Experiment 2b

DETERMINATION OF THE PERCENT CARBONATE IN AN UNKNOWN SAMPLE

Suggested Reading:
Quantitative Chemical Analysis, 9th ed.
Ch. 10: Polyprotic acid-base equilibria
Ch. 11: Acid-base titrations

Introduction

A solution containing CO_3^{2-} can be determined by titration with a strong acid such as HCl. The titration can be stopped either when one mole of HCl per mole of CO_3^{2-} has been added (at the first equivalence point) or when two moles of HCl per mole of CO_3^{2-} have been added (at the second equivalence point).

$H^+ + CO_3^{2-} \rightleftharpoons HCO_3^-$ (1st equivalence point)

$H^+ + HCO_3^- \rightleftharpoons H_2CO_3$ (2nd equivalence point)

The first equivalence point can be detected by the one color indicator phenolphthalein, which goes from pink to colorless. The second equivalence point can be determined by the two-color indicator bromocresol green, which goes from blue to yellow. Advantage may be had from the dissociation of H_2CO_3 to H_2O and CO_2 to obtain a very sharp endpoint with bromocresol green. If HCl is added until the solution is blue-green in color (pH ~ 4.5) and then the solution is *warmed gently*, the CO_2 will be expelled and the buffer capacity of the solution will be lowered. The addition of a fraction of a drop of HCl will cause a sharp drop in the pH of the solution and it should be possible to locate the second equivalence point very accurately.

Pre-lab questions:

1. Sketch of the titration curve for carbonate (pH versus volume of acid added), showing the changes in pH at the two equivalence points. Be sure to label all of the important parts/regions of the titration curve!
2. What criterion is used to select suitable indicators for the two equivalence points? Give some other indicators that could be used instead of phenolphthalein and bromocresol green.
3. Once the first equivalence point has been passed, the solution is buffered. Using the Henderson-Hasselbach equation, demonstrate how this works.
4. How does boiling off the CO_2 change the pH of the solution? Again use the Henderson-Hasselbach equation to demonstrate this.
5. Sketch the titration curve for the back titration. How does this titration curve differ from the curve for the direct titration?

Standardization of a Solution of HCl:

An approximately 0.1M solution of HCl may be prepared by adding 9mL of the concentrated HCl to about 1liter of water. This solution is mixed thoroughly to ensure that the solution has a uniform concentration.

The HCl solution is standardized with the primary standard Na_2CO_3. It is important to dry the Na_2CO_3 thoroughly before weighing it. If possible, dry the Na_2CO_3 overnight at 110°C. Weigh by difference three portions of Na_2CO_3 (0.1-0.15 g) into three titration flasks. Add about 50 mL of distilled water to dissolve the Na_2CO_3. Add 4 drops of 0.1% bromocresol green indicator and titrate with the HCl solution until the blue color of the indicator becomes blue green. Warm the solution gently and swirl the flask to expel the CO_2. Cool and continue to titrate by the addition of fractional drops until the solution becomes yellow. Figure 1 shows the representative colors for acid-base titrations with bromocresol green. Calculate the molarity of the HCl solution from the three titrations.

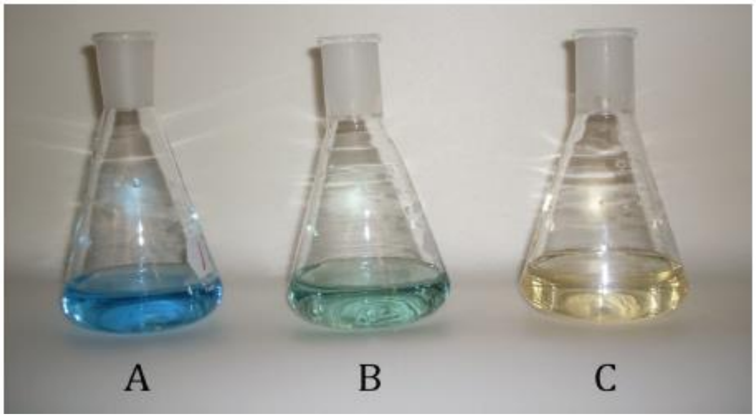

Figure 1. (A) Blue color observed after the addition of bromocresol green to the basic solution. (B) Blue-green intermediate color. (C) Yellow color that indicates that the end point of the titration has been reached.

Determination of the Percent Carbonate in an Unknown.

Dry the unknown sample at 110°C for several hours (preferably overnight). Weigh out by difference three portions (0.1-0.15 g) into three titration vessels, dissolve in deionized water and titrate with the standard HCl solution using bromocresol green as the indicator. The solid is fairly insoluble in water, and will only dissolve completely when the titration is partially completed. You will need to heat and cool several times before the titration is complete. Calculate the percentage of calcium carbonate in the sample and report the answer as percent $CaCO_3$.