# CONDUCTOMETRIC TITRATIONS IN THE PRESENCE OF INDIFFERENT ELECTROLYTES USING BRIGHT PLATINUM ELECTRODES

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# SOEN H. TAN

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To Irene

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## INTRODUCTION

Conductometry is a useful method in analytical chemistry and can be widely applied. It is known to be unsuitable, however, for the titration of ions in the presence of a large amount of indifferent electrolytes. One reason is that the conductivity changes of the solution used for determining the titration endpoint in this titration are small and difficult to measure. Another reason is that polarization effects may become apparent and distort the titration curve. Polarization effects can be effectively eliminated by using a conductance cell with platinized electrodes. However, platinized electrodes may cause induction reactions and adsorption of the ions titrated, thereby reducing the accuracy of the titration result. Bright platinum electrodes do not cause these difficulties and are therefore to be preferred.

This report presents the results of a study on the feasibility of conductometric titrations in the presence of indifferent electrolytes using bright platinum electrodes. First, the factors which determine the accuracy of the endpoint location will be discussed; next, the titration arrangement, the nature and cause of polarization effects, and the elimination of these effects; and finally, the results of acid-base, redox, chelatometric, and precipitation titrations in the presence of indifferent electrolytes.

While conductometric titrations can be carried out with low frequency sine wave alternating current (30–15,000 cycles), high frequency alternating current (megacycles), low frequency square wave current,\* or direct current, this study is concerned exclusively with low frequency alternating current conductometric titrations.

\* Wijnen, M. D., Yzermans, A. B., and Schieman, J. A., Rec. Trav. Chim., 83, 21 (1964).

#### CHAPTER I

# CONDUCTOMETRIC TITRATION CURVES

#### **I.1 Introduction**

A conductometric titration is based on the electrical conductivity of the solution examined being the summation of the conductivities of all the ions present in the solution. Each ion contributes a definite amount to the total electrical conductivity. Consequently, during a titration the conductivity of the solution varies proportionally with the volume of titrant added. And on plotting the conductivity against the volume of titrant, a titration curve is obtained which essentially consists of two straight lines, the *reaction line* and the *excess line*. The reaction line represents the conductivity change of the solution up to the equivalence point, whereas the excess line represents the conductivity change due to the excess of titrant. The intersection of these lines corresponds to the equivalence point.

Accordingly, the endpoint of a conductometric titration is readily determined by making a number of measurements of the electrical conductivity of the solution during the titration. Under favorable conditions, and if the approximate volume of titrant required for the reaction is known, usually five measurements on either side of the equivalence point is sufficient; otherwise more experimental points would be necessary. The conductivity of the solution is then plotted against the volume of titrant added in order to locate the intersection of the straight portions of the plot (by drawing the best straight lines through the experimental points).

The volume of titrant corresponding to the titration endpoint is directly obtained from the location of the intersection of the titration lines on the graph paper, or it is found by solving the two linear equations of the titration lines simultaneously. Regardless of the method used to derive the endpoint, the accuracy of the result of the titration depends on the following factors: (a) whether the titration lines show a curvature, (b) the difference in the magnitudes of the slopes of the titration lines, and (c) the precision of the measurements.

This chapter discusses the above factors which determine the accuracy of the result of a conductometric titration.

#### Principle

A conductometric titration is performed in a conductance cell; that is, a suitable vessel equipped with a stirrer and two inert metal electrodes, which are usually of platinum. During the titration the electrical resistance of the solution between the electrodes is measured with a measuring bridge, which generally employs alternating current. The electrical resistance is related to the conductivity of the solution by

$$k = \frac{K}{R} \tag{I.1}$$

where R is the resistance (ohms); k, the specific conductance or conductivity of the solution (ohm<sup>-1</sup> cm<sup>-1</sup>); and K, the cell constant of the conductance cell (cm<sup>-1</sup>). Thus, the reciprocal of the resistance, 1/R, usually called the conductance (ohm<sup>-1</sup> or mho), differs from the conductivity only by the cell constant. Therefore, instead of the conductivity, the conductance of the solution can be used for the construction of the titration curve.

Contrary to absolute conductivity measurements, in conductometric titrations the cell constant, which depends on the geometry of the conductance cell, need not be known. It should be noted, however, that undesirable polarization effects may arise from using a conductance cell with too small a cell constant (see chapter II). Therefore, in conductometric titrations it is desirable to know the approximate value of the cell constant derived from measurements with potassium choride solutions of known conductivity.

The underlying principle of the conductometric method is the relation

$$k = \frac{1}{V} \sum_{i} n_{i} f_{i} \lambda_{i}^{0} \tag{I.2}$$

where  $n_i$  is the number of gram equivalents of ion *i* in V cm<sup>3</sup> of the solution,  $f_i$ is the conductance coefficient, and  $\lambda_i^0$  is the equivalent ion conductance at infinite dilution (ohm<sup>-1</sup>cm<sup>2</sup>); the conductance coefficient gives an account of the variation of the ion conductance with the concentration of the ions in the solution. From (I.1) and (I.2) it follows that the electrical conductivity of the solution varies linearly with the amount of the ions being titrated and thus with the volume of titrant added. But this is true only when the titrant is sufficiently concentrated so that the effect of the dilution is negligible. Otherwise the titration lines will not be straight, since the conductivity is inversely proportional to the volume of the solution, which increases during the titration owing to the addition of titrant. Because of this, it is common practice to correct the observed values of the conductance to the initial volume of the solution by multiplying the observed conductance values by  $V/V_0$ ,  $V_0$  being the initial volume of the solution, and V, the volume corresponding to the particular conductance value being considered. In constructing the titration curve,  $(V/V_0)/R$  is then plotted against the volume of titrant added.

In our experiments, however, the titration curves were obtained by plotting  $(V/V_0) \Delta k/k_0$  against the volume of titrant added,  $\Delta k/k_0$  being the *relative* 

change in conductivity of the solution. The reason was that the relative conductivity change can be more readily calculated from experimental data obtained with a simple Wheatstone bridge (which measures the resistance of the solution), particularly when the conductivity change is relatively small. From (I.1) it is readily derived that

$$\frac{k}{k_0} = \frac{R_0}{R} \tag{I.3}$$

 $k_0$  being the initial conductivity, and  $R_0$  being the initial resistance of the solution in the conductance cell. By inserting  $k = k_0 + \Delta k$  and  $R = R_0 + \Delta R$  into the above equation, it follows that the relative conductivity change is

$$\frac{\Delta k}{k_0} = \frac{R_0 - R}{R} = \frac{-\Delta R}{R} \tag{I.4}$$

where  $\Delta k$  and  $\Delta R$  represent the increase in conductivity and resistance, respectively. Another reason was that the strain indicator, the measuring bridge used in our experiments for measuring small conductivity changes, measured the relative resistance change  $\Delta R/R_0$ . From this, the relative conductivity change can be obtained by means of the equation

$$\frac{\Delta k}{k_0} = -\frac{\Delta R}{R_0} + \left(\frac{\Delta R}{R_0}\right)^2 - \dots$$
(I.5)

which can be approximated to

$$\frac{\Delta k}{k_0} = -\frac{\Delta R}{R_0} \tag{I.6}$$

if  $\Delta R/R_0$  is 1 per cent or less.

Ideal titration curves consisting of perfectly straight lines will now be considered, and next, curves deviating from the ideal straight lines because of the effect of dilution and incompleteness of reaction.

Deviations due to polarization effects will be discussed in chapter II.

## I.2 Ideal titration curves

Ideal titration curves consist of straight lines that can be represented by equations of the form y = ax + b, where y is the conductance, the conductivity or the relative conductivity change of the solution; x is the volume of titrant added or the fraction of the substance titrated; and a and b are constants. In the derivation of titration curves, the literature on conductometric titrations usually neglects the effect of the conductance coefficient variation with the dilution (see, e.g., ref. 3), a factor affecting the slope of the titration lines and possibly causing curvature. This is allowable in the titration of solutions of

ordinary concentration, but it is not in the titration of solutions containing large amounts of indifferent electrolyte. Since the latter is the object of the present study, in the derivation given below, the change in the conductance coefficient of the solution is taken into account. It will be assumed that no deviation from the ideal straight lines occurs because of dilution effects, incompleteness of reaction, or the like.

A useful equation is obtained by modifying equation (I.2) as follows,

$$k = \frac{n_0 f}{V} \sum_{i} \frac{n_i}{n_0 v_i} \frac{f_i}{f} v_i \lambda_i^0$$
$$= \frac{n_0 f}{V} \sum_{i} m_i \lambda'_i$$
(I.7)

where  $n_1$  is the number of gram equivalents of the *i*-th ion in  $V \text{ cm}^3$  of the solution in the conductance cell;  $m_1$  is the coefficient of the *i*-th ion in the reaction equation;  $v_1$  is the electrovalency of the ion;  $n_0$  is a proportionality constant which is equal to  $n_1/v_1 m_1$ ; and  $\lambda'_1 = v_1 \lambda_1^0 f_1/f$  (see below). In the titration of 1 milli-equivalent of hydrochloric acid with sodium hydroxide,  $n_0 = 1 \times 10^{-3}$  gram equivalent; in the titration of 1 (electrochemical) milli-equivalent of ferrous sulphate with potassium permanganate (section III.3),  $n_0 = 0.5 \times 10^{-4}$  gram equivalent (m = 10, v = 2). This constant is not important, however, since it does not appear in the equation (I.11) to be derived. Further, in the above equation,  $f_1$  is the conductance coefficient of the *i*-th ion, whereas f is the mean conductance coefficient of the mixture of electrolytes. Both change but very little during a titration (approximately 0.15 per cent in our titrations of hydrochloric acid in 5 M sodium chloride with sodium hydroxide); as a result, the ratio  $f_1/f$  is practically a constant.

By introducing

$$G = \sum_{i} m_i \lambda'_i \tag{I.8}$$

which may be called the *conductance sum*, equation (I.7) is further simplified, so that

$$k = \frac{n_0 f G}{V} \,. \tag{I.9}$$

The variables in this equation are functions of the volume of the titrant added,  $\Delta V$ . Writing  $V = V_0 + \Delta V$ ,  $k = k_0 + \Delta k$ ,  $f = f_0 + \Delta f$ , and  $G = G_0 + G$ , where  $\Delta k$ ,  $\Delta f$ , and  $\Delta G$  represent the increase in conductivity, conductance coefficient, and conductance sum, respectively, by the addition of titrant, it follows from (I.9) that

$$\frac{V}{V_0}\frac{k}{k_0} = \frac{f}{f_0}\frac{G}{G_0}$$
 (I.10)

and thus

$$\frac{V}{V_0}\frac{\Delta k}{k_0} = \frac{\Delta G}{G_0} + \frac{\Delta f}{f_0} + \frac{\Delta f}{f_0}\frac{\Delta G}{G_0} - \frac{\Delta V}{V_0}.$$

This, in turn, when the insignificant second order term is neglected (in our titrations,  $\Delta f/f_0$  smaller than 0.0015), reduces to

$$\frac{V}{V_0}\frac{\Delta k}{k_0} = \frac{\Delta G}{G_0} + \frac{\Delta f}{f_0} - \frac{\Delta V}{V_0}.$$
 (I.11)

The above equation, which applies to the reaction line as well as the excess line of a conductometric titration, shows that the conductivity change of the solution (corrected for volume change by the factor  $V/V_0$ ) is the summation of the conductivity changes brought about by the chemical reaction, the change in conductance coefficient, and the change in volume. The equation can be used for deriving conductometric titration curves by expressing the quantities on the right-hand side of the equation in terms of the volume of titrant added,  $\Delta V$ , or the ratio of titrant to titrand, x. This will be illustrated below by the titration of hydrochloric acid with sodium hydroxide in the presence of sodium chloride.

Because the titration curves in this study consist of but two titration lines, the reaction line and the excess line, only these will be considered. All quantities referring to the reaction line will be denoted by the suffix I, while the quantities referring to the excess line will be denoted by the suffix II. For example,  $G_{I}$  is the conductance sum of the solution, defined by (I.8), up to the equivalence point, where x = 1; and  $G_{II}$ , the conductance sum for values of x greater than 1. Quantities referring to x = 0, x = 1, and x = 2 will be denoted by  $G_{0}$ ,  $G_{1}$ , and  $G_{2}$ , respectively.

Also, to save writing, the ion conductances  $\lambda'_{\rm H}$ ,  $\lambda'_{\rm Cl}$ , etc., will simply be represented by H<sup>+</sup>, Cl<sup>-</sup>, etc., wherever applicable.

Further, since the ratio  $f_i/f$  for the ionic species is generally not known, and therefore evaluation of  $\lambda'_i$  not possible, for calculation purposes the known values of the ion conductances at infinite dilution,  $\lambda_i^0$ , multiplied by the electrovalency of the ion, will be used. The relation between  $\lambda'_i$  and  $\lambda_i^0$  is

$$\lambda'_{i} = \frac{f_{i}}{f} \nu_{i} \lambda_{i}^{0} \tag{I.12}$$

cf. equation (I.7).

In the titration of hydrochloric acid with sodium hydroxide in the presence of a p-fold excess of sodium chloride, the reaction or mass balance equation, including the sodium chloride for studying the effect of the variation of the conductance coefficient with dilution, up to the equivalence point is

$$HCl + x[NaOH] + p NaCl = (1 - x)HCl + x NaCl + x H_2O + p NaCl$$

x being the fraction of the hydrochloric acid titrated and the brackets denoting the titrant. (Generally, though, the indifferent electrolyte need not be considered in deriving equations of conductometric titrations.) Thus, up to the equivalence point, the conductance sum is

$$G_{\rm I} = (1 - x)({\rm H}^+ + {\rm Cl}^-) + x({\rm Na}^+ + {\rm Cl}^-) + p({\rm Na}^+ + {\rm Cl}^-).$$
(I.13)

Beyond the equivalence point no further reaction takes place; therefore,

$$G_{\rm II} = (x - 1)({\rm Na^+} + {\rm OH^-}) + {\rm Na^+} + {\rm Cl^-} + p({\rm Na^+} + {\rm Cl^-}).$$
 (I.14)

From the above equations (I.13) and (I.14), it follows that for x = 0,

$$G_0 = H^+ + Cl^- + p(Na^+ + Cl^-).$$
 (I.15)

Thus,

$$\frac{\Delta G_{\rm I}}{G_0} = \frac{G_{\rm I} - G_0}{G_0} = \frac{{\rm Na}^+ - {\rm H}^+}{{\rm H}^+ + {\rm Cl}^- + p \left( {\rm Na}^+ + {\rm Cl}^- \right)} x \tag{I,16}$$

and

$$\frac{\Delta G_{\rm II}}{G_0} = \frac{G_{\rm II} - G_0}{G_0} = \frac{{\rm Na^+ - H^+}}{{\rm H^+ + Cl^- + p(Na^+ + Cl^-)}} + \frac{{\rm Na^+ + OH^-}}{{\rm H^+ + Cl^- + p(Na^+ + Cl^-)}} (x - 1) .$$
(I.17)

For simplification, equations (I.13) and (I.14) can also be written

$$G_{I} = G_{0} + G'_{I}x$$
 (I.18)

and

$$G_{\rm II} = G_0 + G'_{\rm I} + G'_{\rm II}(x - 1) \tag{I.19}$$

 $G'_{I}$  and  $G'_{II}$  being the derivatives of  $G_{I}$  and  $G_{II}$ , respectively, so that

$$\frac{\Delta G_{\mathbf{I}}}{G_0} = \frac{G'_{\mathbf{I}}}{G_0} x \tag{I.20}$$

and

$$\frac{\Delta G_{\rm II}}{G_0} = \frac{G'_{\rm I}}{G_0} + \frac{G'_{\rm II}}{G_0} \left(x - 1\right). \tag{I.21}$$

 $G'_{I}$  and  $G'_{II}$  in the above equations are readily obtained, using

$$G'_{\rm I} = G_1 - G_0 \tag{I.22}$$

and

$$G'_{II} = G_2 - G_1 \tag{I.23}$$

derived by substituting x = 1 and x = 2 in (I.18) and (I.19), respectively.  $G'_{I}$  can thus be obtained by means of the reaction equation by subtracting the

conductance sum for x = 0 from the conductance sum for x = 1. Similarly,  $G'_{II}$  is found by subtracting the conductance sum for x = 1 from the conductance sum for x = 2.

In calculations use can be made of the relation obtained as follows. For a solution of a binary electrolyte, e.g., sodium chloride,

$$f^{0}_{\mathrm{NaCl}}(\lambda^{0}_{\mathrm{Na}}+\lambda^{0}_{\mathrm{Cl}})=f^{0}_{\mathrm{NaCl}}\left(\frac{f^{0}_{\mathrm{Na}}}{f^{0}_{\mathrm{NaCl}}}\lambda^{0}_{\mathrm{Na}}+\frac{f^{0}_{\mathrm{Cl}}}{f^{0}_{\mathrm{NaCl}}}\lambda^{0}_{\mathrm{Cl}}\right).$$

If now the solution is diluted with water,

$$f_{\mathrm{NaCl}}(\lambda^{0}_{\mathrm{Na}} + \lambda^{0}_{\mathrm{Cl}}) = f_{\mathrm{NaCl}}\left(\frac{f_{\mathrm{Na}}}{f_{\mathrm{NaCl}}} \lambda^{0}_{\mathrm{Na}} + \frac{f_{\mathrm{Cl}}}{f_{\mathrm{NaCl}}} \lambda^{0}_{\mathrm{Cl}}\right).$$

Similar equations can be derived for an electrolyte solution consisting of more than two ionic species. It follows then, generally, that

$$\sum_{i} \left( \frac{f_{i}}{f} \lambda_{i}^{0} \right)_{0} = \sum_{i} \frac{f_{i}}{f} \lambda_{i}^{0} = \sum_{i} \lambda_{i}^{0}$$

where the first summation refers to the initial condition. Hence, in the above titration of hydrochloric acid with sodium hydroxide,

$$G_0 = \left(\mathrm{H}^+ + \mathrm{Cl}^- + p\left(\mathrm{Na}^+ + \mathrm{Cl}^-\right)\right)_0 = \mathrm{H}^+ + \mathrm{Cl}^- + p\left(\mathrm{Na}^+ + \mathrm{Cl}^-\right)$$
$$= \lambda^0_{\mathrm{H}} + \lambda^0_{\mathrm{Cl}} + p\left(\lambda^0_{\mathrm{Na}} + \lambda^0_{\mathrm{Cl}}\right)$$

Next the relation between the change in the conductance of the mixture of electrolytes and the change in volume of the solution will be derived. In general, such a relationship is not known; however, if the indifferent electrolyte is present in great excess, an approximation can be made, and the solution can be considered as being entirely composed of this electrolyte. The present discussion and the equation derived below refer particularly to sodium chloride solutions, but they also are essentially applicable to other electrolyte solutions.

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C  $\Lambda$ f  $\ln f$ 0 126.45 1.000 0 0.5 93.62 0.740 -0.3011 85.76 0.678 -0.3902 74.71 0.590 -0.5303 65.57 0.518 -0.6604 -0.79657.23 0.453 5 -0.94049.46 0.391

Conductance coefficient as a function of concentration for sodium chloride solutions  $(25^{\circ}C)$ 

In Table I.1 the conductance coefficient of the sodium chloride calculated by means of  $f = \Lambda/\Lambda^0$  using data of the equivalent conductance of the solutions<sup>5</sup> is shown as a function of concentration. *C* is the molar concentration,  $\Lambda$  is the equivalent conductance for a particular concentration,  $\Lambda^0$  is the equivalent conductance for zero concentration (ohm<sup>-1</sup>cm<sup>2</sup>), and ln *f* is the natural logarithm of the conductance coefficient.



The natural logarithm of the conductance coefficient of sodium chloride solution,  $\ln f$ , as a function of concentration (moles/liter).

In Fig. I.1 it is seen that between 1 and 5 M the logarithm of the conductance coefficient varies almost linearly with the concentration. Thus, in this concentration range the curve may be well represented by

$$\ln f = -aC + \text{constant} \tag{I.24}$$

thus,

$$f = A \exp\left(-aC\right) \tag{I.25}$$

*a* and *A* being constants. In regions where the curve is not linear, the above equation holds only for a narrow concentration range. The constant *a* can be obtained from Fig. I.1; for example, for 1 to 5 M solutions,  $a = -d \ln f/dC = 0.138$ .

As sodium chloride is present in great excess, during a titration the total mass of electrolyte remains practically constant. Thus we may write  $VC = V_0C_0$ , where V is the volume of the solution in the conductance cell, and C is the concentration of the sodium chloride (the suffixes refer to these quantities at the beginning of the titration). Combined with (I.25), this relation yields

$$f = A \exp\left(-a \frac{V_0}{V} C_0\right). \tag{I.26}$$

The above equation gives the relation between the conductance coefficient and the volume of the solution. For a small increase in volume, it is readily derived from (I.26) that

$$\frac{\Delta f}{f_0} = aC_0 \frac{\Delta V}{V} \,. \tag{I.27}$$

By writing  $\Delta V/V$  in series of  $\Delta V/V_0$  , and by neglecting the third and higher order terms

$$\frac{\Delta f}{f_0} = aC_0 \frac{\Delta V}{V_0} - aC_0 \left(\frac{\Delta V}{V_0}\right)^2. \tag{I.28}$$

If the titration is carried out with a sufficiently concentrated titrant, the second order term in (I.28) is negligible. Then the equation reduces to

$$\frac{\Delta f}{f_0} = aC_0 \frac{\Delta V}{V_0} \tag{I.29}$$

which may be written in terms of the fraction of the ions titrated, x, by means of

$$\Delta V = x V_{e} \tag{I.30}$$

where  $V_e$  is the volume of titrant at the equivalence point.

The general equation for the titration curve is now obtained by substituting the expressions for  $\Delta G/G_0$  (see (I.20) and (I.21)) and  $\Delta f/f_0$ , derived above, into equation (I.11). It is assumed that equation (I.29) is applicable. In fact, in a conductometric titration the titrant should be sufficiently concentrated to render the second order term in (I.28) negligible. Otherwise no straight titration lines would be obtained, even though volume corrections  $(V/V_0)\Delta k/k_0$  were applied to the observed values of the conductivity change (see section I.3).

By making the above substitutions, it follows that the reaction line is

$$\frac{V}{V_0} \frac{\Delta k_{\rm I}}{k_0} = \left\{ \frac{G'_{\rm I}}{G_0} + (aC_0 - 1) \frac{V_{\rm e}}{V_0} \right\} x \tag{I.31}$$

and the excess line is

$$\frac{V}{V_0} \frac{\Delta k_{\rm II}}{k_0} = \frac{G'_{\rm I} - G'_{\rm II}}{G_0} + \left\{ \frac{G'_{\rm II}}{G_0} + (aC_0 - 1) \frac{V_{\rm e}}{V_0} \right\} x \,. \tag{I.32}$$

Simplification of these equations is obtained by representing the *slope* of the titration lines by

$$S_{I} = \frac{G'_{I}}{G_{0}} + (aC_{0} - 1)\frac{V_{e}}{V_{0}}$$
(I.33)

and

$$S_{\rm II} = \frac{G'_{\rm II}}{G_0} + (aC_0 - 1)\frac{V_{\rm e}}{V_0}.$$
 (I.34)

The reaction line then becomes

$$\frac{V}{V_0} \frac{\Delta k_{\rm I}}{k_0} = S_{\rm I} x \tag{I.35}$$

and the excess line

$$\frac{V}{V_0} \frac{\Delta k_{\rm II}}{k_0} = S_{\rm I} + S_{\rm II}(x-1) . \tag{I.36}$$

The difference or change in slope of the titration line, i.e., the intercept on the vertical axis,  $S_{II} - S_I$ , which has great bearing on the accuracy in endpoint location (see section I.5), is obtained from (I.33) and (I.34):

$$S_{\rm II} - S_{\rm I} = \frac{G'_{\rm II} - G'_{\rm I}}{G_0} \,. \tag{I.37}$$

Equations (I.35) and (I.36) can be used to derive the equations of the titration lines of any conductometric titration. To illustrate this, the titration of hydrochloric acid with 0.5 M sodium hydroxide in the presence of a 5000-fold excess of sodium chloride (mixture of 0.5 ml of 0.1 M hydrochloric acid with 50 ml of 5 M sodium chloride solution) will be considered.

The mass balance equation is

$$HCl + [NaOH] + 5000 NaCl = NaCl + H_2O + 5000 NaCl$$

Thus,

$$G_{0} = H^{+} + Cl^{-} + 5000(Na^{+} + Cl^{-})$$

$$G_{1} = Na^{+} + Cl^{-} + 5000(Na^{+} + Cl^{-})$$

$$G'_{I} = G_{I} - G_{0} = Na^{+} - H^{+}$$

$$\frac{G'_{I}}{G_{0}} = \frac{Na^{+} - H^{+}}{H^{+} + Cl^{-} + 5000(Na^{+} + Cl^{-})} = -4.76 \times 10^{-4}$$

Beyond the equivalence point

$$G'_{II} = G_2 - G_1 = Na^+ + OH^-$$

and thus

$$\frac{G'_{\rm II}}{G_0} = \frac{{\rm Na^+ + OH^-}}{{\rm H^+ + Cl^- + 5000(Na^+ + Cl^-)}} = 3.94 \times 10^{-4}$$

(using  $H^+ = 350$ ,  $Na^+ = 50$ ,  $OH^- = 198$ , and  $Cl^- = 76$  ohms<sup>-1</sup>cm<sup>2</sup> at infinite dilution and 25 °C). Since the constant a = 0.138 applies for a 5 M sodium

chloride solution,  $aC_0 = 0.69$ . Further, we have  $V_0 = 50.5$  ml and  $V_e = 0.1$  ml (the volume of sodium hydroxide solution required for neutralization); hence,  $(aC_0 - 1)V_e/V_0 = -6.2 \times 10^{-4}$ .

It follows that the slope of the reaction line is

$$S_{I} = \frac{G'_{I}}{G_{0}} + (aC_{0} - 1)\frac{V_{e}}{V_{0}} = -0.0011$$
.

The slope of the excess line is

$$S_{\rm II} = \frac{G'_{\rm II}}{G_0} + (aC_0 - 1)\frac{V_{\rm e}}{V_0} = -0.00023$$
.

The reaction line is

$$\frac{V}{V_0} \frac{\Delta k_{\rm I}}{k_0} = S_{\rm I} x = -0.0011 x \,.$$

And the excess line is

$$\frac{V}{V_0} \frac{\Delta k_{\rm II}}{k_0} = S_{\rm I} + S_{\rm II}(x-1) = -0.0011 - 0.00023(x-1) \,.$$

The change in slope of the titration line can be directly obtained by means of (I.37);

$$S_{\rm II} - S_{\rm I} = \frac{{\rm H}^+ + {\rm OH}^-}{{\rm H}^+ + {\rm Cl}^- + 5000 ({\rm Na}^+ + {\rm Cl}^-)} = 0.00087 \,.$$



Fig. I.2.

Titration of hydrochloric acid in 50 ml of 5 M sodium chloride with 0.5 N sodium hydroxide. The intercept on the ordinate,  $S_{II}-S_{I}$ , is the difference in slope of the titration lines.

The experimental titration curve is shown in Fig. I.2. The reaction line is

$$\frac{V}{V_0} \frac{\Delta k_{\rm I}}{k_0} = -0.105x \text{ per cent}$$

and the excess line

$$\frac{V}{V_0} \frac{\Delta k_{\rm II}}{k_0} = -0.105 - 0.037 (x - 1) \text{ per cent}.$$

Here the conductivity change of the solution is expressed as a percentage. To find the absolute values of the slopes, the constants in the above equations are divided by 100. Hence,  $S_{\rm I} = -0.00105$ ,  $S_{\rm II} = -0.00037$ , and  $S_{\rm II} - S_{\rm I} = 0.00068$  (expressed as a percentage,  $S_{\rm II} - S_{\rm I} = 0.068$  per cent).

It is to be noted that to find the slope of the titration lines the volume of titrant corresponding to the equivalence point must be taken as the unit of length on the horizontal axis.

To express the above equations in  $\Delta V$  (the volume of sodium hydroxide added) instead of x, equation (I.30),  $\Delta V = xV_e$ , is used. Experimentally,  $V_e = 0.1017$  ml. Substituting  $x = \Delta V/0.1017$  into the above equations gives

$$\frac{V}{V_0} \frac{\Delta k_{\rm I}}{k_0} = -1.032 \Delta V \text{ per cent}$$

this being the equation of the reaction line, and

$$\frac{V}{V_0} \frac{\Delta k_{\rm II}}{k_0} = -0.068 - 0.367 \Delta V \text{ per cent}$$

being the equation of the excess line. (See also section III.2.)

The discrepancy between calculated and experimental values in the above illustration is primarily due to using the conductance values for infinite dilution  $\lambda_{0_{\rm H}}$  and  $\lambda_{0_{\rm OH}}$  for obtaining  $G'_{\rm I}$  and  $G'_{\rm II}$ , instead of those pertaining to the actual conditions,  $(f_{\rm H}/f)\lambda_{0_{\rm H}}$  and  $(f_{\rm OH}/f)\lambda_{0_{\rm OH}}$ , which cannot be evaluated because there are no data for  $f_{\rm H}$  and  $f_{\rm OH}$ . (It may be recalled that  $G_0 = \Sigma \lambda_{0_1}$ ; the value for this is therefore correct). Experimentally, the value for  $S_{\rm II}-S_{\rm I}$  is smaller than the value calculated (0.00068 compared with 0.00087). Also,  $S_{\rm I}$  is greater, whereas  $S_{\rm II}$  is smaller than the theoretical value. It appears therefore that under experimental conditions, the conductance values for H<sup>+</sup> and OH<sup>-</sup> are smaller than the values for infinite dilution.

Neglecting the second order term in equation (I.11) cannot account for the above discrepancy, for the error in  $S_{II}-S_I$  as a result of this is of the same order of magnitude as  $(\Delta f/f_0)\Delta G/G_0$  at the equivalence point:  $(\Delta f/f_0)G'_I/G_0$ . And this is only  $-6.6 \times 10^{-7}$  ( $\Delta f/f_0 = 1.38 \times 10^{-3}$ ;  $G'_I/G_0 = -4.76 \times 10^{-4}$ ), which is in absolute terms considerably smaller than  $-1.9 \times 10^{-4}$ , the value for the

difference between the calculated and the experimental  $S_{II}$ - $S_{I}$  found above.

Generally, the constant  $aC_0$  pertaining to the conductance coefficient of the electrolyte solution is not known and really need not be considered, since this constant primarily affects the slope of the titration lines, and not the accuracy in endpoint location. The latter is determined by the difference in slope which is not dependent on the conductance coefficient.

The effect of indifferent electrolytes on the slopes of the titration lines is due to the term  $(aC_0 - 1)\Delta V/V_0$ . This is the combined effect of the change in conductance coefficient and the change in volume on the conductivity of the solution. It gives rise to the *dilution line*, which is the titration line obtained by titrating the solution with distilled water (Fig. I.2). Clearly, the greater the volume change of the solution (using a titrant too dilute), the greater is the slope of the dilution line, and the more evident is its influence on the shape of the conductogram, since the latter is the summation of the dilution line and the line  $\Delta G/G_0$  (cf. equation (I.11)). Further, since the conductance sum,  $G_0$ , increases with increasing amounts of indifferent electrolyte, and since  $\Delta G$ remains unaffected, the above effect is the more pronounced in titrations in the presence of indifferent electrolyte. A titration curve as shown in Fig. I.5, curve I, will then be obtained.

The intersection of such titration lines cannot be determined accurately. To facilitate endpoint location, it is advantageous to transform the curve into a V-shaped curve by plotting  $(V/V_0)\Delta k_0 + B\Delta V$  versus volume of titrant added,  $\Delta V$ . The first term represents the experimental values of the conductivity change, whereas B in the second term is a constant of such magnitude that the reaction line is negative and the excess line positive. Generally, B equals approximately  $(aC_0 - 1)V_e/V_0$ .

Although the accuracy of the endpoint location is improved by this method, it is recommended that a titrant of suitable concentration or a titrant containing indifferent electrolyte which does not interfere with the reaction be used to reduce or eliminate the above dilution effect. The latter is illustrated by the titration of Fe(II)-ions in 0.5 M sulphuric acid with dichromate dissolved in 0.5 M sulphuric acid (see section III.3).

# I.3 Curvature due to volume change

A plot of relative conductivity change (or conductivity) against volume of titrant added produces straight lines if the reaction at the equivalence point is complete and if the volume change of the solution throughout the titration is negligible. If the volume change is not negligible, straight lines are obtained only if a correction for volume change is made. This is done by multiplying the values for the conductivity change by the factor  $V/V_0$ ; that is,  $1 + \Delta V/V_0$ , where  $V_0$  is the initial volume of the solution in the conductance cell, and  $\Delta V$  is

the volume of titrant added for the particular value of the conductivity change being considered.

When the above corrections are not applied, the lines are no longer straight. This is illustrated in Fig. I.3, which represents the titration of acetic acid with sodium hydroxide (see section III.2 for experimental conditions). Curve I is the plot  $(V/V_0)\Delta k/k_0$  against  $\Delta V$ , whereas curve II is  $\Delta k/k_0$  against  $\Delta V$ . The latter curve shows a deviation from linearity, so that an error in the endpoint location may result when the endpoint is taken as the intersection of extrapolated straight lines. This error is derived below.



Titration of acetic acid (in 100 ml of 0.02 M potassium chloride) with 0.1 N sodium hydroxide. Curve I is corrected for volume change. Curve II is uncorrected. The error in endpoint location due to deviation of the titration curve from the ideal straight lines.

A general expression for the error in endpoint location due to a deviation of the titration curve from linearity is obtained as follows. In Fig. I.4, OA and AB represent the ideal titration lines; CD and DE, the straight lines for the location of the endpoint; and the curved line, the experimental titration curve. The coordinates of the intersections of lines CD and DE with the experimental titration curve are represented by  $(x_1, y_1)$ ,  $(x_2, y_2)$ ,  $(x_3, y_3)$ , and  $(x_4, y_4)$ , where it is assumed that  $x_1 = 0.25$ ,  $x_2 = 0.75$ ,  $x_3 = 1.25$ , and  $x_4 = 1.75$ . The equations of the above lines are therefore

$$y_{I} = y_{1} + 2(y_{2} - y_{1}) (x_{I} - 0.25)$$

and

$$y_{II} = y_3 + 2(y_4 - y_3) (x_{II} - 1.25)$$

respectively. It follows that at the intersection of these lines

$$x = \frac{3y_1 - y_2 - 7y_3 + 5y_4}{4(y_1 - y_2 - y_3 + y_4)}$$

and the error in endpoint location

$$\Delta = x - 1 = -\frac{y_1 - 3y_2 + 3y_3 - y_4}{4(y_1 - y_2 - y_3 + y_4)}.$$
 (I.38)

The deviations of the titration curve from the ideal straight lines for the above values of  $x_1$ ,  $x_2$ ,  $x_3$ , and  $x_4$ , are  $d_{0.25}$ ,  $d_{0.75}$ ,  $d_{1.25}$ , and  $d_{1.75}$ , respectively. Hence, from (I.35) it follows that

$$y_1 = 0.25S_1 + d_{0.25}$$

 $y_2 = 0.75S_1 + d_{0.75}$ 

whereas from (I.36)

$$v_3 = S_1 + 0.25S_{11} + d_{1,2}$$

and

and

$$y_4 = S_{\rm I} + 0.75S_{\rm II} + d_{1.75} \; .$$

Substituting the above equations in (I.38) gives

$$\Delta = \frac{-d_{0.25} + 3d_{0.75} - 3d_{1.25} + d_{1.75}}{2(S_{\rm II} - S_{\rm I}) + 4(d_{0.25} - d_{0.75}) - 4(d_{1.25} - d_{1.75})} \,. \tag{I.39}$$

In deriving the error in endpoint location should no volume corrections be applied, the titration lines can be represented by

$$\frac{\Delta k_{\mathrm{I}}}{k_{0}} = S_{\mathrm{I}}x - \frac{xV_{\mathrm{e}}}{V_{0} + xV_{\mathrm{e}}}S_{\mathrm{I}}x$$

$$\frac{\Delta k_{\rm II}}{k_0} = S_{\rm I} + S_{\rm II}(x-1) - \frac{xV_{\rm e}}{V_0 + xV_{\rm e}} \{S_{\rm I} + S_{\rm II}(x-1)\}$$

derived from (I.35) and (I.36). When in the above equations the term  $xV_e$  is neglected with respect to  $V_0$ , the deviations of the reaction line and the excess line from the ideal straight lines become

$$d_{\mathrm{I}} = -\frac{V_{\mathrm{e}}}{V_{\mathrm{0}}} S_{\mathrm{I}} x^2 \tag{I.40}$$

and

$$d_{\rm II} = -\frac{V_{\rm e}}{V_0} \{S_{\rm I} + S_{\rm II}(x-1)\}x \tag{I.41}$$

respectively. Substituting x = 0.25 and x = 0.75 into (I.40) gives  $d_{0.25}$  and  $d_{0.75}$ ; and substituting x = 1.25 and x = 1.75 into (I.41),  $d_{1.25}$  and  $d_{1.75}$ .

Finally, inserting these values for d into (I.39) gives

$$\Delta = -\frac{0.375 \frac{V_{\rm e}}{V_{\rm 0}} (S_{\rm II} - S_{\rm I})}{2(S_{\rm II} - S_{\rm I}) - 4 \frac{V_{\rm e}}{V_{\rm 0}} S_{\rm II}}$$

which by neglecting the second term in the denominator becomes

$$\Delta \simeq -0.2 \, \frac{V_{\rm e}}{V_0} \,. \tag{I.42}$$

The error given by the above equation (I.42) is in agreement with the findings of Righellato and Davies,<sup>4</sup> that the endpoint in a conductometric titration may occur 2 per cent earlier when the concentration of the titrant is 10 times that of the substance titrated ( $V_e/V_0$  is 0.1; thus  $\Delta \simeq -0.02$ ).

Equation (I.42) shows that without the application of volume corrections the error in endpoint location is proportional to the volume change at the equivalence point. The error is, therefore, negligible when the titrant is added at a concentration considerably greater than that of the substance titrated. When  $V_{\rm e}/V_0$  is 0.01 or less, it is appropriate to plot simply the observed relative conductivity change,  $\Delta k/k_0$ , against the volume of titrant added, to locate the endpoint.



Fig. I.5.

Titration of hydrochloric acid in 40 ml of 5 M sodium chloride with 0.1 N sodium hydroxide. The curvature in curve II caused by the change in conductance coefficient is eliminated by correction with a quadratic term (curve III).

When  $V_{\rm e}/V_0$  is greater than 0.01, it is usually necessary to apply corrections for volume change, to produce straight lines. Yet a curvature in the titration lines may occur, and that as a result of the second order term in (I.28),  $aC_0 (\Delta V/V_0)^2$ , which has been neglected in the preceding equations. This is illus-

trated in Fig. I.5, showing the actual titration of the following solution with 0.1 N sodium hydroxide.

Titration mixture: 40 ml of 5 M sodium chloride solution, 0.200 ml of 0.5 N hydrochloric acid. For the experimental conditions, see section III.2.

Curve I is the plot

 $\frac{V}{V_0} \frac{\Delta k}{k_0}$  vs.  $\Delta V$  (ml of 0.1 N sodium hydroxide),

whereas curve II is

$$\frac{V}{V_0} \frac{\Delta k}{k_0} - (aC_0 - 1) \frac{\Delta V}{V_0} \quad \text{vs.} \quad \Delta V$$

and curve III is

$$\frac{V}{V_0}\frac{\Delta k}{k_0} - (aC_0 - 1)\frac{\Delta V}{V_0} + aC_0\left(\frac{\Delta V}{V_0}\right)^2 \quad \text{vs.} \quad \Delta V$$

calculated with  $aC_0 = 0.69$  (see section I.2) and  $V_0 = 40$  ml. From curve II, it follows that curve I actually does not consist of straight lines. It deviates from linearity due to the quadratic term,  $aC_0(\Delta V/V_0)^2$  or  $aC_0(V_e/V_0)^2x^2$ , which gains importance as the dilution increases. (In the present example,  $V_e/V_0$  is 0.021, compared with 0.002 in Fig. I.2.) Hence, correction with the quadratic term was necessary to obtain curve III consisting of straight lines.

(Note that in Fig. I.5 the deviation from linearity of curve II appears greater than that of curve I, as a result of the greater unit of length on the vertical axis of the lower figure.)

The constant  $aC_0$  required for the above correction can be derived from data of the conductance coefficient of the electrolyte solution as a function of concentration, or, if such data are not available, it may be estimated by titrating the solution with distilled water prior to the addition of titrant and determining the slope of the plot of  $(V/V_0)\Delta k/k_0$  against the volume of water added. The equation of this plot is  $(V/V_0)\Delta k/k_0 = (aC_0 - 1)\Delta V/V_0$ , derived by inserting  $\Delta G/G_0 = 0$  into equation (I.11) and by making use of (I.29). From the slope,  $(aC_0 - 1)/V_0$ , the constant  $aC_0$  is readily determined.

However, since such corrections are impracticable, it is best to avoid curvature in the titration lines by using a sufficiently concentrated titrant to render the quadratic term  $aC(\Delta V/V_0)^2$  in the conductance coefficient equation (I.28) negligible.

#### I.4 Curvature due to incompleteness of reaction

In our experiments titrations were made of divalent metal ions with EDTA. In such titrations roundness of the titration curve near the equivalence point may occur as a result of incompleteness of reaction. Consequently, an error in endpoint location may result when the endpoint is taken as the intersection of extrapolated straight lines. This error is calculated below.

The titration of a divalent metal with EDTA at pH = 5 (using acetic acidacetate buffer) will be taken as an example. The conclusions are also applicable to EDTA titrations at a pH other than 5, and are generally applicable to titrations where the titration lines show a curvature from incomplete reaction in the region of the equivalence point.

In the titration of metal ions with EDTA in the presence of acetic acid-acetate buffer, two reactions are taking place simultaneously, viz., the reaction of the metal with EDTA and the reaction of the acetate ions of the buffer with the hydrogen ions released in the first reaction. Hence, the overall reaction up to the equivalence point is

assuming completeness of reaction. However, a fraction of the complex ions,  $\beta_1$ , based on the total amount of metal, dissociates, forming M<sup>+2</sup> and Y<sup>-4</sup> ions, and the latter immediately combine with acetic acid to give H<sub>2</sub>Y<sup>-2</sup> and Ac<sup>-</sup> ions. Hence,

$$x MY^{-2} + 2\beta_I HAc = (x - \beta_I) MY^{-2} + \beta_I H_2 Y^{-2} + 2\beta_I Ac^{-} + \beta_I M^{+2}.$$
 (I.44)

Further, since at pH = 5 EDTA mainly forms  $H_2Y^{-2}$  ions

$$\frac{\alpha_{\rm H}}{K} = \frac{[{\rm M}^{+2}] [{\rm H}_2 {\rm Y}^{-2}]}{[{\rm M} {\rm Y}^{-2}]} \tag{I.45}$$

where K is the stability constant of the metal-EDTA complex,  $\alpha_{\rm H}$  is a factor dependent on the  $\rho$ H of the solution (see section III.4). The concentrations

$$[M^{+2}] = (1 - x + \beta_{I})C$$
$$[H_{2}Y^{-2}] = \beta_{I}C$$
$$[MY^{-2}] = (x - \beta_{I})C$$

can be found by means of (I.43) and (I.44); the concentration of the metal ion, C (moles/liter), is considered constant throughout the titration. By substituting the latter equations in (I.45) and solving for  $\beta_{I}$ , is obtained

$$\beta_{\mathrm{I}} = -\frac{1}{2} \left( 1 - x + \frac{\alpha_{\mathrm{H}}}{KC} \right) + \sqrt{\frac{1}{4} \left( 1 - x + \frac{\alpha_{\mathrm{H}}}{KC} \right)^2 + \frac{\alpha_{\mathrm{H}}}{KC} x} .$$
(I.46)

Beyond the equivalence point we have

 $MY^{-2} + (x - 1) [Na_2H_2Y] = MY^{-2} + 2(x - 1)Na^+ + (x - 1)H_2Y^{-2}$ . (I.47) Due to dissociation of the complex,

 $MY^{-2} + 2\beta_{II}HAc = (1 - \beta_{II})MY^{-2} + \beta_{II}H_2Y^{-2} + \beta_{II}M^{+2} + 2\beta_{II}Ac^-$ . (I.48) It follows that

$$\begin{split} [M^{+2}] &= \beta_{\rm II}C \\ [H_2 Y^{-2}] &= (x - 1 + \beta_{\rm II})C \\ [MY^{-2}] &= (1 - \beta_{\rm II})C \end{split}$$

Substituting these equations in (I.45) and solving for  $\beta_{II}$ , we obtain

$$\beta_{\rm II} = -\frac{1}{2} \left( x - 1 + \frac{\alpha_{\rm H}}{KC} \right) + \sqrt{\frac{1}{4} \left( x - 1 + \frac{\alpha_{\rm H}}{KC} \right)^2 + \frac{\alpha_{\rm H}}{KC}}.$$
 (I.49)

The difference in slope of the titration lines for complete reaction is given by (I.37),

$$S_{\rm II} - S_{\rm I} = \frac{G'_{\rm II} - G'_{\rm I}}{G_{\rm 0}}$$

where  $G'_{I}$  and  $G'_{II}$  can be obtained by differentiating the righthand side of (I.43) and (I.47) with respect to x, or obtained by means of (I.22) and (I.23) through neglecting the non-ionic acetic acid, HAc,

$$G'_{I} = MY^{-2} + 2Na^{+} - M^{+2} - 2Ac^{-},$$
  
 $G'_{II} = 2Na^{+} + H_{2}Y^{-2}.$ 

Hence, the difference in slope

$$S_{II} - S_{I} = \frac{H_2 Y^{-2} + M^{+2} + 2Ac^{-} - MY^{-2}}{G_0}.$$

Up to the equivalence point, the increase in conductance sum of the solution due to dissociation of the metal-EDTA complex is

$$(H_2Y^{-2} + M^{+2} + 2Ac^{-} - MY^{-2})\beta_I$$

as may be derived from (I.44) by subtracting the ion conductance  $xMY^{-2}$ , from the conductance sum of the ions on the righthand side of the equation. It then follows that the increase in relative conductivity is

$$d_{\rm I} = \frac{{\rm H}_2 {\rm Y}^{-2} + {\rm M}^{+2} + 2{\rm Ac}^- - {\rm M} {\rm Y}^{-2}}{G_0} \beta_{\rm I}$$
  
=  $(S_{\rm II} - S_{\rm I}) \beta_{\rm I}$ .

Similarly, for the deviation of the excess line can be derived

$$d_{\mathrm{II}} = (S_{\mathrm{II}} - S_{\mathrm{I}})\beta_{\mathrm{II}} \,.$$

The deviations of the titration curve from the ideal straight lines,  $d_{0.25}$  and  $d_{0.75}$  can be found by means of (I.46), whereas  $d_{1.25}$  and  $d_{1.75}$  can be obtained by means of (I.49). By substituting these values for d in (I.39) the theoretical

error in endpoint location can now be calculated for different values of  $\alpha_{\rm H}/KC$ . This is shown in Table I.2.

Theoretical error in endpoint location, $\Delta$ , in EDTA titrations.					
α <sub>H</sub> /KC	$\beta_{0.25}$	β0.75	$\beta_{1.25}$	$\beta_{1.75}$	Δ
10-4	0.00003	0.0003	0.0004	0.00013	-0.0001
$2.5 \times 10^{-3}$	0.00083	0.0073	0.0095	0.0032	-0.0022
10-2	0.0032	0.0263	0.0340	0.0129	-0.0081
$2.25 \times 10^{-2}$	0.0071	0.0520	0.0664	0.0278	-0.0135

Table I.2.		
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The error is seen to be dependent on the concentration of metal ions, the stability constant of the metal-EDTA complex, and the pH-dependent constant,  $\alpha_{\rm H}$ . For small values of  $\alpha_{\rm H}/KC$ , approximately,  $\Delta \simeq \alpha_{\rm H}/KC$ .

It is evident that in EDTA titrations, to prevent appreciable error due to incompleteness of reaction, the condition of the titration should be such that

$$\frac{\alpha_{\rm H}}{KC} \le 0.0025 \tag{I.50}$$

if the error is not to exceed -0.0022, or -0.22 per cent. This corresponds to a conversion of approximately 95 per cent of the metal ion into the complex at the equivalence point, for the fraction of metal not reacted with EDTA at the equivalence point (where the deviation from the ideal straight lines is a maximum) is

$$\beta_1 \simeq \sqrt{\frac{\alpha_{\rm H}}{KC}} \simeq 0.05$$
 (I.51)

obtained by substituting x = 1 into (I.46) or (I.49).



Fig. I.6.



Fig. I.6 shows the effect of the magnitude of  $\alpha_{\rm H}/KC$  on the deviation of the titration curve from the ideal straight lines, where, for convenience, it is assumed that  $S_{\rm I} = 0$ .

The condition for conductometric EDTA titration derived above, namely, that  $\beta_1$  be not greater than 0.05, may also be applied to other titrations. For example, in the titration of silver with chloride or vice versa, at the equivalence point

$$AgCl = (1 - \beta_1)AgCl + \beta_1Ag^+ + \beta_1Cl^-$$
$$[Ag^+] = [Cl^-] = \beta_1C$$
$$S = [Ag^+] [Cl^-]$$
$$\frac{S}{C^2} = \beta_1^2.$$

Thus,

$$\beta_1 = \frac{\sqrt{S}}{C} \le 0.05 \tag{I.52}$$

where S is the solubility product of silver chloride and C is the concentration of the silver or the chloride ions to be determined (moles/liter). In titrations of ions forming a 1:1 precipitate, this means that the concentration of the ions in question should be greater than  $20\sqrt{S}$ , in order to avoid appreciable error in endpoint location.

## I.5 Accuracy in endpoint location

It has been shown in the preceding sections that deviation of the titration curve from the ideal straight lines may give rise to errors in endpoint location. To avoid such deviations and thus to improve accuracy, it is recommended (a) that volume change corrections be applied, (b) that a sufficiently concentrated titrant be used, and (c) that appropriate reaction conditions (pH, concentration, etc.) be arranged. Nevertheless, even in the absence of curvature, the endpoint location may be erroneous as a result of experimental inaccuracy—insufficient compensation of temperature fluctuations, for example. This not only applies to the graphical, but also to the analytical endpoint determination (made by evaluating the constants of the two linear equations from the experimental values of the conductivity change and the corresponding titrant volumes, and by solving these equations simultaneously).

An expression for the possible error in endpoint location due to experimental inaccuracy is obtained by writing equations (I.35) and (I.36) for the reaction line and the excess line, respectively, as follows

$$y_{\mathrm{I}} = S_{\mathrm{I}} x \pm \mathrm{d} y , \qquad (\mathrm{I}.53)$$

$$y_{\rm II} = S_{\rm I} + S_{\rm II}(x - 1) \pm dy$$
, (I.54)

dy being the uncertainty in the experimental values. Further,

$$\mathrm{d}y = \frac{V}{V_0} \frac{\mathrm{d}k}{k_0} \tag{I.55}$$

since  $y = (V/V_0)\Delta k/k_0$ . Equating equations (I.53) and (I.54) gives

$$x=1\pm\frac{\mathrm{d}y}{S_{\mathrm{II}}-S_{\mathrm{I}}}\,.$$

Hence, the possible error in endpoint location is

$$\Delta = \frac{\mathrm{d}y}{S_{\mathrm{II}} - S_{\mathrm{I}}} \,. \tag{I.56}$$

Since k = K/R (equation (I.1)), it follows that  $dk/k_0 = -(R_0/R) dR/R$ , where dR/R is the uncertainty in the resistance measurements. Equation (I.55) now becomes  $dy = (V/V_0)(R_0/R)(dR/R)$ , omitting the negative sign. This equation may be approximated to dy = dR/R, because the effects of  $V/V_0$ and  $R_0/R$  are only of second order. (In our experiments, the relative conductivity,  $R_0/R$ , varied at the most by 100 per cent; the variation in  $V/V_0$  was less than 5 per cent.)

Now the term 2dy (=2dR/R) in equation (I.56) is the combined effect of three factors. The first is the adjustment error of the measuring bridge, dR'/R. The second is the error due to temperature fluctuations of the solution, cdT, where dT is the magnitude of the temperature fluctuation and c the temperature coefficient of the conductivity of the solution (ca. 2 per cent per degree C). And the last is the uncertainty in the observed value of the conductivity change due to the error in making a buret reading. This may be expressed by  $(S_{II} - S_{I})dV/V_{e}$ . Hence, the possible error in the result is

$$\Delta = \frac{\frac{\mathrm{d}R'}{R} + c\mathrm{d}T}{S_{\mathrm{II}} - S_{\mathrm{I}}} + \frac{\mathrm{d}V}{V_{\mathrm{e}}}.$$
 (I.57)

From the above equation it is evident that the accuracy in a conductometric titration depends not only on instrumental factors (precision of the measuring bridge, temperature constancy, and volume error), but also on the difference in slope of the titration lines,  $S_{II} - S_{I}$ . The latter decreases as the amount of indifferent electrolyte in the solution under examination increases. This means that in the titration of such solutions, a measuring bridge with a high degree of precision should be used, and care should also be taken to eliminate or reduce temperature fluctuations in the solution.

Equation (I.57) shows that the difference in slope  $S_{II} - S_I$  of the titration lines is essential for the accuracy in endpoint location. It has been generally accepted, however, that the magnitude of the angle ABF in a conductometric plot (Fig. I.7) is the factor which determines the accuracy in endpoint location

(see, e.g., ref. 1). For example, it has been frequently stated that in the titration of silver ions, lithium chloride would give a better accuracy than potassium chloride. And, for the same reason, in the titration of sulphate ions, barium acetate would be preferable to barium chloride.





Titration of silver nitrate: (I) with potassium chloride, and (II) with lithium chloride. No gain in accuracy is obtained by using lithium chloride instead of potassium chloride.

Indeed no exact endpoint location is possible if the bend in the titration line at the equivalence point is small (curve I in Fig. 1.5). However, as already mentioned in section I.2, such a titration curve can be transformed into a Vshaped curve, to improve endpoint location. By this method the titration curve of the titration of silver with potassium chloride can be made coincident with that using lithium chloride, since the change in slope of the titration lines at the equivalence point,  $S_{II}$ - $S_{I}$ , is the same in both titrations. Clearly, it is the difference in slope of the titration lines and the accuracy of the measurements that determine the accuracy of the endpoint location, and not the magnitude of the angle ABF.

Referring to titrations where the magnitude of the conductivity of the solution has little effect on the accuracy of the measurements, Lydersen<sup>2</sup> also has stated that the difference in slope of the titration lines is the determining factor for the accuracy in endpoint location. The same conclusion was reached by Liteanu *et al.*\* in studying the factors which determine the accuracy in endpoint location.

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#### CHAPTER II

## APPARATUS

#### **II.1 Introduction**

In conductance measurements on electrolyte solutions, use is made of a measuring bridge and a conductance cell. The measuring bridge, almost invariably a Wheatstone type, usually employs alternating current to reduce polarization at the electrodes and to obtain increased sensitivity by amplification of the unbalance potential. The conductance cell is a suitable vessel equipped with two inert metal electrodes, usually of platinum, and a stirrer for titrations. The resistance of the solution in the cell between the electrodes is measured with the measuring bridge. In accurate work, such as titrations in the presence of large amounts of indifferent electrolyte, it is important that a conductance cell free from polarization effects be employed, since under unfavorable conditions, these effects cause a drift in the bridge readings as well as a distortion in the titration curve, which thus diminish the accuracy of the endpoint location.<sup>14,23</sup>

Polarization effects can be reduced by the following methods recommended by Kohlrausch:<sup>16</sup> (a) using a frequency of 1000 cps or more, (b) using large electrodes (1 cm<sup>2</sup> or more), (c) platinizing the electrodes, and (d) designing the conductance cell so that the resistance to be measured is high (100 ohms or more). A suitable frequency is 1000-5000 cps; a higher frequency may cause inconvenience due to capacitance effects from the connecting leads. Platinization, which increases the active surface area of the electrodes, is most effective. but may introduce errors due to adsorption of the ions being determined or induction of undesirable chemical reactions at the electrodes: moreover, platinized electrodes are more readily subjected to fouling, especially in titrations involving the formation of precipitates. Bright platinum electrodes are therefore to be preferred. However, the resistance of the solution and hence the cell constant of the conductance cell must then be sufficiently large, and therefore in some cases, a conductance cell with a cell constant of at least  $1000 \text{ cm}^{-1}$ or a conductance cell of special design (see, e.g., ref. 26) must be used to make it possible to titrate solutions containing large amounts of indifferent electrolyte. Conductance cells having cell constants up to about 200 cm<sup>-1</sup> are commercially available, but they have been especially designed for absolute conductance measurements and they are not suitable for titrations.

Besides the polarization effects mentioned above, the effect originating from

the geometrical capacitance of the conductance cell composed of the intercapacitance of the two electrodes and the connecting leads must also be considered. Although readily compensated by a capacitor in an adjacent arm of the bridge, the geometrical capacitance should be minimized by proper design of the cell.

In this chapter the polarization resistance, the geometrical capacitance, the frequency of the a.c. source of the measuring bridge, the platinization and the size of the electrodes, the cell constant of the conductance cell, and the effects of all these on the titration curve will be studied. First the bridge measurements and also the balance conditions will be discussed.

# **II.2** The measuring bridge

#### II.2.1 Bridge arrangement for conductance measurements

Two types of instruments were used in our experiments: (a) the Philoscop and (b) the Electronic Strain Indicator, manufactured by the firms Philips in Eindhoven, and Peekel in Rotterdam, respectively. The Philoscop was applied in the titration of solutions with a total conductivity change of 1 per cent or more. The Peekel measuring bridge was used in the titration of solutions with a total conductivity change of less than 1 per cent.

#### (a) The Philoscop

The Philoscop is a measuring bridge of the Wheatstone type; see Fig. II.1. To the bridge network an a.c. voltage of 1000 or 50 cps is applied. The unbalance voltage across CD is amplified and indicated by a magic-eye detector, ND. A number of built-in standard resistances,  $R_2$ , may be placed in the second branch of the bridge, AC, so that measurements of unknown resistances,  $Z_1$  (actually an impedance), in the range of 0.5 ohm to 10 megohms are possible by successively adjusting the ratio arm  $R_3/R_4$  and the capacitor  $C_2$  (placed parallel with  $R_2$ ) until balance is attained. The value of the unknown resistance is directly read off on a scale. When measuring in the open bridge position (appropriate dial on the instrument set at ''Open Bridge''), an external decade resistance box connected to the terminals A and C is employed instead of the built-in standard resistors. A higher accuracy was obtainable with this method (about 1 in 10,000 ohms). For this reason, all titrations using the Philoscop were performed with the instrument set at ''Open Bridge'' and with the ratio arm set at unity.

In performing a titration, the conductance cell with the solution being examined was placed in a thermostat. The resistance of the cell was measured with a dial decade resistance unit,  $R_2$ , using a variable capacitor  $C_2$  (1000 pF) to secure phase balance. In most cases  $R_2$  was a decade box of 10,000 ohms reading down to 1 ohm; in measuring higher resistances, however, two or more such

resistance boxes were used, whereas in measuring lower resistances, a decade with lowest steps of 0.1 or 0.01 ohm was necessary. Balancing was accomplished by successive adjustments of  $R_2$  and  $C_2$ .

The titration curves were constructed by plotting the relative conductivity change corrected for volume change,  $(V/V_0) \Delta k/k_0$ , against the volume of titrant added;  $\Delta k/k_0$  is given by  $(R_0 - R)/R$ ,  $R_0$  being the resistance of the solution at the beginning of the titration. See equation (I.4).



a. c. source

Fig. II.1. Arrangement for measuring electrolytic conductance. ND is the null detector.



Fig. II.2. Circuit arrangement of Peekel measuring bridge.

#### (b) The Electronic Strain Indicator

The Peekel strain indicator is an instrument for measuring stresses and strains in structures and machines utilizing the resistance variation in a strain gauge applied to the surface of the object studied.<sup>14,15</sup> The apparatus is essentially a sensitive measuring bridge that can be used for measuring small variations in the resistance or conductance of electrolyte solutions. Measurements can be made either by the deflection or by the zero method. The zero method, being more accurate than the deflection method, was adopted in our measurements.

Fig. II.2 shows a diagram of the circuit arrangement. Two bridge networks I and II may be distinguished, to which an a.c. voltage of ca. 3 volts is applied

(1000 cps bridge, 3 volts; 2500 cps bridge, 5 volts; 5000 cps bridge, not measured). In the lower bridge I are placed two conductance cells of the same cell constant,  $Z_1$  and  $Z_2$  (to balance out conductance changes due to temperature fluctuations in the solution; see ref. 1), and in the opposite arms, two resistors of 500 ohms each,  $R_3$  and  $R_4$ . In the zero method (with the appropriate dial on the instrument set at ''C-Balance''), a potential change in C, brought about by the addition of reagent to the solution being titrated in one of the cells, is compensated by adjusting the slide-wire setting in the upper bridge II. The null detector is a four-stage amplifier connected to a galvanometer. Phase balance is secured by means of the built-in, or external capacitor  $C_2$  (1000 pF). The percentage resistance change of the solution,  $\Delta R/R_0$ , is found from the difference between two readings on a calibrated scale.

Three apparatus were available for operating with 1000, 2500, and 5000 cps. These were found suitable, although the one operating with 5000 cps showed increased capacitance effects which, however, were largely reduced by shielding the connecting leads. (The instruments operating with 2500 and 5000 cps have been calibrated in micro-strain; 500 micro-strains correspond to a resistance change of 0.1 per cent.)

In performing a titration, two conductance cells of practically equal cell constants were filled with equal amounts of the solution under examination, were placed in a thermostat, and were then titrated successively. The result of the second titration served as a check on the first. The titration curves were obtained by plotting  $(V/V_0) \Delta k/k_0$  against the volume of titrant added.  $\Delta k/k_0$  is the relative conductivity change of the solution, given by equation (I.5). When the relative resistance change was sufficiently small – less than 1 per cent – the approximate relation (I.6) was used.

In the titrations using the Philoscop and the Peekel measuring bridge, it was most important to earth the measuring bridge and the thermostat, to shield the connecting leads to the conductance cells, and to ensure good connections. Further, since the circuit breaker of the electric heater of the thermostat caused fluctuations in the temperature of the water bath, this heater (and the cooling water to the cooler) was disconnected to eliminate the temperature fluctuations. (A temperature rise of the solution during a titration was of no consequence.) All titrations were performed at ordinary temperatures.

The Peekel measuring bridge can be used for the titration of solutions where the difference in the slopes of the reaction and excess lines is as low as 0.05 per cent. Compared with the Philoscop, this is 20-fold higher in accuracy. Nevertheless, since corrections  $(\Delta R/R_0)^2$  must be applied if the resistance change is greater than 1 per cent, the Peekel measuring bridge can only be advantageously employed in titrations where the total resistance change of the solution is less than 1 per cent. In contrast, the Philoscop was found suitable for titrations involving a resistance change greater than 1 per cent.

It was observed that the precision in the conductivity measurements with the Peekel measuring bridge was limited by the temperature inconstancy of the solution during a titration, and not by the sensitivity of the measuring bridge. The accuracy in taking a reading was  $\pm 0.0002$  per cent conductivity change; the actual accuracy, however, was only  $\pm 0.001$  per cent, because of temperature fluctuations in the solution. Further improvement of the accuracy of the titrations may therefore be expected by improving the method of elimination of temperature effects.

In the titrations with the Philoscop, the sensitivity of the measuring bridge was the limiting factor to the accuracy of the measurements.

# II.2.2 The balance conditions

The relation between the impedances in the 4 arms of a Wheatstone bridge when the detector shows a minimum current is discussed below. It is assumed that the detector is of infinitely high impedance and measures voltage independently of its phase – this is approximated by the Philoscop and the Peekel measuring bridge.

Generally, balancing an a.c. bridge consists in successively adjusting two parameters until the detector shows no current. With the Philoscop arrangement in Fig. II.1 (with  $R_3/R_4 = 1$ ), balance is secured by successively adjusting the two components in the second arm of the bridge,  $R_2$  and  $C_2$ ;  $R_2$  is varied until a minimum in the detector signal is reached, and after this,  $C_2$  is adjusted, etc. During this balancing process the unbalance voltage across CD decreases until it becomes zero at true balance. With the Peekel measuring bridge, balance is attained by adjusting the ratio arm  $R_3/R_4$  and the capacitor  $C_2$ . (Actually the ratio arm in the upper bridge network II is adjusted; still, this is equivalent to adjusting  $R_3/R_4$  in the lower bridge network.)

Contrary to d.c. bridge measurements where at balance  $R_1R_4 = R_2R_3$ , here we have

$$\mathbf{Z}_1 R_4 = \mathbf{Z}_2 R_3 \tag{II.1}$$

or,

$$Z_1 R_4 = Z_2 R_3 \tag{II.2a}$$

and

$$\theta_1 = \theta_2 \tag{II.2b}$$

 $Z_1$  is the impedance of the conductance cell, and  $Z_2$  is the impedance of the second conductance cell (in the measurements with the Peekel measuring bridge), or the impedance of the combination of  $R_2$  and  $C_2$  parallel in the second arm of the bridge.  $Z_1$  and  $Z_2$  are the magnitudes, whereas  $\theta_1$  and  $\theta_2$  are the direction angles or phase displacements of  $Z_1$  and  $Z_2$ , respectively.

The above impedances can be represented by

$$\mathbf{Z}_1 = Z_1' - j Z_1'' \tag{II.3}$$

$$\mathbf{Z}_2 = Z_2' - j Z_2'' \tag{II.4}$$

where  $Z_1'$  and  $Z_2'$  are the real parts, and  $Z_1''$  and  $Z_2''$ , the imaginary parts of the impedances.  $Z_1', Z_2', Z_3''$ , and  $Z_4''$  are positive quantities; further,  $j = \sqrt{-1}$ . Thus, in a bridge measurement with  $R_3 = R_4$  and with  $R_2$  and  $C_2$  parallel in the second arm of the bridge, at balance we have

$$Z_{1}' - jZ_{1}'' = Z_{2}' - jZ_{2}''.$$
(II.5)

It follows that

$$Z_{1}' = Z_{2}' = \frac{R_2}{1 + R_2^2 \omega^2 C_2^2}$$
(II.6)

and

$$Z_1'' = Z_2'' = \frac{R^2 \omega C_2}{1 + R_2^2 \omega^2 C_2^2} . \tag{II.7}$$

Further,

$$-\operatorname{tg}\,\theta_1 = -\operatorname{tg}\,\theta_2 = R_2\omega C_2 \tag{II.8}$$

and

$$Z_1 = Z_2 = \frac{R_2}{(1 + R_2^2 \omega^2 C_2^2)^{\frac{1}{2}}}.$$
 (II.9)

Equations (II.2a) and (II. 2b) hold if there is magnitude as well as phase balance. In the measurements with the Peekel measuring bridge, however, the relation  $Z_1R_4 = Z_2R_3$  approximatively holds true, even though no adjustment



Fig. II.3.

When a minimum in the detector signal, M, is attained by merely adjusting the ratio  $R_3/R_4$  ( $C_2 = \text{constant}$ ), the relation  $Z_1R_4 = Z_2R_3$  approximatively holds true, although there is no true balance.

for phase equilibrium is made (the minimum in the detector signal being attained only by varying the ratio  $R_3/R_4$ ). This may be derived as follows. In Fig. II.3 the voltage vector  $E_{\rm AC}$  is

$$E_{\rm AC} = \frac{Z_2}{Z_1 + Z_2} E_{\rm AB} \tag{II.10}$$
The vector  $E_{CB}$  connects the extremity of  $E_{AC}$  with that of the unit voltage vector  $E_{AB}$ . By substituting (II.3) and (II.4) into (II.10) and evaluating this, the following equation is obtained:

$$E_{AC} = \left\{ \frac{Z_{2'}(Z_{1'} + Z_{2'}) + Z_{2''}(Z_{1''} + Z_{2''})}{(Z_{1'} + Z_{2'})^{2} + (Z_{1''} + Z_{2''})^{2}} + j \frac{Z_{1''}Z_{2'} - Z_{1'}Z_{2''}}{(Z_{1'} + Z_{2'})^{2} + (Z_{1''} + Z_{2''})^{2}} \right\} E_{AB}$$
(II.11)

In Fig. II.3,  $E_{AC}$  has been calculated with  $Z_{1'} = 220$ ,  $Z_{1''} = 419$ ,  $Z_{2'} = 357$ , and  $Z_{2''} = 225$  ohms.  $Z_{2'}$  and  $Z_{2''}$ , calculated by means of (II.6) and (II.7), respectively, refer to a combination of  $R_2 = 500$  ohms parallel with  $C_2 = 0.2 \,\mu$ F, and a frequency f = 1000 cps. Since  $R_3$  and  $R_4$  are ohmic resistances, on varying the ratio  $R_3/R_4$ , the extremity of the voltage vector

$$E_{\rm AD} = \frac{R_4}{R_3 + R_4} E_{\rm AB}$$
 (II.12)

moves along the horizontal axis. At M, corresponding to  $R_3/R_4 = 1.131$ , a minimum is reached in the unbalance voltage  $E_{CD}$ ; here, this vector is perpendicular to the horizontal axis, and so,

$$\frac{E_{\rm CB}\cos\alpha_1}{E_{\rm AC}\cos\alpha_2} = \frac{E_{\rm DB}}{E_{\rm AD}}.$$

In practice, as in the above illustration,  $\alpha_1$  nearly equals  $\alpha_2$ ;  $\cos \alpha_1/\cos \alpha_2$  therefore practically equals unity. Accordingly, the relation between the voltages is closely approximated by

$$\frac{E_{\rm CB}}{E_{\rm AC}} = \frac{E_{\rm DB}}{E_{\rm AD}}.$$

Hence,

$$Z_1R_4=Z_2R_3.$$

During a titration with the Peekel measuring bridge (sections III.2 and III.3), it was therefore not necessary to adjust the capacitor to maintain phase balance.

On the other hand, in the measurements with the Philoscop, no simple relation as (II.2a) exists for the minimum in the detector signal reached by adjusting the resistor  $R_2$ , if at the same time there is no phase balance. See Fig. II.4. If in the above illustration with  $R_2 = 500$  ohms and  $C_2 = 0.2 \ \mu$ F, the resistor  $R_2$  is varied from 500 to 5000 ohms, a circular locus with center in P is described by the extremity of the vector  $E_{AC}$ ; this locus may be calculated by means of equation (II.11). The minimum in the detector signal  $E_{CD}$  occurs at M, a point on the locus found by drawing the straight line from P through

the extremity of  $E_{AD}$  until it intersects the locus. For this minimum no simple relation can be derived between the vector magnitudes  $E_{AC}$  and  $E_{CB}$  on one hand, and the vector magnitudes  $E_{AD}$  and  $E_{DB}$  on the other; hence, in this case the impedance magnitudes  $Z_1$  and  $Z_2$  cannot be related simply to the resistances  $R_3$  and  $R_4$ .



Fig. II.4.

When a minimum in the detector signal, M, is attained by merely adjusting the resistor  $R_2$  ( $C_2 = \text{constant}$ ), no simple relation exists between the ratio  $R_3/R_4$  and the impedance magnitudes  $Z_1$  and  $Z_2$ .

Generally, in bridge measurements it is best to balance for magnitude as well as for phase.

#### **II.3** The conductance cell

In conductance measurements on electrolyte solutions the elimination of polarization effects is most important because these effects may impair the accuracy of the bridge readings and may, furthermore, distort the titration curve so that no exact location of the titration endpoint can be made.

In devising methods for elimination of polarization effects, it is useful to consider the equivalent electric circuit of the conductance cell.

It is also interesting to study the effect of the geometrical capacitance on the shape of the titration curve.

### II.3.1 The electric model

The impedance of a conductance cell comprises (a) the electrolytic resistance of the solution  $R_1$ , (b) the electrode impedance at the electrodes  $\mathbf{Z}_e$ , and (c) the geometrical capacitance  $C_1$ . See Fig. II.5, representing a conductance cell of the type used in precision conductance measurements, and its equivalent circuit, which is essentially identical with the circuit proposed by Feates *et al.*<sup>5</sup>. The geometrical capacitance,  $C_1$ , originating from the intercapacitance of the leads and the electrodes, is shown as a capacitance shunted across the conductance cell. There may be other capacitances – for example, the capacitance between A and B, or between A and D, not included in  $C_1$ , through which electricity may flow. These may interfere in the measurements and give rise



Fig. II.5.

A conductance cell and its equivalent electric circuit.  $R_1$  is the electrolytic resistance,  $\mathbf{Z}_e$  is the electrode impedance, and  $C_1$  is the geometrical capacitance.

to the so-called Parker effect.<sup>11,18</sup> This effect was observed by Parker as a small but perceptible increase in the cell constant of a given cell (0.03 per cent), which was found in measuring the cell constant with potassium chloride solutions of decreasing concentration. Parker-capacitance is not cancelled out by the capacitance  $C_2$  parallel with the resistance  $R_2$  in the adjacent arm of the bridge. Therefore, in absolute conductance measurements Parker-capacitance should be avoided by proper design of the conductance cell – for example, by spacing such protruding parts (indicated by *B* and *D* in Fig. II.5) well away from parts of the cell containing solution. Or, it may be reduced by using oil instead of water as thermostat liquid, because of the comparatively smaller dielectric constant of oil. However, in conductrometric titrations where only a relative quantity is measured, Parker-capacitance is not important.

The electrode impedance has been intensively studied.<sup>21,22</sup> It follows that the electrode impedance may be represented by the electric circuit in Fig. II.6. *C* is the double layer capacitance,  $\rho$  is the resistance due to activation polarization of the electrode reaction, and *W* is the Warburg impedance due to diffusion polarization. The quantities  $\rho$  and *W* are given, respectively, by

$$\varrho = \frac{RT}{n^2 F^2 k_{\rm sh} (C_{\rm ox}^*)^{\alpha} (C_{\rm red}^*)^{(1-\alpha)}}$$

$$W = \sigma \omega^{-\frac{1}{2}} - j \sigma \omega^{-\frac{1}{2}}$$

where

$$\sigma = \frac{RT}{n^2 F^2 \sqrt{2}} \Big[ \frac{1}{C_{\text{ox}}^* \sqrt{D_{\text{ox}}}} + \frac{1}{C_{\text{red}}^* \sqrt{D_{\text{red}}}} \Big].$$

 $\omega$  is the angular frequency of the a.c. source of the measuring bridge, R is the gas constant, T is the absolute temperature, n is the number of electrons involved in the electrode reaction, F is the Faraday constant,  $k_{\rm sh}$  is the standard heterogeneous reaction rate constant,  $C_{\rm ox}^*$  and  $C_{\rm red}^*$  are the concentrations of oxidized and reduced forms of the reacting species in the bulk of the solution,  $\alpha$  is the transfer coefficient of the electrode reaction, and  $D_{\rm ox}$  and  $D_{\rm red}$  are the diffusion constants of the reacting species.

For the impedance of the equivalent circuit (Fig. II.6) the following equations may be derived:

$$\mathbf{Z}_{\mathrm{e}} = Z_{\mathrm{e}}' - jZ_{\mathrm{e}}'' \tag{II.13}$$

where

$$Z_{e}' = \frac{\varrho + \sigma \omega^{-\frac{1}{4}}}{(C \varrho \omega^{\frac{1}{4}} + 1)^2 + \omega^2 C^2 (\varrho + \sigma \omega^{-\frac{1}{4}})^2}$$
(II.14)

and

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Fig. II.6. Equivalent electric circuit of the electrode impedance,  $Z_e$ . W is the Warburg impedance;  $\varrho$ , the resistance due to activation polarization; and C, the double layer capacitance.

Fig. II.7. Locus diagram of the electrode impedance.  $Z'_{e}$  is the real component;  $Z_{e}''$ , the imaginary component; and  $\theta_{e}$ , the phase displacement at the electrode.

Sluyters<sup>21</sup> has shown that the electrode impedance may be represented by the diagram as in Fig. II.7.  $Z_{e'}$  is the real part of the impedance and  $Z_{e''}$ , the imaginary part.  $R_1$  is the electrolytic resistance of the solution. The curve in the complex plane is the locus described by the extremity of the vector of the

and

electrode impedance  $Z_e$  when the frequency is varied. For high frequencies the locus is a semicircle, whereas for lower frequencies the locus is a straight line making a slope of 45° with the horizontal axis. The semicircle is due to the activation polarization resistance,  $\rho$ , and the double layer capacitance, C. The straight line is related to the Warburg impedance, W, which is inversely proportional to the square root of the frequency.

Although the dependency of the electrode impedance on the frequency is of considerable interest in the study of electrode reactions, for our purpose it is sufficient to consider the electrode impedance as a complex quantity,  $Z_e = Z_e' - jZ_e''$ . The impedance of a conductance cell with two identical electrodes which is free from Parker-capacitance may then be derived as follows.

The impedance of the equivalent network in Fig. II.5, consisting of two branches with impedances

$$\mathbf{Z}_{\mathrm{I}} = R_{\mathrm{1}} + 2Z_{\mathrm{e}'} - 2jZ_{\mathrm{e}''}$$

and

$$\mathbf{Z}_{\mathrm{II}} = \frac{1}{j\omega C_1}$$

is

$$Z_1 = rac{Z_1 Z_{11}}{Z_1 + Z_{11}} \, .$$

Evaluating the above equation gives

$$\mathbf{Z}_{1} = \frac{\frac{R_{1} + 2Z_{e}'}{1 + 2Z_{e}''\omega C_{1}} - j\left(2Z_{e}'' + \frac{(R_{1} + 2Z_{e}')^{2}\omega C_{1}}{1 + 2Z_{e}''\omega C_{1}}\right)}{1 + 2Z_{e}''\omega C_{1} + \frac{(R_{1} + 2Z_{e}')^{2}\omega^{2}C_{1}^{2}}{1 + 2Z_{e}''\omega C_{1}}}.$$
 (II.16)

In equation (II.16),  $Z_{e''}$  is of the order of 5 ohms (Table II.7) and  $C_1$  is ca. 20 pF (Table II.2). For a frequency of 1000 cps, as in our experiments,  $2Z_{e''}\omega C_1$  is then of the order of 10<sup>-6</sup>. Hence, the term  $2Z_{e''}\omega C_1$  may be neglected.

The equation for the impedance of the conductance cell now becomes

$$\mathbf{Z}_1 = Z_1' - j \, Z_1'' \tag{II.17}$$

where

$$Z_{1}' = \frac{R_{1} + 2Z_{e}'}{1 + (R_{1} + 2Z_{e}')^{2}\omega^{2}C_{1}^{2}}$$
(II.18)

and

$$Z''_{1} = \frac{2Z_{e}'' + (R_{1} + 2Z_{e}')^{2}\omega C_{1}}{1 + (R_{1} + 2Z_{e}')^{2}\omega^{2}C_{1}^{2}}.$$
 (II.19)

The tangent of the phase displacement across the cell

$$\operatorname{tg} \theta_1 = -\frac{Z_1^{\prime\prime}}{Z_1^{\prime\prime}}.$$

Hence

$$- \operatorname{tg} \theta_{1} = \frac{2Z_{e}^{\prime\prime}}{R_{1} + 2Z_{e}^{\prime}} + (R_{1} + 2Z_{e}^{\prime})\omega C_{1}.$$
 (II.20)



The impedance of a conductance cell on varying the geometrical capacitance  $C_1$  and the electrolytic resistance  $R_1$ .

In Fig. II.8 the cell impedance is shown diagrammatically. The extremity of the impedance vector moves along curve I with increasing values of the geometrical capacitance. Curve II is the locus of the extremity of the impedance vector when, in a given cell having appreciable geometrical capacitance, the electrolytic resistance is increased. This can be done, for example, by decreasing the concentration of the solution in the cell. Finally, when the geometrical capacitance is negligible or zero and the electrolytic resistance is increased, the locus is the horizontal line III.

Measuring with equal ratio arms,  $R_3/R_4 = 1$ , it follows from (II.6) and (II.18) that at balance,

$$\frac{R_1 + 2Z_{e'}}{1 + (R_1 + 2Z_{e'})^2 \omega^2 C_1^2} = \frac{R_2}{1 + R_2^2 \omega^2 C_2^2}.$$
 (II.21)

Further, from (II.8) and (II.20), that

$$\frac{2Z_{e''}}{R_1 + 2Z_{e'}} + (R_1 + 2Z_{e'})\omega C_1 = R_2\omega C_2.$$
(II.22)

If the phase difference is sufficiently small, for example,  $-\text{tg }\theta_2 = R_2 \omega C_2$  is smaller than 0.1, then  $R_2^2 \omega^2 C_2^2$  and consequently  $(R_1 + 2Z_e')^2 \omega^2 C_1^2$  in the

above equation (II.21) may be neglected, so that

$$R_1 + 2Z_e' = R_2. (II.23)$$

It is seen that in conductance measurements we always measure the real part of the electrode impedance in addition to the electrolytic resistance of the solution. Therefore,  $Z_{e}'$  may be called the *polarization resistance*.

# II.3.2 The geometrical capacitance

The geometrical capacitance,  $C_1$ , may be derived from the measurements by Jones and Bollinger<sup>11</sup> on the phase displacement across conductance cells of the type shown in Fig. II.5, with the cell constants tabulated in Table II.1.

Cell	Cell constant $cm^{-1}$	Area of electrodes (platinum), cm <sup>2</sup>	Platinization Coulombs/cm <sup>2</sup>		
			Light	Heavy	
I	4.29	0.8	7.07	46.5	
II	1.23	3.1	7.8	81	
III	4.39	3.8	9.5	113	
IV	51.47	2.0	5.4	54	

Table II.1.

Cell constant, electrode area, and degree of platinization of cells I, II, III, and IV in Fig. II.9.

The cells have been tabulated in order of decreasing polarization effect, i.e., cell constant times area of electrodes. The tangent of the phase displacement, tg  $\theta_1$ , was determined as a function of the resistance of potassium chloride solutions,  $R_2$ , by varying the concentration of the solution from 1 to 0.0005 M. Measurements were made at two frequencies: 1090 and 2280 cps.

In Fig. II.9  $-\text{tg }\theta_1$  has been plotted against  $R_2$  on log-to-log coordinates. The curves show a good agreement with equation (II.20),  $-\text{tg }\theta_1 = 2Z_e''/(R_1 + 2Z_e') + (R + 2Z_e')\omega C_1$ , where  $R_1 + 2Z_e' = R_2$ . According to this equation, the curve should consist of two straight lines with slopes of -1 and +1, and a minimum at a certain resistance value. Experimentally, the slope of the lines is not exactly -1 and +1. This may be ascribed to the fact that  $Z_e''$  is not constant but is dependent on the concentration of the solution. Furthermore, Parker capacitance not included in the above equation might also be present in the cells.

It is noted that the minimum in the curves occurs at about 1000 ohms. For higher resistance values, the contribution of the electrode impedance  $Z_e$  to

the phase displacement across the cell becomes negligible, and for 10,000 ohms, tg  $\theta_1$  is approximately equal to  $-R_2\omega C_1$ , so that the geometrical capacitance  $C_1$  can be represented by  $C_1 \simeq -\text{tg } \theta_1/\omega R_2$ . With this equation, the geometrical capacitance of the conductance cells was calculated from the value of  $-\text{tg } \theta_1$  at 10,000 ohms. In Table II.2 the values of this capacitance for cell IV are shown.



Fig. II.9.

Phase displacement across conductance cell,  $- \operatorname{tg} \theta_1$ , versus cell resistance,  $R_2$  (ohms), of 4 different conductance cells (see Table II.1). (A) slightly platinized, (B) heavily platinized, (a) 1090 cps, and (b) 2280 cps. (Constructed with data from Jones and Bollinger.<sup>11</sup>)

Table II.2.

The geometrical capacitance	of	cell	IV	in	Fig.	II.9.
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Platinization Coulomb/cm <sup>2</sup>	$- tg\theta_1$ 1090 cps	$-$ tg $\theta_1$ 2280 cps	C <sub>1</sub> , pF 1090 cps	C <sub>1</sub> , pF 2280 cps
5.4	0.0015	0.0028	22	20
54	0.0013	0.0025	19	17

Average values for cells I, II, III, and IV are 20, 9, 14, and 20 pF, respectively.

In practice, the geometrical capacitance of conductance cells can be higher than the values found above. For example, when the leads to the conductance

cell are shielded, the geometrical capacitance can be 100 pF or even higher. To show the effect of a higher geometrical capacitance on the titration curve, titrations were made in a conductance cell shunted by fixed capacitors of increasing magnitude. Phase balance was secured only at the beginning of the titration, not during the titration.

Fig. II.10 represents the titration of ferro ions in 0.5 M sulphuric acid with potassium dichromate in a conductance cell shunted with capacitors of increasing magnitude. Curves I, II, and III refer to the titration with capacitors of 0, 2000, and 4100 pF, respectively. It is seen that the slope of the reaction lines decreases as the capacitance increases. The excess lines also show a decrease in slope.

Titration mixture: 45 ml of Fe(II) solution. The titrant was a solution of potassium dichromate in 0.5 M sulphuric acid to eliminate dilution effects (see section III). Apparatus: conductance cell with cell constant of 2000 cm<sup>-1</sup> of the type shown in Fig. II.27 and Peekel measuring bridge, frequency 5000 cps. The initial resistance of the solution measured with the Philoscop was 11,500 ohms.

The decrease in the slope of the titration lines may be derived as follows. Because of the high resistance, the cell may be considered as a resistance  $R_1$ and a capacitance  $C_1$  in parallel. In accordance with (II.9) the resistance of the cell, actually the magnitude of the impedance, is then  $Z_1 = R_1/\sqrt{1 + R_1^2\omega^2 C_1^2}$ , and its relative change,  $dZ_1/Z_1 = (1 + R_1^2\omega^2 C_1^2)^{-1}dR_1/R_1$ . It follows that the relative slope of the titration lines

$$\frac{\mathrm{d}Z_1/Z_1}{\mathrm{d}R_1/R_1} = (1 + R_1^2 \omega^2 C_1^2)^{-1}$$
(II.24)

decreases as the capacitance  $C_1$  increases.

Table II.3 shows a comparison of calculated and found values of the relative slope of the titration lines.

C <sub>1</sub> pF	$R_1\omega C_1$		$(1+R_1^2\omega^2C_1^2)^{-1}$		
		Calc.	Found reaction line	Found excess line	
0	0	1	1	1	
2000	0.72	0.66	0.63	0.26	
4100	1.48	0.31	0.32	0.43	

Table II.3.

The relative slope of the titration lines in Fig. II.10.

Satisfactory agreement between theory and results is obtained with regard to the effect on the slope of the reaction lines. The effect of increasing capacitance on the slope of the excess lines is not quite so obvious, and this may be caused by factors not included in equation (II.24). However, from these results it is evident that the slope of the titration lines decreases with increasing values of  $R_1\omega C_1$ .

It is to be noted that the difference in slope,  $S_{II}-S_{I}$ , also decreases as the capacitance increases.

The above results explain why the deflection method of measurement yields flat titration curves when using a conductance cell with a large cell constant or resistance (cf. Mika<sup>17</sup>), for adjustment of phase balance during the titration is not possible with this method.



Fig. II.10.

Titration of ferro ions in 45 ml of 0.5 M sulphuric acid with 0.1 N potassium dichromate. Capacitance across the conductance cell: (I) 0 pF, (II) 2000 pF, and (III) 4100 pF. Phase balance was secured only at the beginning of the titration.



Fig. II.11.

Titration of sodium hydroxide in 45 ml of 0.1 M potassium chloride solution with 0.5 N hydrochloric acid. Capacitance across conductance cell: (I) 0 pF and (II) 4100 pF. Phase balance was maintained during the titration.

When adjustments of the phase balance during the titration are made, there will be practically no effect on the slope of the titration line. This is shown in Fig. II.11, referring to the titration of sodium hydroxide with 0.5 N hydrochloric acid. Curve I refers to the titration without shunted capacitance, whereas curve II refers to the titration with a capacitance of 4100 pF. There is practically no effect on the slope of the titration lines, even though  $-\text{tg }\theta_1 = 6.1$ . The slight deviation of curve II from curve I is probably due to leakage resistance within the capacitor.

Titration mixture: 0.2 ml of 0.5 N sodium hydroxide solution, and 45 ml of 0.1 M potassium chloride solution. Apparatus: cell constant of conductance cell, 1000 cm<sup>-1</sup>; Peekel measuring bridge, 2500 cps. Resistance of the solution was 95,000 ohms.

The above illustration shows that it is quite possible to titrate a solution even when its resistance is about 100,000 ohms. The geometrical capacitance of the conductance cell can be readily compensated by means of the capacitor  $C_2$  in the adjacent arm of the bridge. A lower resistance not exceeding 20,000 ohms is recommended, though, because the sensitivity of the measuring bridge decreases as the resistance increases. (Compare this with equation (II.24), which can be seen as a measure of the sensitivity of the bridge to resistance change.)

Finally, it may be noted that the imaginary part of the electrode impedance of the conductance cells,  $Z_{e}$ ", can also be derived from the measurements by Jones and Bollinger.<sup>11</sup> For a resistance of 100 ohms the phase displacement across the cell is practically determined by the electrode impedance only (see Fig. II.9) so that the term  $(R_1 + 2Z_{e'})\omega C_1$  in equation (II.20) may be neglected and the following relation results

$$-\operatorname{tg} \theta_1 \simeq \frac{2Z_{\mathrm{e}^{\prime\prime}}}{R_1 + 2Z_{\mathrm{e}^{\prime}}} \simeq \frac{2Z_{\mathrm{e}^{\prime\prime}}}{R_2}$$

Hence,

$$Z_{\rm e}'' \simeq \frac{-R_2 \, {\rm tg} \, \theta_1}{2}.$$
 (II.25)

The values in Table II.4 have been calculated with equation (II.25), using the values for  $- \text{tg } \theta_1$  at 100 ohms from Fig. II.9 (cell I). It is seen that  $Z_e''$ decreases with increasing frequency and platinization.  $Z_e''$  is almost inversely proportional to the number of coulombs per cm<sup>2</sup> of electrode surface.

Table II.4.

Platinization Coulomb/cm <sup>2</sup>	$-\operatorname{tg} \theta_1$ 1090 cps	$-\mathrm{tg} \ \theta_1$ 2280 cps	Z <sub>e</sub> ", ohm 1090 cps	Ze", ohm 2280 cps
7.07	0.008	0.005	0.4	0.3
46.5	0.0010	0.0006	0.05	0.03

Imaginary part of the electrode impedance of cell I in Fig. II.9.

Generally, the phase displacement across a conductance cell should be small —smaller, for example, than 0.1. A large phase displacement indicates the presence of a relatively large geometrical capacitance or polarization resistance. To establish whether geometrical capacitance or polarization resistance is responsible for the phase displacement, the frequency of the a.c. source of the measuring bridge is varied. When  $- \text{tg } \theta_1$  increases as the frequency is decreased, for example, from 1000 to 50 cps, polarization resistance predominates. On the other hand, when  $- \text{tg } \theta_1$  decreases, the phase displacement is due to geometrical capacitance. (See also equation (II.20)).

## II.3.3 The polarization resistance

## (1) Measurement

Jones *et al.*<sup>12,13</sup> also have determined the polarization resistance by measuring the resistance of the solution under examination in a suitable conductance cell (a) as a function of the distance between the electrodes and (b) as a function of the frequency of the a.c. source of the measuring bridge. But these methods are not suitable for the measurement of the polarization resistance during a titration. Therefore, the arrangement shown in Fig. II.12 was used.





Arrangement for measuring polarization resistance and for titrations. The platinum electrodes are denoted by 1, 2, and 3. *ND* is the null detector. plugs New York

### Fig. II.13. Conductance cell with three electrodes for measuring polarization resistance and for performing titrations. Cell constant approximately 0.4 cm<sup>-1</sup>.

The measuring bridge is the Philoscop with equal ratio arms  $(R_3/R_4 = 1)$ .  $R_B$  and  $R_2$  are dial decade resistance boxes, and  $C_2$  is a variable capacitor. The conductance cell, which is in principle similar to the one employed by Shedlovsky,<sup>20</sup> has three electrodes of bright platinum of the same size, 1 cm<sup>2</sup> each (Fig. II.13). The distance between the first and the second electrode,  $l_{12}$ , is 2 mm, and between the second and the third electrode,  $l_{23}$ , 15 mm. Accordingly, the electrolytic resistance of the solution within the two compartments of the cell may be represented by  $\alpha R$  and R,  $\alpha$  being the ratio  $l_{12}/l_{23}$ .

Measurements were made according to the following procedure. First the resistance of the solution in the right compartment of the cell is measured, with the switch in position I; balance is attained by adjusting  $R_2$  and  $C_2$ . At balance we have

$$R_1 + R_B + 2Z_e' - 2jZ_e'' = \frac{R_2}{1 + R_2^2 \omega^2 C_2^2} - j \frac{R_2^2 \omega C_2}{1 + R_2^2 \omega^2 C_2^2}.$$
 (II.26)

Thus,

$$Z_{1}' = R_1 + R_B + 2Z_e' = \frac{R_2}{1 + R_2^2 \omega^2 C_2^2}$$
 (II.27)

It follows that

$$Z_{\rm e}' = \frac{(Z_{\rm e}' - R_{\rm B})_{\rm I} - R_{\rm I}}{2}.$$
 (II.28)

The suffix I is to denote measurements with the switch in position I. In the above equations the term  $R_2^2 \omega^2 C_2^2$  may be neglected if  $-\operatorname{tg} \theta_2 = R_2 \omega C_2$  is sufficiently small, e.g.,  $-\operatorname{tg} \theta_2 = 0.1$ . This can be effected by means of the resistor  $R_B$ . The greater is  $R_B$ , the smaller,  $R_2 \omega C_2$ . If  $-\operatorname{tg} \theta_2 = 0.1$  or less than this, it is allowable to write  $Z_1' = R_2$ .

Subsequently, the resistance of the solution is measured with the switch in position II. In this measurement no capacitance  $C_2$  is required to attain phase balance if the electrodes (electrode impedances) are equal in magnitude. At balance,

$$R_1 + R_B + 2Z_{e'} - 2jZ_{e''} = R_2 + \alpha R_1 + 2Z_{e'} - 2jZ_{e''}.$$
 (II.29)

Thus,

$$R_1 = \frac{1}{1 - \alpha} \left( R_2 - R_B \right)_{\text{II}} \tag{II.30}$$

the suffix II refers to measurements with the switch in position II.

The polarization resistance can now be found by means of

$$Z_{e'} = \frac{(Z_{1'} - R_{B})_{I} - \frac{1}{1 - \alpha} (R_{2} - R_{B})_{II}}{2}$$
(II.31)

obtained by substituting (II.30) into (II.28). It follows from the equality of the complex terms in (II.26) that

$$Z_{e}^{\prime\prime} = \frac{R_{2}^{2}\omega C_{2}}{2(1 + R_{2}^{2}\omega^{2}C_{2}^{2})}.$$
 (II.32)

The tangent of the phase displacement across the electrodes,

$$-\operatorname{tg} \theta_{\mathrm{e}} = \frac{Z_{\mathrm{e}}''}{Z_{\mathrm{e}'}} \tag{II.32}$$

which is derived from equation (II.13).

The factor  $\alpha$  in (II.31) can be found from the known values of  $l_{12} = 2$  mm and  $l_{23} = 15$  mm; thus,  $\alpha = 2/15 = 0.133$ . This was further checked as follows. With the same arrangement as in Fig. II.12, the resistances  $R_{12}$ ,  $R_{23}$ , and  $R_{13}$  are measured. These are the resistances of the solution between the electrodes 1-2, 2-3, and 1-3, i.e.,  $R_{12} = \alpha R_1 + 2Z_e'$ ,  $R_{23} = R_1 + 2Z_e'$ , and  $R_{13} = (1+\alpha)R_1 + 2Z_e'$ , respectively, obtained by means of  $R_2/(1 + R_2^2\omega^2C_2^2)$ ; see equation (II.27). Hence,  $R_{13} - R_{23} = \alpha R_1$ ,  $R_{13} - R_{12} = R_1$ , and  $\alpha = (R_{13} - R_{23})/(R_{13} - R_{12})$ .

Measurements on a 0.01 M potassium chloride solution, using a frequency of 1000 cps, yielded the values shown in Table II.5.

Table II.5.

Measurements on 0.01 M KCl solution

$R_{\rm B}$ ohms	$R_2$ ohms	$C_2$ $\mu F$	
 300	394	0.014	
0	368	0.018	
0	413	0.014	

Therefrom it may be derived that  $R_{12} = 94$  ohms,  $R_{23} = 368$  ohms, and  $R_{13} = 413$  ohms. Hence,  $\alpha = 45/319 = 0.141$ . This value of  $\alpha$  was used for the measurements mentioned below instead of the calculated value (0.133).

Measurements were conducted to determine the polarization resistance of bright platinum electrodes in potassium chloride and hydrochloric acid solutions of varying concentration; area of electrodes 1 cm<sup>2</sup>, and frequency 1000 cps. (See Table II.6). The position of the switch in the measuring arrangement (Fig. II.12) is denoted by I and II. The components of the electrode impedance were calculated as follows: for example, for the 0.01 M potassium chloride solution,  $Z_{e'} = (368 - 1.164 \times 274)/2 = 24$  ohms;  $Z_{e''} = (368 \times 4.2 \times 10^{-2})/2 = 7.7$  ohms, and  $-tg \theta_e = 7.7/24 = 0.3$ . The results have been tabulated in Table II.7.

It is seen that  $Z_e'$  is of the same order of magnitude as  $Z_e''$ . It follows that

Table II.6.

Solution		$R_{\rm B}$	$R_2$	$C_2$	$R_2\omega C_2$
		011110		<i>p</i>	
0.01 M KCl	I	0	368	0.018	0.042
	II	0	274.0	0	
0.1 M KCl	I	100	144	0.086	0.078
	II	10	41.4	0	
saturated KCl	Ι	200	204	0.039	0.050
	II	20	21.3	0	
0.01 M HCl	I	80	215	0.046	0.062
	II	20	119.0	0	
0.1 M HCl	I	150	167	0.060	0.063
	II	20	29.5	0	
1.0 M HCl	I	100	105	0.160	0.106
	II	20	20.9	0	

Measurements for determining polarization resistance of bright platinum electrodes in KCl and HCl solutions.

the polarization resistance can also be roughly estimated by measuring the phase displacement across the conductance cell and by making use of equation (II.25),  $Z_{e'} \simeq Z_{e''} = -\frac{1}{2}R_2 \operatorname{tg} \theta_1$ .

From Table II.7 it is evident that the polarization resistance in a conductance cell with (two) bright platinum electrodes may amount to 48 ohms or more, depending upon the size of the electrodes and the electrolyte concentration of

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Polarization resistance at smooth platinum electrodes of 1 cm<sup>2</sup> (1 electrode), and corresponding phase displacement (1000 cps; 23°C).

Solution	Ze'	$Z_{e}^{\prime\prime}$	$-tg \theta_e$
	ohms	ohms	
Potassium chloride			
0.01 M	24	7.7	0.3
0.1 M	3.6	5.6	1.6
saturated	1.2	5.2	4
Hydrochloric acid			
0.01 M	10	6.6	0.7
0.1 M	3	5.3	1.7
1.0 M	2	5.5	2.7

the solution being examined. Consequently, errors may arise not only in absolute conductance measurements, but also in conductometric titrations. These errors are discussed below.

# (2) Polarization effects

As has been noted, polarization effects may interfere in conductometric titrations. Instead of straight lines, curved lines may then result. Since in a conductance measurement, the sum of the electrolytic resistance and the polarization resistance,  $R_2 = R_1 + 2Z_e'$  (equation (II.23)), is measured, it is evident that the deviation from linearity is a result of the simultaneous change in the polarization resistance and electrolytic resistance. This view was verified by actual measurements on the polarization resistance during a titration of sodium hydroxide in 100 ml of 0.1 M potassium chloride solution (1 ml of ca. 0.5 N sodium hydroxide, 10 ml of 1 N potassium chloride, and 89 ml of water) with 0.5 N hydrochloric acid, using the same conductance cell and arrangement shown in Fig. II.12, with the switch in position II; further,  $R_3/R_4 = 1$ ,  $R_B = 0$ ,  $C_2 = 0$ , and frequency 1000 cps.

Table II.8.

Measurement of the polarization resistance of platinum electrodes during the titration of sodium hydroxide with hydrochloric acid

	II	I						
ml HCl	$R_2$ ohms	$R_2$ ohms	$C_2$ $\mu F$	$-\operatorname{tg} \theta_1$ ( $R_2\omega C_2$ )	$Z_1'$ ohms	Ζ <sub>e</sub> ′ ohms	Ze" ohms	$-tg \theta_e$
0	29.92	42.2	0.47	0.1250	41.54	3.52	2.64	0.750
0.2	30.18	42.6	0.48	0.1285	41.90	3.55	2.74	0.771
0.4	30.48	43.0	0.48	0.1300	42.27	3.54	2.80	0.791
0.6	30.67	43.5	0.50	0.1366	42.69	3.65	2.97	0.815
0.8	30.76	44.0	0.52	0.1436	43.10	3.81	3.16	0.829
1.0	30.41	42.4	0.43	0.1146	41.84	3.37	2.43	0.721
1.2	29.66	41.3	0.43	0.1117	40.78	3.27	2.30	0.705
1.4	28.86	40.3	0.45	0.1140	39.78	3.24	2.30	0.710
1.6	28.17	39.3	0.47	0.1160	38.77	3.15	2.28	0.723
1.8	27.46	38.4	0.50	0.1206	37.84	3.07	2.31	0.753

Table II.8 shows the results of the measurements. The figures in column 2 were obtained with the bridge in position II. They represent the values for the electrolytic resistance,  $R_2 = (1 - \alpha)R_1$ , derived from (II.30); they do not include the polarization resistance. On the other hand, the values for  $Z_1' = R_2/(1 + R_2^2\omega^2C_2^2) = R_1 + 2Z_e'$  (equation (II.27),  $R_B = 0$ ), calculated with  $R_2$  and  $C_2$  in columns 3 and 4, and obtained with the bridge in position I, do include the polarization resistance. The polarization resistance itself,  $Z_e'$ , was calculated with (II.31), and  $Z_e''$  with (II.32), whereas the phase displacement across the electrodes,  $-\text{tg } \theta_e$ , was calculated with (II.33). The values for the tangent of the phase displacement across the conductance cell,  $-\text{tg } \theta_1 = R_2\omega C_2$ , are shown in column 5.

In Figure II.14 curve I is the titration curve obtained by plotting  $(V/V_0) (R_0 - R)/R$  against ml's of hydrochloric acid. (R is  $R_2$  in the second column of Table II.8.). It may be noted that  $(R_0 - R)/R = \Delta k/k_0$ ; see equation (I.6). The titration endpoint agrees well with the phenolphtalein endpoint, 0.848 ml. In contrast, curve II calculated with values of  $Z_1$ , shows a deviation. Moreover, the titration endpoint found by extrapolation of the straight portions of the curve gave a result which was too low. Stock<sup>23</sup> found a similar deviation from linearity due to polarization effects in the titration of hydrochloric acid with sodium hydroxide.



The polarization effect illustrated by the titration of sodium hydroxide in 100 ml of 0.1 M potassium chloride solution with 0.5 N hydrochloric acid. Curve I: polarization resistance eliminated. Curve II: polarization

resistance not eliminated.

The percentage change in (I) the electrolytic resistance and (II) the polarization resistance during the titration of sodium hydroxide with hydrochloric acid.

The distortion in the titration curve is a result of the simultaneous change in polarization resistance and electrolytic resistance during titration. Curves I and II in Fig. II.15 represent the percentage change in the electrolytic resistance and polarization resistance, respectively. It is seen that the polarization resistance changes somewhat abruptly at the equivalence point, whereas the electrolytic resistance shows a more gradual change.

Obviously, the extent of the deviation from the normal course of the titration curve depends on the percentage change in both the polarization resistance and the electrolytic resistance. Representing these changes by  $p_z$  and  $p_R$ , it is readily shown that the relative deviation of the observed resistance change  $(2p_z Z_e' + p_R R_1)$  from the actual change in electrolytic resistance  $(p_R R_1)$  is

$$\Delta \simeq \frac{2p_z Z'_e}{p_R R_1} \,. \tag{II.34}$$

It follows that the vertical deviation of the titration curve from the ideal straight lines can be reduced by decreasing the ratio of polarization resistance to electrolytic resistance,  $2Z'_{e}/R_{1}$ .





Fig. II.16.

The accompanying change in the phase displacement (I) across the electrode and (II) across the conductance cell during the titration of sodium hydroxide with hydrochloric acid. Fig. II.17. The equivalent electric circuit of the conductance cell with three electrodes and the arrangement for titrations. ND is the null detector.

Finally, Fig. II.16 shows the accompanying change in the phase displacement across the electrodes and the conductance cell. At the equivalence point there is also a rather abrupt change in the curve.

## (3) Elimination of polarization effects

It was shown in the above example of the titration of sodium hydroxide with hydrochloric acid that polarization effects can be eliminated or reduced by using a conductance cell with three electrodes. The same effect is also achieved by decreasing the polarization resistance or increasing the electrolytic resistance, thus decreasing the ratio of polarization resistance to electrolytic resistance,  $2Z_{\rm e}'/R_{\rm 1}$ , by methods which will be discussed below.

### Conductance cell with three electrodes

In principle, the three-electrode cell shown in Fig. II.13 consists of two cells with unequal cell constants. In a conductance measurement, the polarization resistances in the two adjoining cells cancel each other, so that only the difference in electrolytic resistance of the solution within the two cells is measured. Fig. II.17 shows the equivalent electric circuit of the three-electrode cell.

Balance is attained by adjusting the variable resistor  $R_2$ . When measuring with equal ratio arms,  $R_3/R_4 = 1$ , and if the polarization resistances in the two compartments of the cell are equal in magnitude, at balance,

$$\frac{R_1 + 2Z_{e'}}{1 + (R_1 + 2Z_{e'})^2 \omega^2 C_1^2} = R_2 + \frac{\alpha R_1 + 2Z_{e'}}{1 + (\alpha R_1 + 2Z_{e'})^2 \omega^2 C_2^2}$$

where  $\alpha$  is the ratio of the cell constants, and  $C_1$  and  $C_2$ , the geometrical capacitances of the two cells. Since  $C_1$  and  $C_2$  are in the order of 10 to 50 pF (Table II.2), the effect of these capacitances may be neglected  $(R^2\omega^2C^2)$  is only ca.  $10^{-6}$  when R = 10,000 ohms and f = 1000 cps) so that the above balance equation becomes  $(1 - \alpha)R_1 = R_2$ . Thus,  $R_2$ , which does not include the polarization resistance, can be used for the construction of the titration curve. An example has been given in Fig. II.14.

In the above equations it has been assumed that the polarization resistances at the electrodes are equal in magnitude. In practice this may be realized by making the electrodes of the same size and material. If the polarization resistance is eliminated, magnitude and phase balance can be attained without using additional capacitance across the cell or the adjacent arm of the bridge. Further, balance may not be greatly disturbed when the frequency of the a.c. source of the measuring bridge is changed, for example, from 1000 to 50 cps. However, a capacitance of about 100 pF either across the first or the second arm of the bridge may be necessary to compensate for capacitance from the leads, particularly at higher resistances.

If more capacitance is necessary for securing phase balance, this may indicate the incomplete elimination of polarization resistance. Allowance for this can be made by choosing another ratio of  $R_3/R_4$ ; for example, when the polarization resistance in the left compartment of the cell is *a*-times greater than the polarization resistance in the other compartment of the cell, at balance,

$$R_1 + 2Z_{e'} = \frac{R_3}{R_4} (R_2 + \alpha R_1 + 2aZ_{e'}).$$

It follows that the resistance ratio must be  $R_3/R_4 = 1/a$ , in order to obtain  $(a - \alpha)R_1 = R_2$  free from polarization resistance. The value for the ratio *a* can be found by successively adjusting  $R_3/R_4$  and  $R_2$ , until the bridge is balanced for magnitude and phase.

If the electrodes are of the same size and material, it is usually sufficient to set the ratio  $R_3/R_4$  at unity. Any residual capacitance is then compensated by

means of a variable capacitor placed across AC or CB. In this way, effective elimination of polarization resistance can be achieved.

It is to be noted that the second electrode, which is a common electrode of the two adjoining cells, need not be of the same size.

# Decreasing the polarization resistance

Polarization resistance, especially with platinum electrodes, can be minimized (a) by increasing the frequency of the a.c. source of the measuring bridge, (b) by platinizing the electrodes, and (c) by increasing the effective surface area of the electrodes. The effect of frequency and platinization is shown in Fig. II.18 and Fig. II.19. These represent the measurements by Jones and Bollinger<sup>13</sup> on the polarization resistance at platinum electrodes in a platinizing solution (0.025 M hydrochloric acid containing 0.3 per cent of platinum chloride and 0.025 per cent of lead acetate), recalculated for 1 cm<sup>2</sup> of electrode, assuming inverse proportionality of the polarization resistance to the electrode area.







Polarization resistance of platinum electrodes versus degree of platinization. (Data from Jones and Bollinger<sup>13</sup>.)

From the slope of the curves in Fig. II.18 it is evident that the polarization resistance decreases as the frequency increases. The polarization resistance is almost inversely proportional to the square root of the frequency. (However,

this is not necessarily so; see equation (II.14) and Fig. II.17.) Further, it is seen that by platinization the polarization resistance is decreased by approximately 100 times. The first deposit of platinum black has a great effect. With increasing platinization the polarization resistance is inversely proportional to the number of Coulombs per cm<sup>2</sup> of electrode. After reaching a minimum, the polarization resistance increases. Accordingly, the optimum effect of platinization is obtained with about 10 Coulombs per cm<sup>2</sup> of electrode surface.

The effects of frequency and platinization on the titration curve are shown in Fig. II.20, representing the titration of sodium hydroxide in 40 ml of 0.1 M potassium chloride solution with 0.5 N hydrochloric acid. The effect of frequency is evident from curves I and II. Curve I was obtained with 1000 cps, whereas curve II was obtained with 2500 cps. The effect of platinization is seen in curves II and III, obtained with 2500 cps. Curve II: using bright platinum electrodes. Curve III: using the same electrodes, but after platinization. With 1000 instead of 2500 cps the same titration curve as III was obtained.



The effect of frequency and platinization illustrated by the titration of sodium hydroxide in 0.1 M potassium chloride solution (40 ml) with 0.5 N hydrochloric acid. Curve I: bright platinum electrodes, 1000 cps. Curve II: bright platinum electrodes, 2500 cps. Curve III: platinized electrodes, 2500 cps. (Cell resistance 89 ohms.) The effect of electrode surface area in the titration of sodium hydroxide in 2 N potassium chloride solution (40 ml) with 0.5 N hydrochloric acid. Curve I:  $1.7 \text{ cm}^2$ . Curve II:  $0.5 \text{ cm}^2$ .

The above titrations were carried out in a conductance cell with bright platinum electrodes and a cell constant of  $1.2 \text{ cm}^{-1}$  (electrodes 1 cm<sup>2</sup> each), and the conductivity changes were recorded with the Peekel measuring bridge.

Fig. II.21 shows the effect of the size of the electrodes. It refers to the titration of sodium hydroxide in 40 ml of 2 N potassium chloride solution with 0.5 N

hydrochloric acid (in a conductance cell with bright platinum electrodes and a cell constant of 1000 cm<sup>-1</sup>, using the Peekel measuring bridge and a frequency of 1000 cps). Curve I was obtained with electrodes of about 1.7 cm<sup>2</sup>, whereas curve II was obtained with electrodes of about 0.5 cm<sup>2</sup>. It is seen that polarization effects are practically eliminated by using electrodes of about 1.7 cm<sup>2</sup> (and a high resistance which was 5400 ohms).

From the above examples it is evident that platinization has a greater effect than increasing the frequency or the size of the electrodes. While by increasing the frequency (for example, from 1000 to 2500 cps) and size of electrodes, the polarization resistance may be decreased by a factor of 2 or 3, by platinization, the polarization resistance may be reduced by roughly 100 times.

On the other hand, platinization has the disadvantage that other errors may become apparent, examples being errors due to (a) catalytic effects of the electrodes on certain reactions or (b) adsorption of ions to be determined by the platinized electrodes. Adsorption may cause a drift in the meter readings (the resistance of the solution increases) before starting with the actual titration, as

%

 $V/V_0$ )  $\Delta k/k_0$ ,

-3

-5





The effect of cell resistance (brought about by varying the electrolyte concentration) in the titration of sodium hydroxide with 0.5 N hydrochloric acid. Curve I: 1 M KCl, 530 ohms. Curve II: 0.33 M KCl, 1440 ohms. Curve III: 0.01 M KCl, 4550 ohms. (Curves I and II yield erroneous endpoints.) The effect of cell resistance (brought about by increasing the cell constant) in the titration of sodium hydroxide in 0.1 *M* potassium chloride solution (40 ml) with 0.5 N hydrochloric acid. Curve I: 89 ohms (cell constant 1.2 cm<sup>-1</sup>). Curve II: 95,000 ohms (cell constant 1000 cm<sup>-1</sup>).

ml of 0.5 N HCl

Fig. II.23.

0.1

0.2

0.3

was found in the titration of 0.001 M zinc solution with EDTA, using the conductance cell with platinized electrodes and cell constant of  $1.2 \text{ cm}^{-1}$  (see also ref. 16).

Some workers attempted to reduce polarization effects by using electrodes of other materials: gold,<sup>2</sup> tin, tungsten,<sup>6</sup> silver,<sup>1</sup> and graphite.<sup>24</sup> But these electrodes do not seem to have specific advantages over platinum. Only relatively small differences in polarization resistance may be expected.

Bright platinum electrodes are still to be preferred, and in some cases even polarization effects are tolerated.  $^{3,25}$ 

## Using a large cell constant

The polarization effect is small when the electrolytic resistance of the solution,  $R_{1}$ , is relatively large compared with the polarization resistance at the electrodes of the conductance cell,  $2Z_{e}$ '; see equation (II.34). This can be effected by using a conductance cell with a large cell constant. It follows from (I.1) that the larger the cell constant, the larger is the electrolytic resistance.

The effect of a large electrolytic resistance is shown in Fig. II.22. The curves represent the titration of sodium hydroxide in potassium chloride solutions of decreasing concentration (40 ml) with 0.5 N hydrochloric as titrant. Apparatus: conductance cell with cell constant of 60 cm<sup>-1</sup> and bright platinum electrodes of 1.7 cm<sup>-2</sup>, and Peekel measuring bridge, frequency 1000 cps. Curve I: 1 M KCl, molar ratio KCl/NaOH = 480, and R = 530 ohms. Curve II: 0.33 M KCl, KCl/NaOH = 160, and R = 1440 ohms. Curve III: 0.095 M KCl, KCl/NaOH = 46, and R = 4550 ohms. It is seen that the deviation of the titration curve from the ideal straight lines decreases as the resistance of the solution increases. In curve III, where the resistance was about 5000 ohms, there is practically no polarization effect.

Fig. II.23 shows the effect of a higher resistance by using a conductance cell with a large cell constant. It refers to the titration of sodium hydroxide in 40 ml of 0.1 M potassium chloride solution with 0.5 hydrochloric acid (using the Peekel measuring bridge and a frequency of 1000 cps.) Curve I: K = 1.2 cm<sup>-1</sup> and R = 89 ohms. Curve II: K = 1000 cm<sup>-1</sup> and R = 95,000 ohms. In curve II, with a resistance of 95,000 ohms, the deviation in the titration curve is virtually eliminated.

However, the resistance need not be so high. From Fig. II.24 it is evident that curve II, as compared with curve I, does not show the typical deviation due to polarization effects. Curve I:  $K = 1.2 \text{ cm}^{-1}$  and R = 89 ohms. Curve II:  $K = 60 \text{ cm}^{-1}$  and R = 4550 ohms. Hence, approximately 5000 ohms is sufficient.

It is to be noted that the cell constants mentioned above are only approximations and may differ by 10 per cent from the values indicated.

The value of the cell resistance required for eliminating polarization effects depends on the frequency of the a.c. source of the measuring bridge, the size of the electrodes, and the degree of platinization. See Table II.9. R is the cell resistance (ohms), and A, the surface area of the electrodes (cm<sup>2</sup>). In our

titrations, we found that the resistance should be at least 5000 ohms, using bright platinum electrodes of about 1.7 cm<sup>2</sup> and a frequency of 1000 cps. Thus, RA should be not less than 8500 ohms cm<sup>2</sup> (1000 cps). This value particularly applies to titrations in the presence of large amounts of indifferent electrolyte. In the titration of solutions of ordinary concentration, the required minimum value for RA may be different from the value just mentioned, because the polarization resistance and, hence, the ratio  $2Z_{e'}/R_{1}$  depends on the electrolyte concentration. (See Table II.7.)

RA	RA	Frequency	References
bright Pt	platinized Pt	a.c. source	
-	100	(inductor)	Jander <sup>9</sup>
2500	50	(inductor)	Fajans <sup>4</sup>

Table II.9.						
Value of J	RA	for	bright	and	platinized	electrodes.

### Conclusion

In conductometric titrations, bright platinum electrodes are to be preferred to platinized electrodes. Polarization effects from these electrodes may be reduced or eliminated by the following methods: (a) using a conductance cell with three electrodes and (b) using a conductance cell with large cell constant so that the resistance to be measured is at least 5000 ohms. In the latter case, the cell constant must be not less than 1000 cm<sup>-1</sup>, especially in titrations in the presence of large amounts of foreign electrolyte – redox titrations, for instance.

# II.3.4 Design of the conductance cell

Two types of conductance cells with bright platinum electrodes have been constructed – namely, cells with three electrodes, and cells with a large cell constant.

### Cell with three electrodes

To take advantage of the sensitivity of the measuring bridge, the cell constant of the conductance cell should not be too low. For example, with the cell shown in Fig. II.13 the resistance of a 0.1 M potassium chloride solution was 31.4 ohms. This would require a dial decade resistance box having lowest steps of 0.001 ohm, to take the most of the sensitivity of the Philoscop (1 in 10,000 ohms). It is advantageous to use a cell constant so that the resistance would be 1000– 10,000 ohms. Then a dial decade resistance box reading down to 0.1 ohm could be used.

A cell constant of about 26 cm<sup>-1</sup> was achieved by giving the liquid column

between the electrodes a length of approximately 10 cm and a cross-section of 0.2 cm<sup>2</sup>, by means of a glass tube with an inside diameter of 0.5 cm. See Fig. II.25, where also other dimensions are indicated. Stirring is effected with the aid of a glass stirrer attached directly to a small electric motor with variable speed by means of a short length of rubber tubing. The liquid enters the tube through the funnelshaped openings I and II, and passes through the tubular (bright) platinum electrodes 1, 2, and 3 ( $D_1 = 0.5$  cm). Electrodes 1 and 3 (length 1 cm) are placed diametrically, whereas electrode 2 (length 0.5 cm) at a distance of 1 mm from electrode 1. Measured with the arrangement in Fig. II.17, the resistance of a 0.1 M potassium chloride solution was 2204 ohms (20°C). Accordingly, the cell constant of the cell is  $K = kR = 0.01167 \times 2204 = 26$  cm<sup>-1</sup>.





A cell resistance of about 5000 ohms is sufficient to reduce polarization effects effectively. Illustrated by the titration of sodium hydroxide in 40 ml of 0.1 M potassium chloride solution with 0.5 N hydrochloric acid. Curve I: 89 ohms, K = 1.2 cm<sup>-1</sup>. Curve II: 4550 ohms, K = 60 cm<sup>-1</sup>







If required, a higher cell constant may be obtained by using a longer or narrower tube (e.g.,  $D_i = 0.3$  cm).

In performing a titration, the cell was dipped into the solution under examination. The solution was contained in a beaker of 250 ml, placed in a thermostat. After each addition of titrant from the buret, constancy in the bridge reading was attained within a few seconds.

The above type of cell, which is similar to the one employed by Walisch and Barthel<sup>26</sup> (except for the use of three electrodes instead of two), was also useful for precipitation titrations.

The circuit arrangement is shown in Fig. II.17.

### Cell with a large cell constant

A tube in which the solution is circulated may be used to obtain a large cell constant — see Fig. II.26. If L is the total length of the tube, and the tubular bright platinum electrodes (inside diameter 0.5 cm, length 1.4 cm) are at a distance of  $\frac{1}{2}L$  from each other, the cell constant is

$$K = \frac{L}{\pi D_i^2}$$

where  $D_i$  is the inside diameter of the tube. A number of conductance cells of the type shown in Fig. II.26 have been constructed with the following (approximate) cell constants: 60 cm<sup>-1</sup> (type A, L = 45 cm,  $D_i = 0.5$  cm), 1000 cm<sup>-1</sup> (type A, L = 45 cm,  $D_i = 0.1$  cm), and 2000 cm<sup>-1</sup> (type B, L = 90 cm,  $D_i = 0.1$  cm). See Fig. II.27 (and also ref. 14). In the cell with cell constant 2000 cm<sup>-1</sup>, the resistance of 5 M sodium chloride and 7 M sodium nitrate solutions, approximating the saturated solutions, was about 10,000 ohms. (Measured





Fig. II.27. Design of conductance cell with large cell constant.

with the aid of a 5 M sodium chloride solution, the actual cell constant of this cell was  $2100 \text{ cm}^{-1}$ .)

The solution in the cell is circulated by means of a centrifugal stirrer, driven by an electric motor with 30 rps connected to the shaft of the stirrer with rubber tubing (diameter of the 6 vanes semi-open impeller<sup>7</sup> made of Teflon, 2 cm, and width, 0.5 cm). The titrant is added from a piston buret, placed on an adjustable stand, through an opening in the glass stopper. Through a second opening inert gas may be introduced if it is required. In the conductance cell with cell constant of 2000 cm<sup>-1</sup> complete mixing was attained within 30 seconds after each addition of titrant. In the cells with lower cell constants, complete mixing was attained within a shorter time.

For the purpose of design, the rate of mixing may be estimated by means of the head-capacity curve of the pump and the well-known equation for flow resistance (see e.g., ref. 19). For low flow rates the pump head, H, may be approximated by  $H = \omega^2 r^2/g$ , where  $\omega$  and r are the angular velocity and the radius of the impeller, respectively, and g is the acceleration of gravity. Because of its lower flow resistance, type B cell, which is essentially identical with the cell designed by Jander<sup>8,17</sup> is to be preferred if a cell constant higher than 2000 cm<sup>-1</sup> is desired. (A cell of 5000 cm<sup>-1</sup> of this type, with L = 100 cm,  $D_1 = 0.08$  cm, r = 1.25 cm,  $\omega = 30$  rps, would require approximately 40 seconds for mixing.)

For cleaning the conductance cell a water pump is used. The liquid in the circulation tube of the cell is sucked off by means of a 20 cm glass tube with one end provided with a short length of rubber tubing pressed against the entrance of the circulation tube at the bottom of the titration cell, while the other end is connected to the water pump. After being rinsed well, the tube is kept filled with water. Care must be taken to avoid air bubbles trapped in the tube.

To perform a titration, two conductance cells equal in cell constant and filled with the solution under examination are used. The solutions in both cells are titrated successively. The result of the second titration may serve as a check on the first.

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### CHAPTER III

# TITRATIONS

### **III.1** Introduction

Conductometric titrations were performed using the conductance cells of the design discussed in chapter II, in order to test the suitability of these cells for the titration of solutions which has to be carried out in the presence of relatively large amounts of indifferent electrolyte.

The conductance cells with large cell constants up to 2000 cm<sup>-1</sup> were used mainly for acid-base and redox titrations. In these cases the solutions were highly conducting, so it was necessary to use a large cell constant to obtain a resistance of about 5000 ohms. Moreover, because the conductivity change of the solutions titrated was smaller than 1 per cent, the (Peekel) precision measuring bridge was employed in titrations with these cells.

For the chelatometric and precipitation titrations the three-electrode cell having a cell constant of  $26 \text{ cm}^{-1}$  was used in conjunction with the Philoscop measuring bridge. In these titrations the conductivity change was in most cases larger than 1 per cent. The use of this measuring bridge was therefore justified.

Two piston burets with the following capacities were used: 2 ml (actual volume of 1 ml at 20°C, 0.9618 ml; smallest division 0.001 ml) and 5 ml (actual volume of 1 ml at 20°C, 1.0194 ml; smallest division 0.002 ml). The inside diameter of the buret tip was approximately 0.4 mm. This small diameter was necessary to reduce the drop error.

In performing a titration, the buret was placed on an adjustable stand. Whenever titrant was being added, the stand was lowered and the tip of the buret dipped into the solution for about 5 seconds. This method was followed in order to minimize the drop error resulting from any droplet of liquid adhering to the buret tip. Otherwise this drop error would give a spread in the observed values of the conductivity change. For the same purpose, before adding the first portion of titrant, but after adjusting the buret to the zero mark, the buret tip was dipped into distilled water contained in a beaker. In this way the drop error was smaller than the error in making a buret reading, which was estimated at less than  $\frac{1}{2}$  of a smallest division of the buret scale.

The titrant was added in decimal fractions of a millilitre to facilitate construction of the titration curve. A sufficient number of measurements (5 to 10) was made on either side of the equivalence point not only to detect any

possible deviation from linearity in the titration curve due to polarization effects or incompleteness of reaction, but also to permit accurate location of the endpoint. In most cases the latter was determined graphically. When the titration curve is plotted in such a way that the equivalence point corresponds to a length of at least 10 cm on the horizontal axis, for practical purposes, this graphical method yields sufficiently accurate results.

A problem was encountered in verifying the results of the chelatometric titrations. Some titrations using metallochrome indicators did not yield exact results due to the relatively wide color change interval. Because of this, the following method was adopted:  $V_{\rm M1}$  ml of the approximately 0.1 M metal solution to be determined is added from a buret to the diluted buffer solution in the titration cell. Using a second buret this solution is then titrated with an excess of 0.1 M EDTA solution. This titration yields  $V_{\rm E1}$  ml (the volume at the titration endpoint) and  $V_{\rm E2}$  ml of EDTA solution (the excess of EDTA). Subsequently, the excess of EDTA is back-titrated with the metal solution; this titration yields  $V_{\rm M2}$  ml as its endpoint. A titration may be considered satisfactory if  $V_{\rm E1}/V_{\rm M1}$  minus  $V_{\rm E2}/V_{\rm M2}$  is  $\pm 0.02$  or less.

Where necessary, volume corrections were made by multiplying the observed values of the conductivity change by  $V/V_0$ .

(For further details on titration arrangement, conductance cells, and titration procedure, see sections II.2.1 and II.3.4.)

# **III.2** Acid-base titrations

Titrations in 5 M sodium chloride and 7 M sodium nitrate solutions which will be described below show that the conductance cell with cell constant of  $2000 \text{ cm}^{-1}$  is suitable for titrations of relatively small amounts of acid or base in concentrated salt solutions.

The titration of acetic acid illustrates the effect of using ammonium hydroxide instead of sodium hydroxide as titrant.

## Titration in 7 M sodium chloride

Titrations of hydrochloric acid in 5 M sodium chloride solutions were carried out with 0.508 N sodium hydroxide as titrant, using the conductance cell with a cell constant of 2000 cm<sup>-1</sup> and the Peekel measuring bridge, frequency 1000 cps. (See also ref. 8.) The titration mixture consisted of 50 ml of 5 M sodium chloride solution prepared from a C.P. product and 0.500 ml of 0.1 N hydrochloric acid exactly measured with a piston buret. The resistances of the two conductance cells in the arrangement were practically equal (8500 ohms). About 100 pF across one of the cells was necessary to balance for capacitance unsymmetry by means of an external capacitor. The total capacitance change during the titration was 5 pF. It was not necessary to adjust the capacitor to maintain phase balance during the titration because the effect of the capacitance change on the slopes of the titration lines was negligible ( $R_1\omega C_1 \simeq 0.005$ ; see section II.3.2). During a titration carbon dioxide-free nitrogen was passed over the solution through a second opening in the glass stopper of the conductance cell.

Carbonate-free sodium hydroxide for the titration was prepared by passing 0.5 N sodium hydroxide (C.P. product) solution through a column with a basic ion-exchanger.<sup>6</sup> The latter was prepared by treating 67 g of Amberlite 410 in the column subsequently with  $\frac{1}{2}$  1 of 2 N hydrochloric acid, 3 l of 1 N sodium hydroxide, and finally distilled water, until no chloride was detected, using a flowrate of about 5 ml per minute.

To check the results, potentiometric titrations of the same amount of hydrochloric acid were carried out in 50 ml of 5 M sodium chloride solution and also in 50 ml of distilled water, using a glass electrode.



Fig. III.1

Conductometric and potentiometric titrations of hydrochloric acid in 5 M sodium chloride with 0.5 N sodium hydroxide.

Fig. III.1 compares the conductometric with the potentiometric titration curve. Table III.1 shows the results of the titrations. The data in column (Ia) refer to the conductometric titrations in 5 M sodium chloride; the titration endpoints were determined by solving simultaneously the equations of the

titration lines obtained by the least squares method.<sup>12</sup> (Ib) The data were obtained by plotting the observed values, fitting the best straight lines, and finding the intersection of these lines by eye. (II) refers to the potentiometric titrations in water. (III) refers to the potentiometric titrations in 5 M sodium chloride. The means of these results,  $\bar{X}$ , are (Ia) 0.1017 ml, (Ib) 0.1017 ml, (II) 0.1000 ml. The estimated standard errors of the means,  $s_{\bar{x}}$ , are (Ia) 0.00028 ml, (Ib) 0.00026 ml, (II) 0.00016 ml, and (III) 0.00013 ml.

Ia	Ib	II	III
0.1008	0.1018	0.1015	0.1001
0.1009	0.1013	0.1016	0.1001
0.1020	0.1020	0.1005	0.1005
0.1006	0.1005	0.1007	0.1005
0.1020	0.1018	0.1005	0.0995
0.1019	0.1010	0.1008	0.1000
0.1025	0.1030	0.1010	0.0995
0.1027	0.1015	0.1015	0.1000

					Tabl	le	[11.1					
ml	of	0.508	N	sodium	hydroxide	in	the	titration	of	hydrochloric	acid	

The *t*-test<sup>12</sup> can be applied to the above results to ascertain significant differences between the means. According to this test, the difference between the means  $\bar{X}_1$  and  $\bar{X}_2$  is not significant if  $t = (\bar{X}_1 - \bar{X}_2)/\sqrt{s_{\bar{x}_1}^2 + s_{\bar{x}_2}^2}$  is not greater than 2.15 (14 degrees of freedom and 5 per cent level of significance). The following values are found: t = 0.13 for the means Ia and Ib, t = 2.03 for the means Ia and II, and t = 4.65 for the means II and III. Accordingly, there is no significant difference between the results of Ia obtained by the least squares method, and the results of Ib obtained by the graphical method. In a conductometric titration, therefore, the graphical method can be used to obtain comparably accurate results.

Nor was any significant difference between the results of Ia (or Ib) and II found. On the other hand, the potentiometric titrations in 5 M sodium chloride solution (III) shows a highly significant difference in result, probably due to the salt effect.

As may be seen in Fig. III.1, the difference in slope  $S_{II} - S_I$  in the conductometric titration is 0.00068 (0.068 per cent). The calculated value, using the equivalent conductances at infinite dilution (H<sup>+</sup> = 350, Na<sup>+</sup> = 50, OH<sup>-</sup> = 198 Cl<sup>-</sup> = 76 for 25 °C) and the concentration ratio NaCl/HCl = 5000, is

$$S_{II} - S_{I} = \frac{H^{+} + OH^{-}}{H^{+} + Cl^{-} + 5000(Na^{+} + Cl^{-})} = 0.00087$$
.

The difference between observed and calculated values may be ascribed to the effect of the concentrated sodium chloride solution on the equivalent conductances of the ionic species  $H^+$  and  $OH^-$ . (See section I.2.)

Still smaller quantities of hydrochloric acid may be determined in the presence of 0.5 M sodium chloride. If in the above titration instead of 0.05 milliequivalent, 0.01 milli-equivalent of hydrochloric acid were used, the intersection of the titration lines in Fig. III.1 would occur with 0.02 ml of sodium hydroxide. This may still give usable results.

Further improvement of the applicability of the titration setup is possible by improving the method of elimination of temperature effects in the solution being titrated. But it should be noted that the titration of a solution with a total conductivity change of 0.05 per cent already required very high accuracy and precision of performance. This makes the method less attractive than potentiometry, for example, where temperature variations are not a problem.

For the discussion of the titration curves, see section I.2.

## Titration in 7 M sodium nitrate

In a titration of about 0.1 milli-equivalent of sodium hydroxide in 40 ml of 7 M sodium nitrate solution with 0.485 N hydrochloric acid, two endpoints were found: the first corresponding to the amount of sodium hydroxide, and the second apparently indicating the presence of alkaline impurities in the sodium nitrate. To determine the amount of these impurities more accurately, only the 40 ml of 7 M sodium nitrate solution was titrated using the conductance cell with cell constant of 2000 cm<sup>-1</sup> and the Peekel measuring bridge of 1000 cps. Initial resistance of the solution was 11,000 ohms. The results were compared with potentiometric titrations (using glass electrode).

Fig. III.2 depicts the titration curves obtained by conductometry and potentiometry. The titration endpoint corresponds to 0.060 ml of 0.485 N hydrochloric acid, and calculated as sodium hydroxide, the percentage of alkaline impurities was 0.0050. The potentiometric titration curve shows only a very gradual change in pH, so that the endpoint cannot be determined accurately, in contrast to the conductometric titration curve, which has a distinct endpoint. Thus, in this particular instance conductometry has a definite advantage over potentiometry.

The results of the above titrations in concentrated salt solutions can be compared with the following. In the titration of perchloric acid with barium hydroxide in the presence of barium perchlorate, Jander and Ebert<sup>7</sup> attained a total salt concentration of 0.1 M. Walisch and Barthel<sup>14</sup> performed satisfactory titrations of sodium hydroxide in 2 M potassium chloride solution. And Morrison<sup>10</sup>, using a linear conductance bridge for high conductance solutions, succeeded in titrating acids and bases in the presence of up to 3.5 M electrolytes, whereas Liteanu *et al.*\* succeeded in titrating hydrochloric acid in 5 M sodium

\* Liteanu, C., and Hopîrtean, E., Studia Universitatis Babeș-Bolyai, Series Chemia, 135 (1966).

chloride solution. Compared with these results, a higher electrolyte concentration was therefore achieved in our titrations. In addition, in titrations of concentrated salt solutions of 3.5 M and higher, titration curves consisting of straight lines were obtained, in contrast to those obtained by Morrison and Liteanu.



Fig. III.2.

Conductometric and potentiometric titrations of alkali content (0.0050 per cent) in 7 M sodium nitrate solution.

### Titration of acetic acid

The titration of acetic acid with sodium hydroxide or any other strong base gives a \_/-shaped titration curve, whereas with a weak base such as ammonium hydroxide, the titration curve is /<sup>-</sup>-shaped. It has been commonly accepted that the latter type of titration curve permits a more accurate endpoint location

than the type mentioned first. On that ground, ammonium hydroxide would be preferable to sodium hydroxide in the titration of a weak acid. (See, e.g., ref. 9.)

In section I.5, however, we noted that the accuracy in the endpoint location was determined by the difference in slope  $S_{II}$ — $S_I$  of the titration lines. Accordingly, the above view that ammonium hydroxide is preferable to sodium hydroxide in the titration of a weak acid is incorrect. It may be shown theoretically as well as experimentally that sodium hydroxide yields a greater difference in slope than ammonium hydroxide. This is illustrated by the following titration (Fig. III.3).

V	R	$\Delta R$	$\Delta R \left( 1 + \Delta V \right) 0/$
ml	ohms	ohms	$= \frac{1}{R} \left( \frac{1}{V_0} \right), \frac{1}{V_0}$
0	8642	0	0
1	8770	128	-1.74
2	8643	1	-0.01
3	8505	-137	1.66
4	8350	-292	3.64
5	8191	-451	5.78
6	8043	-599	7.90
7	7923	-710	9.72
8	7660	-982	13.84
9	7242	-1397	21.02
10	6885	-1757	28.3
11	6557	-2085	35.3
12	6295	-2347	41.7
13	6022	-2620	49.2
14	5819	-2823	55.3
15	5612	-3030	62.1
16	5412	-3230	69.2

 $\label{eq:Table III.2.} Table III.2.$  Titration of acetic acid with sodium hydroxide. ( $\Delta R\!=\!R\!-\!R_0$ .)

Titration mixture: 100 ml of a solution which was 0.01 M with respect to acetic acid and 0.02 M with respect to potassium chloride. The addition of potassium chloride was to demonstrate the suitability of the titration set up for titrations in the presence of indifferent electrolyte. Apparatus: conductance cell with three electrodes and cell constant of 26 cm<sup>-1</sup>, and the Philoscop measuring bridge operating at 1000 cps (Fig. II.25). The solution was titrated with 0.1 N sodium hydroxide and 0.1 N ammonium hydroxide. The percentage change in conductivity for the titration with sodium hydroxide is shown in Table III.2. Volume corrections have been applied, because the volume change at the endpoint  $V_e/V_0$  was more than 0.01 ( $V_0 = 100$  ml).

Fig. III.3 shows titration curve I using sodium hydroxide and titration curve II using ammonium hydroxide, the difference in slope being 36% = 0.36 (*AB*) and 25% = 0.25 (*BC*), respectively. The ratio *AB/BC* is therefore 36/25 = 1.44; theoretically,

$$\frac{AB}{BC} = \frac{\text{OH}^- - \text{AC}^-}{\text{NH}^+ + \text{Ac}^-} = 1.38$$

using the values of the equivalent conductances at infinite dilution (OH<sup>-</sup> = 198, NH<sub>4</sub><sup>+</sup> = 73, Ac<sup>-</sup> = 41).



Fig. III.3.

Titration of acetic acid (I) with sodium hydroxide and (II) with ammonia. The transformed curves III and IV show that sodium hydroxide produces a greater change in slope (AB) than ammonia (BC).
That the titration with sodium hydroxide is more accurate than with ammonium hydroxide is clearly demonstrated by curves III and IV. These curves have been obtained by subtracting 21 per cent conductivity change per ml from curve I and 14 per cent conductivity change per ml in case of curve II, respectively; the values have been plotted against the ratio of titrant to titrand,  $x = \Delta V/V_e$ . By this transformation the positions of A, B, and C on the vertical axis are not affected; this is also true for the magnitude of the error in the experimental points.

From curves III and IV it may be concluded that the accuracy in endpoint location is less when using ammonium hydroxide as a titrant because of the smaller change in the slope of the titration lines at the equivalence point. It is then improper to state that ammonium hydroxide is capable of giving greater accuracy than sodium hydroxide in the titration of a weak acid.

It may be noted that the deviation in the titration curve from the ideal (straight) reaction line, OB, is due to the dissociation of the acetic acid in the beginning of the tiration. The dissociation constant of the acetic acid itself can be calculated from the ratio OB/AB and the concentration of the acid.

## **III.3 Redox titrations**

Redox titrations were also carried out using the conductance cell with cell constant of 2000 cm<sup>-1</sup> and the Peekel measuring bridge. This is illustrated by the titrations of Fe(II)-ions with potassium permanganate and potassium dichromate. Although these titrations show that it is quite possible to perform redox titrations conductometrically, it is concluded that potentiometric endpoint indication is to be preferred because of its simplicity with regard to apparatus and performance.

### Titration of Fe(II) with potassium permanganate

In a redox titration the change in slope of the titration line at the equivalence point is usually small, owing to the presence of a large excess of indifferent electrolyte in the solution. For the titration with potassium permanganate of a mixture of 10 ml of 0.006 M Fe(II)-solution (ca. 600 mg of Mohr's salt dissolved in 250 ml 0.5 M sulphuric acid) and 35 ml of 0.5 M sulphuric acid, the change in slope may be calculated as follows.

The reaction equation which includes all ions present in the solution is

$$10 \text{ FeSO}_4 + 10 (\text{NH}_4)_2 \text{SO}_4 + 8 \text{ H}_2 \text{SO}_4 + p \text{ H}_2 \text{SO}_4 + 2 [\text{KMnO}_4] = 10 \text{ FeSO}_4 + 10 (\text{NH}_4)_2 \text{SO}_4 + 8 \text{ H}_2 \text{SO}_4 + p \text{ H}_2 \text{SO}_4 + 2 [\text{KMnO}_4] = 10 \text{ FeSO}_4 + 10 \text{ (NH}_4)_2 \text{SO}_4 + 10 \text{ (NH}_4)_$$

$$5 \text{ Fe}_2(\text{SO}_4)_3 + 10 (\text{NH}_4)_2 \text{SO}_4 + \text{K}_2 \text{SO}_4 + 2 \text{ MnSO}_4 + p \text{ H}_2 \text{SO}_4 + 8 \text{ H}_2 \text{O}_4$$

where p represents the amount of sulphuric acid not taking part in the reaction.

For simplification it is assumed that the sulphuric acid is dissociated into  $H^+$  and  $HSO_4^-$  ions mainly.

From the above reaction equation, it follows that

$$G'_{I} = 10 \text{ Fe}^{+3} + 2 \text{ K}^{+} + 2 \text{ Mn}^{+2} - 10 \text{ Fe}^{+2} - 16 \text{ H}^{+},$$
  
 $G'_{II} = 2 \text{ K}^{+} + 2 \text{ MnO}_{4}^{-}$ 

and

$$G_0 = 10 \text{ Fe}^{+2} + 20 \text{ NH}_4^+ + 20 \text{ SO}_4^- + (p + 8) (\text{H}^+ + \text{HSO}_4^-)$$

(See equations (I.22) and (I.23).)

Since a great excess of sulphuric acid is present, the conductance sum at the beginning of the titration may be approximated by  $G_0 \simeq (p + 8)$  (H<sup>+</sup> + HSO<sub>4</sub><sup>-</sup>). From the molar ratio of ferrous sulphate to sulphuric acid,

$$\frac{\text{FeSO}_4}{\text{H}_2\text{SO}_4} = \frac{10}{\phi + 8} = \frac{10 \times 0.006}{45 \times 0.5}$$

is obtained p + 8 = 3750. Hence,  $G_0 \simeq 3750$  (H<sup>+</sup> + HSO<sub>4</sub><sup>-</sup>). Finally, the difference in slope

$$S_{\rm II} - S_{\rm I} = \frac{G'_{\rm II} - G'_{\rm I}}{G_0}$$
$$= \frac{2 \,\mathrm{MnO_{4^-}} + 10 \,\mathrm{Fe^{+2}} + 16 \,\mathrm{H^+} - 10 \,\mathrm{Fe^{+3}} - 2 \,\mathrm{Mn^{+1}}}{3750 \,(\mathrm{H^+} + \mathrm{HSO_{4^-}})}$$

Inserting the respective equivalent ion conductances into the above equation gives  $S_{II} - S_I = 0.0030$ . (Fe<sup>+2</sup> = 107, Fe<sup>+3</sup> = 204, Mn<sup>+2</sup> = 107, H<sup>+</sup> = 350, MnO\_4<sup>-</sup> = 61, HSO\_4<sup>-</sup> = 52.)\*

Experimental. Apparatus: conductance cell, 2000 cm<sup>-1</sup>, and Peekel measuring bridge, 2500 cps. The cell resistance was 10,800 ohms. The titration endpoint accords with the result of potentiometric titrations and the appearance of the pink permanganate color at the equivalence point (Fig. III.4). The change in slope is  $S_{II} - S_I = 0.0024$  (0.24 per cent).

### Titration of Fe(II) with potassium dichromate

As in the above example, accurate results were also obtained in the titration of ferrous ions with potassium dichromate; this is illustrated in Fig. III.5. The endpoint corresponds with the results of potentiometric titrations.

Titration mixture: 10 ml of 0.006 N ferro-solution (in 0.5 M sulphuric acid) and 35 ml of 0.5 M sulphuric acid. Apparatus: conductance cell, 2000 cm<sup>-1</sup>, and Peekel measuring bridge, 2500 cps; cell resistance, 10,000 ohms.

\* The literature usually gives the values of the equivalent ion conductance rather than the values of the ion conductance. To obtain the ion conductance, multiply the value of the equivalent conductance by the valency of the ion considered.

When titrating with 0.1 N potassium dichromate solution, this solution should be prepared by dissolving potassium dichromate in 0.5 M sulphuric acid (curve I). With 0.1 N aqueous solution of potassium dichromate, a flat titration curve pointing downwards was obtained (conductivity change at endpoint, -1.7 per cent, and  $S_{II} - S_{I} = 0.003$ ). Corrections by adding 2 per



Fig. III.4.







Titration of Fe(II) in 0.5 M sulphuric acid (I) with 0.1 N solution of potassium dichromate in 0.5 M sulphuric acid, and (II) with 0.5 N aqueous solution of potassium dichromate. (In both titrations the difference in slope is 0.3 per cent.)

cent conductivity change per ml of potassium dichromate to the experimental values were then necessary to obtain a V-shaped titration curve and to permit accurate location of the endpoint. Titration with 0.5 N aqueous solution of potassium dichromate was possible without volume corrections (curve II).

The difference in slope of the titration lines in the above titrations is only determined by the ratio of ferrous ions to sulphuric acid of the solution; consequently, in all three cases  $S_{II} - S_{I} = 0.003$  (0.3 per cent).

# **III.4 Chelatometric titrations**

Titrations with ethylenediamine tetra-acetic acid (EDTA) using conductance methods have been studied by Hall<sup>4</sup> and Vydra,<sup>13</sup> and, using high frequency technique, by other workers.<sup>1,5</sup> It has been found that many metal ions can be determined conductometrically. In these titrations, usually a /<sup>-</sup>-shaped titration curve is obtained when no buffer is used to control the pH of the solution within narrow limits. However, the curve does not permit exact endpoint location, because the titration lines are not straight, in contrast to a titration using buffer. On the other hand, when a buffer is used, the total change in conductivity is decreased, so that precise measurements have to be made, in order to secure accurate results. In their measurements, Hall and Vydra used an oscilloscope to detect bridge balance.

In our experiments we used the simpler Philoscop measuring bridge and a conductance cell with three electrodes (cell constant  $26 \text{ cm}^{-1}$ ). The purpose was, first, to test the suitability of this titration setup, and second, to study the effect of the *p*H of the solution, as well as the effect of the buffer on the titration curves in order to establish the optimum conditions for conductometric EDTA titrations.

The titrations were carried out in a beaker of 250 ml (Fig. II.25). For a titration, 0.5-2 ml of the 0.1 M weakly acidic metal solution exactly measured with a piston buret was added to the buffer solution in the beaker and then diluted with redistilled water up to 100 ml. The resulting approximately 0.001 M metal solution was subsequently titrated with an excess of 0.100 M EDTA solution (prepared by dissolving a weighed amount of the disodium salt in redistilled water) by means of a second piston buret. Finally, to check the accuracy of the result, the excess EDTA was back-tritated with the metal solution. (See section III.1.)

## The effect of the pH

Ethylenediamine tetra-acetic acid, commonly abbreviated to EDTA, is a four basic acid having the following dissociation constants:

$$K_1 = \frac{[\mathrm{H}^+] [\mathrm{H}_3 \mathrm{Y}^-]}{[\mathrm{H}_4 \mathrm{Y}]}$$
(III.1)

$$K_{2} = \frac{[\mathrm{H}^{+}] [\mathrm{H}_{2} \mathrm{Y}^{-2}]}{[\mathrm{H}_{3} \mathrm{Y}^{-}]}$$
(III.2)

$$K_{3} = \frac{[\text{H}^{+}] [\text{H}\text{Y}^{-3}]}{[\text{H}_{2} \text{Y}^{-2}]}$$
(III.3)

$$K_4 = \frac{[\mathrm{H}^+][\mathrm{Y}^{-4}]}{[\mathrm{H}\mathrm{Y}^{-3}]}$$
(III.4)

with  $pK_1 = 2.0$ ,  $pK_2 = 2.76$ ,  $pK_3 = 6.16$ , and  $pK_4 = 10.3$  (pK is the negative logarithm of the dissociation constant). The square brackets denote concentrations in moles per litre. As usual, in the above expressions the acid and the anions of the acid are denoted by H<sub>4</sub>Y, H<sub>3</sub>Y<sup>-</sup>, H<sub>2</sub>Y<sup>-2</sup>, HY<sup>-3</sup>, and Y<sup>-4</sup>. The disodium salt, which is now exclusively used in analytical chemistry, is Na<sub>2</sub>H<sub>2</sub>Y.2H<sub>2</sub>O.

With many metal ions  $M^{+n}$  of oxidation state n, EDTA forms a 1:1 complex. Its stability is expressed by

$$K = \frac{\left[\mathbf{M}\mathbf{Y}^{+n-4}\right]}{\left[\mathbf{M}^{+n}\right]\left[\mathbf{Y}^{-4}\right]} \tag{III.5}$$

where K is the (true) stability constant, i.e., the reciprocal of the dissociation constant of the complex ion. A list of stability constants of EDTA complexes of some common metals is given in Table III.3. Although the values given apply strictly to a medium of ionic strength 0.1 and a temperature of 20 °C, they may be used for approximate calculations. (See also ref. 3.)

Cation	$\log K$	Cation	$\log K$
Ag+	7.3	Cd+2	16.46
Ba+2	7.76	Zn+2	16.50
Sr+2	8.63	Pb+2	18.04
$Mg^{+2}$	8.69	Ni <sup>+2</sup>	18.62
Ca+2	10.70	Cu+2	18.80
Mn+2	13.79	$Hg^{+2}$	21.80
Fe <sup>+2</sup>	14.33	Cr+3	23.0
A1+3	16.13	Th+4	23.2
Co+2	16.31	Fe <sup>+3</sup>	25.1

Table III.3.

Stability constants of EDTA complexes for a medium of ionic strength 0.1 at 20°C.

It should be pointed out that in a titration the concentration of unreacted metal ion at the equivalence point,  $[M^{+n}]$ , is not equal to  $[Y^{-4}]$ , but  $[M^{+n}] = [Y]^*$ ,

since other protonated forms of the EDTA anion may be present. The concentration

$$[Y]^* = [Y^{-4}] + [HY^{-3}] + [H_2Y^{-2}] + [H_3Y^{-}] + [H_4Y].$$
(III.6)

The ratio

$$\frac{[Y]^*}{[Y^{-4}]} = \alpha_{\rm H} \tag{III.7}$$

which may be derived by means of the above equations, is a function of the pH of the solution, as shown in Fig. III.6.



It is seen that only at a pH higher than 12, where  $\alpha_{\rm H}$  is nearly unity, will practically all of the EDTA be present as Y<sup>-4</sup>. At lower pH, increasing amounts of the other possible ionic forms of EDTA or the free acid may be present, the relative amount of each attaining a maximum at a certain pH (Fig. III.7). The curves, which may also be derived by means of the above equations, show, for example, that at a pH of 4–5, practically all of the EDTA is present as H<sub>2</sub>Y<sup>-2</sup>, whereas at a pH of 8–9, HY<sup>-3</sup> is the main ionic form.

Generally,  $[Y]^*$  is not equal to  $[Y^{-4}]$ . Because of this, the completeness of the reaction between the metal ions,  $M^{+n}$ , and EDTA at the equivalence point strongly depends on the pH of the solution. This is seen by substituting (III.7) into (III.5):

$$\frac{K}{\alpha_{\rm H}} = \frac{[\rm MY^{+n-4}]}{[\rm M^{+n}][\rm Y]^*}.$$
(III.8)

If the total concentration of metal, complexed and uncomplexed, is denoted by

C moles per litre, we may write

$$[\mathbf{M}^{+n}] = [\mathbf{Y}]^* = \beta_1 C$$

and

$$[\mathrm{MY}^{+n-4}] = (1 - \beta_1)C \simeq C$$

On substitution in (III.8),  $\beta_1 \simeq \sqrt{\alpha_{\rm H}/KC}$  is then obtained,  $\beta_1$  being neglected with respect to unity. (See also equation (I.51).) This equation represents the relative amount of unreacted metal and EDTA. It shows that at a given metal concentration the completeness of the reaction depends on  $\alpha_{\rm H}$ , and thus it depends on the pH.





Titration of calcium with EDTA using acetic acid-acetate buffer. The deviation from linearity is due to incompleteness of reaction (pH = 5.3 too low).

When the reaction is not complete, a deviation in the titration curve may become apparent, as is illustrated in Fig. III.8. This is the titration of calcium (mixture of 2 ml of 0.1 M calcium chloride solution, 10 ml of 0.5 M-0.5 M acetic acid-acetate buffer, and 88 ml of water) with EDTA at a pH of 5.3. The titration curve shows considerable curvature, so that the endpoint is not exactly located.

If the reaction had been complete, the line ABE (drawn approximately) would have been obtained. If on the other hand, no reaction took place at all, the line AD, which is parallel to BE, would be followed. It follows that B corresponds to 100 per cent conversion of the metal into the complex, whereas D corresponds to zero per cent conversion. Hence, the ratio  $BC/BD = \beta_1$  corresponds to the relative amount of unreacted calcium and EDTA.

The experimental value  $\beta_1 = 0.13$  agrees reasonably well with the calculated

value, 0.1, obtained by means of (I.51) and the following:  $\log K$  of CaY<sup>-2</sup> is 10.7,  $\log \alpha_{\rm H}$  at  $p \rm H = 5.3$  is 6, and the calcium concentration is 2 × 0.1/100 = 0.002 M.

Section I.4 has shown that  $\alpha_{\rm H}/KC$  should not be greater than 0.0025 in order to avoid curvature in the titration curve. Consequently, at  $p \rm H = 9$  (log  $\alpha_{\rm H} = 1$ ) all metals with log  $K \ge 7$  (K is the stability constant) may be titrated with EDTA if the metal concentration is not less than 0.001 M. According to Table III.1, these metals are the alkaline-earth metals barium, strontium, magnesium, and calcium.

The accurate titration of calcium with EDTA at pH = 9 (curve I) as well as the back-titration (curve II) is shown in Fig. III.9. Practically no deviation



Fig. III.9.

Titration of calcium at pH = 9 using borax buffer (curve I). The back-titration of the excess of EDTA (curve II) can be used to check the result. ( $V_{Ca_1} = 2.000$  ml, and  $V_{E_2} = 1.440$  ml.)



Fig. III.10.

Barium, having the lowest complex stability constant of the alkaline-earth metals, can also be determined accurately (curve I). Curve II is the back-titration of the excess of EDTA. ( $V_{Ba_1} = 0.500$  ml, and  $V_{E_2} = 0.615$  ml.)

from linearity can be seen, since  $\beta_1$  was only  $7 \times 10^{-4}$ , calculated with log  $\alpha_{\rm H} = 1.5$ , log K = 10.7, and C = 0.002 M.

Titration mixture: 2 ml of 0.1 M calcium chloride solution, 25 ml of 0.05 M borax solution, and 73 ml of water.

Even barium, with a lower stability constant than calcium, can be titrated at pH = 9, using 20 ml of 0.05 M borax solution per 100 ml, although the titration curve already shows a deviation from linearity (Fig. III.10; $\beta_1 = 0.013$ ).





Titration of copper. Without buffer the titration lines are not straight due to change in pH (I and II). Straight lines are obtained when using buffer (III and IV). Curves II and IV are the back-titrations of the excess of EDTA. ( $V_{Cu_1} = 0.500$  ml, and  $V_{E_2} = 1.100$  ml.

The other metals having greater stability constants can be titrated at a lower pH. Very suitable is pH = 5 (log  $\alpha_{\rm H} = 6$ ), using acetic acid-acetate buffer. Metals which can be titrated at this pH are those having stability constants corresponding to log K > 12, i.e., Mn<sup>+2</sup>, Zn<sup>+2</sup>, etc.

### The effect of buffer

Metal ions forming stable complexes with EDTA can be titrated without buffering the solution. This is illustrated in Fig. III.11. Curve I represents the titration of 100 ml of 0.0001 M Cu<sup>+2</sup> solution with 0.100 M EDTA, and curve II is the back-titration of the excess of EDTA with Cu<sup>+2</sup> solution. It is seen that the titration lines are not straight, so the endpoint cannot be located exactly.

Obviously, the curvature in the titration curve is a result of the following. During the reaction between  $Cu^{+2}$  and EDTA, hydrogen ions are released according to the equation

$$Cu^{+2} + [Na_2H_2Y] = CuY^{-2} + 2 H^+ + 2 Na^+.$$
 (III.9)

As a consequence, the pH of the solution drops (at the beginning of the titration pH = 6, whereas at the equivalence point pH = 3-4, using universal indicator paper) and a greater part of the complex which is already formed dissociates. This dissociation will become apparent as a curvature in the reaction line.

Beyond the equivalence point (pH = 3-4) the pH of the solution increases, owing to the reaction

$$H^+ + [Na_2H_2Y] = 2 Na^+ + H_3Y^-$$
 (III.10)

which consumes hydrogen ions. As the pH increases, however, the reaction

$$[Na_2H_2Y] = 2 Na^+ + H_2Y^{-2}$$
 (III.11)

brought about by the addition of an excess of EDTA, is gaining importance; this may be easily deduced from Fig. III.7. Reaction (III.10) will cause the conductivity of the solution to decrease, since the equivalent conductance H<sup>+</sup> is greater than the sum of the equivalent conductances  $2 \text{ Na}^+ + \text{H}_3\text{Y}^-$ . On the other hand, reaction (III.11) will cause the conductivity to increase. As a result, the excess line will show a curvature.

In order to prevent this, it is necessary to use a buffer to control the pH within narrow limits. The beneficial effect of using buffer is shown in Fig. III.11, curves III and IV, which represent the titration of the same amount of copper solution, but now using 20 ml of an 0.5 M-0.5 M acetic acid-acetate buffer per 100 ml. In contrast to curves I and II, the titration lines are straight and the endpoint can be located exactly.

It is of importance to distinguish two types of buffers: (a) *basic* buffers, derived from weak bases, e.g., ammonia-ammonium chloride buffer, and (b) *acidic* buffers, derived from weak acids, e.g., borax, which in solution may be considered as half-neutralized boric acid:  $Na_2B_4O_7 + 5H_2O = 2NaH_2BO_3 + 2H_3BO_3$ .

A basic buffer, e.g.,  $NH_3/NH_4^+$ , reacts with the hydrogen ions released during titration:  $NH_3 + [H^+] = NH_4^+$ . This increases the conductance of the solution

by forming ammonium ions, whereas an acidic buffer, such as borax, reacts with the hydrogen ions according to  $H_2BO_3^- + [H^+] = H_3BO_3$ , giving rise to a decrease in the conductance by the removal of  $H_2BO_3^-$  ions. As a result, not only a better shape of titration curve is obtained with an acidic buffer, but also a greater difference in slope of the titration lines at the equivalence point. This will be shown in the following section.

#### Borax buffer

In a conductometric titration with EDTA, borax buffer gives a greater difference in slope of the titration lines than ammonia-ammonium buffer of the same concentration.

When using ammonia-ammonium buffer, the reaction taking place up to the equivalence point (considering the titration of a divalent metal ion) is

 $M^{+2} + 2NH_3 + [Na_2H_2Y] = MY^{-2} + 2Na^+ + 2NH_4^+.$ 

beyond the equivalence point,

$$NH_3 + [Na_2H_2Y] = 2 Na^+ + HY^{-3} + NH_4^+$$

It follows that the difference in slope,

$$(S_{\rm II} - S_{\rm I})_{\rm A} = \frac{{\rm M}^{+2} + {\rm HY}^{-3} - {\rm MY}^{-2} - {\rm NH}_4^+}{(G_0)_{\rm A}}$$
(III.12)

where  $(G_0)_A$  is the conductance sum of the solution at the beginning of the titration, the suffix A referring to ammonia-ammonium buffer.

When using borax buffer the reaction up to the equivalence point is

 $M^{+2} + 2 H_2 BO_3^- + [Na_2 H_2 Y] = MY^{-2} + 2 Na^+ + 2 H_3 BO_3$ 

beyond the equivalence point (pH = 9):

 $H_2BO_3^- + [Na_2H_2Y] = 2 Na^+ + HY^{-3} + H_3BO_3.$ 

Thus, here the difference in slope is

$$(S_{\rm II} - S_{\rm I})_{\rm B} = \frac{M^{+2} + HY^{-3} + H_2 BO_3^{-} - MY^{-2}}{(G_0)_{\rm B}}$$
(III.13)

where the subscript B refers to borax buffer.

Considering the numerator in (III.12),  $M^{+2} + HY^{-3} - MY^{-2} - NH_{4^+}$ , which refers to the titration using ammonia-ammonium buffer, and the numerator in (III.13),  $M^{+2} + HY^{-3} + H_2BO_3^- - MY^{-2}$ , which refers to the titration using borax as a buffer, it follows that the difference in the conductance sums of these equations is  $H_2BO_3^- + NH_4^+$ . As a result, if the ionic concentrations of the buffer in both titrations are approximately equal, i.e.,  $(G_0)_A \simeq (G_0)_B$ , the difference in slope will be greater when using borax buffer. Hence,  $(S_{II} - S_I)_B > (S_{II} - S_I)_A$ . This is illustrated in Fig. III.12.

Curve I represents the titration using ammonia-ammonium buffer

 $(S_{II} - S_I = 0.016)$ . Curve II is the titration using borax buffer  $(S_{II} - S_I = 0.113)$ . It is seen that borax gives a greater change in slope than ammonia-ammonium buffer, and consequently, a greater accuracy in endpoint location. Borax is therefore preferable to ammonia-ammonium buffer.



Fig. III.12.

The titration of calcium, showing the favorable effect of borax (curve II) as compared to ammonia buffer (curve I).



Fig. III.13.

Titration of magnesium. (I) Using ethanolamine. (II) Using borax buffer.

Experimental. Curve I: 2 ml of 0.1 M calcium chloride solution, 5 ml of 1 M – 1 M NH<sub>3</sub>/NH<sub>4</sub>Cl buffer, and 93 ml of water; pH = 9 (indicator paper); initial resistance of solution 3608 ohms. Curve II: 2 ml of 0.1 M calcium chloride solution, 25 ml of 0.05 M borax solution, and 73 ml of water; pH = 9; initial resistance 12,692 ohms.

Borax giving a greater change in slope of the titration lines at the equivalence point is true only if as in the above titrations the buffer is approximately of the same ionic concentration (5 milli-equivalents of  $NH_4Cl$  and 2.5 milliequivalents of  $NaH_2BO_3$  per 100 ml). However, if only the weak base (not halfneutralized with acid) is used, then the difference in slope using borax buffer is less. This is shown in Fig. III.13, referring to the titration of magnesium. Curve I is the titration using ethanolamine, a substance similar to ammonia, and curve II is the titration using borax as buffer. With ethanolamine the difference in slope was 0.195 (19.5 per cent), whereas with borax buffer, only 0.083 (8.3 per cent).

Experimental. Curve I: 1 ml of 0.1 M magnesium chloride solution, 50 ml of 0.01 M ethanolamine, and 49 ml of water; cell resistance 43,530 ohms, and pH 10. Curve II: 1 ml of 0.1 M magnesium chloride solution, 20 ml of 0.05 M borax solution, and 79 ml of water; cell resistance 17,010 ohms, and pH 9.

Nevertheless, in this case the greater difference in slope when using ethanolamine is of no advantage, particularly, if the titration endpoint is determined graphically. The reason is that the slope of the reaction line using ethanolamine is relatively large. For accurate determination of the endpoint, the titration curve must then be transformed into a V-shaped curve.

In Fig. III.14 this was done by subtracting 27 per cent conductivity change per ml from the observed values of the conductivity change used for the construction of curve I in Fig. III.13, this after correcting for volume change by multiplying by  $V/V_0$ .



Fig. III.14.

The V-shaped titration curve, obtained by transformation of curve I in Fig. III.13.

Practically identical results were obtained in the titrations of magnesium using ethanolamine and borax buffer. Curve I in Fig. III.13 and Fig. III.14: endpoint 0.1050 ml. Curve II in Fig. III.13: endpoint 0.1053 ml. It should be

noted, however, that the titration curve using ethanolamine already shows departure from linearity. The accuracy of the endpoint location is therefore less compared with the titration using borax.

The above illustration shows that in principle ammonia, ethanolamine, and similar weak bases may be used for controlling the pH in an EDTA titration. Generally, however, transformation of the titration curve into a V-shaped curve will be necessary to determine the endpoint. Hence, borax buffer or another acidic buffer is to be preferred to a basic buffer such as ammonia.

A titration curve similar to curve I in Fig. III. 13 was obtained by using triethylamine instead of ethanolamine.

#### Acetic acid-acetate buffer

Acetic acid-acetate buffer has the same favourable effect on the titration curve as borax buffer. This is illustrated by the titrations of zinc shown in



Titration of zinc. (I) Using hexamethylene tetramine. (II) Using acetic acid-acetate buffer.

Fig. III.15. It compares the titration using hexamethylenetetramine as buffer, curve I, with the titration using acetic acid-acetate buffer, curve II. With hexamethylenetetramine the exact determination of the endpoint requires transformation of the titration curve into a V-shaped curve; the curve, particularly the reaction line, is also not straight. Generally, the curves obtained are comparable to the curves in Fig. III.13.

Experimental. Curve I: 1 ml of 0.1 M zinc chloride solution, 3 g of hexamethylenetetramine, and 99 ml of 'water; cell resistance = 60,000 ohms, pH = 5.5, and  $S_{II} - S_I = 0.15$ . Curve II: 2 ml of 0.1 M zinc chloride solution, 10 ml of 0.5 M - 0.5 M acetic acid-acetate buffer, and 88 ml of water; cell resistance = 9776 ohms, pH = 5, and  $S_{II} - S_I = 0.067$ .

Curves similar to curves I and II in Fig. III.15 were found in the titration of



Fig. III.16.



manganese (sulphate) with 0.1 M EDTA using ammonia-ammonium chloride and acetic-acetate buffers.

The favorable effect of acetic acid-acetate buffer on the slopes of the titration lines can be derived in a similar manner as the one shown for borax buffer.

# The amount of buffer

The amount of buffer should be sufficient to minimize the change in the pH of the solution. Otherwise, a curvature in the titration curve may become apparent. This is shown in Fig. III.16, referring to the titrations of cadmium with EDTA using different concentrations of acetic acid-acetate buffer (0.5 M - 0.5 M). With 5 ml of buffer per 100 ml of solution the titration line – especially the reaction line – shows considerable curvature. Straight titration lines were obtained by using 15 ml of the buffer solution.

Experimental. Curve I: 1 ml of 0.2 M cadmium nitrate solution, 5 ml of 0.5 M-0.5 M acetic acid-acetate buffer, and 94 ml of water; cell resistance = 14,432 ohms. During the titration, the pH of the solution varied from 5 to 3-4 (measured with universal indicator paper). Curve II: 0.5 ml of 0.2 M cadmium nitrate solution, 15 ml of 0.5 M - 0.5 M acetic acid-acetate buffer, and 85 ml of water.



Fig. III.17.

Titration of magnesium. The change in slope decreases with increasing amounts of buffer; (I) with 10 ml and (II) with 20 ml of 0.05 M borax solution per 100 ml. (Cell resistance: (I) 26,510 ohms, (II) 17,010 ohms, Change in slope: (I) 15 per cent and (II) 8.3 per cent.)

On the other hand, too much buffer should be avoided. Otherwise, this will decrease the change in slope and render the location of the endpoint less

accurate. This is illustrated in Fig. III.17. Curve I is the titration of magnesium chloride (1 ml of a 0.1 M solution) with 0.100 M EDTA using 10 ml of 0.05 borax solution per 100 ml. Curve II is the titration of the same amount of magnesium, but using 20 ml of 0.05 M borax solution.

It is best to check the solution for pH change at the end of the titration by means of a strip of universal indicator paper.

## Results

The bridge arrangement with the three-electrode cell and the Philoscop was found useful for conductometric titrations with EDTA. With this arrangement, satisfactory titrations using borax buffer were made of barium, magnesium, strontium, and calcium; and using acetic acid-acetate buffer, titrations of manganese, cadmium, cobalt, zinc, and copper.

The results of the above chelatometric titrations were checked for accuracy by titrating the metal solution with an excess of EDTA and back-titrating this excess with the metal solution according to the procedure described in section III.1. Values of -0.0068 to -0.018 were found as the difference in the volume ratios  $V_{\rm E1}/V_{\rm M1}$  and  $V_{\rm E2}/V_{\rm M2}$ . In the titration of calcium using borax buffer (Fig. III.9) the value was 2.160/2.000 - 1.440/1.325 = -0.0068. The results were satisfactory for values of  $\pm 0.02$  or less for the above difference.

Some titrations were also carried out using metallochrome indicators and visual observation of the color change at the equivalence point. Compared with the conductometric titrations, these titrations were unsatisfactory, since no exact endpoint location was possible because of the color change interval. For example, in the titration of calcium using ammonia as buffer and murexid as indicator, the color change was observed after addition of 2.18–2.40 ml of 0.1 M EDTA (conductometrically 2.160 ml; see Fig. III.9). Therefore, the above conductometric method of over-titration and back-titration was used to verify the results.

Other metals which form stable complexes with EDTA, such as lead, nickel, iron(II), lanthanum, and cerium(III) may also be determined conductometrically.<sup>4</sup>

### **III.5** Precipitation titrations

The conductometric cell with three electrodes and a cell constant of 26 cm<sup>-1</sup> was also found suitable for precipitation titrations, as illustrated by the titration of silver ions with chloride.

It is to be noted that in the titration of ions forming 1:1 precipitates (e.g., silver chloride), the concentration of the ions should be such that  $\sqrt{S/C} < 0.05$  (see equation (I.52)).

Thus, in the titration of silver with chloride, the concentration of silver ions

should be 0.0002 M or greater, in order to prevent undue curvature in the titration lines at the equivalence point  $(S = 10^{-10})$ .

In the experiment 1 ml of 0.1 M potassium chloride solution acidified with 1 ml of 2 M nitric acid and diluted with water up to 100 ml was titrated with an excess of 0.1 M silver nitrate, and this excess, back-titrated with the 0.1 M potassium chloride solution. The Philoscop measuring bridge was used; frequency 1000 cps, and cell resistance 5167 ohms. Results:  $V_{Ag1} = 0.948$  ml,  $V_{Cl1} = 1.000$  ml,  $V_{Ag2} = 1.052$  ml,  $V_{Cl2} = 1.096$  ml,  $V_{Ag1}/V_{Cl1} - V_{Ag2}/V_{Cl2} = -0.012$ , and  $S_{II} - S_{I} = 0.023$ .



Fig. III.18.

Titration of silver with potassium chloride. Curve I is  $(V/V_0)\Delta k/k_0$  vs. volume of chloride solution,  $\Delta V$ . Curve II represents the plot of conductance,  $(V/V_0)R_0/R$  (minus 100%) vs.  $\Delta V$ . The vertical difference between the two plots is  $\Delta V/V_0$ .

Curve I in Fig. III.18 shows the back-titration of the excess of silver with potassium chloride. It is seen that the titration curve is V-shaped, whereas according to literature<sup>2</sup> the curve should be \_/-shaped (curve II); for curve I is the plot of the relative change in conductivity  $(V/V_0)\Delta k/k_0$ , while curve II is the plot of the relative conductance  $(V/V_0)R_0/R$  (minus 100 per cent) against the volume of titrant.

By means of equations (I.3) and (I.10) it is readily shown that the vertical difference between the two plots is equal to the relative change in conductivity resulting from the change in the volume of the solution,  $\Delta V/V_0$ . From these equations it follows that  $(V/V_0)R_0/R - 1 = \Delta G/G_0 + \Delta f/f_0$ , the second order term  $(\Delta f/f_0)(\Delta G/G_0)$  being neglected. According to equation (I.11),

 $(V/V_0) \Delta k/k_0 = \Delta G/G_0 + \Delta f/f_0 - \Delta V/V_0$ . Thus, the two equations differ by the term  $\Delta V/V_0$ .

It has been frequently stated (see, e.g., ref. 2) that in the titration of silver, lithium chloride, which produces a V-shaped curve, is superior to potassium chloride because with potassium chloride a \_/-shaped curve is obtained. However, a \_/-shaped curve can be transformed into a V-shaped curve (see section I.5), and on that ground, it is immaterial whether lithium chloride or potassium chloride is used in the titration of silver ions.

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## SUMMARY

Conductometric titration of solutions having a high concentration of indifferent electrolytes can be satisfactorily performed with the use of bright platinum electrodes. The principal problems in this titration are the elimination of polarization effects and the measurement of the small conductivity changes of the solution. Elimination of polarization effects is necessary, because these effects bring about a distortion in the titration curve and diminish the accuracy of the endpoint location. Polarization effects were found to be a result of the simultaneous change of the electrolytic resistance of the solution and the polarization resistance at the electrode-solution in the torn the conductance cell relatively large compared with the polarization resistance. This was accomplished by using conductance cells with a large cell constant (up to 2000 cm<sup>-1</sup>) and conductance cells with three electrodes.

Conductance cells with a large cell constant were used in conjunction with a strain indicator for acid-base and redox titrations. Conductance cells with three electrodes were used in conjunction with an ordinary measuring bridge for chelatometric and precipitation titrations.

The effect of various factors on the titration curves was studied. These factors include incomplete reaction and concentration of indifferent electrolytes. The effect of a buffering agent in chelatometric titrations was also investigated.

### SAMENVATTING

Dit proefschrift beschrijft de resultaten van een onderzoek naar de mogelijkheid van konduktometrische titraties in aanwezigheid van veel indifferent elektrolyt in geleidbaarheidscellen met blanke platina elektroden. De voornaamste problemen bij deze titraties zijn de eliminatie van polarisatie-effekten en de meting van de geringe geleidbaarheidsveranderingen van de oplossing. Eliminatie van polarisatie-effekten is noodzakelijk omdat deze effekten de titratiekurve en de nauwkeurigheid van de eindpuntsbepaling ongunstig beïnvloeden. Gevonden werd dat polarisatie-effekten een gevolg zijn van de gelijktijdige verandering van de grenslaag tussen elektrode en oplossing. Deze werden geëlimineerd door gebruikmaking van geleidbaarheidscellen met grote celconstante (2000 cm<sup>-1</sup>) en geleidbaarheidscellen met drie elektroden.

De geleidbaarheidscellen met grote celconstante werden gebruikt met een rekmeter voor zuur-base en redox titraties. De geleidbaarheidscellen met drie elektroden werden gebruikt samen met een gewone meetbrug voor chelatometrische titraties en titraties waarbij een neerslag ontstaat.

Het effekt van verschillende faktoren op de titratiekurven werd bestudeerd. Deze faktoren zijn o.a. onvolledige omzetting en concentratie van het indifferente elektrolyt. Ook het effekt van een buffer bij chelatometrische titraties werd onderzocht.

## ZUSAMMENFASSUNG

Diese Arbeit enthält die Ergebnisse einer Untersuchung nach der Durchführbarkeit konduktometrischer Titrationen in Anwesenheit einer hohen Konzentration von Fremdelektrolyt unter Verwendung von blanken Platinelektroden. Wichtige Probleme bei diesen Titrationen sind die Unterdrückung der Polarisationseffekte und die Messung der geringen Leitfähigkeitsänderungen der Lösung. Elimination der Polarisationseffekte ist notwendig, weil diese Effekte die Titrationskurve und die Genauigkeit der Endpunktsbestimmung nachteilig beeinflussen. Es wurde gefunden, dass Polarisationseffekte hervorgerufen werden durch die gleichzeitige Änderung des Elektrolytwiderstandes und des Polarisationswiderstandes an der Grenzschicht zwischen Elektrode und Lösung. Diese wurden eliminiert durch Anwendung von Titrationszellen mit grosser Zellkonstante (2000 cm<sup>-1</sup>) und Titrationszellen mit drei Elektroden.

Die Titrationszellen mit grosser Zellkonstante wurden verwendet zusammen mit einer Dehnungsmessbrücke für Säure-Base und Redoxtitrationen. Die Titrationszellen mit drei Elektroden wurden verwendet mit einer gewöhnlichen Messbrücke für chelatometrische Titrationen und Niederschlagstitrationen.

Der Effekt verschiedener Faktoren auf die Titrationskurven wurde untersucht. Diese Faktoren sind u.a. ungenügende Umsetzung und Konzentration des Fremdelektrolytes. Der Effekt eines Puffers bei chelatometrische Titrationen wurde auch untersucht.

#### STELLINGEN

(I) De vergelijking, waarmee Müller en Clegg de stijgsnelheid van een vloeistof in een strook filtreerpapier beschrijven, is onjuist.

Müller, R. H. en Clegg, D. L., Anal. Chem., 21, 408 (1951).

(2) De interpretatie, die Perry geeft aan de door hem in gaschromatografische experimenten waargenomen daling van de schotelhoogte met toenemende kolomlengte, is onjuist. Het gekonstateerde effekt kan worden toegeschreven aan overlading van de kolommen.

Perry, J. A., J. of Gas Chromatography, 4, 194 (1966). Van Deemter, J. J., Zuiderweg, F. J. en Klinkenberg, A., Chem. Eng. Science, 5, 271 (1956).

(3) De toepassing van de gaspyknometer voor de bepaling van het specifiek oppervlak van poeders is slechts voldoende verantwoord indien niet al te hoge nauwkeurigheidseisen worden gesteld.

> Tuul, J. en DeBaun, R. M., Anal. Chem., **34**, 814 (1962). Tuul, J. en Innes, W. B., Anal. Chem., **34**, 818 (1962).

(4) De zienswijze van Sillén aangaande de pH van zeewater steunt te veel op de mogelijkheid dat het zeewater in chemisch evenwicht verkeert met silicaten.

> Sillén, L. G., Oceanography, ed. M. Sears, The Horn-Shafer Co., Baltimore, Md., 1961. Kleijn, H. F. W., Int. J. Air Wat. Poll., 9, 401 (1965).

(5) Het fasendiagram van het stelsel  $CoSO_4$ -H<sub>2</sub>O zoals voorgesteld door Kohler en Zäske is aanvechtbaar.

Kohler, K. en Zäske, P., Z. anorg. allg. Chem., **331**, 7 (1964). Broers, P. M. A. en Van Welie, G. S., Z. anorg. allg. Chem., **346**, 221 (1966).

(6) Een konduktogram biedt de mogelijkheid om de dissociatiekonstante van zwakke zuren en basen te bepalen zonder dat een systematische fout optreedt tengevolge van het milieu. (7) Tegen de door English en Van Winkle afgeleide correlatie voor de berekening van de Murphree schotel efficiency van distillatiekolommen zijn bedenkingen in te brengen.

English, G. E. en Van Winkle, M., *Chem. Eng.*, **69**, Nov. 11, 1963, p. 241.

(8) De algemene opvatting dat in de konduktometrische titratie van bariumionen met sulfaat het gebruik van lithiumsulfaat een grotere nauwkeurigheid dan kaliumsulfaat zou geven is onjuist.

> Britton, H. T. S., Conductometric Analysis, in *Physical Methods in Chemical Analysis*, ed. W. G. Berl, Vol. II, Academic Press, New York, 1951. Lingane, J. L., *Electroanalytical Chemistry*, Interscience Publishers,

> New York, 1953.

(9) Bij konduktometrische titraties is het aan te bevelen in plaats van de geleidbaarheid van de oplossing de procentuele verandering van de geleidbaarheid tegen het volume van het reagens uit te zetten.