Tracking Reaction Progress via Electrochemical Methods

Following a reaction’s progress:
- Reactions with visible changes
  - Bubbles of gases
  - Color changes (colored reactant and/or product or indicator added)
- Reactions with Non-visible changes
  - How do we follow these?
- Electrochemical methods are one way:
  - Measuring changes in
    - Conductivity
    - pH

Conductometric methods

For a solution to conduct an electrical current, what is required?

Solid NaCl is composed of ions, will it conduct electrical current?

Do all ions behave the same in terms of conductance in solution?

Na⁺: I⁻

Ionic Conductances @ 25°C and infinite dilution or Mobility of Ions

<table>
<thead>
<tr>
<th>Cations</th>
<th>λ⁺</th>
<th>Anions</th>
<th>λ⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>H⁺</td>
<td>350</td>
<td>OH⁻</td>
<td>199</td>
</tr>
<tr>
<td>Na⁺</td>
<td>50</td>
<td>Cl⁻</td>
<td>76</td>
</tr>
<tr>
<td>K⁺</td>
<td>74</td>
<td>Br⁻</td>
<td>78</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>73</td>
<td>NO₃⁻</td>
<td>71</td>
</tr>
<tr>
<td>Ca⁺</td>
<td>120</td>
<td>CH₃COO⁻</td>
<td>41</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SO₄²⁻</td>
<td>160</td>
</tr>
</tbody>
</table>

What ion has the greatest mobility?

For strong electrolytes:

\[ \Lambda = \sum n \lambda_{\text{ions}} = n \lambda_+ + n \lambda_- \]

- NaCl: 50 + 76 = 126
- Na₂SO₄: 2(50) + 160 = 260
If you apply an electrical current to a conductive solution, such as aqueous CuCl₂, what happens?

We want to measure the voltage across two electrodes, such as the paper clips in the home-made conductivity probe.

However, we would like to limit the electrolysis reactions at the electrodes.

What influences conductivity?
The conductivity of a solution depends on the following factors:

- Directly on the surface area of the electrodes
- Inversely on the distance between the electrodes
- Directly on the concentration of the ions in solution
- Directly on the mobility of the ions
- Directly on the temperature

Conductometric Titration

- How does the conductivity change during an acid-base neutralization reaction?
- Measure conductivity as titrant is added.
- A change in conductivity must occur at equivalence point.

A piece-wise function is generated and the intersection of the two lines locates the equivalence point.

What is present at various points?
Laboratory titration reaction

- CH$_3$COOH + NH$_3$ $\rightarrow$ CH$_3$COO$^-$ NH$_4^+$
  where the ammonia is the titrant
- Can ammonia conduct current?
- How is conductivity going to change?

Potentiometric methods

Direct measurement
Does a reaction occur in the cell?

Cell generates a voltage!
- reactions occur at the electrodes!

Simple potentiometer

known current - + known variable E

Potentiometric Balance

NO current flows

unknown current Zn Cu

For an electrode measurement, the cell must consist of:

- Reference electrode
  - Maintains a fixed constant potential
  - Composition must not change
  - Common references: Calomel, Silver chloride
- Indicator electrode
  - Potential depends on concentration of electroactive species
  - For glass electrode, the electroactive species is H$^+$

Must have two electrodes!

Combination Glass Electrode

external reference electrode (porous plug)
potential develops across membrane due to pH difference
constant pH
External solution
solution level
internal reference electrode
glass membrane-hydrated (50 µm thick)
at 25°C: \( E = E' - 0.0591 \text{pH} \)

depends on internal reference electrode and membrane behavior, which changes with time

Must calibrate with a buffer!

Potentiometric Titration
- How does the pH change during an acid-base neutralization reaction?
- Measure pH as titrant is added.

Potentiometric Titration

\[
\text{HCl} + \text{NaOH} \rightarrow \text{NaCl} + \text{H}_2\text{O}
\]

Volume of titrant (mL NaOH)

Calculating the derivative of the titration curve

We calculate the slope or \( \Delta \text{pH}/\Delta \text{volume} \) between each pair of data points.

<table>
<thead>
<tr>
<th>Volume (mL)</th>
<th>pH</th>
<th>( \Delta \text{pH} )</th>
<th>( \Delta \text{volume} )</th>
<th>( \Delta \text{pH}/\Delta \text{vol} )</th>
<th>Ave. Vol.</th>
</tr>
</thead>
<tbody>
<tr>
<td>24.00</td>
<td>2.69</td>
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<td></td>
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<td>24.50</td>
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<td>25.10</td>
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</tr>
<tr>
<td>25.50</td>
<td>11.00</td>
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</tr>
</tbody>
</table>

Find the maximum of the derivative?
Using the derivative to locate the equivalence point

The maximum of the derivative locates the equivalence point.

Some questions

- What indicator would work?
- How do you calculate the pKₐ of the weak acid?
- How do you calculate the molar mass of the weak acid?

- Some pH meters are calibrated using only one buffer, a single point calibration. Using E = E' - 0.0591pH, explain how this can be done.
- What is the advantage of a two point calibration on a pH meter?
- All of the conductivity measurements were done without calibration of the conductivity probe. Why did things work?

- Which compound has the greater conductivity in 0.1 M solution? Explain why.
  - NaCl or CaCl₂
  - HCl or KCl
  - KOH or NaOH
- Why are pH meters calibrated using buffers of known pH instead of acid or base solutions of known concentration and pH?

- How does the ionic conductance vary with temperature? Use this equation to describe the variation:
  \[ \lambda_T = \lambda_{25} [1 + 0.020 (T-25)] \]
  where T is Celsius temperature and \( \lambda \) is the ionic conductance. Values for \( \lambda_{25} \) were given earlier.