

1 Electrochemistry: galvanic cells

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

- | | |
|--|---|
| <input type="checkbox"/> jumbo test tubes | <input type="checkbox"/> 0.1M solutions of KNO_3 , KCl , KOH , HCl , and $\text{Ca}(\text{NO}_3)_2$ |
| <input type="checkbox"/> conductivity meter | <input type="checkbox"/> an unknown solution |
| <input type="checkbox"/> 6M solution of NH_3 | <input type="checkbox"/> 5mL, 10mL, 25mL pipets (preferred Mohr's) |
| <input type="checkbox"/> 6M solution of CH_3COOH | <input type="checkbox"/> 250mL and 50mL beakers |
| <input type="checkbox"/> Ethyl alcohol | <input type="checkbox"/> 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, $\text{S}\cdot\text{cm}^{-1}$. 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 $10\mu\text{S}\cdot\text{cm}^{-1}$.
- × **Weak electrolyte.** When the aqueous solution of that substance conducts electricity poorly. In general terms, these electrolytes present medium conductivities, between $10\text{-}1000\mu\text{S}\cdot\text{cm}^{-1}$.
- × **Strong electrolyte.** When the conductivity of the aqueous solution of that substance is high. In general terms, these electrolytes present large conductivities, larger than $1000\mu\text{S}\cdot\text{cm}^{-1}$.

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^∞ ($10^5\text{cm}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$)	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.

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.

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 ,

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

The same values apply for KCl.

We can see that the addition of the separate conductivities (κ) is very close to the total conductivity of the mixture with the same concentrations for each electrolyte.

$$\begin{aligned}\kappa(\text{HNO}_3\ 0.05\text{ M}) + \kappa(\text{KCl}\ 0.05\text{ M}) &= 19.6\text{ mS/cm} + 9.6\text{ mS/cm} = 29.2\text{ mS/cm} \\ \kappa(\text{HNO}_3\ 0.05\text{M} + \text{KCl}\ 0.05\text{M}) &= 29.6\text{ mS/cm}\end{aligned}$$

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:* – 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 4:* – Now press Standardize (top right menu) and input 0.999 mS/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 5:* – 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.

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 6:* – Following the procedure outlined above, measure the conductivity of distilled water. Record the value in the Results section.
- ☐ *Step 7:* – Following the procedure outlined above, measure the conductivity of tap water. Record the value in the Results section.
- ☐ *Step 8:* – Following the procedure outlined above, measure the conductivity of Ethyl alcohol ($\text{C}_2\text{H}_5\text{OH}$). Record the value in the Results section.
- ☐ *Step 9:* – Classify the substance as strong, weak, or nonelectrolyte.

Part C. Series of electrolytes.

- ☐ *Step 10:* – 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 11:* – 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 12:* – 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 13:* – In a clean 50 mL beaker, add 20 mL of 0.10 M KNO₃ 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 14:* – In a clean 50 mL beaker, add 20 mL of 0.10 M Ca(NO₃)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 15:* – 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 16:* – 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 17:* – Measure the conductivity of a 0.1 M solution of HCl. Write down the result in the Results section.
- ☐ *Step 18:* – 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 19:* – 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 KNO₃.

- ☐ *Step 20:* – Write down the conductivity of the 0.050 M solution of HCl from the previous section in the Results section.
- ☐ *Step 21:* – Write down the conductivity of the solution of KNO₃ from the previous section in the Results section.
- ☐ *Step 22:* – In a clean 50 mL beaker, add 20 mL of 0.10 M HCl and 20 mL of 0.10 M KNO₃. 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 $\text{HC}_2\text{H}_3\text{O}_2$.

- ☐ *Step 23:* – Prepare the following dilutions: 100mL of acetic acid ($\text{HC}_2\text{H}_3\text{O}_2$) 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 24:* – 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 25:* – In a clean 50 mL beaker, add 20 mL of 0.12 M $\text{HC}_2\text{H}_3\text{O}_2$ 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 26:* – In a clean 50 mL beaker, add 20 mL of 0.12 M NH_3 and 20 mL of 0.12 M $\text{HC}_2\text{H}_3\text{O}_2$. 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?

STUDENT INFO

Name:

Date:

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 ($\text{HC}_2\text{H}_3\text{O}_2$) 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	$\mu\text{S} \cdot \text{cm}^{-1}$	_____
FeCl_3	0.05M	10000	$\mu\text{S} \cdot \text{cm}^{-1}$	_____
$\text{C}_6\text{H}_{12}\text{O}_6$	0.05M	120	$\mu\text{S} \cdot \text{cm}^{-1}$	_____
CH_3COOH	0.05M	320	$\mu\text{S} \cdot \text{cm}^{-1}$	_____

STUDENT INFO

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**Results
EXPERIMENT****Conductivity of electrolyte solutions****Part B: Pure substances**

	Conductivity	Units	Electrolyte type
Distilled water	_____	_____	_____
Tap water	_____	_____	_____
C ₂ H ₅ OH	_____	_____	_____

Part C: Electrolytes

	Concentration (M)	Conductivity	Units	Electrolyte type
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+KNO₃ mixture

	Concentration (M)	Conductivity	Units
HCl	_____	_____	_____
KNO ₃	_____	_____	_____
HCl+KNO ₃	_____	_____	_____

Part F: HC₂H₃O₂+NH₃ mixture

	Concentration (M)	Conductivity	Units
HC ₂ H ₃ O ₂	_____	_____	_____
NH ₃	_____	_____	_____
HC ₂ H ₃ O ₂ +NH ₃	_____	_____	_____

STUDENT INFO

Name:

Date:

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?

