

Exp.: Determine the strength of given AgNO₃ solution by conductance measurement.

Theory in Brief: The principle of conductometric titration is based on the fact that during the titration, one of the ions is replaced by the other and invariably these two ions *differ in the ionic conductivity* with the result that conductivity of the solution varies during the course of titration. The equivalence point is located graphically by plotting the *change in conductance* as a function of the *volume of titrant* added. In order to reduce the influence of errors in the conductometric titration to a minimum, the angle between the two branches of the titration curve should be as small as possible (like the conductance curve obtained on titration between strong acid with a strong base).

The reaction that takes place in solution for this experiment is:



Since the ionic conductance of Ag⁺ (= 61.9 S.cm².mol⁻¹) is nearly same with K⁺ (= 73.5 S.cm².mol⁻¹), which replaces Ag⁺ when KCl is added in AgNO₃ solution in beaker, the change the conductance is nearly negligible. However, after the equivalence point is reached (i.e., all AgNO₃ is consumed), excess addition of KCl increases the conductance drastically increases due to presence of excess K⁺ and Cl⁻ [Ionic conductance in infinite dilution at 25 °C of Cl⁻ (=76.3 S.cm².mol⁻¹) and NO₃⁻ (=71.5 S.cm².mol⁻¹)]. Point of equivalence is obtained from the intersection of two slopes.

Typical Experimental Procedure:

- 1) Standard KCl solution (100mL, N/10) was prepared in a 100mL volumetric flask (by weighing 0.745 g, eq. wt. of KCl= 74.5).
- 2) This KCl solution is filled in burette (make sure that burette is not leaking).
- 3) 50 mL of given (unknown strength) AgNO₃ solution was taken in a 100 mL beaker.
- 4) Conductivity cell was properly washed with water and calibrated. This conductivity cell is then dipped into 50 mL AgNO₃ solution and attached to conductivity meter.
- 5) Magnetic stirrer was used to stir the solution for a proper mixing.
- 6) This solution was then titrated by KCl solution filled in the burette (each time addition: 1 mL) and conductivity reading was noted on each addition.
- 7) A graph between conductance (in millisiemens at Y-axis) versus volume of KCl added (in mL, at X-axis) was plotted. The equivalent point is determined from the intersection of two slopes.

Observation:

Weight of the KCl taken: -----

Normality of the prepared KCl: $\frac{\text{weight} \times 1000}{74.5 \times 100}$ N

Volume of AgNO₃ solution taken in 100 mL beaker: 50 mL

Table 1: Data obtained from the conductometric titration:

Vol. of KCl added (in mL)	Conductance (milli Siemens, ms)
0.0	1.60 (example)
1.0	1.60 (example)
.....
20.0	4.95 (example)

Calculation:

From the graph, the equivalent point = x.x mL, i.e., volume of KCl required.

Using the relation, $N_{\text{AgNO}_3} \times V_{\text{AgNO}_3} = N_{\text{KCl}} \times V_{\text{KCl}}$, the strength (in normality) of AgNO₃ solution was determined.

Therefore, the strength (in g/L) of AgNO₃ solution = $N_{\text{AgNO}_3} \times 169.87$ (eq. wt. of AgNO₃)

Result: The strength of the given AgNO₃ solution was found to be X.XXX g/L.

Typical graph (taken from P C Rakshit's Physical chemistry book):

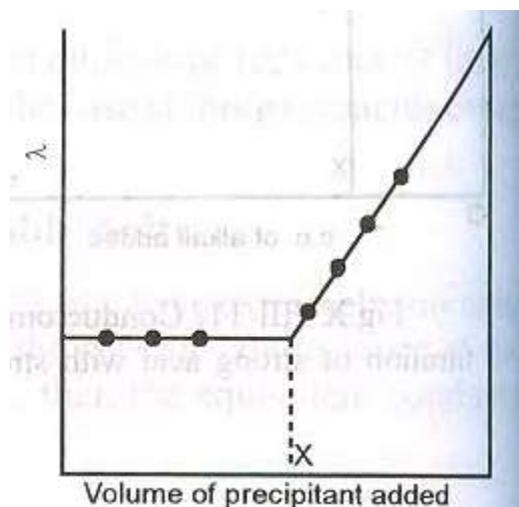


Fig.XVIII. 13. Titration of KCl soln. by AgNO₃ soln.

[P.S.: The same experiment must be done with HCl as well (in addition to KCl), in order to establish that “the smaller the conductivity of the ion which replaces the reacting ion (here Ag⁺), the more accurate will be the results”.]

Some important points to remember:

- 1) The smaller the conductivity of the ion which replaces the reacting ion, the more accurate will be the result. Thus it is preferable to titrate a silver salt with lithium chloride or KCl rather than with HCl.
- 2) The larger the conductivity of the anion of the reagent which reacts with the cation to be determined, or vice versa, the more acute is the angle of titration curve.
- 3) The titration of a slightly ionized salt does not give good results, since the conductivity increases continuously from the commencement. Hence, the salt present in the cell should be virtually completely dissociated; for a similar reason; the added reagent should also be as strong electrolyte.
- 4) Throughout a titration the volume of the solution is always increasing, unless the conductance is corrected for this effect, *non-linear titration curves* result. The correction can be accomplished by multiplying the observed conductance either by total volume ($V+V'$) or by the factor $(V+V')/V$, where V is the initial volume of solution and V' is the total volume of the reagent added. The correction presupposes that the conductivity is a linear function of dilution, this is true only to a first approximation.
- 5) In the interest of keeping V small, the reagent for the conductometric titration is ordinarily several times more concentrated than the solution being titrated (at least 10-20 times).
- 6) Advantage: The main advantages to the conductometric titration are its applicability to *very dilute, and coloured solutions* and to *system that involve relative incomplete reactions*. For example, which neither a potentiometric, nor indicator method can be used for the neutralization titration of phenol ($K_a = 10^{-10}$) a conductometric endpoint can be successfully applied.
- 7) Disadvantage: The conductance is a non-specific property, presence or slight concentration of another electrolyte can be troublesome. For this reason, direct conductance measurement is of little use unless the solution contains only the electrolyte to be determined. Conductometric titrations, in which the species in the solution are converted to non-ionic for by neutralization, precipitation, etc. are of more value.



Typical conductivity meter.