

07

POTENTIOMETRIC TITRATIONS OF CHLORIDE AND IODIDE

In this experiment the concentrations of chloride and of iodide in an unknown solution will be determined by potentiometric titration with standard solution of silver nitrate. The potential of a silver electrode immersed in the solution is measured with respect to a reference electrode. In this experiment a glass electrode will serve as a reference electrode, since the pH of the solution is invariant during the titration. The position of the titration curve with respect to the volume axis does not depend on any knowledge of the electrode potential for either the measuring electrode or the reference electrode.

The data obtained also enable calculation of the solubility (solubility product) of AgCl and AgI. AgI (ca. $K_{sp} = 1 \times 10^{-16}$) precipitates first since it is less soluble than AgCl (ca. $K_{sp} = 1 \times 10^{-10}$). Silver chloride starts precipitation near the equivalence point of the iodide titration. The potential rise* of the iodide titration curve will level off at the point when the chloride starts precipitating, that is near the iodide equivalence point inflection. This will be followed by a typical S-shaped chloride potentiometric end point. The error in determining the iodide end point is small if it is taken at the point at which the potential levels off.

[* Depending on the manner in which the reference and working electrodes are connected, you may observe potential decrease, instead of potential rise.]

APPARATUS:

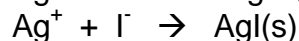
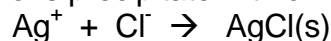
Potentiometer (commercial pH/mV meter)
Indicator electrode, silver wire or silver billet electrode
Reference electrode, with KNO₃ salt bridge.
Magnetic stirrer with stirring bar
Burette, 25 ml
Pipette, 25 ml
Beaker, 100 ml, and graduated cylinder, 100 ml

REAGENTS:

Silver nitrate, 0.100 mol/l, standardized
Unknown: solution containing chloride and iodide approximately 0.04-0.05 mol/l in each ion

THEORY:

Silver ions precipitate with chloride and iodide:



Throughout the titration the potential of the cell (potential difference between the glass and silver electrodes) should conform (at 25 °C) to the Nernst equation

$$E = E_{\text{Ag}} - E_{\text{ref}} = E^{\circ} + 0.0591 \log [\text{Ag}^+],$$

where E° incorporates both the potential of the reference electrode and any liquid

junction potentials.

Prior to the first break on the titration curve (the equivalence point corresponding to complete precipitation of silver iodide) the cell potential is governed by the iodide concentration. After the first but prior to the second break on the titration curve (the equivalence point for precipitation of silver chloride), the cell potential is governed by the chloride concentration. Beyond the second break, the silver ion concentration is in excess and can be reliably calculated from the Nernst equation and free silver ion concentration.

PROCEDURE:

Obtain an unknown (solid sample) which contains a mixture of KI and KCl. Pour your unknown carefully into a 50- or 100-ml beaker. Dissolve the sample in approximately 20 ml of water and transfer it quantitatively into a 100-ml volumetric flask. Dilute to mark.

Dry 1.7 g of AgNO_3 at 105°C for 1 hour and cool in a desiccator for 30 minutes, shielded from light. Weigh accurately approximately 1.7 g and dissolve it in 100-ml volumetric flask.

Pipette a 25 ml aliquot of the unknown into a 100-ml beaker. Add 25 ml of distilled water. Titrate with standard silver nitrate using 1-ml increments up to near the first end point ("break"), then use 0.10 ml increments as required until the E values become nearly constant past the first end point. Then add 1-ml increments again until the second end point is close, and then use 0.10 ml increments. Continue the titration past the second end point by a few milliliters. As at some point during the titration the potential may go from positive to negative, do not forget to note the sign of the measured potential as well.

Repeat the titration two more times. Be sure to rinse the electrodes between titrations with distilled water.

TREATMENT OF DATA:

1. Calculate and report the percent of iodide and chloride in your sample (calculated for the dry sample). Include the error, based on the three repetitions.

2. Calculate the ratio of K_{sp} of AgI and AgCl from the measured potentials of the titration curve equivalence points.

PRE-LAB PROBLEMS:

(1) Give a chemical reason why a saturated calomel reference electrode is not placed in direct contact with the silver solutions (in contrast to the usual pH meter application wherein the pH electrode is in direct contact with the titrating solution) and a KNO_3 bridge is used.

(2) Consider a potentiometric titration of 100.0 ml of 0.0300 mol/l NaCl with 0.100 mol/l AgNO_3 . After 15.0 ml of the AgNO_3 solution have been added, the observed potential between a silver electrode and a reference saturated calomel electrode (which you will not be using in your experiment) is +0.095 V. Find:

(a) $[\text{Cl}^-]$ at this point,

(b) $[\text{Ag}^+]$ at this point, and

(c) K_{sp} for AgCl in water.

(3) What is meant by the phrase "weigh accurately approximately 1.7 g?"