VIDEO EXPERIMENT 3
THERMOMETRIC TITRATIONS

In this experiment, the progress of several titrations is followed by using a thermistor immersed in the titrated solution to detect minute temperature changes.

The two acid-base titrations studied first are of the type you may have performed yourself by more conventional means. Next several reactions will be done in which an aqueous metal ion solution is titrated with a solution which can function as a precipitating and/or complexing agent. The reactions are all exothermic and the temperature of the liquid in the stirred reaction vessel rises sufficiently during the reaction to overcome the cooling effect of the added solution (i.e., the titrant). This is minimized by using a titrant of high concentration compared with that of the solution in the reaction vessel. In turn, this necessitates the steady and accurate addition of very small volumes of titrant, for which an automatic microburette is used. The thermistor in the reaction vessel is incorporated in a Wheatstone bridge circuit and as the temperature of the solution varies, the change in resistance of the thermistor produces an imbalance in the bridge circuit which is displayed by a pen trace on the chart recorder.

At the endpoint of a titration, the reaction no longer raises the temperature of the solution and the cooling effect of excess titrant produces a pronounced change in the trace gradient. If intermediate products are formed or the reaction occurs in stages, then appropriate changes in gradient of the trace may be observed. By determining the position of the inflections and relating them to the volume of titrant added we can determine the stoichiometry of the reaction.

After the titration of the solution of phosphoric acid with standard 1 M sodium hydroxide, the molarity of the acid solution can be calculated by using any of the three separate endpoints corresponding to the neutralization of all three acidic protons on the tribasic acid. The accuracy of the endpoint measurement depends on how distinct the gradient change is. It is interesting to note that this technique detects the reaction of the third acidic proton in phosphoric acid, whereas indicators are insensitive to the pH change which accompanies the process. In the remaining reactions, the addition of titrant to aqueous solutions of silver(I), zinc(II), nickel(II) and iron(III) ions is investigated. Here precipitates are formed which redissolve in excess titrant to form complex ions. From the inflections of each trace, the stoichiometry of the reactants can be determined and the constitution of the intermediate and final products deduced. Metal ions in solution can be regarded as aqua complex ions \([\text{M(H}_2\text{O)}_n]^m\) and as such the coordinated water molecules (in the coordination sphere of the metal ion) may be replaced by other ligands to form energetically more stable products. A change to a thermodynamically more stable state will be accompanied by evolution of heat. This aspect of compound formation is illustrated by interacting hydrated silver(I) ions first with ammonia solution to form a cationic ammine complex, then with potassium cyanide to form the insoluble cyanide which finally redissolves to give an anionic cyano complex. Intermediates are also observed in the reactions of potassium cyanide with the other metal ions except iron(III). In this titration, precipitation of an intermediate has been suppressed by the addition of glycerol, which acts as a weak complexing agent.
THE STUDENT'S PART IN THE EXPERIMENT

The technique is demonstrated using the titration of hydrochloric acid with sodium hydroxide. No readings need to be taken during this titration, but you should be ready to record the volumes and precise concentrations of the solutions used in the vessel for the titrations of

a. phosphoric acid, $\text{H}_3\text{PO}_4$ with sodium hydroxide
b. silver(I) nitrate with ammonia solution (including the silver(I)ammine with potassium cyanide)
c. zinc(II) sulfate with potassium cyanide
d. nickel(II) sulfate with potassium cyanide
e. ammonium iron(III) sulfate with potassium cyanide.

(Note that the concentration of the iron(III) solution is based on the formula $(\text{NH}_4)_2\text{SO}_4\cdot\text{Fe}_2(\text{SO}_4)_3\cdot24\text{H}_2\text{O}$.

It is useful during the titration to take brief notes on, say, the presence and color of any precipitate at each stage. After each titration, the traces are presented so that you can record the volumes of titrant corresponding to the separate inflections of the trace. The ratio of the reactants at the intermediate and final endpoints is related to the stoichiometries of the chemical species present at different stages.

Note: The video experiment Applications of an Electrochemical Cell also involves the stoichiometry of the silver(I)-ammine complex. Your report for that experiment should include a comparison of the results obtained there with those obtained here.