The overall balanced redox equation is:

$$\text{Oxidation:} -3\text{e}^-$$
$$2\,\overset{0}{\text{Al}}\,(s) + 3\,\overset{II}{\text{Cu}}{}^{2+}\,(aq) \longrightarrow 2\,\overset{III}{\text{Al}}{}^{3+}\,(aq) + 3\,\overset{0}{\text{Cu}}\,(s)$$
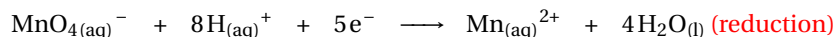$$\text{Reduction:} +2\text{e}^-$$

Redox reactions happen in either basic or acidic medium. Here we will go over how to balance redox reactions in acidic medium. In order to do this we will first separate the reaction in two half-reactions. In each semi-reaction we will balance all elements but hydrogen and oxygen. When all elements are balanced, we will proceed to balance O by adding $H_2O$ molecules and we will balance H by adding $H^+$. Finally, we all add electrons to compensate the charge of the reaction. Let us work on an example:

$$MnO_{4\,(aq)}{}^- \quad + \quad Fe_{(aq)}{}^{2+} \quad \longrightarrow \quad Mn_{(aq)}{}^{2+} \quad + \quad Fe_{(aq)}{}^{3+}$$
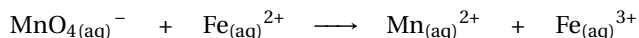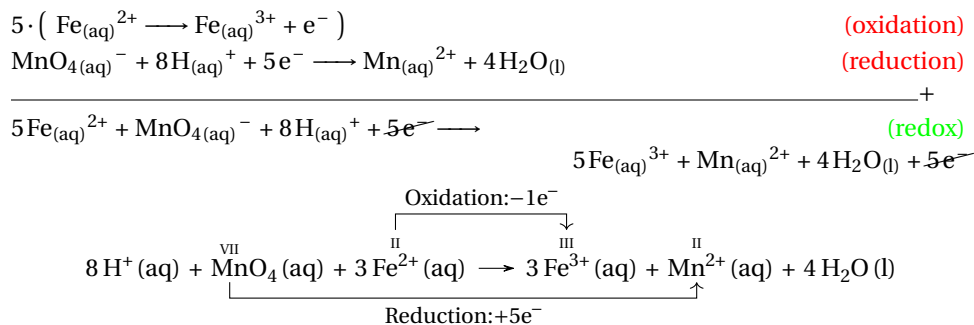
One of the semi-reactions involve Manganese whereas the other involves Iron. The redox number of Mn in permanganate is VII hence Manganese is being reduced, as its redox number decreases from VII to II, whereas Iron is being oxidized as its redox number increases from II to III. The oxidation half-reaction does not contain hydrogen or oxygen hence we will only have to balance the charger with one electron:

$$Fe_{(aq)}{}^{2+} \quad \longrightarrow \quad Fe_{(aq)}{}^{3+} \quad + \quad e^- \text{ (oxidation)}$$
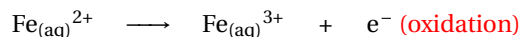
The reduction half-reaction contains oxygen. Hence, we will have to add $H_2O$ molecules to balance oxygen and $H^+$ to balance hydrogen. In particular, we will need two water molecules–as $MnO_4{}^-$ has four oxygens and we will have to add eight protons as we are adding four molecules of water. Finally, we need to add three electrons to equalize the charge:

$$MnO_{4\,(aq)}{}^- \quad + \quad 8\,H_{(aq)}{}^+ \quad + \quad 5\,e^- \quad \longrightarrow \quad Mn_{(aq)}{}^{2+} \quad + \quad 4\,H_2O_{(l)} \text{ (reduction)}$$

As the oxidation involves one electron and the reduction three, we need to time the oxidation by three:

$$5 \cdot \left( Fe_{(aq)}{}^{2+} \longrightarrow Fe_{(aq)}{}^{3+} + e^- \right) \qquad \text{(oxidation)}$$
$$MnO_{4\,(aq)}{}^- + 8\,H_{(aq)}{}^+ + 5\,e^- \longrightarrow Mn_{(aq)}{}^{2+} + 4\,H_2O_{(l)} \qquad \text{(reduction)}$$
$$\overline{\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad}+$$
$$5\,Fe_{(aq)}{}^{2+} + MnO_{4\,(aq)}{}^- + 8\,H_{(aq)}{}^+ + \cancel{5\,e^-} \longrightarrow \qquad \text{(redox)}$$
$$5\,Fe_{(aq)}{}^{3+} + Mn_{(aq)}{}^{2+} + 4\,H_2O_{(l)} + \cancel{5\,e^-}$$



$$8\,H^+\,(aq) + \overset{VII}{Mn}O_4\,(aq) + 3\,\overset{II}{Fe}{}^{2+}\,(aq) \longrightarrow 3\,\overset{III}{Fe}{}^{3+}\,(aq) + \overset{II}{Mn}{}^{2+}\,(aq) + 4\,H_2O\,(l)$$

Oxidation:$-1e^-$
Reduction:$+5e^-$

In order to balance a redox in basic medium we need first to balance the reaction in acidic medium. After, we will compensate all $H^+$ with $OH^-$ in both sides of the reaction. Mind that when combining $H^+$ with $OH^-$ we obtain $H_2O$. For example, in order to balance the following reaction in basic medium:

$$3\,Fe_{(aq)}{}^{2+} \quad + \quad MnO_{4\,(aq)}{}^- \quad + \quad 4\,H_{(aq)}{}^+ \quad \longrightarrow \quad 3\,Fe_{(aq)}{}^{3+} \quad + \quad Mn_{(aq)}{}^{2+} \quad + \quad 2\,H_2O_{(l)}$$
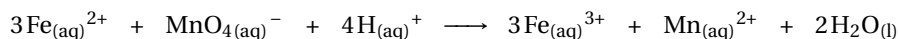
we will add four $OH^-$ in both sides:

$$3\,Fe_{(aq)}{}^{2+} \quad + \quad MnO_{4\,(aq)}{}^- \quad + \quad 4\,H_{(aq)}{}^+ \quad + \quad 4\,OH_{(aq)}{}^- \quad \longrightarrow \quad 3\,Fe_{(aq)}{}^{3+} \quad + \quad Mn_{(aq)}{}^{2+} \quad + \quad 2\,H_2O_{(l)}$$
$$+\,4\,OH_{(aq)}{}^-$$
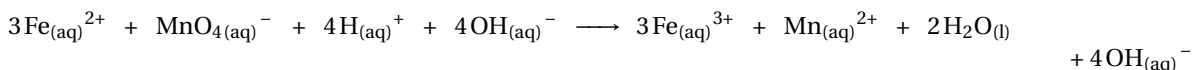
And after cancelling the four protons with the four hydroxyls, we have:

$$3\,Fe_{(aq)}{}^{2+} \quad + \quad MnO_{4\,(aq)}{}^- \quad + \quad 4\,H_2O_{(l)} \quad \longrightarrow \quad 3\,Fe_{(aq)}{}^{3+} \quad + \quad Mn_{(aq)}{}^{2+} \quad + \quad 2\,H_2O_{(l)} \quad + \quad 4\,OH_{(aq)}{}^-$$
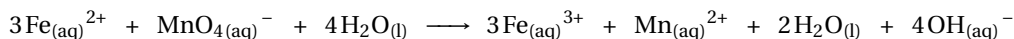
Now we have four water molecules in the left and two in the right. We will cancel two molecules from each side in order not to report water molecules twice:

$$3\,Fe_{(aq)}{}^{2+} \quad + \quad MnO_{4\,(aq)}{}^- \quad + \quad 2\,H_2O_{(l)} \quad \longrightarrow \quad 3\,Fe_{(aq)}{}^{3+} \quad + \quad Mn_{(aq)}{}^{2+} \quad + \quad 4\,OH_{(aq)}{}^-$$
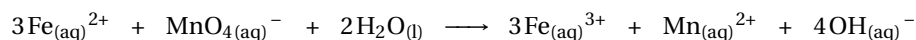
**Example**

*Balance the following redox in acidic medium:*

$$Cr_2O_7{}^{2-} \quad + \quad SO_3{}^{2-} \quad \longrightarrow \quad Cr^{3+} \quad + \quad SO_4{}^{2-}$$

**Answer**:
We locate the same element in both sides of the reaction with different redox number. We found Chromium in the form of dichromate ($Cr_2O_7{}^{2-}$) with redox number VI and Chromium in the product side with redox III. Therefore Chromium is being reduced, as its redox number decreases. Differently, we found sulphur in the reactants side in the form of sulfite ($SO_3{}^{2-}$) with redox number of IV and in the product side with redox number of VI. Therefore Sulphur is being oxidized. We will first set up the oxidation half-reaction knowing that we have different amounts of Cr in both side and that we will have to add water molecules to balance O and protons to balance H. As we have seven oxygens in $Cr_2O_7{}^{2-}$ we will have to add seven water molecules. Also, as we add seven water molecules we will have to add fourteen protons. We will need six electrons to compensate the charge:

$$Cr_2O_7{}^{2-} \; + \; 14\,H^+ \; + \; 6\,e^- \; \longrightarrow \; 2\,Cr^{3+} \; + \; 7\,H_2O \text{ (reduction)}$$
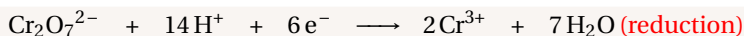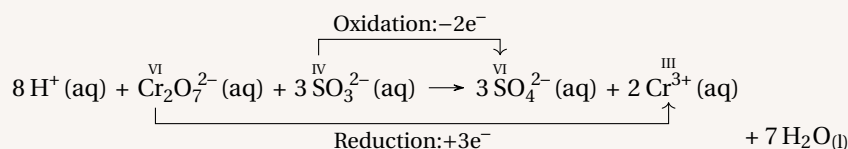
For the reduction half-reaction, we have a difference of one oxygen atoms and hence we will need one water molecule and two protons; we will need two electrons to compensate the charge:

$$SO_3{}^{2-} \; + \; H_2O \; \longrightarrow \; SO_4{}^{2-} \; + \; 2\,H^+ \; + \; 2\,e^- \text{ (oxidation)}$$
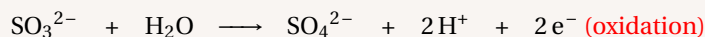
In order to add both half-reactions as the reduction involves two electrons and the oxidation six, we will have to multiply the reduction half-reaction by three:

$$1 \cdot \left( Cr_2O_7{}^{2-} + 14\,H^+ + 6\,e^- \longrightarrow 2\,Cr^{3+} + 7\,H_2O \right) \qquad \text{(reduction)}$$
$$3 \cdot \left( SO_3{}^{2-} + H_2O \longrightarrow SO_4{}^{2-} + 2\,H^+ + 2\,e^- \right) \qquad \text{(oxidation)}$$

$$Cr_2O_7{}^{2-} + 14\,H^+ + 3\,SO_3{}^{2-} + 3\,H_2O + \cancel{6\,e^-} \longrightarrow \qquad \text{(redox)}$$
$$2\,Cr^{3+} + 7\,H_2O + 3\,SO_4{}^{2-} + 6\,H^+ + \cancel{6\,e^-}$$
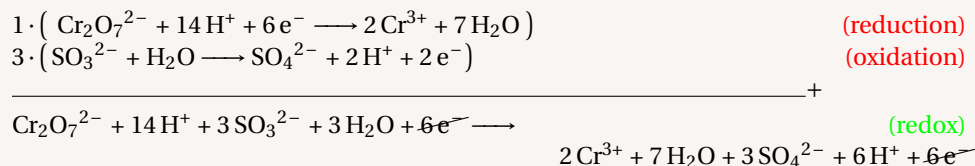
After we cancel the electrons and eliminate protons and water molecules, the balanced reaction is:

$$8\,H^+\,(aq) + \overset{VI}{Cr_2}O_7{}^{2-}\,(aq) + 3\,\overset{IV}{S}O_3{}^{2-}\,(aq) \longrightarrow 3\,\overset{VI}{S}O_4{}^{2-}\,(aq) + 2\,\overset{III}{Cr}{}^{3+}\,(aq) + 7\,H_2O_{(l)}$$

Oxidation: $-2e^-$

Reduction: $+3e^-$

## The experiment

The experimental part consists of a trial titration and an exact titration. The trial titration will be used to estimate the volume added at the endpoint of the titration. It is conducted quickly, adding portions of 1 mL until the endpoint is exceeded. The final result is not used for calculations. In the exact titration, an initial amount is added rapidly. This amount is calculated by subtracting 5 mL from the volume used in the trial titration. Like this it is possible to stop before the endpoint of the titration and to continue carefully, adding the titrant on a drop-by-drop basis until the precise endpoint. If time allows, the exact titration should be repeated and the mean volume used in calculations.

# Procedure

## Part A. Trial titration.

☐ *Step 1:* – Obtain a solution of bleach (the instructor might give you an unknown bleach sample, if so write down the Unknown # in the results section).

☐ *Step 2:* – Obtain a buret, a stand, and a clamp. Rinse the buret with distilled water and make sure the valve works properly.

☐ *Step 3:* – In a 100 mL beaker, obtain 70 mL of 0.025 M solution of $Na_2S_2O_3$. Use a small portion of the solution to rinse the buret. Discard the rinsing liquid and fill up the buret above the zero mark. Bring the volume in the buret to zero or below, discarding the excess liquid through the tip of the buret.

☐ *Step 4:* – In a 125 mL Erlenmeyer, obtain about one inch of a spatula of KI.

⚠CAUTION!

⚠ Bleach is a base.

⚠ Bases and acids can cause burns and clothes color loss.

⚠ Always wear eye protection and handle carefully.

!

☐ *Step 5:* – In a 50 mL beaker, obtain about 30 mL of a 10% bleach solution.

☐ *Step 6:* – Obtain a 10 mL transfer pipet. Pipet 10.0 mL of the bleach into the KI containing Erlenmeyer. Add 20 mL of distilled water from a graduated column and 20 drops of HCl 2 M. Homogenize the mixture by stirring the flask.

☐ *Step 7:* – Record the buret initial reading to the closest hundredth of mL.

☐ *Step 8:* – Place the Erlenmeyer under the buret and start the titration by adding 1 mL portions until the solution turns from brown to yellow.

☐ *Step 9:* – Add 40 drops of a 0.2% starch solution to the yellow solution in the Erlenmeyer.

☐ *Step 10:* – Proceed with the titration adding the $Na_2S_2O_3$ in 1 mL portions until it turns from dark color to colorless.

☐ *Step 11:* – Record the buret final reading and calculate the volume added.

☐ *Step 12:* – Discard the solution in the Erlenmeyer in the corresponding waste container.

**Part B. Exact titration.**

☐ *Step 1:* – Refill the buret with $Na_2S_2O_3$ 0.025 M. At this point you know how much volume you will need from the trial titration. You don not need to fill the buret up to zero but add a few milliliters more than the expected volume.

☐ *Step 2:* – In a 125 mL Erlenmeyer, obtain about one inch of a spatula of KI.

☐ *Step 3:* – Pipet 10.0 mL of the diluted bleach into the KI containing Erlenmeyer. Add 20 mL of distilled water from a graduated column and 20 drops of HCl 2 M. Homogenize the mixture by stirring the flask.

☐ *Step 4:* – Record the buret initial reading to the closest hundredth of mL.

☐ *Step 5:* – Place the Erlenmeyer under the buret and add 3 mL less than the volume used in the trial titration.

☐ *Step 6:* – Add 40 drops of a 0.2% starch solution to the solution in the Erlenmeyer.

☐ *Step 7:* – Continue the titration adding the titrant drop by drop until the solution turns transparent.

☐ *Step 8:* – Record the buret final reading in your notes.

☐ *Step 9:* – Discard the solution in the Erlenmeyer. If the time allows, do two exact titration replicates.

☐ *Step 10:* – When finished empty the buret and rinse it with plenty of distilled water. The buret should be stored empty, open, and upside down.

## Calculations

①This is the initial reading of the buret (often is zero if the buret is all filled up).

②This is the final reading of the buret after the endpoint has been reached.

③This is the volume of titrant used, $v_{S_2O_3^{-2}}$:

$$v_{S_2O_3^{-2}} = ② - ①$$

④This is the moles of thiosulfate used in the titration:

$$n_{S_2O_3^{-2}} = ③ \times 0.025 \times 10^{-3}$$

⑤ These are the moles of bleach in the (diluted) sample:

$$n_{\text{OCl}^{-1}} = \frac{n_{\text{S}_2\text{O}_3^{-2}}}{2} = \frac{④}{2}$$

⑥ This is the molarity of bleach in the (diluted) sample:

$$c_{\text{OCl}^{-1}}^{diluted} = \frac{n_{\text{OCl}^-}}{1 \times 10^{-2}} = \frac{⑤}{1 \times 10^{-2}}$$

⑦ This is the molarity of bleach in the (original, concentrated) sample:

$$c_{\text{OCl}^{-1}}^{concentrated} = c_{\text{OCl}^{-1}}^{diluted} \times 10 = ⑥ \times 10$$

**STUDENT INFO**

Name:                              Date:

**Pre-lab Questions**

# Strength of Laundry Bleach

1. Balance the following redox reaction, indicating the oxidizing and reducing agents:

$$\underline{\quad}H^+_{(aq)} \;+\; \underline{\quad}ClO^-_{(aq)} \;+\; \underline{\quad}I^-_{(aq)} \;\longrightarrow\; \underline{\quad}I_{2(s)} \;+\; \underline{\quad}Cl^-_{(aq)} \;+\; \underline{\quad}H_2O_{(l)}$$
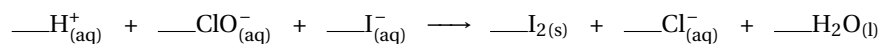
2. Balance the following redox reaction, indicating the oxidizing and reducing agents:

$$\underline{\quad}I_{2(s)} \;+\; \underline{\quad}S_2O_3^{2-}{}_{(aq)} \;\longrightarrow\; \underline{\quad}I^-_{(aq)} \;+\; \underline{\quad}S_4O_6^{2-}{}_{(aq)}$$
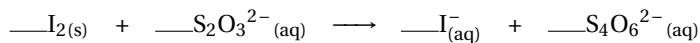
3. What is the proportion of bleach to water necessary to make water safe to drink?

4. What is the active ingredient in liquid bleach? And the active ingredient in bleach powder?

5. Indicate the oxidation state of all elements in the following species:

   × $H^+$
   × $H_2O$
   × $Cl^-$
   × $ClO^-$
   × $I^-$
   × $I_2$
   × $S_2O_3^{2-}$
   × $S_4O_6^{2-}$

**Results**
**EXPERIMENT**

# Strength of Laundry Bleach

| | Trial | Exact | | |
|---|---|---|---|---|
| | | 1 | 2 | 3 |
| (1) Initial buret reading (mL) | _____ | _____ | _____ | _____ |
| (2) Final buret reading (mL) | _____ | _____ | _____ | _____ |
| (3) $Na_2S_2O_3$ added (mL) | _____ | _____ | _____ | _____ |
| (4) Moles $Na_2S_2O_3$ | | _____ | _____ | _____ |
| (5) Moles NaOCl | | _____ | _____ | _____ |
| (6) [NaOCl] (diluted) (M) | | _____ | _____ | _____ |
| (7) [NaOCl] (original) (M) | | _____ | _____ | _____ |

Average Molarity,[NaOCl] (M)                    _____

Unknown number ( if given )                    _____

**STUDENT INFO**

Name:                                    Date:

**Post-lab Questions**

# Strength of Laundry Bleach

1. Commercial bleach claims a 5.25% NaClO by weight. Assuming a density of 1.0 g/mL for NaClO obtain the molarity of the solution. Consider your results in the laboratory, is the claim true?

2. Considering the bleach-water ratio of eight bleach drops per water gallon, what is the concentration, in molarity, of NaClO in the dilution?

**10** Relative strength of some acids

<div align="center">

EXPERIMENT

# Acids Strength

</div>

## Goal

The goal of this laboratory is to learn three different techniques to measure pH.

## Materials

- ☐ 5 jumbo testube and rack

- ☐ 100mL, 50mL beaker

- ☐ Indicator solutions

- ☐ 0.1 M $H_3PO_4$, 0.1 M $CH_3COOH$, 0.1 M $NaH_2PO_4$, 0.1 M $Zn(NO_3)_2$, and 0.1 M $NH_4NO_3$

- ☐ Distilled water and tap water

- ☐ Unknown solution

## Background

Acids are considered dangerous substances and while it is true that special care must be taken when handling some of these products, many acids are used in daily life with great simplicity. For example, aspirin's active principle ingredient is acetylsalicylic acid, vinegar is a 5% solution of acetic acid, and vitamin C is ascorbic acid.

Acids are defined by Brønsted-Lowry as proton ($H^+$) donors because when dissolved in water, acids dissociate by releasing protons. Strong acids dissociate completely into two ions: the anion is the acid conjugate base and the the cation is a proton. For stoichiometric reasons, the concentration of each ion in the solution equals the initial concentration of the acid. Weak acids do not dissociate completely but, instead, only do so to a certain extent. The strength of weak acids depends on how much they dissociate, a ratio characterized by the acid dissociation constant, $K_a$.

For a certain weak acid

$$HA \quad \rightleftharpoons \quad H^+ \quad + \quad A^-$$

The equilibrium can be characterized by the expression:

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

where $K_a$ (capital letter) is the dissociation constant and the brackets represent the concentrations of the respective species.

### pH

The acidity depends on the concentration of $H^+$ in the solution, which will always be a value between $10^{-14}$ and 1. To avoid using such a large and complex range, a logarithmic scale is preferred, ranging from 0 to 14.

This scale is called the pH, defined by Danish biochemist Sørensen in 1909 as the "power of Hydrogen".

$$pH = -log[H^+]$$

Considering that the strength of acids is their power to generate $H^+$, and to compare the strength of different acids, pH should be measured.

In this experiment, the pH for different solutions will be measured using three different approaches; indicators, pH paper, and a pH meter. Each of these techniques has a different accuracy. While using **pH indicators** it is only possible to determine a range for the pH, **pH paper** will provide an estimated unit, and the **pH-meter** will read down to the decimals.

## Indicators

There are several techniques to locate the endpoint during a titration. On one hand, we can use a PH meter and measure PH during the titration. The endpoint locates between the initial and final plateau. We can also use an automatic titrator, a machine that automatically mixes the acid and the base while displaying the PH. Another technique uses an indicator that changes color when the PH changes from acidic to basic or the opposite. Acid-base indicators are water-soluble organic dyes that have a different color depending on PH. Halochromism is the effect of changing color due to changes on a external force such as PH. Many flowers or plants exhibit this quality. For example, the french hydrangea is a plant that changes color depending on the acidity of the soil. Turmenic is a specie that turn from yellow to brown when the PH increases. indicator can be extracted from many plants and fruits such as red cabbage, geranium, poppy, rose petals or blueberries. Indeed, indicators are weak acids that exist in a conjugate base form as well. Both the acid (the indicator form with the hydrogen attached) and the conjugate base have a different color due to differences in their electronic structure that transform into differences absorbing light. For example, phenolphthalein is a common acid-base indicator that is transparent when the PH is acidic and pink when the PH is basic. The equivalency point of a titration (when acid and base are neutralized) is not necessarily the end point (when the indicator changes color). However, if both points are close enough chemical indicators are an accurate way to visually locate the equivalency point during a titration. As indicators are weak acids, each particular indicator is characterized by a constant of acidity referred to as $K_{In}$ so that

$$HIn_{(aq)} \quad \overset{H_2O}{\rightleftharpoons} \quad H^+_{(aq)} \quad + \quad In^-_{(aq)} \qquad K_{In} \quad = \quad \frac{\left[H^+\right]\cdot\left[In^-\right]}{\left[HIn\right]}$$
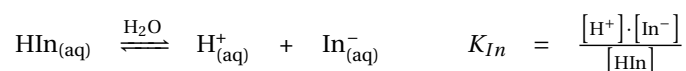
The change in color is considered to happen when the difference between the acidic and basic form of the indicator is an order or magniture–ten times–different. This is the ten times rule. For this difference, we have that

$$PH \quad = \quad PK_{In} \, \pm \, 1$$

We can always use a different value for the difference ($\Delta$) between the acid and basic form of an indicator so that the PH range will be given by

$$PH \quad = \quad PK_{In} \, \pm \, log(\Delta)$$

This expression helps with the selection of the indicator for a given titration. For example, if we want to select an indicator that changes color when the difference between acid and base form is 5 times ($\Delta = 5$), then the OH range would be: $PH = PK_{In} \pm 0.7$ A good indicator will turn into a different color within the transition between acid and basic PH during a titration. For example, for the titration of hydrochloric acid with sodium hydroxide, the PH changes from 5 before the equivalency point to 8 after. Any indicator with $PK_{In}$ between 5 and 8 would be able to accurately indicate the stoichiometric point. Examples are bromothymol blue, m-nitrophenol, and even phenolphthalein that transition color at 8. For the titration of a weak acid and a strong base, the selection of an indicator is more difficult as the difference between the acidic and basic plateaus during the titration is less pronounced. We must choose an indicator that changes color more closely to the end point. Litmus paper is an indicator heavily used for quick PH testing in labs. It contains a mixture of dyes that were extracted originally from lichens. There are two main types of litmus paper, red and blue litmus. Light blue litmus paper turns red when the medium is acidic, whereas red litmus paper turns blue in basic mediums. By wetting a piece of litmus paper one can also test for the acidity of gases, and for example, ammonia vapor would turn blue a piece of wet red litmus paper.

| Acid-base indicators showing ample representations of their colors | | | |
|---|---|---|---|
| Name | PH Range | Color acid form | Color basic form |
| Thymol blue (acid range) | 1.2-2.8 | red | yellow |
| Thymol blue (basic range) | 8.0-9.6 | yellow | blue |
| Methyl orange | 3.1-4.4 | red | orange |
| Methyl red | 4.4-6.2 | red | yellow |
| Bromomethyl blue | 6.0-7.6 | yellow | blue |

## The experiment

The experiment today is divided into the following parts:
   i) Determining pH range using indicators. ii) Determining pH using pH paper. iii) Determining pH using a pH meter.

## Part A. Determining pH range using indicators.

A pH indicator is a chemical substance that, when added to a solution, changes its color depending on the solution's pH. The pH at which color changes is called the **equivalence point**. Some indicators have one equivalence point while others have more than one equivalence points. By using an indicator it will be possible to determine a pH range only. Combining different indicators the range can be narrowed down.

---

**Example**

*We test a sample with three different indicators by dividing the sample into three small samples. Each small sample is tested using an indicator from the following list: i) Indicator A is colorless for pH values lower than 10 and turns pink for a pH greater than 10. ii) Indicator B is blue up to pH 3, then it turns colorless. iii) Indicator C is colorless for a pH lower than 6, when it turns red. The red color changes to yellow between pH 9 and pH 10, and stays yellow for higher pH values. Estimate the pH range for the solution if the three samples are colorless.*

- - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - -

**Answer**: Indicator A tells that the solution's pH is lower than 10. Therefore, the range must be 0 < pH < 10. Indicator B shows that the solution's pH is greater than 3 (3 to 14). This information, combined with that of indicator A, narrows the pH range to 3 < pH < 10. Indicator C tells that the solution's pH is lower than 5. The final range is 3 < pH < 5.

---

## Parts B. Determining pH using pH-paper.

pH paper, or **universal pH paper** is a strip of paper impregnated with a mixture of indicators. The paper changes color smoothly for each pH value and the pH is determined by matching the color of the paper with that in a chart attached to the pH paper. In the best case, by using pH paper it will be possible to select one value for the pH, although in some situations when the color is not one in the chart, it will be possible to indicate a range of two numbers only.

## Parts C. Determining pH using a pH-meter.

pH meters are scientific instruments that measure the pH of solutions. The tool has a probe that is inserted in the liquid and measures the concentration of protons based on the voltage between two electrodes. Their use is similar to that of a conductivity-meter, and some instruments can perform both tasks. Probes need to be cleaned after each measurement to avoid contamination and should never be touched with the hands or paper towels. Calibration of the tool with solutions of known pH ensures the best accuracy. After use, probes are best kept moist, typically in distilled water. A pH meter can offer a precision down to the hundredth of the unit of pH.

# Procedure

## Part A. Determining pH range using indicators.

☐ *Step 1:* – Obtain 5 jumbo test tubes and a rack. Clean the test tubes and let them drain upside down in the rack.

☐ *Step 2:* – Obtain a 100 mL beaker with plenty of distilled water and transfer 4.0 mL in a graduated cylinder.

☐ *Step 3:* – Label one test tube with the letter R, and pour the 4.0 mL of distilled water into it. This test tube will be used as a volume reference for the following test tubes.

☐ *Step 4:* – In a 50 mL beaker get 40 mL of one of the following list of solutions (you will use the others further in the experiment). These solutions are going to be referred to here as the acid or base solutions.

1. $0.1 \, M \, H_3PO_4$
2. $0.1 \, M \, CH_3COOH$
3. $0.1 \, M \, NaH_2PO_4$
4. $0.1 \, M \, Zn(NO_3)_2$
5. $0.1 \, M \, NH_4NO_3$
6. Distilled water
7. Tap water
8. Unknown solution

> **⚠ CAUTION!**
>
> ⚠ Handle concentrated acids with care to avoid chemical burns.
>
> ⚠ Are you wearing your goggles? Do you know where the eye-washer is?

☐ *Step 5:* – Obtain a 250 mL beaker for waste, a medicine dropper or a plastic pipette

☐ *Step 6:* – Label the rest of the test tubes from 1 to 4. Use test tube R as a reference for the volume to add in the following test tubes. Rinse the dropper with the distilled water (discarding it in the waste beaker) between different solutions. Add 4.0 mL of the solution chosen to each test tube.

☐ *Step 7:* – Add two drops of Thymol Blue to test tube 1. Using the color table provided in the background section, indicate the PH range of the solution.

☐ *Step 8:* – Add two drops of Methyl Orange to test tube 2. Using the color table provided in the background section, indicate the PH range of the solution.

☐ *Step 9:* – Add two drops of Methyl Red to test tube 3. Using the color table provided in the background section, indicate the PH range of the solution.

☐ *Step 10:* – Add two drops of Bromothymol Blue to test tube 4. Using the color table provided in the background section, indicate the PH range of the solution.

☐ *Step 11:* – Record the colors on the results page.

☐ *Step 12:* – Reserve the acid or base solution for Parts B and C (the beaker you used to fill the test tubes). Set the beaker on a paper towel and label it.

☐ *Step 13:* – Discard the colored solutions tested with the indicator and clean the test tubes.

☐ *Step 14:* – Repeat steps 4 to 12 all other solutions given in Step 4. Make sure to rinse the dropper.

## Part B. Determining pH using pH-paper.

☐ *Step 1:* – Obtain a stirring rod and the universal indicator paper. Be careful not to contaminate the paper with dirty gloves or bare hands. Always set the (small) pieces of paper on a clean paper towel.

☐ *Step 2:* – Rinse the stirring rod with the wash bottle over the waste beaker. Rinse thoroughly between different solutions.

☐ *Step 3:* – Immerse the tip of the stirring rod in one solution and touch a piece of pH paper with the rod.

☐ *Step 4:* – Match the color of the drop on the paper with the color chart on the plastic case. Record the pH value in the results section.

☐ *Step 5:* – Repeat the same process; rinsing, dipping, and touching, for the rest of the solutions.

☐ *Step 6:* – Reserve the solutions in the beakers for part C.

## Part C. Determining pH using a pH-meter.

☐ *Step 1:* – Install the pH meter. The probe of the instrument is immersed in a buffer solution that must be kept aside until the end of the experiment.

☐ *Step 2:* – Press Calibrate (top right menu) and make sure the PH is set to the buffer solution's value (i.e. 4.00).

☐ *Step 3:* – Cleaning and measuring. It is very important to follow the cleaning steps before each measurement. You will need a 100 mL beaker labeled waste a wash bottle and a 100 mL beaker with distilled water.

1. Rinse the probe using the wash bottle over the waste beaker.
2. Dip the probe 3-4 times into the 250 mL beaker with clean distilled water.
3. Dip the probe into the solution to be measured. Use a 50 mL beaker with at least 25 mL of solution.
4. Repeat cleaning steps 1 and 2.

☐ *Step 4:* – Following the procedure outlined in the step above, measure the eight solutions.

☐ *Step 5:* – Record all the values.

☐ *Step 6:* – Make sure you leave the PH meter's probe immersed in the buffer solution, as you originally found it.

**Pre-lab Questions**

# Acids Strength

1. Find the definition of the following concepts:

   (a) Acids (according to Brønsted-Lowry definition).

   (b) pH.

2. You add a few drops of tymol blue to a clear solution and its color quickly changes to red. What is the PH range of the solution?

3. You add a few drops of tymol blue to a clear solution and its color quickly changes to orange. What is the PH range of the solution?

4. Name the three methods to determine pH to be used in this laboratory.

5. Order the three methods from the most accurate to the least accurate, according to your expectations.

6. We test a sample with three different indicators by dividing the sample into three small samples. Each small sample is tested using an indicator from the following list: i) Indicator A is colorless for pH values lower than 10 and turns pink for a pH greater than 10. ii) Indicator B is blue up to pH 3, then it turns colorless. iii) Indicator C is colorless for a pH lower than 6 when it turns red. The red color changes to yellow between pH 9 and pH 10, and stays yellow for higher pH values. Estimate the pH range for the solution if the samples tested with indicators A and B become colorless and the one tested with indicator C turns reddish.

**Results**
**EXPERIMENT**

# Acids Strength

| Solution | Indicators | | | | | | | | PH Paper | PH Meter |
|---|---|---|---|---|---|---|---|---|---|---|
| | Thymol Blue | | Methyl Orange | | Methyl Red | | Bromothymol Blue | | | |
| | Color | PH Range | Color | PH Range | Color | PH Range | Color | PH Range | PH | PH |
| $H_3PO_4$ | ___ | ___ | ___ | ___ | ___ | ___ | ___ | ___ | ___ | ___ |
| $CH_3COOH$ | ___ | ___ | ___ | ___ | ___ | ___ | ___ | ___ | ___ | ___ |
| $NaH_2PO_4$ | ___ | ___ | ___ | ___ | ___ | ___ | ___ | ___ | ___ | ___ |
| $Zn(NO_3)_2$ | ___ | ___ | ___ | ___ | ___ | ___ | ___ | ___ | ___ | ___ |
| $NH_4NO_3$ | ___ | ___ | ___ | ___ | ___ | ___ | ___ | ___ | ___ | ___ |
| Distilled water | ___ | ___ | ___ | ___ | ___ | ___ | ___ | ___ | ___ | ___ |
| Tap water | ___ | ___ | ___ | ___ | ___ | ___ | ___ | ___ | ___ | ___ |
| Unknown | ___ | ___ | ___ | ___ | ___ | ___ | ___ | ___ | ___ | ___ |

Unknown # ___　　　　Unknown Indentity ___

**Post-lab Questions**

# Acids Strength

1. Based on your observation, identify the unknown.

2. Based on your observation, which of the three techniques is the most accurate?

3. Calculate the concentration of $H_3O^+$ ions in the most acidic solution, using the pH-meter value.

4. Calculate the concentration of $H_3O^+$ ions in the less acidic solution, using the pH-meter value.

## 11  Entropy

<div align="center">

**EXPERIMENT**

# Entropy and spontaneity

</div>

## Goal

The goal of this laboratory experiment is to calculate the minimum entropy change for a chemical reaction involving the dissolution of sodium nitrate.

## Materials

☐ A coffee-cup calorimeter

☐ A thermometer and a lit for the calorimeter

☐ $NaNO_3(s)$

## Background

### Standard molar entropy

The standard molar entropy of a substance is the absolute entropy of one more substance at 1 atm. Entropies are absolute properties in contrast to other relative thermodynamic functions like the enthalpy in which a set of molecular states act as a reference. The tabulated standard entropy values are listed at the end of the chapter at one bar and 25 °C, the conventional temperature for reporting thermodynamic data. The units of molar entropy are J/molK. Molar entropies tend to be small values–as the unit joule is a small unit of energy. Finally, entropies can be positive or negative values.

### Factors affecting entropy

We can qualitatively rationalize the trends between the standard molar entropy values for different substances and different conditions (temperature, volume, pressure) by using some simple rules described below:

ℽ **The state of matter:** The standard entropy of gases is larger than the standard entropy of liquids as gases present a larger degree of freedom (possible configurations) than liquids. The standard entropy of liquids is larger than the standard entropy of solids as liquids present a large degree of freedom than solids. The molecules of a liquid molecules can jiggle more in comparison with the molecules of a solid. Overall, we can assume that liquids and solid has almost null entropy whereas gases have very large entropy. For example, the entropies of ice, water, and steam are respectively 41, 69.95, and 69.95 J/molK.

ℽ **Molar mass:** For monoatomic substances (e.g. Ne, Ar, etc.) the larger the atomic weight the larger entropy. This is because the energy levels of larger molecules are more packed, and hence are easier to access at a given temperature.

ℽ **Molecular complexity:** For substances with comparable molar mass ($O_3$ and $F_2$), the more complex the molecule the larger entropy, as the number of degrees of freedom is directly correlated with the number of microstates.

ℽ **Temperature:** Temperature increases entropy as the system has more accessible microstates. The plot below represents the entropy change with temperature for a substance.

ℽ **Number of particles:** The larger the number of particles of a system, the larger the entropy, as the more particles the more microstates or possible configurations.

ℽ **Volume:** The larger the volume of a system, the larger the entropy, as the larger volume the more microstates of possible configurations.

## Calculating entropy changes in reactions

We can calculate the standard entropy of a reaction in a similar way as we calculate the standard enthalpy of a reaction:

$$\boxed{\Delta S_R^\circ = \Delta S_{products}^\circ - \Delta S_{reactants}^\circ} \quad \text{Entropy change} \tag{1}$$

where:

$\Delta S_R^\circ$ is the standard entropy change of the reaction

$\Delta S_{products}^\circ$ is the standard entropy of all products

$\Delta S_{reactants}^\circ$ is the standard entropy of all reactants

It is important to take into account the stoichiometric coefficients. For example, for the reaction:

$$2\,CH_3OH_{(g)} \quad + \quad 3\,O_{2\,(g)} \quad \longrightarrow \quad 2\,CO_{2\,(g)} \quad + \quad 4\,H_2O_{(l)}$$

We have the entropy values of: $S^\circ(CH_3OH_{(g)})$=239.7 J/K· mol, $S^\circ(O_{2\,(g)})$=161.1 J/K· mol, $S^\circ(CO_{2\,(g)})$=213.79 J/K· mol, and $S^\circ(H_2O_{(l)})$=69.95 J/K· mol. We can calculate $\Delta S_R^\circ$:

$$\Delta S_R^\circ = \Delta S_{products}^\circ - \Delta S_{reactants}^\circ =$$
$$\left(2 \cdot S^\circ(CO_{2\,(g)}) + 4 \cdot S^\circ(H_2O_{(l)})\right) - \left(2 \cdot S^\circ(CH_3OH_{(g)}) + 3 \cdot S^\circ(O_{2\,(g)})\right)$$
$$= \left(2 \cdot 213.79 + 4 \cdot 69.95\right) - \left(2 \cdot 239.7 + 3 \cdot 161.1\right) = -255.32\, J/K$$

## Estimating the sign of the entropy changes in reactions

Oftentimes times were are more interested in predicting the sign of the entropy change of a reaction than in computing the exact value. This is because the sign can be used to estimate whether a reaction proceeds spontaneously. Two basic rules are used to estimate the entry change sign:

⚥ **The state of matter:** solids and liquids have very low entropy in comparison to gases. For example, in the case below, we have the production of liquid water from ice produces entropy as liquids have more entropy than solids:

$$H_2O_{(s)} \longrightarrow H_2O_{(l)} \qquad\qquad\qquad \Delta S_R^\circ > 0$$

On the other hand, the condensation of water vapor to produce a liquid consumes entropy, as liquids have less entropy than gases:

$$H_2O_{(g)} \longrightarrow H_2O_{(l)} \qquad\qquad\qquad \Delta S_R^\circ < 0$$

⚥ **The number of molecules:** the larger the number of molecules of gas the larger entropy. For example, in the reaction below we have that we produce three molecules from two molecules. Hence, the entropy increases.

$$2\,SO_{3\,(g)} \longrightarrow 2\,SO_{2\,(g)} + O_{2\,(g)} \qquad\qquad\qquad \Delta S_R^\circ < 0$$

However, this rule only works if we only take into account the number of gas molecules. For example, in the reaction below we produce two gas molecules from three gas molecules and hence we lose entropy:

$$2\,H_2S_{(g)} + SO_{2\,(g)} \longrightarrow 3\,S_{(s)} + 2\,H_2O_{(g)} \qquad\qquad\qquad \Delta S_R^\circ < 0$$

## Gibbs free energy

The Gibbs free energy is just a combination of enthalpy and entropy for a given temperature:

$$G = H - T \cdot S \tag{2}$$

Working at constant temperature, we can compute the change in Gibbs free energy as:

$$\boxed{\Delta G^T = \Delta H - T\Delta S} \quad \text{Gibbs free-energy} \tag{3}$$

where:

$\Delta G^T$ is the Gibbs free-energy change at constant temperature

$\Delta H$ is the enthalpy change

$\Delta S$ is the entropy change

$T$ is the temperature

Gibbs free energy is a state function that only depends on the final and initial state and not the path followed. At the same time, Gibbs free energy depends on temperature and pressure–we will discuss more about this at the end of the section. More importantly, the change in Gibbs free energy is associated with the spontaneity of the process. Gibbs free-energy decreases with temperature and the decrease is sharper for gases in comparison to liquids, and at the same time, the decrease is also sharper for liquids in comparison to solids.

## Gibbs free energy and spontaneity

The Gibbs free-energy change of a reaction is associated with the spontaneity of the process or with its state of equilibrium. In particular, reactions that produce Gibbs free energy are nonspontaneous. Differently, reactions consuming free energy are indeed spontaneous. Finally, reactions without a change in free energy are in equilibrium.

- ɤ $\Delta G < 0$**:** The reaction is spontaneous

- ɤ $\Delta G = 0$**:** The reaction is in equilibrium

- ɤ $\Delta G > 0$**:** The reaction is nonspontaneous

This is because the expression of Gibbs free energy is related to the total entropy change of the universe given by the second law of thermodynamics:

$$\Delta G^T = \Delta H - T\Delta S \quad \text{and} \quad T\Delta S^{T,P}_{univ} = -(\Delta H - T\Delta S) \tag{4}$$

Hence, we have that

$$\Delta G^T = T\Delta S^{T,P}_{univ} \tag{5}$$

This last expression means that an increase in total entropy is accompanied by a decrease in Gibbs free energy at constant pressure and temperature. At the same time, the expression indicates that the direction of spontaneous change corresponds to a decrease of Gibbs free energy, at constant temperature and pressure.

# How to find extrapolated temperature

A calorimeter is ideally an isolated system. That means the heat produced does not leave the cup. If a reaction is exothermic–if it produces heat–the temperature inside the calorimeter will increase. Differently, for an endothermic reaction–a reaction that consumes heat–the temperature inside the calorimeter will decrease. When the reaction stops, as there is no more heat being produced or consumed, the temperature inside the calorimeter will change. To estimate the temperature at that point, we need to extrapolate the temperature inside the calorimeter. If you plot temperature versus time you will see that for early times, the temperature inside a calorimeter in which a reaction happens changes abruptly. After that, the temperature slowly decreases with time. To calculate the temperature when the reaction stops you need to connect the dots of the later stages, when the reaction already has stopped. We call this interpolation. All these points will be part of a line. If you extend the line, it will cross the Y-axis, and that crossing point is the temperature at which the reaction has stopped. We call this the extrapolation method.

**Example**

*The following data reports the temperature inside a cup calorimeter. Indicate whether the reaction is exothermic or endothermic and calculate the temperature when the reaction stops employing the extrapolation method.*

| t (min) | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|---------|-----|-----|-----|-----|-----|-----|------|-----|------|------|-----|
| T (°C) | 10 | 10 | 20 | 28 | 29 | 30 | 29.5 | 29 | 28.5 | 27.5 | 27 |

**Answer**: if we plot temperature versus time we will see the two different regions of the plot. In early times, the temperature increased and hence the reaction in the calorimeter was exothermic. At later times, the reaction stops and temperature decreases due to the lack of heat release. We will use the last points and connect them with a line. The crossing point with the Y axis is 33 °C and that is the final temperature of the reaction.
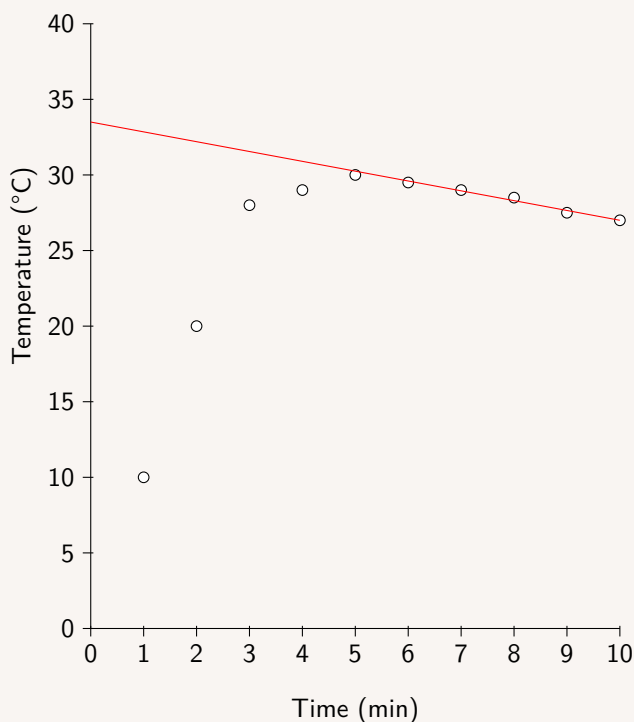


## Procedure

☐ *Step 1:* – Obtain a coffee cup calorimeter with a thermometer and a plastic lid.

☐ *Step 2:* – Weight about 8.5g of $NaNO_3$. Write down the mass you weighed in the results section.

☐ *Step 3:* – Use a 100mL graduated cylinder to add 100mL of distilled water in the calorimeter.

☐ *Step 4:* – Measure the temperature of water in the calorimeter. Record this temperatures as your initial temperature $t_i$.

☐ *Step 5:* – Get the timer ready. Time should be taken as soon as the solid reactant is added.

☐ *Step 6:* – Add the $NaNO_3$ to the calorimeter. If you are using a magnetic stirrer set the speed to a medium speed and make sure the heating option is off. Then add the solid. Start the timer immediately and place the lid on the calorimeter.

☐ *Step 7:* – Record the temperature for 4 min. Do not stop the timer during the experiment. Record the results in the results table.

☐ *Step 8:* – Replicate the experiment one more time.

☐ *Step 9:* – Plot the temperature of the calorimeter against time and use a straight line to extrapolate your results against the starting time (time = 0 s). Plot the results for both replicates in the same plot. Record the extrapolated temperature as $t_f$.

☐ *Step 10:* – Do not carry out any calculation before finishing the plot from the previous step. Calculate the change of enthalpy, $\Delta H$.

☐ *Step 11:* – Calculate the average enthalpy change using the two replicated experiments.

☐ *Step 12:* – If your instructor assigns you an unknown solute, repeat the previous procedure with this new solute.

---

**Good Lab Practice**

✎ Make sure you always use the same thermometer all through the experiment so that the results are consistent.

---

## Calculations

①This is the initial temperature before you add the solid.

② This is the final temperature after the dissolution reaction stops. You need to plot the data and extrapolate to get this value.

③ This is the maximum temperature during the experiment. Comparing the initial and final temperatures you can figure out of the reaction is endothermic or exothermic.

④This is the mass of salt weighed.

⑤This is the number of moles of salt:

$$④ /\ 84.9947$$

⑥You can calculate the enthalpy change ($\Delta H$ in KJ/mol) by means of the following formula:

$$\Delta H = -\frac{1 \times 10^{-3}}{⑤} \cdot \left(4.184 \cdot 1.0 \cdot 100.0 \cdot (② - ①) + 10 \cdot (② - ①)\right)$$

⑦This is the average enthalpy.

⑧This is the average maximum temperature.

⑨ Calculate the minimum entropy change for equilibrium using the maximum temperature and the average enthalpy (remember enthalpy is expressed in KJ/mol and entropy in J/molK)

$$\Delta S_{min} = \frac{\Delta H}{T_m} = \frac{⑦ \times 1000}{⑧}$$

**STUDENT INFO**

Name:                                    Date:

**Pre-lab Questions**

# Entropy and spontaneity

1. Ammonium nitrate ($NH_4NO_3$) is dissolved in a coffee-cup calorimeter. We recorded the temperatures with time and the data is given below. The initial temperature, $t_i$ was 25.0 °C.

| t (s) | 0 | 30 | 60 | 90 | 120 | 150 | 180 | 210 | 240 |
|-------|-----|------|------|------|------|------|------|------|------|
| T (°C) | 25 | 40.8 | 40.7 | 40.6 | 40.5 | 40.4 | 40.3 | 40.2 | 40.1 |

   (a) Plot T (vertical axis) vs. t (horizontal axis).
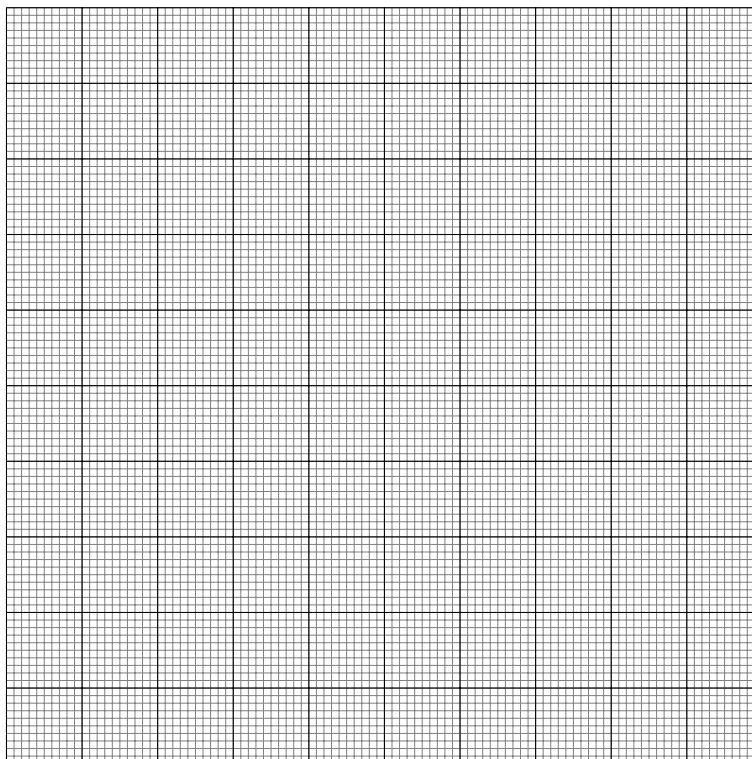
   (b) Obtain $t_f$, the final temperature after the reaction starts, by extrapolating to the time of mixing (time = 0 s) with a straight line.

   (c) Indicate whether this is an exothermic or an endothermic reaction.

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(d) Explain the change of temperature inside the calorimeter.

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2. Predict the sign of the entropy change for the dissolution of $NH_4NO_3$.

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3. Predict the spontaneity of the dissolution of $NH_4NO_3$ using the signs of the entropy and enthalpy estimated above.

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4. Calculate the $NaNO_3$ (MW=84.9947 $g \cdot mol^{-1}$) mass needed to prepare 100mL of a 1M solution of this salt.

# Entropy and spontaneity

**STUDENT INFO**

Name: _____     Date: _____

## NaNO₃ Trial 1

| t(s) | 0 | 30 | 60 | 90 | 120 | 150 | 180 | 210 | 240 |
|------|---|----|----|----|-----|-----|-----|-----|-----|
| T (°C) | | | | | | | | | |

| $T_i$ (°C) | $T_f$ (°C) | $T_m$ (°C) | $m$ (g) | $n$ (moles) | $\Delta H(kJ/mol)$ |
|------------|------------|------------|---------|-------------|---------------------|
| ① | ② | ③ | ④ | ⑤ | ⑥ |
| | | | | | |

## NaNO₃ Trial 2

| t(s) | 0 | 30 | 60 | 90 | 120 | 150 | 180 | 210 | 240 |
|------|---|----|----|----|-----|-----|-----|-----|-----|
| T (°C) | | | | | | | | | |

| $T_i$ (°C) | $T_f$ (°C) | $T_m$ (°C) | $m$ (g) | $n$ (moles) | $\Delta H(kJ/mol)$ |
|------------|------------|------------|---------|-------------|---------------------|
| | | | | | |

Average $\Delta H (kJ/mol)$ = ⑦

Average $T_m (K)$ = ⑧

$\Delta S_{min} (J/molK)$ = ⑨

**Unknown Trial 1**

| t (s) | 0 | 30 | 60 | 90 | 120 | 150 | 180 | 210 | 240 |
|---|---|---|---|---|---|---|---|---|---|
| T (°C) | | | | | | | | | |

| $T_i$ (°C) ① | $T_f$ (°C) ② | $T_m$ (°C) ③ | $m$ (g) ④ | $n$ (moles) ⑤ | $\Delta H$ (kJ/mol) ⑥ |
|---|---|---|---|---|---|
| | | | | | |

**Unknown Trial 2**

| t (s) | 0 | 30 | 60 | 90 | 120 | 150 | 180 | 210 | 240 |
|---|---|---|---|---|---|---|---|---|---|
| T (°C) | | | | | | | | | |

| $T_i$ (°C) | $T_f$ (°C) | $T_m$ (°C) | $m$ (g) | $n$ (moles) | $\Delta H$ (kJ/mol) |
|---|---|---|---|---|---|
| | | | | | |

Average $\Delta H$ (kJ/mol) = ⑦

Average $T_m$ (K) = ⑧

$\Delta S_{min}$ (J/molK) = ⑨

Figure 9: time (X axis) vs. Temperature (Y axis)

**Post-lab Questions**

# Entropy and spontaneity

1. Predict the sign of the entropy change for the dissolution of $NaNO_3$

2. Use the data below to compute the entropy change in the dissolution process of sodium nitrate at 298K. Compare your experimental result with the calculated giving reasons for the difference.

| | $NaNO_{3(s)}$ | $\longrightarrow$ | $Na^+_{(aq)}$ | + | $NO_3^-{}_{(aq)}$ |
|---|---|---|---|---|---|
| $S°(J/molK)$ | 116.32 | | 59.0 | | 146.4 |
| $n$ | | | | | |
| $S° \cdot n$ | | | | | |
| $\Delta S°(J/molK)$ | | | | | |

3. Use the data below to compute the enthalpy change in the dissolution process of sodium nitrate at 298K. Compare your experimental result with the calculated giving reasons for the difference.

| | $NaNO_{3(s)}$ | $\longrightarrow$ | $Na^+_{(aq)}$ | + | $NO_3^-{}_{(aq)}$ |
|---|---|---|---|---|---|
| $H°(KJ/mol)$ | -466.68 | | -240.1 | | -207.36 |
| $n$ | | | | | |
| $H° \cdot n$ | | | | | |
| $\Delta H°(KJ/mol)$ | | | | | |

4. Was the dissolution of sodium nitrate spontaneous in the conditions of the experiment?

5. Calculate the value of Gibbs free energy at 298K using the entropy and enthalpy calculated above.

**EXPERIMENT**

# A Solubility Product Constant: Solubility product of an iodate salt

## Goal

The goal of this laboratory experiment is to calculate the solubility product of a iodate salt.

## Materials

- ☐ A 10mL pipet, a 150mL beaker, stiring rod
- ☐ Filter paper, funnel, stand, ring
- ☐ A burete, stand and fisher clamp
- ☐ A 1M $Ca(NO_3)_{2\,(aq)}$ solution

- ☐ solid $KI_{(s)}$
- ☐ A 0.2M $KIO_{3\,(aq)}$ solution
- ☐ 2M $HCl_{(aq)}$ and 2% starch solution
- ☐ A series of 125mL (or 250mL) erlenmeyers

## Background

When insoluble compounds dissolve in water an equilibrium between the solid and the dissolved ions establishes. Based on the stoichiometry of the compound we will obtain a different number of moles of ions in solution.

This experiment can be carried out in two different forms. The instructor can either give you an unknown saturated solution, or you can prepare it yourself. At the same time, the standardization of sodium thiosulfate can be carried out optionally, based on the instructor's indications.

### Solubility equilibrium

Insoluble compounds dissolve in small amounts in water. Solubility equilibrium is the equilibrium that describes the dissolution of an insoluble compound to produce an aqueous solution of ions. For example, in the case of silver chloride, we have:

$$AgCl_{(s)} \rightleftharpoons Ag^+_{(aq)} + Cl^-_{(aq)}$$
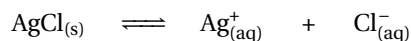
The solubility equilibrium above represents the dissolution of the insoluble salt–a solid–to produce ions, silver, and chloride in solution. In general terms, solubility equilibriums start with a solid and generate ions in solution. To break down the insoluble compound into ions, we just need to take into account the stoichiometry of the compound. For example, for the case of Cobalt(II) phosphate, we have:

$$Co_3(PO_4)_{2\,(s)} \rightleftharpoons 3\,Co^{2+}_{(aq)} + 2\,PO_4{}^{3-}{}_{(aq)}$$
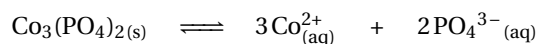
### Solubility product in terms of molarities, $K_{sp}$

Silver chloride, AgCl is an insoluble compound in water which means this compound will not fully dissolve in water. Still, small quantities of the salt will indeed dissolve leading to a small amount of silver and chlorine ions. As this compound is insoluble the ion concentration will be very small. The dissociation equilibrium involved in the dissolution indicated below, is characterized by an equilibrium constant $K_{sp}$ called *solubility product constant* or simply *solubility product*:

$$AgCl_{(s)} \rightleftharpoons Ag^+_{(aq)} + Cl^-_{(aq)} \qquad\qquad K_{sp} = [Ag^+] \cdot [Cl^-]$$

As pure solids are not included in any equilibrium constant, the formula above does not include $AgCl_{(s)}$. Hence, all solubility products simply result from the product of the molarities of the ions involved in the dissociation with the corresponding powers based on the stoichiometry of the salt. This is why the term *product* is included in its name. $K_{sp}$ will have a different explicit expression depending on the formula of the insoluble compound–depending on its stoichiometry. For example, $K_{sp}$ for calcium fluoride–a 1:2 compound–would be:

$$CaF_{2(s)} \rightleftharpoons Ca^{2+}_{(aq)} + 2F^-_{(aq)} \qquad\qquad K_{sp} = [Ca^{2+}] \cdot [F^-]^2$$

Solubility products are related to the solubility of chemicals. However, the relationship is not one-on-one. In other words, a larger $K_{sp}$ does not necessarily imply a larger solubility. For example, $K_{sp}$ for $PbBr_2$ is $6.6 \times 10^{-3}$ M whereas $K_{sp}$ for $MgCO_3$ is $4.0 \times 10^{-5}$ M. We have that $K_{sp}$ for $PbBr_2$ is smaller than $K_{sp}$ for $MgCO_3$. However, the solubility of $PbBr_2$ is indeed larger than the solubility of $MgCO_3$.

## Relating solubility to the concentration of ions

We have that insoluble compounds dissolve to produce small amounts of ions in solutions. The concentration of these ions is directly related to solubility $s$ using the stoichiometry of the compound. For example, for silver chloride–a salt with a 1:1 stoichiometry–we have that solubility has a 1 and 1 relationship with the concentration of ions:

$$[Ag^+] = s \text{ and } [Cl^-] = s$$

Similarly, for barium sulfate we have that solubility has a 1:1 relationship with the concentration of ions:

$$[Ba^{+2}] = s \text{ and } [SO_4^{-2}] = s$$

When the stoichiometry of the compound is not 1:1 we need to include the stoichiometry coefficients in the relationship between solubility and ion concentration. For example, for $Ag_2SO_4$–a compound with 2:1 stoichiometry, we have that

$$[Ag^+] = 2 \cdot s \text{ and } [SO_4^{-2}] = s$$

This is because, for every mole of silver sulfate, we produce two moles of silver–and hence the factor two–and one mole of sulfate in solution. Similarly, for $Nd_2(CO_3)_3$ we have

$$[Nd^{+3}] = 2 \cdot s \text{ and } [CO_3^{-2}] = 3 \cdot s$$

## Relating solubility to the concentration of ions

The solubility product is directly related to molar solubility $s$. We will demonstrate how to obtain this relationship using three examples. First, the solubility product of AgCl is:

$$AgCl_{(s)} \rightleftharpoons Ag^+_{(aq)} + Cl^-_{(aq)} \qquad\qquad K_{sp} = [Ag^+] \cdot [Cl^-]$$

As the concentration of each ion, $Ag^+$ and $Cl^-$, is related to the molar solubility of the salt, we have

$$K_{sp} \quad = \quad [Ag^+] \cdot [Cl^-] \quad = \quad (s) \cdot (s) \quad = \quad s^2$$

Second, for silver sulfide, an insoluble compound with a more complex stoichiometry, we have:

$$Ag_2S_{(s)} \rightleftharpoons 2Ag^+_{(aq)} + S^{2-}_{(aq)} \qquad\qquad K_{sp} = [Ag^+]^2 \cdot [S^{2-}] = (2s)^2 \cdot (s) = 4s^3$$

Third, the solubility equilibrium and $K_{sp}$ expression for $Nd_2(CO_3)_3$ is

$$Nd_2(CO_3)_{3(s)} \rightleftharpoons 2Nd^{3+}_{(aq)} + 3CO_3^{2-}{}_{(aq)} \qquad\qquad K_{sp} = [Nd^{3+}]^2 \cdot [CO_3^{2-}]^3$$

As the ion concentrations are related to solubility, we have

$$K_{sp} \quad = \quad (2s)^2 \cdot (3s)^3 \quad = \quad 108s^5$$

## $K_{sp}$ in terms of molar solubility: general formula

For any insoluble salt $A_xB_y$, we have that $K_{sp}$ is related to $s$ by means of a general formula:

$$K_{sp} = a \cdot s^b \tag{6}$$

where:

$a$ is $x^x \cdot y^y$

$b$ is $x + y$

For example, for $Ba_1F_2$ the constant $a$ would be $1^1 \cdot 2^2$, that is four, whereas the constant $b$ will be $1 + 2$ which equals three. As such, the expression of $K_{sp}$ in terms of $s$ would be: $K_{sp} = 4s^3$. This approach is useful when we need to compute the solubility product constant given the molar solubility.

## Molar solubility in terms of $K_{sp}$: general formula

We previously explored the relationship between $K_{sp}$ and molar solubility. Here we will explore the relationship between molar solubility and $K_{sp}$, simply solving for $s$ in Equation 6. Again, for any insoluble salt $A_xB_y$, we have:

$$s = \left(\frac{K_{sp}}{a}\right)^{\frac{1}{b}} \tag{7}$$

where:

$a$ is $x^x \cdot y^y$

$b$ is $x + y$

For example, for $Ba_1F_2$ the constant $a$ would be $1^1 \cdot 2^2$, that is four, whereas the constant $b$ will be $1 + 2$ which equals three. As such, the expression of $s$ in terms of $K_{sp}$ would be: $s = \left(\frac{K_{sp}}{4}\right)^{\frac{1}{3}}$. This approach is useful when the solubility product constant is given and we need to calculate the molar solubility. As the relation between molar solubility and $K_{sp}$ is not a one-to-one relationship, $K_{sp}$ is not directly related to solubility. For salts with a similar stoichiometry, it would be safe to compare solubilities in terms of $K_{sp}$. For example:

| | | |
|---|---|---|
| CuS | $K_{sp}=8 \times 10^{-37}$ | $s = 6 \times 10^{-19}$ |
| PbS | $K_{sp}=3 \times 10^{-28}$ | $s = 1 \times 10^{-14}$ |
| LiF | $K_{sp}=2 \times 10^{-3}$ | $s = 3 \times 10^{-2}$ |

and we have that the lower $K_{sp}$ the lower solubility. When the salt stoichiometry differs

| | | |
|---|---|---|
| $MgF_2$ | $K_{sp}=5 \times 10^{-11}$ | $s = 2 \times 10^{-4}$ |
| $Li_3PO_4$ | $K_{sp}=2 \times 10^{-4}$ | $s = 7 \times 10^{-2}$ |
| $Li_2CO_3$ | $K_{sp}=8 \times 10^{-4}$ | $s = 6 \times 10^{-2}$ |

then an increase in $K_{sp}$ does not necessarily follow an increase in solubility.

# Procedure

## Part A: Preparation of a saturated solution

☐ *Step 1:* – If your instructor assign you an unknow you can skip Part A.

☐ *Step 2:* – In a 150mL beaker mix 50mL of a 0.2M $KIO_3$ solution and 20mL of a 1M $Ca(NO_3)_2$ solution. Make sure you pick the reagents with the indicated concentration as in the lab there could be more diluted potassium iodate. Stir the resulting mix with a stirring rod. A precipitate will appear.

☐ *Step 3:* – Using gravity filtration (use a filter funnel and not a Büchner funnel), filter the precipitate. Make sure you rinse the beaker with water, to collect all precipitate leftovers.

☐ *Step 4:* – Wash the precipitate on the filter paper with three different volumes of water.

☐ *Step 5:* – Use a spatula to separate the precipitate into two halves. Dispose of each part in a clean labeled 100mL beaker. Put one of the beakers aside to be used in case of an accident. Use the other beaker in the rest of the experiment. If you do not use the first half of the precipitate, dispose of it at the end of the experiment following your instructor's indications.

☐ *Step 6:* – Add 40mL of distilled water to the beaker containing the precipitate. Use a stirring rod to stir the mixtures.

☐ *Step 7:* – This is the saturated solution. Let this solution rest for 30 minutes, occasionally stirring.

☐ *Step 8:* – It is important not to add additional water to this solution.

## Part B: Standardization of thiosulfate: mixture preparation

☐ *Step 1:* – Locate the $KIO_3$ solution and write down its molarity in the results section.

☐ *Step 2:* – Prepare a diluted $KIO_3$ solution by pipetting 5mL of the $KIO_3$ solution into a 100mL volumetric flask and fill up with distilled water.

☐ *Step 3:* – Pipet 10mL of the diluted $KIO_3$ solution prepared in the previous step into a 125mL (or 250mL) Erlenmeyer flask. First, add 20mL of distilled water from a cylinder. Add 20 drops of 2M HCl and the equivalent of 1mL of solid KI, measured with a 10mL cylinder. Mind you can approximately measure the volume of a solid with a cylinder. Finally, add 40 drops of a 0.2% starch solution. Swirl the mixture to obtain a homogeneous mixture.

☐ *Step 4:* – Repeat the previous step two more times, preparing a total of three Erlenmeyers containing the iodate mixture.

## Part B: Standardization of thiosulfate

☐ *Step 1:* – Ask your instructor of the thiosulfate solution is already standarized. If so, you can skip Part B.

☐ *Step 2:* – Rinse a buret with a small portion of $Na_2S_2O_3$ solution, discarding the solution used in the rinses.

☐ *Step 3:* – Fill a buret with $Na_2S_2O_3$ solution.

☐ *Step 4:* – Titrate one of the iodate samples samples adding increments of 1mL of sodium thiosulfate at a time. Swirl the mixture after each addition. You will have reached the equivalency point when the solution becomes colorless. Try placing the flask containing the analyte on a piece of paper. The white background will help see the color change when it occurs.

☐ *Step 5:* – Write down the volume of thiosulfate added to reach the equivalency point to the nearest 0.01mL. This will give an estimate of the volume needed to reach the endpoint.

☐ *Step 6:* – After having estimated the volume of titrate needed to reach the endpoint, we will now speed up the titration by rapidly titrating the second thiosulfate sample.

☐ *Step 7:* – Add thiosulfate ($Na_2S_2O_3$) to a second iodate sample, stopping 3mL before the estimated endpoint.

☐ *Step 8:* – Add $Na_2S_2O_3$ drop by drop until you reach the endpoint and the solution becomes colorless. Record the buret reading to the nearest 0.01mL.

☐ *Step 9:* – Repeat the titration with the last iodate sample.

## Part C: Preparing three mixtures of the saturated solution

☐ *Step 1:* – The goal now is to prepare three samples of an acidified, saturated solution containing iodide. To do this we will first filter the saturated solution to eliminate the solid. After that, we will add acid and iodine to an exact volume of this solution.

☐ *Step 2:* – Filter the saturated solution obtained earlier in the experiment. Make sure the funnel and the paper are dry. Do not wash the precipitate with water. The filtrate is the solution to be titrated.

☐ *Step 3:* – Rinse a 10mL pipet with distilled water making sure the pipet is free of water at the end. Now rinse the same pipet two times with a small amount of the filtrate collected in the previous step (2mL), discarding the solution from the pipet.

☐ *Step 4:* – Pipet 10mL from the filtrate into a 125mL (or 250mL) Erlenmeyer flask. First, add 20mL of water distilled water from a cylinder. Add 20 drops of 2M HCl and the equivalent of 1mL of solid KI, measured with a 10mL cylinder. Mind you can approximately measure the volume of a solid with a cylinder. Finally, add 40 drops of a 0.2% starch solution. Swirl the mixture to obtain a homogeneous mixture.

☐ *Step 5:* – Repeat the previous step two more times to prepare a total of three mixtures.

## Part D: Titration of the saturated solution mixtures: trial titration

☐ *Step 1:* – The final goal here is to calculate the molarity of the saturated solution, which corresponds to the solubility of the insoluble compound. Here we will estimate the equivalence point of the titration of sodium thiosulfate and sodium iodate.

☐ *Step 2:* – Rinse a buret with a small portion of $Na_2S_2O_3$ solution, discarding the solution used in the rinses.

☐ *Step 3:* – Fill a buret with $Na_2S_2O_3$ solution.

☐ *Step 4:* – Titrate one of the samples adding increments of 1mL of sodium thiosulfate at a time. Swirl the mixture after each addition. You will have reached the equivalency point when the solution becomes colorless. Try placing the flask containing the analyte on a piece of paper. The white background will help see the color change when it occurs.

☐ *Step 5:* – Write down the volume of thiosulfate added to reach the equivalency point to the nearest 0.01mL. This will give an estimate of the volume needed to reach the endpoint.

## Part D: Titration of the saturated solution mixtures: exact titration

☐ *Step 1:* – After having estimated the volume of titrate needed to reach the endpoint, we will now speed up the titration by rapidly titrating the second thiosulfate sample.

☐ *Step 2:* – Add thiosulfate to a second sample of saturated solution, stopping 3mL before the estimated endpoint.

☐ *Step 3:* – Add $Na_2S_2O_3$ drop by drop until you reach the endpoint and the solution becomes colorless. Record the buret reading to the nearest 0.01mL.

☐ *Step 4:* – Repeat the procedure with the last saturated sample.

# Calculations

( 0 ) This is the molarity of the potassium iodate solution, $c_{KIO_3}$.

( 1 ) This is the initial volume on the buret.

(2) This is the final volume in the buret.

(3) This is the volume of sodium thiosulfate used in the standardization, $v_{Na_2S_3O_3}$:

$$v_{Na_2S_3O_3} = \boxed{2} - \boxed{1}$$

(4) This is the molarity of thiosulfate, $c_{Na_2S_3O_3}$:

$$c_{Na_2S_3O_3} = 10 \times c_{KIO3}^{diluted} / v_{Na_2S_3O_3} \times 6 = 10 \times 0.05 \times \boxed{0} / \boxed{3} \times 6$$

(5) This is the average sodium thiosulfate concentration. If you do not standardize the reagent this value should be written in the bottle (0.025M).

(6) This is the initial volume in the buret.

(7) This is the final volume in the buret.

(8) This is the volume of thiosulfate used, $v_{Na_2S_3O_3}$:

$$v_{Na_2S_3O_3} = \boxed{7} - \boxed{6}$$

(9) This is the concentration of iodate $IO_3^-$ in the saturated solution, $c_{IO_3^-}$:

$$c_{IO_3^-} = v_{Na_2S_3O_3} \times c_{Na_2S_3O_3} / 60 = \boxed{8} \times \boxed{5} / 60$$

(10) This is the solubility of the iodate salt, $s$.

$$s = c_{IO_3^-}/2 = \boxed{9}/2$$

(11) This is the average solubility.

(12) You obtain the solubility product by doing:

$$s = 4 \times \boxed{11}^3$$

**Pre-lab Questions**

# A Solubility Product Constant: Solubility product of an iodate salt

1. In the experiment, you will react potassium iodate with calcium nitrate to produce a precipitate. Indicate the name of the precipitate formed:

$$KIO_3 \quad + \quad Ca(NO_3)_2 \quad \longrightarrow$$
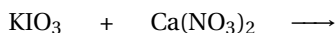
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2. In this experiment the iodate ($IO_3{}^-$) and iodide ions ($I^-$) react to produce molecular iodine ($I_2$) in acidic medium. Hence, in this redox reaction, a reactant is converted into products by simultaneous oxidation and reduction reactions. This type of redox reaction is referred to as disproportionation. Balance the corresponding disproportionation reaction.

$$IO_3{}^- \quad + \quad I^- \quad \longrightarrow \quad I_2$$
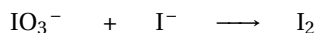
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3. In this experiment thiosulfate ($S_2O_3{}^{-2}$) is used in a redox titration. This compound reacts with molecular iodide ($I^-$), which has a reddish-brown color, to produce the ion colorless iodide ($I_2$) and tetrathionate. Hence, when all thiosulfate is finished along with the titration the reaction becomes colored. Balance the corresponding redox reaction in acidic medium.

$$S_2O_3{}^{-2} \quad + \quad I_2 \quad \longrightarrow \quad I^- \quad + \quad S_4O_6{}^{-2}$$
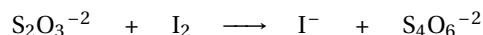
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4. Both reactions in the previous questions happen consecutively during the experiment. In the redox titration, first iodate reacts with iodine to produce iodine, which also reacts with thiosulfate to produce iodine. Combine both reactions to generate the overall reaction happening in the titration.

$$S_2O_3^{-2} \quad + \quad I^- \quad + \quad IO_3^- \quad \longrightarrow \quad I_2 \quad + \quad S_4O_6^{-2} \text{ (unbalanced)}$$
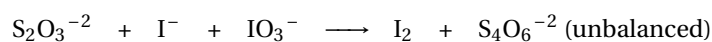
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5. You need 25mL of sodium thiosulfate 0.01M to reach the equivalency point in the titration of a 10mL sample of iodate. Using the balanced reaction from the previous question, carry stoichiometric calculations to calculate the molarity of iodate in the solution.
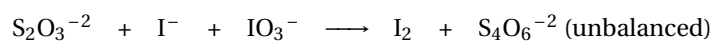
$$S_2O_3^{-2} \quad + \quad I^- \quad + \quad IO_3^- \quad \longrightarrow \quad I_2 \quad + \quad S_4O_6^{-2} \text{ (unbalanced)}$$

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**Results**
**EXPERIMENT**

# A Solubility Product Constant: Solubility product of an iodate salt

## Part B: $Na_2S_3O_3$ standarization

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( 0 )  Molarity of $KIO_3$, $c_{KIO_3}$ =

|  |  | 1 | 2 | 3 | 4 |
|---|---|---|---|---|---|
| ( 1 ) | Initial Buret Volume (mL) |  |  |  |  |
| ( 2 ) | Final Buret Volume (mL) |  |  |  |  |
| ( 3 ) | $Na_2S_2O_3$ Volume used (mL) |  |  |  |  |
| ( 4 ) | $Na_2S_2O_3$ Concentration (M) |  |  |  |  |

( 5 )  Mean $Na_2S_2O_3$ Concentration (M) =

# Part D: Titration of saturated solution

⑤ Molarity of $Na_2S_2O_3$, $c_{Na_2S_2O_3}$ =

| | | 1 | 2 | 3 | 4 |
|---|---|---|---|---|---|
| ⑥ | Initial Buret Volume (mL) | | | | |
| ⑦ | Final Buret Volume (mL) | | | | |
| ⑧ | $Na_2S_2O_3$ Volume used (mL) | | | | |
| ⑨ | $IO_3^-$ Concentration (M) | | | | |
| ⑩ | Solubility (M) | | | | |

Unknown Number = _____   ⑪ Mean solubility (M) =   ⑫ Mean $K_{sp}$ =

**Post-lab Questions**

# A Solubility Product Constant: Solubility product of an iodate salt

1. Write down the solubility equilibrium of calcium iodate.

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2. Write down the expression of the solubility constant of calcium iodate in terms of ion molarities.

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3. Write down the expression of the solubility constant of calcium iodate in terms of solubilities.

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4. Write down the expression of the solubility of calcium iodate in terms of the solubility product constant.

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EXPERIMENT

# Electrochemistry: galvanic cells

## Goal

The goal of this laboratory experiment is to build up a series of galvanic cell as well as a concentration cell.

## Materials

- ☐ A series of 150mL beaker
- ☐ A salt bridge
- ☐ A series of electrodes: Zn, 2 Cu electrodes, Pb, Fe, 2 graphite electrodes, Pt

- ☐ Two sets of banana plug to aligator clip wires and a voltmeter
- ☐ A series of solutions: 0.1M $Cu(NO_3)_2$, 0.1M $Zn(NO_3)_2$, 6M $HNO_3$, 0.1M $Pb(NO_3)_2$, 0.05M $Fe_2(SO_4)_3$ mixed with 0.05M $FeSO_4$ in 1M $H_2SO_4$

## Background

### Introduction to galvanic cells

Galvanic cells–also known as voltaic cells or piles–are electrochemical cells that generate electricity from spontaneous redox reactions. They contain two different metals immersed in electrolyte solutions. Each half-cell contains a metal in contact with a liquid solution of the same metal in ionic form. Both half-cells are either connected by a salt bridge or separated by a porous membrane. Galvanic cells differ from batteries. Batteries are composed of multiple single cells working out of equilibrium while producing electricity. Galvanic cells are textbook batteries. They are reversible devices unable to produce electricity.

### Components of a galvanic cell

Galvanic cells are composed of two different electrodes, an anode, and a cathode, connected by means of a salt bridge or a membrane. The role of the salt bridge or membrane is to complete the electrical circuit. Anodes are sources of electrons, whereas cathodes are electron sinks. At the same time, anodes generate positive cations, whereas cathodes generate negative anions. The role of the salt bridge or membrane is also to allow the charges generated in the cathode to be compensated by the charges generated in the anode. Electrodes contain two different redox states of the same element in contact with each other. An example of an electrode would be a piece of metallic copper Cu in contact with a solution of $Cu^{2+}_{(aq)}$ ions. However, electrodes are not always made of metals. For example, electrodes can contain gas in contact (e.g. $H_{2(g)}$) with an electrolyte solution (e.g. $H^+_{(aq)}$). Electrodes without a metal being directly involved in the redox reaction need to include an external metal to support the charge transfer. Metals such as Pt are normally used for this purpose.

### The electrodes: anode and cathode

Every galvanic cell is composed of two electrodes: an anode and a cathode. Electrodes produce ionic and electronic charges. The oxidation occurs on the anode which is indicated with a negative (−) sign. Electrons are being produced in the anode resulting from an oxidation reaction. The reduction occurs on the cathode, indicated with a positive (+) sign. Electrons are being consumed in the cathode resulting from a reduction reaction. These electrodes also produce ions, in particular cations and anions which have a tendency to migrate inside the cell. Anodes generate cations (and consume anions, depending on

the chemical reaction involved), whereas cathodes generate anions (and consume cations, again, depending on the chemical reaction involved). As such, anions have a tendency to migrate to the anode, as their concentration is lower there, whereas cations have a tendency to migrate to the cathode. The excess ionic charge is compensated in the interface between the electrode and the salt bridge or the membrane. Mind that in a galvanic cell only electrons flow through the circuit, by means of the wire connecting both electrodes. The ions involved have a tendency to migrate inside each of the electrodes but do not leave the electrode. The name of the electrodes–anode and cathode–results from the ionic flow involved in the galvanic cell: anions have a tendency to migrate towards the anode and cations to the cathode.

## Cell potential

Water flows down a waterfall due to the difference of potential energy between the high and low parts of the waterfall. Similarly, heat flows between a hot and a cold reservoir due to the difference in temperature between both locations. The force that drives the flow is heat is temperature. Electricity flows through a galvanic cell resulting from the difference of cell potential $\Delta\mathscr{E}$ between both electrodes, the anode, and the cathode. The cell potential–also referred to as cell voltage, cell electromotive force, or cell *emf*–is the force that drives the flow of electrons. Anodes and cathodes have a characteristic cell potential associated with the electrochemical half-reaction happening in the electrode. The voltage of the anode ($\mathscr{E}_{anode}$) is always lower than the one from the cathode ($\mathscr{E}_{cathode}$). The combination of the anodic and cathodic voltage gives the overall cell potential measured in a galvanic cell. In particular, the overall voltage results from the voltage of the cathode with respect to the anode, so that the overall voltage of a galvanic cell is always positive.

## A galvanic cell example

Below we display a representation of the Daniell cell, a classical galvanic cell in which copper is oxidized by zinc. The name of the cell is in honor of John Daniell, a British chemist from the nineteenth century who was trying to develop an electric power supply to sustain telegraphy. He connected with a metallic wire a zinc electrode in contact with a zinc sulfate solution to a copper electrode in contact with a copper (II) sulfate solution. In this cell, Copper(II) ions are converted into metallic copper in the cathode by means of the reaction $Cu^{2+}_{(aq)} + 2\,e^- \longrightarrow Cu_{(s)}$, whereas metallic zinc is converted into zinc ions in the anode following the reaction $Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2\,e^-$. Copper(II) ions are being reduced whereas zinc is being oxidized. The cathode solution becomes negatively charged whereas the anode solution becomes positively charged. A porous membrane permeable to ions was used to avoid the charge buildup.
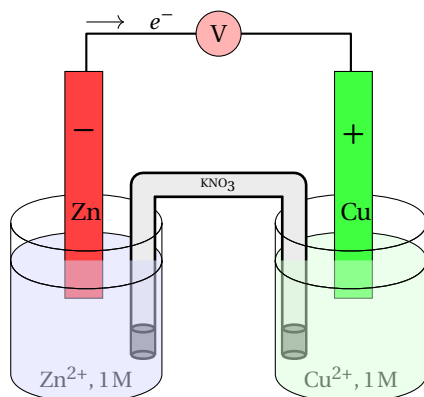


**Figure 10** The Daniell galvanic cell

## Anodes and cathodes

The standard reduction potential of an electrode predicts the tendency of an electrod to act as an anode or cathode. Imagine we have two different electrodes involving the following reaction with the standard potentials indicated on the side, and we need to set up a galvanic cell:

$$Cu^{2+}_{(aq)} + 2\,e^- \longrightarrow Cu_{(s)} \qquad\qquad \mathscr{E}^\circ = +0.34V$$
$$Zn^{2+}_{(aq)} + 2\,e^- \longrightarrow Zn_{(s)} \qquad\qquad \mathscr{E}^\circ = -0.76V$$

How to determine which electrode will act as anode and which will act as cathode? The rule is the smaller the electrode potential the more tendency of the electrode to act as an anode. If we compare the copper and zinc electrodes, as the electrode potential of zinc is smaller–more negative–than the electrode potential of copper. Therefore, zinc will act as an

anode and copper will act as a cathode. The standard reduction potential is not affected by the stoichiometry of the reaction. For example, the standard reduction potential of cesium is −3.03V:

$$Cs^+ + e^- \rightleftharpoons Cs_{(s)} \qquad\qquad \mathscr{E}° = -3.03V$$

At the same time, the standard reduction potential of two moles of cesium is still −3.03V.

$$2\,Cs^+ + 2\,e^- \rightleftharpoons 2\,Cs_{(s)} \qquad\qquad \mathscr{E}° = -3.03V$$

Differently, inverting the reduction reaction switches the sign of the reduction potential. For example, the standard reduction potential of Titanium(II) is −1.63V

$$Ti^{2+} + 2\,e^- \rightleftharpoons Ti_{(s)} \qquad\qquad \mathscr{E}° = -1.63V$$

while the standard potential of oxidation of Titanium into Titanium(II) is +1.63V

$$Ti_{(s)} \rightleftharpoons Ti^{2+} + 2\,e^- \qquad\qquad \mathscr{E}° = +1.63V$$

## The Nernst equation applied to a galvanic cell

We can also apply the Nernst's equation to a galvanic cell, for example the Daniell cell:

$$Zn \,|\, Zn^{2+}(1\,M) \,||\, Cu^{2+}(1\,M) \,|\, Cu$$
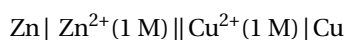
The redox reaction behind this cell oxidizes zinc and reduces copper, with a redox standard potential of 1.10V, with all concentrations fixed at 1M:

$$Zn_{(s)} + 2\,e^- + Cu^{2+}_{(aq)}(1\,M) \longrightarrow Zn^{2+}_{(aq)}(1\,M) + Cu_{(s)} + 2\,e^- \qquad\qquad \mathscr{E}°_{cell} = +1.10V$$

For nonstandard conditions we have that as Zinc is being oxidized, its ionic concentration will increase, whereas as Copper is being reduced its concentration will decrease. One can envision the following galvanic cell,

$$Zn \,|\, Zn^{2+}(1.2M) \,||\, Cu^{2+}(0.8\,M) \,|\, Cu$$
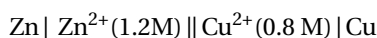
in which the following redox reaction occurs

$$Zn_{(s)} + 2\,e^- + Cu^{2+}_{(aq)}(0.8\,M) \longrightarrow Zn^{2+}_{(aq)}(1.2\,M) + Cu_{(s)} + 2\,e^- \qquad\qquad \Delta\mathscr{E}_{cell}$$

Applying Nernst's equation at 298.15K we have:

$$\Delta\mathscr{E}_{cell} = \Delta\mathscr{E}°_{cell} - \frac{R \cdot T}{n_e \cdot F} \ln Q$$

$$\Delta\mathscr{E}_{cell} = 1.10 - \frac{8.314 \cdot 298.15}{2 \cdot 96485} \ln \frac{1.2}{0.8} = 1.09\,V$$

We have that as the galvanic cell is being consumed, the overall cell potential has decreased. For overall redox reactions behind galvanic cells involving a single ionic species in the anode and cathode, the anode molarity will be on the top side of $Q$ whereas the cathode molarity will be on the bottom:

$$Q = \frac{\text{anode}}{\text{cathode}}$$

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**Example**

*For the galvanic cell below:*

$$Mg \,|\, Mg^{2+}(10^{-4}\ M) \,||\, Au^+(10^{-3}\ M) \,|\, Au$$
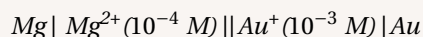
*(a) Calculate the standard voltage of the cell, given $\mathscr{E}°(Au^+/Au)$=1.83V and $\mathscr{E}°(Mg^{2+}/Mg)$=−2.37V (b) calculate the cell potential at 298.15K*

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**Answer**: The redox reaction being this galvanic cell is indicated below with the standard cell voltage obtained by doing $\mathscr{E}°_{cathode} - \mathscr{E}°_{anode}$:

$$Mg_{(s)} + 2\,e^- + 2\,Au^+_{(aq)}(10^{-4}\ M) \longrightarrow Mg^{2+}_{(aq)}(10^{-3}\ M) + 2\,Au_{(s)} + 2\,e^- \qquad \mathscr{E}°_{cell} = 4.20V$$
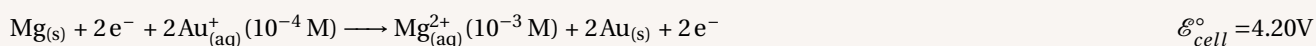
We have that two electrons flow though the cell. To calculate the cell potential at 298.15K we apply Nernst equation. While calculating $Q$ we have to place the anodic concentration on top and the cathodic on the bottom:

$$\Delta\mathcal{E}_{cell} = \Delta\mathcal{E}_{cell}^{\circ} - \frac{R \cdot T}{n_e \cdot F} \ln Q = 4.20 - \frac{8.314 \cdot 298.15}{2 \cdot 96485} \ln \frac{10^{-4}}{(10^{-3})^2} = 4.14V$$

## Concentration cells

What caused a voltage difference in a galvanic cell is the differences in reduction potentials of the anode and cathode. By selecting cathodes with larger positive $\mathcal{E}^{\circ}$ and anodes with large negative $\mathcal{E}^{\circ}$ we can achieve large cell potentials. At the same time, the Nernst equations tell us that $\mathcal{E}$ depends on molarity, hence we could potentially select the same anode and cathode and use the molarity terms in the Nernt equation to drive the potential difference. This is the principle behind concentration cells. These types of galvanic cells contain the same material in the anode and cathode but with different concentrations. The anode is the less concentrated electrode, whereas the cathode is the most concentrated electrode. The concentration difference is what drives the cell potential. Concentration cells in general produce very low voltages, even with very high concentration differences. For example, for the cell:

$$\text{Zn} \,|\, \text{Zn}^{2+}(10^{-5} \text{ M}) \,|\, \text{Zn}^{2+}(10^5 \text{ M}) \,|\, \text{Zn}$$
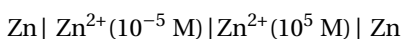
we have that $\mathcal{E}^{\circ} = +0.29$V. At the same time, good concentration cells have very low anodic concentrations and very large cathodic concentrations. For concentration cells we have that as both electrodes are made of the same material $\Delta\mathcal{E}^{\circ}=0$. Hence, Nernst equation for a concentration cell is simplified to:

$$\Delta\mathcal{E}_{cell} = -\frac{R \cdot T}{n_e \cdot F} \ln Q \quad \text{where } Q = \frac{[\text{anode}]}{[\text{cathode}]}$$

### Example

*For the concentration cell below:*

$$Cu \,|\, Cu^{2+}(10^{-8} \text{ M}) \,|\, Cu^{2+}(10^8 \text{ M}) \,|\, Cu$$
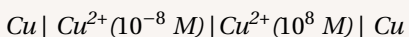
*(a) Identify the anode and the cathode (b) calculate the cell potential at 298.15K*

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**Answer**: The electrode potential depends on concentration. The smaller the concentration the lower the cell potential. On the other hand, we have that electrodes with lower cell potential have a stronger tendency to act as anodes, wheres electrodes with higher cell potential have a stronger tendency to act as cathodes. The less concentrated electrode on the left is the anode, whereas the more concentrated electrode on the right is the cathode. To calculate the cell voltage we use Nernst equation at 298.15K and given that two electrons flow though the cell:

$$\Delta\mathcal{E}_{cell} = -\frac{R \cdot T}{n_e \cdot F} \ln Q = -\frac{8.314 \cdot 298.15}{2 \cdot 96485} \ln \frac{10^{-8}}{10^8} = 0.47V$$

**Table 1 Standard reduction potentials at 298K**

| Element | Reaction | $\mathcal{E}°$ (V) | Element | Reaction | $\mathcal{E}°$ (V) |
|---|---|---|---|---|---|
| Sr | $Sr^+ + e^- \rightleftharpoons Sr_{(s)}$ | -4.10 | H | $2H^+ + 2e^- \rightleftharpoons H_{2(g)}$ | 0.00 |
| Ca | $Ca^+ + e^- \rightleftharpoons Ca_{(s)}$ | -3.80 | Ag | $AgBr_{(s)} + e^- \rightleftharpoons Ag_{(s)} + Br^-$ | +0.07 |
| Li | $Li^+ + e^- \rightleftharpoons Li_{(s)}$ | -3.04 | S | $S_4O_2^{6-} + 2e^- \rightleftharpoons 2S_2O_2-3$ | +0.08 |
| Cs | $Cs^+ + e^- \rightleftharpoons Cs_{(s)}$ | -3.03 | N | $N_{2(g)} + 2H_2O + 6H^+ + 6e^- \rightleftharpoons 2NH_4OH_{(aq)}$ | +0.09 |
| Ca | $Ca(OH)_2 + 2e^- \rightleftharpoons Ca_{(s)} + 2OH^-$ | -3.02 | Hg | $HgO_{(s)} + H_2O + 2e^- \rightleftharpoons Hg(l) + 2OH^-$ | +0.10 |
| Ba | $Ba(OH)_2 + 2e^- \rightleftharpoons Ba_{(s)} + 2OH^-$ | -2.99 | C | $C_{(s)} + 4H^+ + 4e^- \rightleftharpoons CH_{4(g)}$ | +0.13 |
| Rb | $Rb^+ + e^- \rightleftharpoons Rb_{(s)}$ | -2.98 | Sn | $Sn^{4+} + 2e^- \rightleftharpoons Sn_2^+$ | +0.15 |
| K | $K^+ + e^- \rightleftharpoons K_{(s)}$ | -2.93 | Cu | $Cu^{2+} + e^- \rightleftharpoons Cu^+$ | +0.159 |
| Ba | $Ba^{2+} + 2e^- \rightleftharpoons Ba_{(s)}$ | -2.91 | Fe | $3Fe_2O_{3(s)} + 2H^+ + 2e^- \rightleftharpoons 2Fe_3O_{4(s)} + H_2O$ | +0.22 |
| Sr | $Sr^{2+} + 2e^- \rightleftharpoons Sr_{(s)}$ | -2.90 | Ag | $AgCl_{(s)} + e^- \rightleftharpoons Ag_{(s)} + Cl^-$ | +0.22 |
| Sr | $Sr(OH)_2 + 2e^- \rightleftharpoons Sr_{(s)} + 2OH^-$ | -2.88 | Cu | $Cu^{2+} + 2e^- \rightleftharpoons Cu_{(s)}$ | +0.34 |
| Ca | $Ca^{2+} + 2e^- \rightleftharpoons Ca_{(s)}$ | -2.87 | Fe | $Fe^+ + e^- \rightleftharpoons Fe_{(s)}$ | +0.40 |
| Li | $Li^+ + C_{6(s)} + e^- \rightleftharpoons LiC_{6(s)}$ | -2.84 | O | $O_{2(g)} + 2H_2O + 4e^- \rightleftharpoons 4OH-_{(aq)}$ | +0.40 |
| Na | $Na^+ + e^- \rightleftharpoons Na_{(s)}$ | -2.71 | Cu | $Cu^+ + e^- \rightleftharpoons Cu_{(s)}$ | +0.520 |
| Mg | $Mg(OH)_2 + 2e^- \rightleftharpoons Mg_{(s)} + 2OH^-$ | -2.69 | C | $CO_{(g)} + 2H^+ + 2e^- \rightleftharpoons C_{(s)} + H_2O$ | +0.52 |
| Mg | $Mg^{2+} + 2e^- \rightleftharpoons Mg_{(s)}$ | -2.37 | I | $I_{2(s)} + 2e^- \rightleftharpoons 2I^-$ | +0.54 |
| H | $H_{2(g)} + 2e^- \rightleftharpoons 2H^-$ | -2.23 | Mn | $MnO_4^- + 2H_2O + 3e^- \rightleftharpoons MnO_{2(s)} + 4OH^-$ | +0.595 |
| Sr | $Sr^{2+} + 2e^- \rightleftharpoons Sr(Hg)$ | -1.79 | O | $O_{2(g)} + 2H^+ + 2e^- \rightleftharpoons H_2O_{2(aq)}$ | +0.70 |
| Al | $Al^{3+} + 3e^- \rightleftharpoons Al_{(s)}$ | -1.66 | Fe | $Fe_2O_{3(s)} + 6H^+ + 2e^- \rightleftharpoons 2Fe^{2+} + 3H_2O$ | +0.728 |
| Ti | $Ti^{2+} + 2e^- \rightleftharpoons Ti_{(s)}$ | -1.63 | Fe | $Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$ | +0.77 |
| Ti | $Ti^{3+} + 3e^- \rightleftharpoons Ti_{(s)}$ | -1.37 | Ag | $Ag^+ + e^- \rightleftharpoons Ag_{(s)}$ | +0.80 |
| Ti | $TiO_{(s)} + 2H^+ + 2e^- \rightleftharpoons Ti_{(s)} + H_2O$ | -1.31 | Hg | $Hg_2^{2+} + 2e^- \rightleftharpoons 2Hg(l)$ | +0.80 |
| Mn | $Mn^{2+} + 2e^- \rightleftharpoons Mn_{(s)}$ | -1.18 | N | $NO_3^-{}_{(aq)} + 2H^+ + e^- \rightleftharpoons NO_{2(g)} + H_2O$ | +0.80 |
| V | $V^{2+} + 2e^- \rightleftharpoons V_{(s)}$ | -1.13 | Fe | $2FeO_2^{2-} + 5H_2O + 6e^- \rightleftharpoons Fe_2O_{3(s)} + 10OH^-$ | +0.81 |
| Ti | $TiO^{2+} + 2H^+ + 4e^- \rightleftharpoons Ti_{(s)} + H_2O$ | -0.93 | Hg | $Hg^{2+} + 2e^- \rightleftharpoons Hg(l)$ | +0.85 |
| Si | $SiO_{2(s)} + 4H^+ + 4e^- \rightleftharpoons Si_{(s)} + 2H_2O$ | -0.91 | Mn | $MnO_4^- + H^+ + e^- \rightleftharpoons HMnO_4^-$ | +0.90 |
| Fe | $Fe_2O_{3(s)} + 3H_2O + 2e^- \rightleftharpoons 2Fe(OH)_{2(s)} + 2OH^-$ | -0.86 | Hg | $2Hg^{2+} + 2e^- \rightleftharpoons Hg_2^{2+}$ | +0.91 |
| H | $2H_2O + 2e^- \rightleftharpoons H_{2(g)} + 2OH^-$ | -0.828 | Pd | $Pd^{2+} + 2e^- \rightleftharpoons Pd_{(s)}$ | +0.915 |
| Zn | $Zn^{2+} + 2e^- \rightleftharpoons Zn_{(s)}$ | -0.762 | N | $NO_3^-{}_{(aq)} + 4H^+ + 3e^- \rightleftharpoons NO_{(g)} + 2H_2O(l)$ | +0.96 |
| Cr | $Cr^{3+} + 3e^- \rightleftharpoons Cr_{(s)}$ | -0.74 | Fe | $Fe_3O_{4(s)} + 8H^+ + 2e^- \rightleftharpoons 3Fe^{2+} + 4H_2O$ | +0.98 |
| Ni | $Ni(OH)_{2(s)} + 2e^- \rightleftharpoons Ni_{(s)} + 2OH^-$ | -0.72 | Br | $Br_{2(aq)} + 2e^- \rightleftharpoons 2Br^-$ | +1.09 |
| Ag | $Ag_2S_{(s)} + 2e^- \rightleftharpoons 2Ag_{(s)} + S_2-_{(aq)}$ | -0.69 | Ag | $Ag_2O_{(s)} + 2H^+ + 2e^- \rightleftharpoons 2Ag_{(s)} + H_2O$ | +1.17 |
| Pb | $PbO_{(s)} + H_2O + 2e^- \rightleftharpoons Pb_{(s)} + 2OH^-$ | -0.58 | Pt | $Pt^{2+} + 2e^- \rightleftharpoons Pt_{(s)}$ | +1.188 |
| Fe | $Fe^{2+} + 2e^- \rightleftharpoons Fe_{(s)}$ | -0.44 | Cl | $ClO^{-4} + 2H^+ + 2e^- \rightleftharpoons ClO_3^- + H_2O$ | +1.20 |
| Cr | $Cr^{3+} + e^- \rightleftharpoons Cr_2^+$ | -0.42 | O | $O_{2(g)} + 4H^+ + 4e^- \rightleftharpoons 2H_2O$ | +1.229 |
| Cd | $Cd^{2+} + 2e^- \rightleftharpoons Cd_{(s)}$ | -0.40 | Cl | $Cl_{2(g)} + 2e^- \rightleftharpoons 2Cl^-$ | +1.36 |
| Cu | $Cu_2O_{(s)} + H_2O + 2e^- \rightleftharpoons 2Cu_{(s)} + 2OH^-$ | -0.36 | Br | $BrO_3^- + 5H^+ + 4e^- \rightleftharpoons HBrO_{(aq)} + 2H_2O$ | +1.45 |
| Pb | $PbSO_{4(s)} + 2e^- \rightleftharpoons Pb_{(s)} + SO_2-4$ | -0.36 | Br | $2BrO^{3-} + 12H^+ + 10e^- \rightleftharpoons Br_2(l) + 6H_2O$ | +1.48 |
| Pb | $PbSO_{4(s)} + 2e^- \rightleftharpoons Pb(Hg) + SO_2-4$ | -0.35 | Cl | $2ClO^{3-} + 12H^+ + 10e^- \rightleftharpoons Cl_{2(g)} + 6H_2O$ | +1.49 |
| Co | $Co^{2+} + 2e^- \rightleftharpoons Co_{(s)}$ | -0.28 | Mn | $MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn_2^+ + 4H_2O$ | +1.51 |
| Ni | $Ni^{2+} + 2e^- \rightleftharpoons Ni_{(s)}$ | -0.25 | Au | $Au^{3+} + 3e^- \rightleftharpoons Au_{(s)}$ | +1.52 |
| As | $As_{(s)} + 3H^+ + 3e^- \rightleftharpoons AsH_{3(g)}$ | -0.23 | Pb | $Pb^{4+} + 2e^- \rightleftharpoons Pb^{2+}$ | +1.69 |
| Ag | $AgI_{(s)} + e^- \rightleftharpoons Ag_{(s)} + I^-$ | -0.15 | Mn | $MnO_4^- + 4H^+ + 3e^- \rightleftharpoons MnO_{2(s)} + 2H_2O$ | +1.70 |
| Sn | $Sn^{2+} + 2e^- \rightleftharpoons Sn_{(s)}$ | -0.13 | Ag | $AgO_{(s)} + 2H^+ + e^- \rightleftharpoons Ag^+ + H_2O$ | +1.77 |
| Pb | $Pb^{2+} + 2e^- \rightleftharpoons Pb_{(s)}$ | -0.126 | O | $H_2O_{2(aq)} + 2H^+ + 2e^- \rightleftharpoons 2H_2O$ | +1.78 |
| C | $CO_{2(g)} + 2H^+ + 2e^- \rightleftharpoons HCOOH_{(aq)}$ | -0.11 | Au | $Au^+ + e^- \rightleftharpoons Au_{(s)}$ | +1.83 |
| C | $CO_{2(g)} + 2H^+ + 2e^- \rightleftharpoons CO_{(g)} + H_2O$ | -0.11 | Ag | $Ag^{2+} + e^- \rightleftharpoons Ag^+$ | +1.98 |
| Fe | $Fe_3O_{4(s)} + 8H^+ + 8e^- \rightleftharpoons 3Fe_{(s)} + 4H_2O$ | -0.08 | Mn | $HMnO_4^- + 3H^+ + 2e^- \rightleftharpoons MnO_{2(s)} + 2H_2O$ | +2.09 |
| Fe | $Fe^{3+} + 3e^- \rightleftharpoons Fe_{(s)}$ | -0.04 | Fe | $FeO_2^{4-} + 8H^+ + 3e^- \rightleftharpoons Fe_3^+ + 4H_2O$ | +2.20 |
| H | $2H^+ + 2e^- \rightleftharpoons H_{2(g)}$ | 0.00 | F | $F_{2(g)} + 2H^+ + 2e^- \rightleftharpoons 2HF_{(aq)}$ | +3.05 |

Increasing oxidizing strength (decreasing reducing strength)

## Procedure

### Part A: Daniell galvanic cell

☐ *Step 1:* – Obtain a copper and zinc electrodes, a salt bridge as well as a potentiometer.

☐ *Step 2:* – We use a BK Precision potentiometer: make sure the black wire is connected to the COM connnection whereas the red one is connected to the Hz V Ω connection. The potentiometer has to be turned towards the right ro start measuring DC. Make sure you select the scale that that gives Volts.

☐ *Step 3:* – Place 0.1M $Cu(NO_3)_2$ (approximately 50 mL) in one compartment of the cell and 0.1M $Zn(NO_3)_2$ in the other.

☐ *Step 4:* – Obtain a copper and zinc electrodes.

☐ *Step 5:* – Clean the electrodes by dipping them (no more than 3 seconds) into 40mL of 6M $HNO_3$. You will notice that the surface of the electrodes will become bright. Rinse the electrodes with distilled water.

> **Good Lab Practice**
> ✍ Concentrated acid can cause severe burns and ruin your clother.

☐ *Step 6:* – Obtain a salt bridge as well as a potentiometer.

☐ *Step 7:* – Place the electrodes in separate 150-mL beakers, placing the salt bridge between both beakers. Connect each electrode to a terminal of the potentiometer.

☐ *Step 8:* – To find out whether the electrodes are properly connected to the potentiometer, read the voltage from the potentiometer. If the number is negative you need to switch the electrode conetions.

☐ *Step 9:* – Record the cell potential in the results section, as well as the nature of both electrodes (Zn and Cu).

### Part B: A series of galvanic cell

☐ *Step 1:* – Obtain a platinum (or graphite), copper, iron, lead and zinc electrodes.

☐ *Step 2:* – Clean the electrodes by dipping them (no more than 3 seconds) into 40mL of 6M $HNO_3$. You will notice that the surface of the electrodes will become bright. Rinse the electrodes with distilled water.

> **Good Lab Practice**
> ✍ Concentrated acid can cause severe burns and ruin your clother.
>
> ✍ Use globes to handle lead solutions. Lead solutions are poisonous.

☐ *Step 3:* – Gather the following solutions: 0.1M $Cu(NO_3)_2$, $Zn(NO_3)_2$, $Pb(NO_3)_2$, $FeSO_4$, and an iron solution made of 0.05M $FeSO_4$ and $Fe_2(SO_4)_3$ in 1M sulfuric acid (this last solution was made by dissolving $Fe_2(SO_4)_3$ in sulfuric acid as solvent).

☐ *Step 4:* – Set up the following galvanic cells, writing down in the results section its voltage and the nature of the anode and cathode. Mind you can replace Pt by graphite.

☐ Cu| $Cu^{2+}$(0.1 M) and Pb| $Pb^{2+}$(0.1 M)
☐ Cu| $Cu^{2+}$(0.1 M) and Fe| $Fe^{2+}$(0.1 M)
☐ Cu| $Cu^{2+}$(0.1 M) and Pt| $Fe^{2+}, Fe^{3+}$(0.1 M)
☐ Zn| $Zn^{2+}$(0.1 M) and Pb| $Pb^{2+}$(0.1 M)

☐ Zn| $Zn^{2+}$(0.1 M) and Fe| $Fe^{2+}$(0.1 M)
☐ Zn| $Zn^{2+}$(0.1 M) and Pt(or graphite)| $Fe^{2+}, Fe^{3+}$(0.1 M)
☐ Fe| $Fe^{2+}$(0.1 M) and Pt| $Fe^{2+}, Fe^{3+}$(0.1 M)

*Step 5:* – For each cell, write down the measured voltage in the Results section. Every time you change electrodes, makes sure you rinse the salt bridge with water.

## Part C: Concentration cell

*Step 1:* – Obtain two copper electrodes, a salt bridge as well as a potentiometer.

*Step 2:* – Clean the electrodes by dipping them (no more than 3 seconds) into 40mL of 6M $HNO_3$. You will notice that the surface of the electrodes will become bright. Rinse the electrodes with distilled water.

> **Good Lab Practice**
>
> ✍ Concentrated acid can cause severe burns and ruin your clother.

*Step 3:* – Prepare a copper diluted solution by adding 1mL of a 0.1M concentrated $Cu(NO_3)_2$ solution into a 100mL gradated cylinder. Stir well the mixture. Fill the cylinder with distilled water until you reach the 100mL mark.

*Step 4:* – Place some of the concentrated solution in a 150-mL beaker and some of the diluted solution in the other one. Insert one cooper electrode in each beaker, placing the salt bridge between both beakers. Connect each electrode to a terminal of the potentiometer.

*Step 5:* – Record the cell potential in the results section, as well as the nature of both electrodes (Cu| $Cu^{2+}$(0.1 M) and Cu | $Cu^{2+}$(0.01 M)) while identifying the anode and cathode.

*Step 6:* – Add 10 drops of the concentrated 0.1M $Cu(NO_3)_2$ solution to the most diluted electrode of the cell you built up. Record the cell potential in the results section.

## Part D: Electrolysis

*Step 1:* – Obtain two graphite electrodes and a power supply (6V battery).

*Step 2:* – Weight 2g of KI and transfer the solid into a 250mL Erlenmeyer flask. Add 100mL of distilled water and swirl until the solid dissolves.

*Step 3:* – Using a PH meter, measure the PH of the KI solution. Write down the value in the results section.

*Step 4:* – Place two graphite electrodes in a 250mL beaker. Clamp the electrodes so that they don't touch each other. Use a pair of upside-down test tubes to secure the electrodes. Attach the wires to the electrodes but do not connect them yet to the battery.

*Step 5:* – Add 30mL of the KI solution to the beaker.

*Step 6:* – Attach the wires to the battery and record the time in the Results section. Observe the solution.

*Step 7:* – Allow the electrolysis to run for 15 minutes.

*Step 8:* – After the time has elapsed, remove the electrodes from the battery. Remove the electrodes and take a good look at them.

*Step 9:* – Stir the KI solution in the beaker and using a PH meter measure the PH. Write down the results in the results section.

## Calculations

① Write down here the measured voltage.

② Write down here the cathodic reaction.

③ Write down here the cathodic standard potential.

④ Write down here the anodic reaction (revert the reaction from the table of voltages).

⑤ Write down here the anodic standard potential.

⑥ Write down here the overall reaction: add the cathodic reaction and the anodic reaction.

⑦ Write down here the overall standard potential.

⑧ Elapsed time in seconds.

⑨ Measured PH.

⑩ Calculated hydroxyl concentration:

$$[\text{OH}^-] = 1 \times 10^{-14}/10^{-PH}$$

⑪ Change on hydroxyl concentration:

$$\Delta\,[\text{OH}^-] = [\text{OH}^-]_f - [\text{OH}^-]_0$$
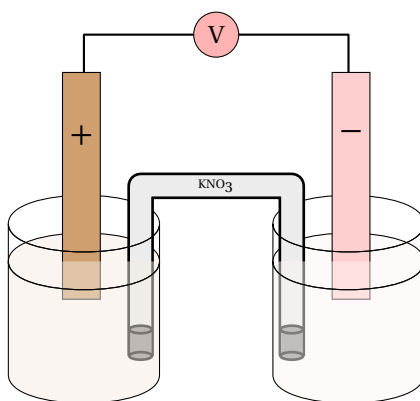
⑫ The intensity in Amperes:
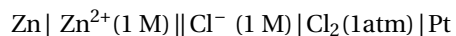
$$⑪ \times 96485/⑧$$

**Pre-lab Questions**

# Electrochemistry: galvanic cells

1. For the galvanic cell below, indicate: (a) the direction of flow of electrons (b) the direction of flow of cations (c) the direction of flow of anions
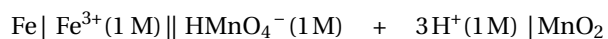


2. Calculate the standard cell potential for the galvanic cell below:

$$\text{Zn} \,|\, \text{Zn}^{2+}(1\text{ M}) \,\|\, \text{Cl}^{-}\ (1\text{ M}) \,|\, \text{Cl}_2\,(1\text{atm}) \,|\, \text{Pt}$$

3. For the unbalanced reaction below, calculate $\mathscr{E}^\circ$ and indicate whether the reaction is spontaneous under standard conditions. Balance the reaction.

$$2\,\text{HMnO}_4{}^{-} \quad + \quad \text{Fe}_2\text{O}_{3\,(s)} \quad + \qquad \rightleftharpoons \quad 2\,\text{Fe}^{2+} \quad + \quad 2\,\text{MnO}_4{}^{-}$$

4. Calculate the standard cell potential for the galvanic cell below:

$$\text{Fe} \,|\, \text{Fe}^{3+}(1\text{ M}) \,\|\, \text{HMnO}_4{}^{-}(1\,\text{M}) \quad + \quad 3\,\text{H}^{+}(1\,\text{M}) \,|\, \text{MnO}_2$$

5. For the concentration cell below:

$$\text{Au} \,|\, \text{Au}^{+}(10^{2}\text{ M}) \,|\, \text{Au}^{+}(10^{-2}\text{ M}) \,|\, \text{Au}$$

(a) Identify the anode and the cathode (b) calculate the cell potential at 298.15K

**Results**
EXPERIMENT

# Electrochemistry: galvanic cells

## Part A

| Electrodes | Cathodic reaction | $\mathscr{E}^{\circ}_{cath}$ | Anodic reaction | $\mathscr{E}^{\circ}_{anod}$ | Total reaction | $\Delta\mathscr{E}^{\circ}$ | $\Delta\mathscr{E}_{exp}$ |
|---|---|---|---|---|---|---|---|
| | ② | ③ | ④ | ⑤ | ⑥ | ⑦ | ① |
| Cu—Zn | | | | | | | |

## Part B

| Electrodes | Cathodic reaction | $\mathscr{E}^{\circ}_{cath}$ | Anodic reaction | $\mathscr{E}^{\circ}_{anod}$ | Total reaction | $\Delta\mathscr{E}^{\circ}$ | $\Delta\mathscr{E}_{exp}$ |
|---|---|---|---|---|---|---|---|
| Cu—Pb | | | | | | | |
| Cu—Fe | | | | | | | |
| Zn—Pb | | | | | | | |
| Cu—$Fe^{3+}$+$Fe^{2+}$ | | | | | | | |

## Part B

| Electrodes | $\Delta\mathscr{E}_{exp}$ ①  | Cathodic reaction ②  | $\mathscr{E}^\circ_{cath}$ ③ | Anodic reaction ④ | $\mathscr{E}^\circ_{anod}$ ⑤ | Total reaction ⑥ | $\Delta\mathscr{E}^\circ$ ⑦ |
|---|---|---|---|---|---|---|---|
| $Zn-Fe^{3+}+Fe^{2+}$ | | | | | | | |
| $Fe, Fe^{2+}-Fe^{3+}+Fe^{2+}$ | | | | | | | |

## Part C

| Electrodes | | | | | | | |
|---|---|---|---|---|---|---|---|
| $Cu^{2+}(0.01\,M)-Cu^{2+}(0.1\,M)$ | | | | | | | |
| $Cu^{2+}(0.01\,M)^{*}-Cu^{2+}(0.1\,M)$ | | | | | | | |

\* After adding 10 drops of $Cu^{2+}$ (0.1 M)

\*\* Use the temperature value of 298K

## Part D

| $PH_0$ ⑨ | $PH_f$ ⑨ | $[OH^-]_0$ ⑩ | $[OH^-]_f$ ⑩ | $\Delta[OH^-]$ ⑪ | $I$ ⑫ |
|---|---|---|---|---|---|
| | | | | | |

**Post-lab Questions**

# Electrochemistry: galvanic cells

1. Calculate the percent error between the measured voltage and the calculated one for all electrodes you measured using the formula below:

$$\%Error = \frac{|\Delta\mathscr{E}_{calc} - \Delta\mathscr{E}_{exp}|}{\Delta\mathscr{E}_{calc}} \times 100$$

| Electrodes | $\Delta\mathscr{E}_{exp}$ ① | $\Delta\mathscr{E}°$ ⑦ | Expression for $-\frac{R\cdot T}{n_e\cdot F}\ln Q$ ⑧ | $\Delta\mathscr{E}_{calc}$ ⑦+⑧ | % Error |
|---|---|---|---|---|---|
| Cu—Zn | | | | | |
| Cu—Pb | | | | | |
| Cu—Fe | | | | | |
| Zn—Pb | | | | | |
| Cu—$Fe^{3+}$+$Fe^{2+}$ | | | | | |
| Zn—$Fe^{3+}$+$Fe^{2+}$ | | | | | |
| Fe, $Fe^{2+}$—$Fe^{3+}$+$Fe^{2+}$ | | | | | |
| $Cu^{2+}$(0.01 M)—$Cu^{2+}$ (0.1 M) | | | | | |
| $Cu^{2+}$(0.01 M)*—$Cu^{2+}$ (0.1 M) | | | | | |

* After adding 10 drops of $Cu^{2+}$ (0.1 M)

2. Using line notation, write down the cell with that gives the largest and the cell that gives the smallest voltage.

<div align="center">EXPERIMENT</div>

# Radioactivity: half-life of K-40

## Goal

The goal of this laboratory experiment is to calculate the half-life of potassium-40 by means of the measurement of its rate of disintegration.

## Materials

- ☐ A Geiger counter
- ☐ Potassium chloride

- ☐ A 100mL beaker
- ☐ A stand and a clamp

## Background

Light elements have normally stable nuclei. Differently, heavier elements with atomic numbers larger than 20 tend to often have several isotopes–remember these are atoms of the element with a different number of neutrons–that have unstable nuclei. For these unstable isotopes, the forces that keep the nucleus together are not strong enough to stabilize the nuclei. An unstable nucleus is radioactive, which means that it will spontaneously emit radiation in the form of small particles. Not all radioactivity is the same and there exist different types of radiation, which we will address in the following. Table 2 reports common nuclear symbols.

### alpha radiation

Alpha radiation–referred to as $\alpha$–is a type of radiation that contains alpha particles. These particles are indeed helium nuclei, with 2 protons, 2 neutrons, and a (2+) positive charge. Alpha particles are often represented as $\alpha$ or $^4_2\text{He}$.

### beta radiation

Beta radiation–referred to as $\beta$–is a type of radiation that contains beta particles. These particles are indeed high-energy electrons with (−) negative charge. Beta particles are often represented as $\beta$ or $^0_{-1}\text{e}$.

### gamma radiation

Gamma radiation–referred to as $\gamma$–is a type of radiation that contains high-energy photons. These particles are indeed photons with no mass or charge. Gamma particles are often represented as $\gamma$ or $^0_0\gamma$.

### protons

Protons in this chapter are often referred to as $p$ or $^1_1\text{H}^+$. These are positive charges.

### positrons

Positrons are the electron antiparticle, often referred to as $\beta^+$ or $^0_{+1}\text{e}$. They do have a positive charge.

## neutrons

Neutrons are nuclear particles with no charge, often referred to as $n$ or $^1_0 n$.

| Table 2 Nuclear symbols | | | | | |
|---|---|---|---|---|---|
| Particle Name | Symbol | Charge | Identity | Penetrating power | Discovery |
| Alpha $(\alpha)$ | $^4_2 He$ | 2+ | Helium nucleus | Minimal | 1899 |
| Beta $(\beta)$ | $^0_{-1} e$ | −1 | Electrons | Short | 1899 |
| Gamma $(\gamma)$ | $^0_0 \gamma$ | 0 | Electromagnetic radiation | Deep | 1900 |
| Neutrons $(n)$ | $^1_0 n$ | 0 | nuclear particle | Maximal | 1932 |
| Proton $(p)$ | $^1_1 H^+$ | +1 | nuclear particle | | 1919 |
| Positrons $(\beta^+)$ | $^0_{+1} e$ | +1 | antiparticle | | 1932 |

Isotopes–called emitters–spontaneously decompose producing new isotopes in a process called radioactive decay. In this decay, radiation is also emitted.

$$\text{Emitter} \longrightarrow \text{radiation} + \text{New isotope}$$

In the following, we will discuss the most important type of radioactive decay.

## alpha decay

Some isotopes produce alpha radiation, that is, they produce $\alpha$ particles on its decay. A nuclear reaction that produces an $\alpha$ particle ($^4_2 He$) is called alpha decay. In alpha decay, the emitter decreases its mass number $A$ four units and its atomic number $Z$ two units.
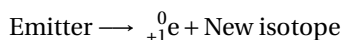
$$\text{Emitter} \longrightarrow {}^4_2 He + \text{New isotope}$$
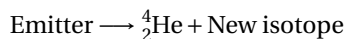
## beta decay

Other isotopes produce beta radiation, that is, they produce $\beta$ particles on its decay. A nuclear reaction that produces a $\beta$ particle ($^0_{-1} e$) is called beta decay. In beta decay, the emitter has the same mass number $A$ as the product isotope. However, its atomic number $Z$ decreases by one unit.

$$\text{Emitter} \longrightarrow {}^0_{-1} e + \text{New isotope}$$
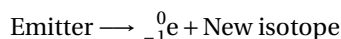
## positron emission

Certain isotopes decay by producing a positron, that is, they produce $^0_{+1} e$ particles on its decay. A nuclear reaction that produces $^0_{+1} e$ is called positron emission. In a positron emission, the emitter has the same mass number $A$ as the product isotope. However, its atomic number $Z$ increases by one unit.

$$\text{Emitter} \longrightarrow {}^0_{+1} e + \text{New isotope}$$

## gamma decay

Some other isotopes produce gamma radiation in the form of $\gamma$ particles on its decay. A nuclear reaction that produces a $\gamma$ particle ($^0_0 \gamma$) is called gamma decay. In this type of decay, no new isotope is produced. Gamma emitters are normally excited, that is they have higher energy than normal; we denote this with a $^*$ symbol. Exited particles tend to lose energy to become more stable. In gamma decay, the emitter and the product isotope, both have the same mass and atomic number.
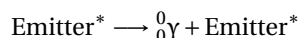
$$\text{Emitter}^* \longrightarrow {}^0_0 \gamma + \text{Emitter}^*$$

| Table 11 Half-life for various isotopes and chemicals | | | | | |
|---|---|---|---|---|---|
| Americium-241 | 432.2 years | Lutetium-177 | 6.71 days | Hydrogen-3 | 12.35 years |
| Barium-133 | 10.74 years | Molybdenum-99 | 66 hours | Technetium-99 | 213,000 years |
| Bismuth-212 | 60.55 minutes | Nickel-63 | 96 years | Indium-111 | 2.83 days |
| Cadmium-109 | 464 days | Phosphorus-32 | 14.29 days | Technetium-99m | 6.02 hours |
| Calcium-45 | 163 days | Potassium-40 | $1.28 \times 10^9$ years | Indium-113m | 1.658 hours |
| Carbon-14 | 5730 years | Plutonium-239 | 24,065 years | Tin-113 115.1 | days |
| Cesium-137 | 30 years | Polonium-210 | 138.38 days | Iodine-123 | 13.2 hours |
| Chlorine-36 | 301,000 years | Radium-226 | 1600 years | Tungsten-188 | 69.4 days |
| Chromium-51 | 27.704 days | Radon-222 | 3.8235 days | Iodine-125 | 60.14 days |
| Cobalt-57 | 270.9 days | Rhenium-188 | 16.98 hours | Uranium-235 | 703,800,000 years |
| Cobalt-58 | 70.8 days | Rubidium-81 | 4.58 hours | Iodine-129 | 15,700,000 years |
| Cobalt-60 | 5.271 years | Selenium-75 | 119.8 days | Uranium-238 | 4,468,000,000 years |
| Copper-62 | 9.74 minutes | Sodium-22 | 2.602 years | Iodine-131 | 8.04 days |
| Copper-64 | 12.701 hours | Sodium-24 | 15 hours | Xenon-127 | 6.41 days |
| Copper-67 | 61.86 hours | Strontium-85 | 64.84 days | Iron-55 | 2.7 years |
| Gallium-67 | 78.26 hours | Strontium-89 | 50.5 days | Xenon-133 | 5.245 days |
| Gold-195 | 183 days | Sulfur-35 | 87.44 days | Iron-59 | 44.529 days |
| Ondansetron | 360 min | Capecitabine | 2400s | Carmustine | 0.25h |

Radioisotopes–isotopes that decay producing radiation–are unstable and with time they eventually disappear given a more stable isotope. Some radioisotopes decay very quickly, such as the ones used in nuclear medicine to fight cancer. Other radioisotopes take longer to disappear.

## The concept of half-live

The half-life of an isotope represented as $t_{1/2}$ is the time it takes for an isotope to disappear reducing the sample mass to half the initial value. For example, $t_{1/2}$ for chromium-51 is 28 days and that means that after 28 days a sample of 1 gram of the radioisotope will indeed weigh 0.5 g. Table 11 reports half-lives of numerous isotopes. Samples of radioisotopes weigh less and less with time as they decompose producing more stable isotopes. Similarly, $t_{1/2}$ for strontium-90 is 38 years which means that a one-gram sample will take 38 years to reduce its mass to 0.5g. We can use the concept of half-life to compare the speed of decomposition of different radioisotopes. For example $t_{1/2}$ for strontium-90 is 38 years whereas $t_{1/2}$ for chromium-51 is 28 years. Hence, strontium-90 will exist longer than chromium-51. The activity of an isotope is indeed its rate of the decomposition $r$ which depends on the amount of radioactive isotope you have in the sample $n$,

$$r = kn$$

where $k$ is the rate constant for the decomposition. At the same time this rate constant is related to half-life, as decomposition is a first order reaction:

$$t_{1/2} = \frac{0.693}{k}$$

## Quantifying half-live

The formula that related the amount of radioisotope with $t_{1/2}$ is:

$$N(t) = N_o \cdot 0.5^{\left(\frac{t}{t_{1/2}}\right)} \tag{8}$$

where $N(t)$ is the amount of isotope at a given time $t$, $N_o$ is the initial amount of isotope, $t$ is the time and $t_{1/2}$ is the half-life. $N(t)$ is often referred to as the activity of the radioisotope at a given time $t$. At the same time, while the radioisotope disappears, a new isotope–this time more stable than the radioisotope–starts forming. The amount of product formed $F(t)$

at a given time is:

$$F(t) = N_o \cdot \left[1 - 0.5^{\left(\frac{t}{t_{1/2}}\right)}\right] \qquad (9)$$

## After several half-lives

So if the half-life is the time it takes for a radioisotope to decompose in half, what would happen after several half-lives? For example, imagine we have 20 grams of iridium-131 with a half-life of 8 days. When we prepare or hypothetically unseal the sample, we will have 20 grams of $^{131}$Ir. After one half-life (8 days) we'll have 10 grams of $^{131}$Ir. After two half-lives (16 days), we'll have 5 grams of $^{131}$Ir. Similarly, after three half-lives (22 days), we'll have 2.5 grams.

---

**Example**

$^{131}_{53}I$ has a half-life of 8days. How many milligrams of a 50mg sample will remain after 10 days.

- - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - -

**Answer**: We will following steps to solve this problem:

**1** **Step one:** list of the given variables.

**2** **Step two:** use the half-life formula $N(t) = N_o \cdot 0.5^{\frac{t}{t_{1/2}}}$ to obtain the mass remaining of the radioisotope

$$N(t) = N_0 \cdot 0.5^{\frac{t}{t_{1/2}}}$$

10d

50mg

8d

**3** **Step three:** solve for $N = 50 \cdot 0.5^{\frac{10}{8}} = 50 \cdot 0.5^{1.25} = 21mg$. The result means that after 10 days from the 50mg sample of radioisotope, only 21mg will remain due to radioactive decay.

---

# Procedure

## Part A: Background measurement

☐ *Step 1:* – Obtain a Geiger counter. Turn it on and let it warm up for five minutes.

☐ *Step 2:* – Start the Geiger counter. Set up the measurement time to 60 seconds and the measuring voltage according to your professor's instructions. Mind to select a voltage of 900V for all measurements (Press Display/High Voltage/Up/Down until you reach 900V). Press measure (press Display until the light cursor is next to count; then press Count until the stop button lights up.) and write down the background radioactivity in counts per minute in the table below.

☐ *Step 3:* – Measure the background radiation by reading the meter 10 times.

☐ *Step 4:* – Compute the average activity and standard deviation.

## Part B: Calculation of $t_{1/2}$ for a set of mass measurements

☐ *Step 1:* – Weight between 10 and 11 grams of KCl in a scale. Write down your measurement. Place the sample in a 100mL beaker.

☐ *Step 2:* – With the help of a stand, clamp the counter as close a possible to the sample but without touching the sample. Be very careful with the membrane at the end of the counter as it is very delicate and tears easily.

☐ *Step 3:* – Set up the measurement time to 60 seconds and the measuring voltage according to your professor's instructions. Mind to select a voltage of 900V for all measurements (Press Display/High Voltage/Up/Down until you reach 900V). Press measure (press Display until the light cursor is next to count; then press Count until the stop button lights up.) and write down the activity in counts per minute in the Results section.

☐ *Step 4:* – Measure radiation by reading the meter 10 times.

☐ *Step 5:* – Repeat Part A for a set of K masses between: 14-15g, 19-20g, and 24-25g.

☐ *Step 6:* – For each sample compute the average activity $\overline{A}$ in cps and the number of 40-K atoms in the sample, $N$.

☐ *Step 7:* – Plot $\overline{A}$ in cps in the vertical axis versus $N$ in the horizontal axis.

☐ *Step 8:* – Compute the half-life for each mass measurement with its average.

☐ *Step 9:* – From the slope of your plot calculate the half-life of the isotope.

☐ *Step 10:* – Compare the calculated half-lives with the experimental value.

## Calculations

⓪ The mass of KCl your weighted, $m$.

① The number of 40-K atoms in you sample, $n$, given its abundance is 0.012%:

$$N = \frac{m \cdot N_o \cdot f}{AW} = \boxed{0} \cdot 6.02 \times 10^{23} \cdot 0.00012 \cdot 39.0983/74.5$$

② The average activity in cpm.

③ The average activity in cps:

$$A(cps) = \boxed{2}/60$$

④ The standard deviation in cps.

⑤ These are the activity values in cpm for the background (without K).

⑥ These are the activity values in cpm for the sample.

⑦ These are the activity values in cpm for the sample without the background. You can susbtract the average value and the standard deviation.

$$\boxed{6} - \boxed{5}$$

$\boxed{8}$ Calculated half-life of the isotope in years (the one measured in the experiment). In the formula below you need to use the Activity in cps.

$$t_{1/2}^{calc.} = \frac{0.693 \cdot \boxed{1}}{\boxed{7} \cdot 31536000}$$

$\boxed{9}$ The sum of activity times mass and mass squared

$\boxed{10}$ The average half-life

$\boxed{11}$ Half-life calculated by means of a linear regression

$$t_{1/2}^{calc.}(LR) = \frac{0.693}{31536000} \times \frac{\sum N^2}{\sum A \cdot N}$$

$\boxed{12}$ Experimental half-life of the isotope in years (the one obtained from the tables)

$\boxed{13}$ The percent error

**STUDENT INFO**

Name:                                    Date:

**Pre-lab Questions**

# Radioactivity: half-life of K-40

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1. Research the half-life of the following isotopes: (a) Chlorine-36 (b) Cadmium-109 (c) Copper-64 (d) Chromium-51 (e) Carbon-14 (f) Gold-195 (g) Calcium-45

2. Classify the following nuclear reactions as: (a) $\alpha$ decay (b) $\beta$ decay (c) $\gamma$ decay (d) positron emission (e) electron capture (i) $^{14}_{6}C \longrightarrow \, ^{14}_{7}N + \, ^{0}_{-1}\beta$ (ii) $^{11}_{6}C \longrightarrow \, ^{11}_{5}B + \, ^{0}_{+1}\beta^{+}$ (iii) $^{55}_{26}Fe + \, ^{0}_{-1}\beta \longrightarrow \, ^{55}_{25}Mn + X-ray$ (iv) $^{234}_{88}Th^{*} \longrightarrow \, ^{234}_{88}Th + \, ^{0}_{0}\gamma$ (v) $^{226}_{88}Ra \longrightarrow \, ^{222}_{86}Rn + \, ^{4}_{2}\alpha$

3. The half-life of bromine-74 is 25 min. How much of a 100 mg sample is still active after 100 min?

4. Identify the unknown radioactive particle involved in the following nuclear equations: (a) $^{9}_{4}Be + \, ^{A}_{Z}X \longrightarrow \, ^{12}_{6}C + \, ^{1}_{0}n$ (b) $^{31}_{15}P + \, ^{1}_{1}H \longrightarrow \, ^{31}_{16}S + \, ^{A}_{Z}X$ (c) $^{3}_{1}H + \, ^{2}_{1}H \longrightarrow \, ^{A}_{Z}X + \, ^{1}_{0}n$ (d) $^{14}_{6}C \longrightarrow \, ^{A}_{Z}X + \, ^{0}_{-1}\beta$

5. Indicate the nuclear symbol for (a) Oxygen-18 (b) Magnesium-24 (c) Lithium-7

**STUDENT INFO**

Name:                    Date:

**Results**
**EXPERIMENT**

# Radioactivity: half-life of K-40

(0) m (K) in g=_____

(1) $N$ (⁴⁰K) in atoms=_____

## Part A

| Activity, A (cpm) | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | $\overline{A}$ (cpm) | $\overline{A}$ (cps) | s(cps) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Background (5) | | | | | | | | | | | (2) | (3) | (4) |
| Sample + Background (6) | | | | | | | | | | | | | |
| Sample (7) | | | | | | | | | | | | | |

(0) m (K) in g=_____

(1) $N$ (⁴⁰K) in atoms=_____

## Part B

| Activity, A (cpm) | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | $\overline{A}$ (cpm) | $\overline{A}$ (cps) | s(cps) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample + Background (6) | | | | | | | | | | | | | |
| Sample (7) | | | | | | | | | | | | | |

⓪ m (K) in g=_____  ① N ($^{40}$K) in atoms=_____

| Activity, A (cpm) | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | $\overline{A}$ (cpm) | $\overline{A}$ (cps) | $s$(cps) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample + Background | ⑥ | | | | | | | | | | | | | |
| Sample | ⑦ | | | | | | | | | | | | | |

⓪ m (K) in g=_____  ① N ($^{40}$K) in atoms=_____

| Activity, A (cpm) | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | $\overline{A}$ (cpm) | $\overline{A}$ (cps) | $s$(cps) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample + Background | ⑥ | | | | | | | | | | | | | |
| Sample | ⑦ | | | | | | | | | | | | | |

| N (atoms) ① | $t_{1/2}$ (s) ⑧ | A (cpm) ② | $A \cdot N$ ①×② | $N^2$ ①×① |
|---|---|---|---|---|
| | | | | |
| | | | | |
| | | | | |
| | | | | |
| | ⑨ Sum ($\Sigma$)= | | | |

⑩ $\overline{t}_{1/2}^{calc.}$ (years)=_____

⑪ $t_{1/2}^{calc.}$(LR) (years)=_____

⑫ $t_{1/2}^{theory}$ (years)=_____  ⑬ % error=_____

⑫ $t_{1/2}^{theory}$ (years)=_____  ⑬ % error=_____

Figure 12: $\overline{A}$ cps (Y axis) vs. N (X axis)

**Post-lab Questions**

# Radioactivity: half-life of K-40

1. Classify the following nuclear reactions as: (a) $\alpha$ decay (b) $\beta$ decay (c) $\gamma$ decay (d) positron emission (e) electron capture (i) $^{238}_{92}U \longrightarrow ^{234}_{90}Th + ^{4}_{2}He$ (ii) $^{42}_{19}K \longrightarrow ^{42}_{20}Ca + ^{0}_{-1}e$ (iii) $^{15}_{8}O \longrightarrow ^{15}_{7}N + ^{0}_{+1}e$ (iv) $^{228}_{88}Ra \longrightarrow ^{228}_{89}Ac + ^{0}_{-1}e$ (v) $^{13}_{6}C + ^{1}_{1}H \longrightarrow ^{14}_{7}N + ^{0}_{0}\gamma$

2. Indicate the name of the following nuclear symbols: (a) $^{0}_{+1}e^{+}$ (b) $^{0}_{0}\gamma$ (c) $^{1}_{1}H$

3. Research the half-life of the following isotopes: (a) Potassium-40 (b) Cesium-137 (c) Cobalt-57 (d) Bismuth-212 (e) Gallium-67 (f) Americium-241

4. The half-life of bromine-74 is 25 min. 20mg of the isotopes remain after 10 minutes of preparing the sample. Calculate the initial mass of the bromine-74 sample.

# Periodic Table of Chemical Elements

| 1 IA | 2 IIA | 3 IIIB | 4 IVB | 5 VB | 6 VIB | 7 VIIB | 8 VIIIB | 9 VIIIB | 10 VIIIB | 11 IB | 12 IIB | 13 IIIA | 14 IVA | 15 VA | 16 VIA | 17 VIIA | 18 VIIIA |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 H 1.0079 Hydrogen | | | | | | | | | | | | | | | | | 2 He 4.0025 Helium |
| 3 Li 6.941 Lithium | 4 Be 9.0122 Beryllium | | | | | | | | | | | 5 B 10.811 Boron | 6 C 12.011 Carbon | 7 N 14.007 Nitrogen | 8 O 15.999 Oxygen | 9 F 18.998 Flourine | 10 Ne 20.180 Neon |
| 11 Na 22.990 Sodium | 12 Mg 24.305 Magnesium | | | | | | | | | | | 13 Al 26.982 Aluminium | 14 Si 28.086 Silicon | 15 P 30.974 Phosphorus | 16 S 32.065 Sulphur | 17 Cl 35.453 Chlorine | 18 Ar 39.948 Argon |
| 19 K 39.098 Potassium | 20 Ca 40.078 Calcium | 21 Sc 44.956 Scandium | 22 Ti 47.867 Titanium | 23 V 50.942 Vanadium | 24 Cr 51.996 Chromium | 25 Mn 54.938 Manganese | 26 Fe 55.845 Iron | 27 Co 58.933 Cobalt | 28 Ni 58.693 Nickel | 29 Cu 63.546 Copper | 30 Zn 65.39 Zinc | 31 Ga 69.723 Gallium | 32 Ge 72.64 Germanium | 33 As 74.922 Arsenic | 34 Se 78.96 Selenium | 35 Br 79.904 Bromine | 36 Kr 83.8 Krypton |
| 37 Rb 85.468 Rubidium | 38 Sr 87.62 Strontium | 39 Y 88.906 Yttrium | 40 Zr 91.224 Zirconium | 41 Nb 92.906 Niobium | 42 Mo 95.94 Molybdenum | 43 Tc 96 Technetium | 44 Ru 101.07 Ruthenium | 45 Rh 102.91 Rhodium | 46 Pd 106.42 Palladium | 47 Ag 107.87 Silver | 48 Cd 112.41 Cadmium | 49 In 114.82 Indium | 50 Sn 118.71 Tin | 51 Sb 121.76 Antimony | 52 Te 127.6 Tellurium | 53 I 126.9 Iodine | 54 Xe 131.29 Xenon |
| 55 Cs 132.91 Caesium | 56 Ba 137.33 Barium | 57-71 La-Lu | 72 Hf 178.49 Halfnium | 73 Ta 180.95 Tantalum | 74 W 183.84 Tungsten | 75 Re 186.21 Rhenium | 76 Os 190.23 Osmium | 77 Ir 192.22 Iridium | 78 Pt 195.08 Platinum | 79 Au 196.97 Gold | 80 Hg 200.59 Mercury | 81 Tl 204.38 Thallium | 82 Pb 207.2 Lead | 83 Bi 208.98 Bismuth | 84 Po 209 Polonium | 85 At 210 Astatine | 86 Rn 222 Radon |
| 87 Fr 223 Francium | 88 Ra 226 Radium | 89-103 Ac-Lr | 104 Rf 261 Rutherfordium | 105 Db 262 Dubnium | 106 Sg 266 Seaborgium | 107 Bh 264 Bohrium | 108 Hs 277 Hassium | 109 Mt 268 Meitnerium | 110 Ds 281 Darmstadtium | 111 Rg 280 Roentgenium | 112 Uub 285 Ununbium | 113 Uut 284 Ununtrium | 114 Uuq 289 Ununquadium | 115 Uup 288 Ununpentium | 116 Uuh 293 Ununhexium | 117 Uus 292 Ununseptium | 118 Uuo 294 Ununoctium |

**Lanthanides**

| 57 La 138.91 Lanthanum | 58 Ce 140.12 Cerium | 59 Pr 140.91 Praseodymium | 60 Nd 144.24 Neodymium | 61 Pm 145 Promethium | 62 Sm 150.36 Samarium | 63 Eu 151.96 Europium | 64 Gd 157.25 Gadolinium | 65 Tb 158.93 Terbium | 66 Dy 162.50 Dysprosium | 67 Ho 164.93 Holmium | 68 Er 167.26 Erbium | 69 Tm 168.93 Thulium | 70 Yb 173.04 Ytterbium | 71 Lu 174.97 Lutetium |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|

**Actinides**

| 89 Ac 227 Actinium | 90 Th 232.04 Thorium | 91 Pa 231.04 Protactinium | 92 U 238.03 Uranium | 93 Np 237 Neptunium | 94 Pu 244 Plutonium | 95 Am 243 Americium | 96 Cm 247 Curium | 97 Bk 247 Berkelium | 98 Cf 251 Californium | 99 Es 252 Einsteinium | 100 Fm 257 Fermium | 101 Md 258 Mendelevium | 102 No 259 Nobelium | 103 Lr 262 Lawrencium |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|

**Key**

z mass
**Symbol**
Name

Legend:
- Alkali Metal
- Alkaline Earth Metal
- Metal
- Metalloid
- Non-metal
- Halogen
- Noble Gas
- Lanthanide/Actinide