Potentiometric Acid-Base Titration

Determination of Sodium Carbonate

A hydrochloric acid solution is standardized using primary standard sodium carbonate. A soda ash sample is then analyzed to determine its % Na_2CO_3. The end point is determined using a pH meter. One of the titrations is done with sufficient detail to allow determination of both end points and pK values for Na_2CO_3. A sample titration curve is attached. The data are analyzed using a spreadsheet computer program - directions for preparing the spreadsheet are attached. A complete report for this experiment is required.

Background: The potential of the glass electrode responds to hydrogen-ion activity according to the Nernst equation:

$$E_{glass} = E^o_{glass} + k \cdot \log a_H \; .$$

Using the definition of pH, this becomes:

$$E_{glass} = E^o_{glass} - k \cdot pH.$$

In an electrochemical cell composed of a glass electrode and a reference electrode the cell voltage is:

$$E_{cell} = E_{glass} - E_{ref} \; .$$
$$E_{cell} = (E^o_{glass} - E_{ref}) - k \cdot pH$$

Both E^o_{glass} and E_{ref} are constant at a given temperature, so the cell potential is linearly related to pH. The pH meter is adjusted to read directly in pH units by calibrating against a standard buffer solution. A correction for the temperature dependence of the slope, k, can be made by using a second standard buffer. This will not be necessary for this experiment (the instrument default value is 25^oC).

The pH meters are equipped with a combination electrode which contains the pH electrode and the reference electrode, a silver-silver chloride electrode, combined in one unit.

Preparation:

- Read Section 12A-2, p 249, in your text; it discusses the titration of sodium carbonate and its use as a primary standard.
- Oven-dry about 1.0 gram of standard Na_2CO_3 and all of your unknown for one hour or more at 110-120 °C. Place these materials in a dessicator to cool before weighing.
- Prepare 1.0 liter of 0.12 M HCl by diluting 10 mL of the concentrated acid (12M HCl). Store in a glass-stoppered bottle.
- Transfer a 1.0 g sample (analytical balance) of sodium carbonate to the 100 mL volumetric flask. Place a funnel in the flask to receive the sample. Dissolve in deionized water and dilute to the mark. Mix very well by inversion.

Operation of the pH Meter:

The pH meter is calibrated at pH = 4.01 using a 0.05 M potassium hydrogen phthalate (KHP) buffer. Dissolve 1.0 g of KHP in 100 mL of deionized water to prepare this solution. **The glass electrode is fragile and expensive. Use it with the plastic guard. Be careful not to hit it against the beaker or the stir bar.** Follow this procedure: Rinse the electrode with distilled water. Locate the fill hole near the top of the electrode and move it from the closed to the open position. Allow the electrode to soak in the buffer for several minutes prior to standardization. Depress the pH key, then depress the STANDARD key (|∠). *The standard symbol will begin flashing indicating a standardization is taking place. The AUTO symbol will begin flashing as the electrode is approaching stabilization. When the signal from the electrode is stable the AUTO READ signal will appear in the display and the instrument is no longer reading the signal from the electrode.*
Use the UP/DOWN keys to adjust the meter reading to the buffer-pH value of 4.01. Then press the pH key again to complete the one-point standardization. *The STANDARD symbol will stop flashing. It now appears with a single point indicating calibration for the instrument <u>offset</u> only.*
To measure the pH of a sample, rinse the electrode with deionized water before placing it in the solution to be measured, then press the pH key. Wait for the AUTO READ symbol to appear and note the pH value.
The meter should be standardized each week with freshly prepared buffer.

General directions for performing the potentiometric titrations:
- Add about 50 mL of water to a 25 mL aliquot of the standard Na_2CO_3 solution.
- Rinse the electrode with deionized water and immerse it in the sample solution. Provide magnetic stirring. Use a low stirring rate and take care that the stir bar does not hit the electrode. Position the buret so that the HCl can be delivered without splashing.
- Measure and record the initial buret reading as well as the initial potential.
- Add fairly large volumes (about 5 mL) initially. Press the pH key to start a measurement and wait for the AUTO READ symbol to appear before recording the solution pH. Thorough, but gentle, mixing is required to insure correct electrode response.
- Judge the volume of reagent to be added each time by estimating a value for $\Delta E/\Delta V$ after each addition. Use the attached theoretical curve as a guide to the expected <u>pH ranges</u> of most interest and to the number of data points needed.
- Continue the titration 2 to 3 mL beyond the equivalence point, increasing the volume elements as $\Delta pH/\Delta V$ again becomes smaller.

Directions for repeat titrations: Once the complete pH titration curve has been established, <u>it is only necessary to determine the second equivalence point in succeeding runs</u>. Data is only needed from about pH = 6 to pH = 2. Proceed quickly to this region. Then add the reagent in small (approx. 0.1 mL) increments before and after the equivalence point. Twelve to fourteen data points should be sufficient. Take readings as quickly as possible because the pH will tend to drift as CO_2 escapes from the solution. If you have already set up a spreadsheet to determine the equivalence point, use it to analyze one set of data before proceeding with repeat determinations. The standardization and the determination of the unknown each require at least three determinations.

Determination of % Na_2CO_3 ***in a soda ash unknown****:* The method of charges is used for the unknown since the appropriate sample size is not known in advance. The unknowns contain from 20% to 50% Na_2CO_3. Weigh out a 0.5 g sample for a preliminary determination and dissolve it in about 75 mL of water. Follow the directions for a repeat titration; <u>it is not necessary to determine the complete titration curve for the unknown</u> . Adjust the size of the charges used for repeat titrations so that the titration volume is about 40 mL.

Report: Provide the results of your unknown determination along with the detailed potentiometry report as described below:
Examine the sample article from *Analytical Chemistry*, one of the leading research journals in the field. This is an unusually short article, but it is typical in its format and writing style. Note the heading, followed by an Abstract, an Introduction, Experimental Section, Results and Discussion, and Acknowledgment. References appear at the bottom of each page in this journal. Your report should be guided by the sample article with the modifications indicated below. It should be prepared using a word processor and a spreadsheet program. Parts, like mathematical equations, that may be difficult for you can be completed, neatly, by hand.

Your report should include:
- A **Title Page** with your name.
- An **Introduction** - this can be brief - one page at most.
- An **Experimental** section - also brief - refer to your handout and/or text for details. Briefly summarize procedures that were followed and the number of experiments carried out.
- A **Results and Discussion** - the heart of the report. Carefully summarize your results referring to tables and graphs as appropriate. Provide <u>sample</u> calculations. Don't include all of your data - they can be found in your notebook, if needed. Several pages are required to include:
  - A graph showing the experimentally determined pH dependence of a sodium carbonate solution. A graph to illustrate the method used for the end point determination. Graphs should be referred to by number in the text. They must have a title, properly labeled axes (with units), and experimentally determined points clearly indicated. Do not include a graph for each determination.
  - Table(s) summarizing results. These are numbered and referred to in the text.
  - Calculation of pK_1 and pK_2. This will be discussed in lecture. Compare your results to literature values.
  - The determination of your unknown with statistics.
  - A discussion of errors. Try to estimate the consequences of each source of error.
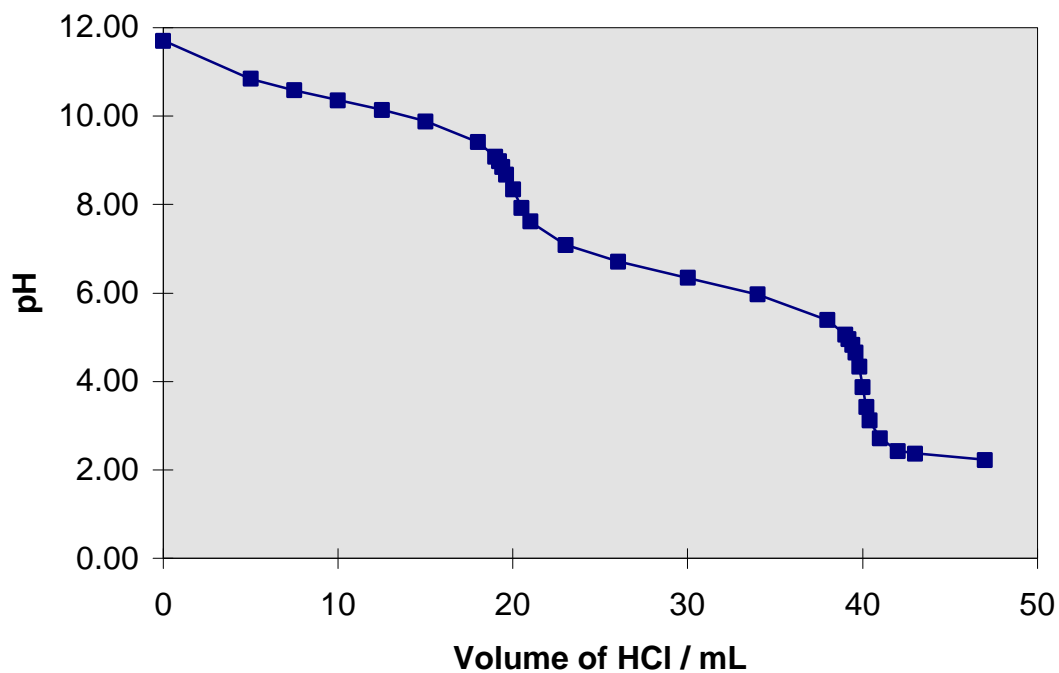
Potentiometric Titration, Data Analysis

	A	B	C	D	E
1	V(HCl)/mL	pH	dpH/dV		
2	0	11.70			
3	5	10.84	0.172		
4	7.5	10.58	0.104		
5	10	10.36	0.088		
6	12.5	10.14	0.088		
7	15	9.88	0.104		
8	18	9.41	0.157		
9	19	9.08	0.330		
10	19.2	8.98	0.500		
11	19.4	8.85	0.650		
12	19.6	8.67	0.900		
13	20	8.35	0.800		
14	20.5	7.93	0.840		
15	21	7.62	0.620		
16	23	7.09	0.265		
17	26	6.71	0.128		
18	30	6.34	0.093		
19	34	5.97	0.093		
20	38	5.39	0.145		
21	39	5.06	0.330		
22	39.2	4.96	0.500		
23	39.4	4.83	0.650		
24	39.6	4.65	0.900		
25	39.8	4.34	1.550		
26	40	3.88	2.300		
27	40.2	3.42	2.300		
28	40.4	3.12	1.500		
29	41	2.72	0.667		
30	42	2.43	0.29		
31	43	2.37	0.06		
32	47	2.23	0.035		
33					
34					

This sheet shows original data in columns A and B.

The formula to calculate the first derivatives in column C is =-(B3-B2)/(A3-A2). This formula is entered in cell C3 (note: there is no cell C2 !) and it should be copied into cells C4 - C32.

Titration of 2.5 mmoles of Na_2CO_3 with 0.125 M HCl

First Derivative