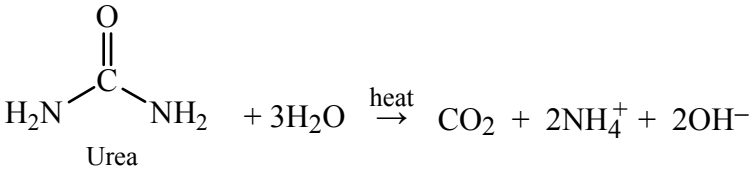
2. Gravimetric Determination of Calcium as $CaC_2O_4 \cdot H_2O$[1]

Green Profile
See Section 0

Calcium ion can be analyzed by precipitation with oxalate in basic solution to form $CaC_2O_4 \cdot H_2O$. The precipitate is soluble in acidic solution because the oxalate anion is a weak base. Large, easily filtered, relatively pure crystals of product will be obtained if the precipitation is carried out slowly. Slow precipitation is achieved by dissolving Ca^{2+} and $C_2O_4^{2-}$ in acidic solution and gradually raising the pH by thermal decomposition of urea:



NOTE: for expediency the sintered-glass funnels should be heated, brought to constant mass, cooled, and then placed in a dessicator the previous lab period.

Reagents

Ammonium oxalate solution: Make 1 L of solution containing 40 g of $(NH_4)_2C_2O_4$ plus 25 mL of 12 M HCl. Each student will need 80 mL of this solution.

Methyl red indicator: Dissolve 20 mg of the indicator in 60 mL of ethanol and add 40 mL H_2O. (Table 11-3 in text).

0.1 M HCl: (225 mL/student) Dilute 8.3 mL of 37% HCl up to 1 L.

Urea: 45 g/student.

Unknowns: Prepare 1 L of solution containing 15–18 g of $CaCO_3$ plus 38 mL of 12 M HCl. Each student will need 100 mL of this solution.

1. C. H. Hendrickson and P. R. Robinson, *J. Chem. Ed.* **1979,** *56,* 341.

Procedure

1. Dry three medium-porosity, sintered-glass funnels for 1–2 h at 105°C. Cool them in a desiccator for 30 min and weigh them on an analytical balance (use the same balance for all of your weighings). Repeat the procedure with 30-min heating periods until successive weighings agree to within 0.3 mg (try for 0.1 mg). Use tongs, not your fingers, to handle the funnels.
2. Use a few small portions of unknown to rinse a 25-mL transfer pipet, and discard the washings. *Use a rubber bulb, not your mouth, to provide suction.* Transfer exactly 25 mL of unknown to each of three 250- to 400-mL beakers, and dilute each with ~75 mL of 0.1 M HCl. Add 5 drops of methyl red indicator solution to each beaker. This indicator is red below pH 4.8 and yellow above pH 6.0.
3. Add ~25 mL of ammonium oxalate solution to each beaker while stirring with a glass rod. Remove the rod and rinse it into the beaker with small portions of deionized water. Add ~15 g of solid urea to each sample, cover it with a watchglass, and boil gently for ~30 min until the indicator turns yellow.
4. Filter each hot solution through a weighed funnel, using suction (Figure 2-17 and Section 2-7 in the textbook). Add ~3 mL of ice-cold water to the beaker, and use a rubber policeman to help transfer the remaining solid to the funnel. Repeat this procedure with small portions of ice-cold water until all of the precipitate has been transferred to the funnel. Finally, use two 10-mL portions of ice-cold water to rinse each beaker, and pour the washings over the precipitate.
5. Dry the precipitate, first with aspirator suction for 1 min (when done filtering first disconnect the suction and then turn off the aspirator to prevent liquid from being sucked back), then in an oven at 105°C for 1–2 h. (Possibly finish next lab period.) Bring each filter to constant mass (see Section 2-8 in the textbook). Keep the filters in a dessicator to prevent moisture accumulation. The product is somewhat hygroscopic, so only one filter at a time should be removed from the desiccator, and weighings should be done rapidly. This drying procedure does not remove the water of crystallization.
6. Calculate the average molarity of Ca^{2+} in the unknown solution, the standard deviation, and the relative standard deviation (s / x = standard deviation/average). Also calculate the average g $CaCO_3$/L.