

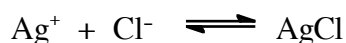
## Experiment 7

### (i) Gravimetric Determination of Chlorine in the Cobalt Complex

#### Discussion

In gravimetric analysis, one takes a known mass of a substance with unknown composition, converts the sample into a product with known composition, measures the weight of the product, and calculates the amount of initial sample. A common approach involves dissolving the sample to be analyzed, reacting this sample to form a precipitate of known composition, isolating the precipitate, and weighing the (dried) product.

In the present experiment, we dissolve a known quantity of a soluble mixture containing chloride ions in water, add an aqueous solution of silver nitrate to precipitate the chloride ions as silver chloride, then filter, wash, dry and weigh the precipitate. The fundamental reactions are



A calculation using the weight of the cobalt sample and the weight of the silver chloride product (using the atomic weights of silver and chlorine) yields the percent chloride ions in the unknown sample.

This procedure not only serves to introduce principles and procedures fundamental to gravimetric analysis, but provides useful experience in careful weighing, filtration, drying, and other techniques basic to laboratory work in the physical sciences.

Acidification with dilute nitric acid prevents the precipitation of silver carbonate and other silver compounds which may precipitate in neutral or basic solution on addition of silver ions. Avoiding an excess of silver nitrate minimizes the tendency of silver chloride to form a colloidal dispersion, and heating the solution promotes coagulation into a filterable precipitate. The filtration is carried out using a porcelain crucible with a porous filtering bed. The use of dilute nitric acid as the wash water prevents the formation of the unfilterable colloidal dispersion which is apt to form when pure water is used. Methanol used in the washing procedure removes most of the water and hastens the drying process.

Clean two 400-mL beakers. The beakers should be rinsed with distilled water and dried. Cover them with close-fitting, plain watch glasses.

Accurately weigh by difference two samples of the cobalt complex, one into each of the beakers. Identify beakers by marking with **lead pencil on the ground-glass area**. Sample weights of about 0.3 gram should be large enough for adequate weighing accuracy and small enough to produce a manageable amount of precipitate.

Dissolve each of these samples in 100 mL of 0.1 M nitric acid at room temperature. Using a tripod and ringstand assembly (construct carefully and sturdily; place away from edge of desk top to minimize accidents), heat the solutions to 80-90° (DO NOT BOIL).

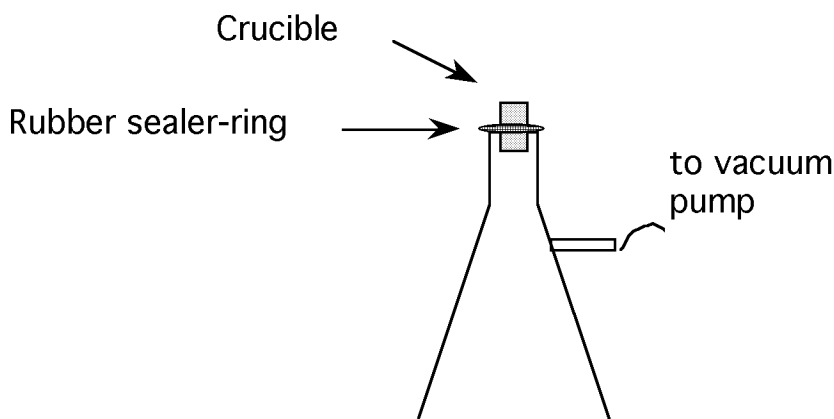
Pour about 30 mL of 5% silver nitrate solution into a 100-mL beaker.

**NOTE WELL:** USE  $\text{AgNO}_3$  CAREFULLY AND SPARINGLY. IT LEAVES DARK STAINS (metallic silver) ON EQUIPMENT, SKIN AND LABORATORY SURFACES. IF SPILL OCCURS WIPE UP IMMEDIATELY AND RINSE THOROUGHLY WITH PLENTY OF WATER.

While heating, using a clean dropper, add the silver nitrate solution slowly and carefully to the hot solution with thorough stirring (NO SPLASHING). Both solutions may be treated simultaneously (use separate stirring rods!). Hold the tip of the dropper close to the surface of the solution to avoid splashing, and carefully rinse stirring rods with distilled water to remove silver chloride. Except when adding silver nitrate and stirring, cover the beakers with plain watch glasses to avoid contamination; when resting watch glasses, be sure to invert them for the same reason.

Complete precipitation of the chloride may require about 15 mL or more of the silver nitrate solution. The stirring and elevated temperature promote flocculation of the precipitate. As the equivalence point is approached, the silver chloride precipitate should noticeably coagulate, although the solution will not become entirely clear. Add about 1 mL more of silver nitrate solution beyond this point. Let the solution stand for a few minutes to allow the supernatant to clear somewhat and then add a drop or two of the silver nitrate solution to test for completeness of precipitation (observe carefully). Hold the tip of the dropper close to the surface of the solution to avoid splashing and near the front of the beaker so you can see clearly. If additional precipitation occurs (appearance of slight turbidity), add about 1 mL of silver nitrate and continue heating. Repeat this procedure until the test for incomplete precipitation is negative. Continue heating and stirring (**care: do not boil**) until solution is clear (perhaps one hour). These procedures will promote the necessary coagulation of the precipitate.

Be sure to weigh your crucibles before beginning the filtration. Look for distinguishing marks (e.g. differences in the logo ink) to tell them apart. Set up the following apparatus to wash and filter the precipitate according to figure 1.



**Figure 1.** Apparatus for filtration using a crucible filter.

Prepare a wash solution by adding 3 mL of 6M  $\text{HNO}_3$  to 300 mL of distilled water and stirring.

If you prepared compound Y in Experiment 6, there may be orange crystals in your beakers at this point. If this is the case, gently warm the beakers to dissolve these crystals. The  $\text{AgCl}$  will not dissolve.

With the suction on, pour as much of the supernatant through the **previously weighed** crucible filter as is possible without transferring an appreciable amount of precipitate. Use a stirring rod to guide the flow of liquid to the crucible. (Examine the filtrate for any precipitate particles, hopefully absent.) Wash down the walls of the beaker with about 25 mL of the prepared wash solution (guiding the flow, as always, with a stirring rod). After the precipitate settles, decant the wash solution into the crucible. Repeat this washing process three or four times. During the last decantation, most of the precipitate should go into the crucible. Transfer the remainder with the aid of the wash bottle.

Remove the particles of precipitate which cling to the walls of the beaker and the stirring rod by gentle rubbing with a rubber "policeman" and transfer them to the crucible. Test the filtrate for remaining silver ions by adding a drop or two of 6M HCl **to 1 mL of the filtrate**.

After the complete transfer of the precipitate to the crucible, draw air through the crucible and precipitate (to dry ppt) for about 5 minutes. Then fill the crucible about four-fifths full with methanol. After about three or four minutes, reapply the suction for 10 minutes to remove the methanol and dry the crucible. Remove the crucible, wipe the outside dry with soft tissue, and dry precipitate in oven. Filter the second solution in the same manner.

Weigh the crucibles carefully. Determine the weight of silver chloride in each case and from it the weight percent of the chloride in the cobalt complex. Report the average and the average deviation on the Worksheet provided for this experiment.

### **Disposal**

Excess  $\text{AgNO}_3$  -give to people who still need more. The rest, if it is still pure, return it to the brown collection bottle. As you may guess, this solution is valuable.

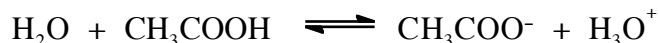
Leave the  $\text{AgCl}_{(s)}$  in the crucible. When you are done weighing the product, return the crucible *with* the AgCl. We will recover the silver.

Other solutions can go down the drain.

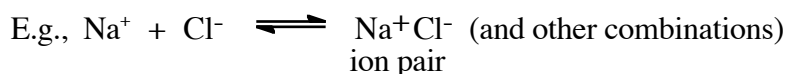
## (ii) Conductometric Analysis of the Cobalt Complex

The ability of a material to conduct electricity is a characteristic property and is due to the movement of charged particles under the influence of the applied electric field (potential gradient).

Aqueous solutions of ionic substances are good conductors because of the presence of positive and negative ions which carry the current (rate of flow of electrical charge per second) when a voltage is applied. The conductance of an electrolyte depends on its concentration since this determines any mass action or electrostatic interionic effects in a particular solvent at a particular temperature and thus determines the number of ions free to take part in conduction. For example, in the case of a weak electrolyte such as acetic acid we have



and there is a shift in the equilibrium point to the left (fewer ions/mole) as the total concentration is increased. In the case of strong electrolytes (such as in this experiment), a shift to the right occurs because of increased electrostatic influences between the ions.



The conductance of the solution is the sum of the contributions of the individual free ions and this in turn depends on their speeds. In a given solvent the speed of an ion depends primarily on its size (effective radius) and charge.

Thus strong electrolytes of the same valence type (1:1, 2:1, etc.) and possessing ions of approximately equal effective radii will have roughly the same conductance at the same concentration in the same solvent.

The strong electrolytes sodium chloride ( $\text{Na}^+\text{Cl}^-$ ), magnesium chloride ( $\text{Mg}^{2+}2\text{Cl}^-$ ) and potassium ferricyanide ( $3\text{K}^+[\text{Fe}(\text{CN})_6]^{3-}$ ) may be compared with the cobaltic complexes  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+\text{Cl}^-$ ,  $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}2\text{Cl}^-$  and  $[\text{Co}(\text{NH}_3)_6]^{3+}3\text{Cl}^-$ , respectively. The complex  $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$  is of course a nonelectrolyte and would show little or no conductance.

By measuring the conductances of approximately 0.01M solutions of NaCl, MgCl<sub>2</sub> and K<sub>3</sub>Fe(CN)<sub>6</sub> and comparing these with the conductance of a 0.01M solution of your complex cobalt compound, you can identify the valence type of the latter and thus obtain additional evidence as to the identity of the complex.

### CONDUCTANCE AND RESISTANCE OF ELECTROLYTE SOLUTIONS

The conductance of a solution is the reciprocal of its electrical resistance, and it is the latter that we measure directly though the meter will display conductance.

#### Electrical resistance and its measurement., Ohm's Law (1827)

When an electric current flows through a solid electrons carry the charge, whereas in the case of an electrolyte solution the ions transport the charge (see figure 1). In either case the current (I) that flows is directly proportional to the applied voltage(U). This is Ohm's Law and is written:

$$I = \frac{U}{R} \quad (7-1)$$

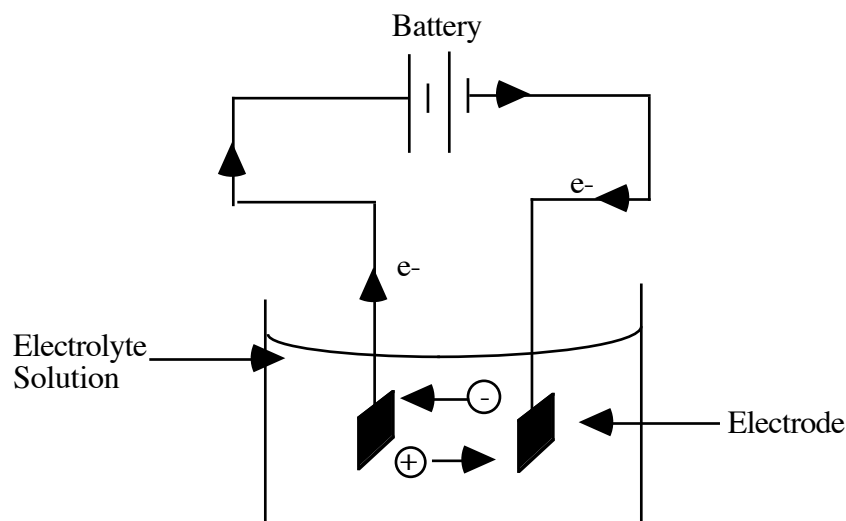
where I is the current in amperes, U is the potential difference in volts, and R is known as the electrical resistance of the sample and is expressed in ohms.

For a homogeneous material of length L and of uniform cross-section A:

$$R \propto \frac{L}{A} \quad \text{that is, we may write} \quad (7-2)$$

$$R = \rho \left( \frac{L}{A} \right) \quad (7-3)$$

where  $\rho$ , the proportionality constant, is termed the specific resistance of the material. The units of specific resistance are ohm-cm.



**Figure 1.** A simple electrochemical cell. **Note:** direction of flow in a circuit is, by convention, defined as the direction of flow of positive charge.

Generally, chemists prefer to speak about the conductance of an electrolytic solution, and the last expression becomes:

$$\text{Conductance} = \frac{1}{R} = \frac{1}{\rho} \left( \frac{A}{L} \right) = \kappa \left( \frac{A}{L} \right) \quad (7-4)$$

where kappa ( $\kappa$ ) is the specific conductance in units of reciprocal ohms per centimeter ( $\Omega^{-1} \text{ cm}^{-1}$ ).

### Procedure

Weigh out accurately 0.25 g of your compound and transfer carefully to a 100 mL volumetric flask. Fill to the mark with distilled water and shake thoroughly to ensure homogeneity.

As demonstrated by the instructor, measure the conductances of the supplied solutions of 0.010 M NaCl, 0.010 M  $\text{MgCl}_2$ , 0.010 M  $\text{K}_3\text{Fe}(\text{CN})_6$  and the solution of your unknown. Record your results in your notebook on a new dated page. Be sure to rinse the conductance cell thoroughly between measurements and use a little of each solution to rinse the cell before carrying out a measurement of that solution.

### Disposal

Solutions can go down the drain with water.



# Experiment 7 Worksheet — Gravimetric and Conductiometric Analysis of Cobalt Compound

Name \_\_\_\_\_

Date of Experiment: \_\_\_/\_\_\_/\_\_\_

Report: \_\_\_/\_\_\_/\_\_\_

Complex Made: X or Y (circle)

## Experimental Results for Gravimetric Analysis of Chlorine

Average Weight % Cl \_\_\_\_\_ ± \_\_\_\_\_

Please attach a sheet that shows your complete results and calculations.

Possible formulae for the complex are:  $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$ ,  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ ,  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ , and  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ . On a separate sheet, calculate the weight percent chlorine for each of these complexes and suggest a formula for your compound based on the result of the gravimetric analysis. Note that in this gravimetric analysis all chlorine is precipitated as  $\text{AgCl}$ , not just the complex counter ions. Discuss your answer briefly.

Probable identity of compound  
as inferred from Gravimetric Analysis \_\_\_\_\_

What is the expected weight percent  
chlorine for this ammine complex? \_\_\_\_\_

## Experimental Results for Conductiometric Analysis

Conductance (or Resistance) (with units)

0.010 M NaCl \_\_\_\_\_

0.010 M  $\text{MgCl}_2$  \_\_\_\_\_

0.010 M  $\text{K}_3\text{Fe}(\text{CN})_6$  \_\_\_\_\_

Your complex in solution \_\_\_\_\_

Probable identity of compound  
as inferred from conductance test \_\_\_\_\_

Based on both the conductance and the percent chlorine, which compound do you think you have?

