


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

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Conductometric methods

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- 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⁺Cl⁻

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

Cations	Λ_+	Anions	Λ_-
H ⁺	350	OH ⁻	199
Na ⁺	50	Cl ⁻	76
K ⁺	74	Br ⁻	78
NH ₄ ⁺	73	NO ₃ ⁻	71
Ca ²⁺	120	CH ₃ COO ⁻	41
		SO ₄ ⁻²	160

What ion has the greatest mobility?

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For strong electrolytes:

$$\mathbf{L} = \mathbf{S} \mathbf{I}_{\text{ions}} = n_+ \mathbf{I}_+ + n_- \mathbf{I}_-$$

$$\blacklozenge \text{NaCl} \quad 50 + 76 = 126$$

$$\blacklozenge \text{Na}_2\text{SO}_4 \quad 2(50) + 160 = 260$$

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- If you apply an electrical current to a conductive solution, such as aqueous CuCl_2 , 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.

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Conductivity probe

Voltage converted to conductivity by CBL

Units of microsiemens per centimeter

Graphite electrode (fairly inert)

Voltage measured with an alternating current to prevent electrolysis (no reaction at electrodes)

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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

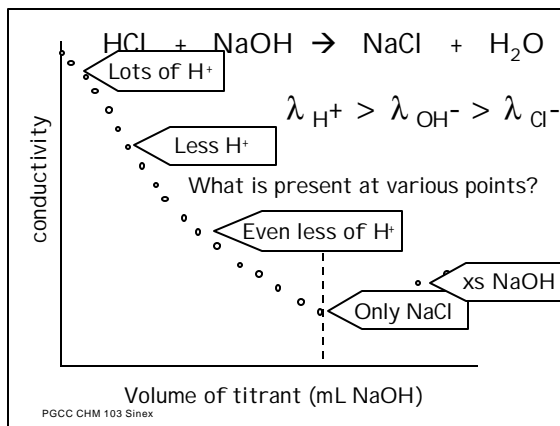
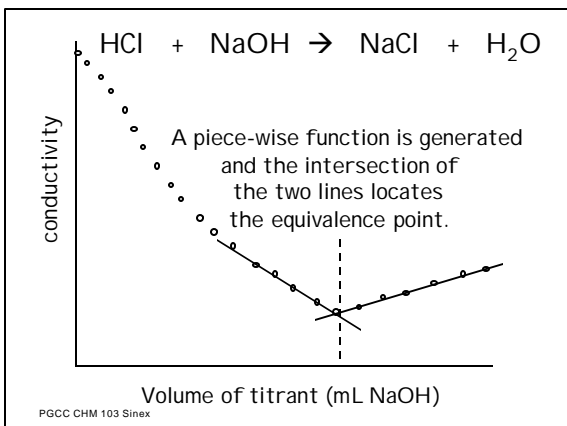
Held constant on probe (for surface area and distance)
Held constant during experiment (for concentration, mobility, and temperature)

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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.

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Laboratory titration reaction

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

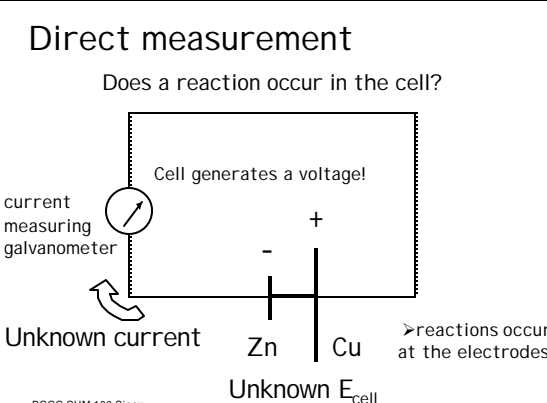
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Potentiometric methods

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Direct measurement

Does a reaction occur in the cell?



Cell generates a voltage!

current measuring galvanometer

Unknown current

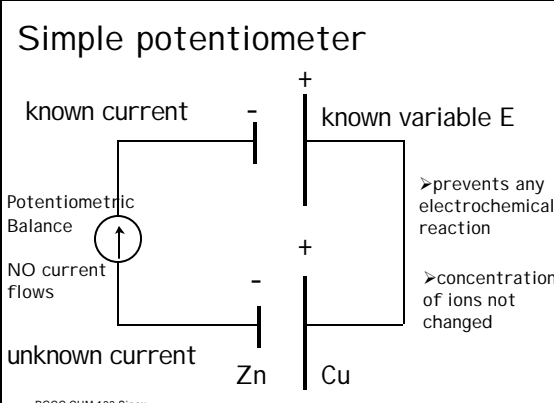
Zn | Cu

Unknown E_{cell}

reactions occur at the electrodes!

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Simple potentiometer



known current

known variable E

Potentiometric Balance

NO current flows

unknown current

Zn | Cu

prevents any electrochemical reaction

concentration of ions not changed

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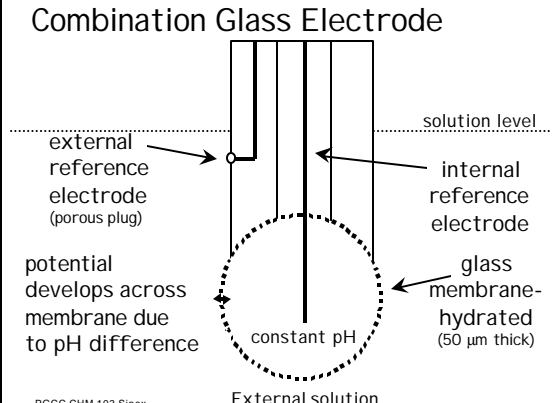
For an electrode measurement, the cell must consist of:

<ul style="list-style-type: none"> ■ Reference electrode <ul style="list-style-type: none"> ■ Maintains a <u>fixed constant potential</u> ■ Composition must not change ■ Common references <ul style="list-style-type: none"> ■ Calomel ■ Silver chloride 	<ul style="list-style-type: none"> ■ Indicator electrode <ul style="list-style-type: none"> ■ Potential depends on concentration of electroactive species ■ For glass electrode, the electroactive species is H^+
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Must have two electrodes!

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Combination Glass Electrode



external reference electrode (porous plug)

internal reference electrode

glass membrane-hydrated (50 μm thick)

constant pH

External solution

potential develops across membrane due to pH difference

solution level

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at 25°C: measured voltage

$$\bar{E} = E' - 0.0591 \text{ pH}$$

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

Must calibrate with a buffer!

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What type of function is this?

$$E = E' - 0.0591 \text{ pH}$$

How does the measured voltage, E, vary with pH?

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Potentiometric Titration

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

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HCl + NaOH -> NaCl + H2O

How do we locate the equivalence point?

Equivalence point pH

pH = 7

Volume of titrant (mL NaOH)

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HCl + NaOH -> NaCl + H2O

What is present at various points?

Just acid

Both acid & salt

Just salt

xs NaOH

Volume of titrant (mL NaOH)

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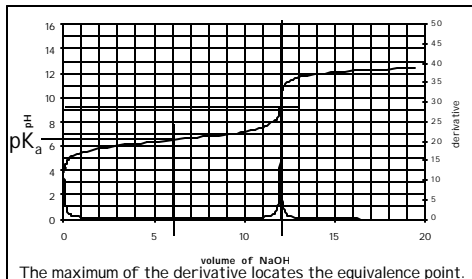
Calculating the derivative of the titration curve

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

Volume	pH	ΔpH	Δvolume	$\Delta\text{pH}/\Delta\text{vol}$	Ave. Vol.
24.00	2.69				
24.50	3.00				
24.90	3.70				
25.00	7.00				
25.10	10.30				
25.50	11.00				

PGCC CHM 103 Sinex Find the maximum of the derivative?

Using the derivative to locate the equivalence point



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Some questions

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

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- Some pH meters are calibrated using only one buffer, a single point calibration. Using $E = E' - 0.0591\text{pH}$, 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?

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- Which compound has the greater conductivity in 0.1 M solution? Explain why.
 - NaCl or CaCl_2
 - 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?

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- 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 λ is the ionic conductance. Values for λ_{25} were given earlier.

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