

CE 554 LABORATORY

ACID - BASE TITRATIONS

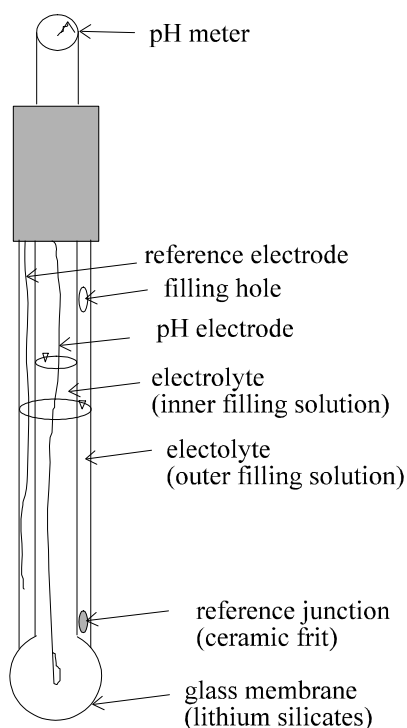
BACKGROUND NOTES

The activity of the hydrogen ion in water, $\{H^+\}$, may be measured directly through measurement of a hydrogen ion selective electrode potential, from which pH ($-\log \{H^+\}$) may be calculated. pH electrodes are glass electrodes, and the selectivity of these electrodes for positive ions follows the sequence: $H^+ \ggg Na^+ > K^+ \ggg Ca^{2+}$.

The complete electrochemical cell consists of contacts between the following elements

inner	electrolyte	glass	reference	electrolyte	reference
electrode	(inner filling	membrane	junction	(outer filling	electrode
(pH)	solution)	- solution	(frit)	solution)	

Combination pH/reference Electrode



The potential is related to the hydrogen ion activity through the Nernst Equation:

$$E = E^{\circ} + \frac{2.3026RT}{F} \log \{H^{+}\}$$

Where: E = the cell potential (volts, V)
 E^o = a constant (depends on the reference electrode, glass, junction, etc.)
 T = Temperature in Kelvin (K)
 R = The gas constant = 8.3144 J / (mol K)
 F = Faraday's Constant = 96,484.6 J / (V mol)

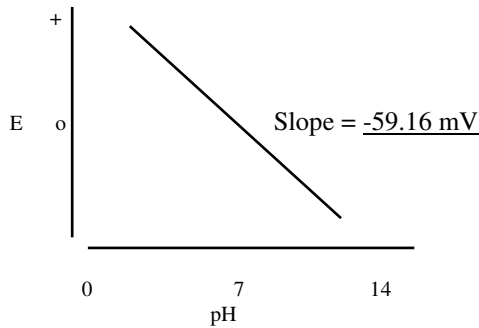
At 25° C, the Nernst equations simplifies to the linear equation (y = b - m·x):

$$E = E^{\circ} - \text{pH} \cdot 59.16 \text{ mV}$$

By definition, at pH = 7, E = 0 volts (assuming the probe's efficiency is 100%). Hence, on manual calibration meters, find the intercept first (because this point is independent of the slope) and then adjust the slope.

To Standardize the Meter:

- (1) At pH=7.0 (the isothermal point)
- (2) At another pH to adjust the slope of the line, usually at pH = 4 or 10)



at pH = 7.0 E = 0.0 rel. mV
 at pH = 4.0 E = ? rel. mV
 at pH = 10.0 E = ? rel. mV

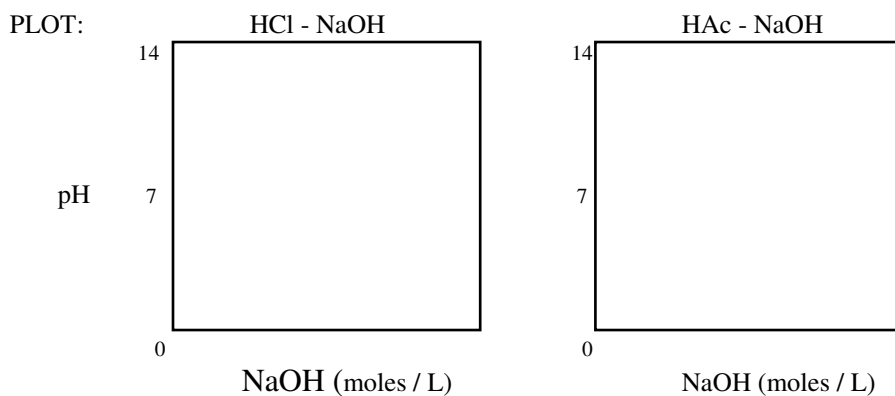
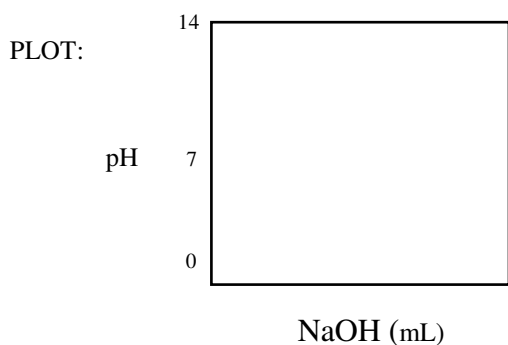
Uses of pH Titrations:

- (1) Measure alkalinity/acidity
 $\text{alk} = [\text{HOC}_3^-] + [\text{OH}^-] + 2[\text{CO}_3^{2-}] - [\text{H}^+]$
 The alkalinity end point is where all carbonate species are converted to H₂CO₃ (pH ≈ 4.5)
- (2) Standardize strong acids or bases for other titrations
- (3) Calculate buffer capacity (same as (1) where the B.C. is due to carbonate species).
- (4) Determine pK_a's

In the lab:

- (1) First standardize the pH meter/probe.
- (2) Read the pH of the acid solution.
- (3) Begin to titrate.

Data analysis:

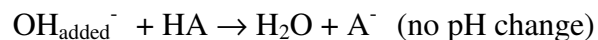


Buffer Capacity (Intensity) - resistance to pH change

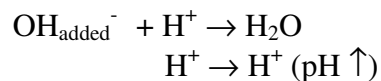
$$B = \frac{\Delta C_{OH}}{\Delta pH} = \frac{\text{change in base added}}{\text{change in pH}}$$

When NaOH is added to solution, the resulting OH^- may:

- (1) neutralize acids:



- (2) react with $[H^+]$, raising the pH. The more acid in solution, the smaller the change in pH for each unit addition of NaOH:



Similarly, addition of HCl to solution may:

- (1) neutralize base, or
 $H^+_{\text{added}} + A^- \rightarrow HA$ (no pH change)
- (2) consume OH^- , decreasing pH.
 $H^+_{\text{added}} \rightarrow H^+$ (pH ↓)

For each titration create a table:

number	mL NaOH	C_{OH}	ΔC_{OH}	pH	ΔpH	β	pH_{AVE}
1							
2							
3							
4							
.							
.							
.							

Alkalinity: Alkalinity is the buffer capacity of a solution measured as a resistance to pH change upon the addition of a strong acid to a designated pH (usually 4.5 for total alkalinity). For most natural waters alkalinity is due to the presence of carbonate species (HCO_3^- and CO_3^{2-}), and hydroxide (OH^-). In some water, other bases may be important, such as silicates, phosphates, ammonia, etc. At the endpoint in an alkalinity titration, the equivalents of acid added to the system equals the equivalents of base neutralized, or:

$$N_{\text{acid}} V_{\text{acid}} = N_{\text{base}} V_{\text{base}}$$

rearranging:

$$\left(\frac{X \text{ eq}_{\text{base}}}{L_{\text{base}}} \right) = \left(\frac{N_{\text{acid}} V_{\text{acid}}}{V_{\text{base}}} \right)$$

converting units:

$$\text{alk} \left(\frac{\text{mg CaCO}_3}{L} \right) = \left(\frac{X \text{ eq}_{\text{base}}}{L_{\text{base}}} \right) \left(\frac{1000 \text{ meq}}{\text{eq}} \right) \left(\frac{50 \text{ mg CaCO}_3}{\text{meq CaCO}_3} \right)$$

LABORATORY PROTOCOL (Acid - Base Titrations)

References:

Standard Methods for the Examination of Water and Wastewater, 14th or 15th edition., American Public Health Association.
Snoeyink and Jenkins, *Water Chemistry*, Wiley and Sons, New York, 1980.

Reagents:

0.2 % phenolphthalein in 90% ethanol (colorless red, 8.2-9.8)
0.2 % phenol red in 90% ethanol (yellow red, 6.8-8.4)
0.05 M NaOH (about 50 mL / group)
0.01 M HCl (about 120 mL / group)
0.01 M CH₃COOH (acetic acid) (about 120 mL / group)
Other Reagents: pH buffers (pH = 4, 7, and 10) (20 mL each of 2 buffers)

Methods:

In this laboratory you will titrate: (1) A strong acid (HCl) with a strong base (NaOH), and (2) a weak acid (CH₃COOH) with a strong base, and three water samples with acid (to measure alkalinity). We will observe the "progress" of (1) and (2) by measuring the pH of the solution as a function of volume of titrant (NaOH) added. We will also monitor the titrations with indicators. (1) and (2) will be compared to predicted titration curves, calculated through knowledge of the acid-base chemistry.

Procedure:

Standardization of the pH meter/probe. (Please be very gentle with the probes). Add approximately 15 mL of the pH = 7.00 buffer to a 20 mL beaker. Rinse the pH probe with distilled water with the squirt bottle, gently blot the probe with a kimwipe (not a paper towel) to remove excess water, and place the probe tip in the buffer past the glass frit. "Calibrate" to pH 7.00, with gentle agitation. Remove the probe and repeat with pH = 10.0 or 4.0 buffer, calibrating this time with either the temperature compensation dial, or other appropriate dial or button; this 2 point calibration sets the pH 7.0 intercept and the "slope" of the electrode.

Strong Acid - Strong Base Titration. Add 50 mL 0.01 M HCl to a 100 mL beaker, and add 1 (or 2) drop(s) of phenol red to the solution and gently stir with the magnetic stirring plate. Rinse the calibrated pH probe and place in the HCl solution. Record the initial pH. Titrate the solution with the 0.05 M NaOH from the burette, taking reading at least every 0.5 mL. Record both pH and mLs titrated, waiting for at least 30 sec for a stable pH reading. Near the equivalence point take reading every 0.2 mL or 0.1 mL. Stop adding NaOH at the point of color change, and record the pH and titrant volume. Continue to titrate with about 2 mL, beyond the change in color. Note the pH at which the indicator changed color.

Weak acid - Strong Base Titration. Repeat the above procedure, titrating 50 mL 0.01 M acetic acid in place of HCl. Use phenolphthalein as the indicator.

Alkalinity Titrations. Replace the NaOH in the burette with 0.01 M HCl. Add 50 mL of (1) tap water to a 100 mL beaker and add 2 drops of phenolphthalein to the solution, stirring with the magnetic stirrer. Record the initial pH, and titrate, taking volumetric readings at pH 8.3 and 4.5. If you over-shoot these pH values, start over. Repeat this procedure with: (2) river water and (3) distilled water.

Data Analysis:

Plot: (a) For the HCl - NaOH titration:

pH (on the y-axis) vs titrant volume (the raw data)

Determine: (b) The volume of titrant necessary to reach the equivalence point of the titration (that point where the pH change is the greatest; it will occur when pH 7.0 is exceeded for these acids). Calculate the exact molarity of the NaOH solution by:

Molarity*Volume = Molarity*Volume.

Plot: (c) For both acids:

pH (on the y-axis) versus moles of OH⁻ added per liter of solution, COH, where,

$C_{OH} = (\text{molarity of NaOH})(\text{titrant volume})/(\text{sample volume})$

(neglect sample dilution by the NaOH, (i.e., sample volume = 0.05 L)

Plot: (d) For the acetic acid titration, the buffer intensity, (yet to be discussed), versus pH (pH on the x axis):

$$\beta = \frac{\Delta C_{OH}}{\Delta pH} \text{ (units = Molar)}$$

Calculate: (e) The alkalinity of each of the three samples titrated with 0.01 M HCl. Report in units of mg / L as CaCO₃.

Questions:

- (1) The pKa of acetic acid occurs at the volume of titrant necessary to reach the equivalence point divided by 2 (0.005 moles / NaOH), which also is at the maximum buffer intensity. Indicate this value (on the pH scale) of both your acetic acid plots.
- (2) From the alkalinity titrations, calculate the amount of each carbonate species in river water. Assume that the total alkalinity equals the total equivalents of carbonate species.

TA's INFORMATION

Reagent Preparation:

1 week in advance: prepare a 50 % NaOH Solution:

Add 30 g NaOH to 30 mL water; Let sit for at least 5 days.

Lab week:

0.2 % phenolphthalein in 90% ethanol (colorless red, 8.2-9.8)

0.2 % phenol red in 90% ethanol (yellow red, 6.8-8.4)

Decant 50 % NaOH solution (Na_2CO_3 precipitates). Add 15 mL to 6 L de-gassed H_2O (15 mL to 6 - 1 L volumes added together in a nalgene carboy; (2.5 mL / L). Standardize with potassium acid phthalate, PAP, (dried at 110° , for 2 hrs):

Place 0.25 g PAP in a 100 mL beaker. Add 50 mL degassed water, 2 drops phenolphthalein, and titrate with the NaOH solution (approximately 25 mL) to a pink endpoint. Store in nalgene or other plastic container.

$$M_{\text{NaOH}} = (\text{mg KHC}_8\text{H}_4\text{O}_4) / ((204.23 \text{ g/mole}) * (\text{ml NaOH}))$$

Make 6 L 0.01 M HCl. Add 5 mL Concentrated HCl to 6 L degassed water, label 0.01 M HCl.

Make 6 L 0.01 M CH_3COOH . Add 3.44 mL Glacial Acetic Acid to 6 L degassed water, label 0.01 M acetic acid.

Store all solutions in tightly stoppered 10-L containers.

Other Reagents: pH buffers (pH = 4, 7, and 10)