

CHAPTER 14

Current Flow Methods

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The property of certain solutes to enable a solvent to conduct electricity when dissolved in it was observed very early in the history of science and was used to distinguish between those classes of solutes called "salts" and those called "nonsalts." The development of our current concept of ions and

dissociation stems directly from efforts to explain the conduction of electricity by solutions of salts. At the culmination of a century of experimental efforts and theoretical interpretations as to the nature of salts in solution, our present concept of ionic dissociation was proposed by Svante Arrhenius in 1887¹ when he suggested that ions are present at all times in solutions of salts, the current the solutions carry being the result of simple passive transfer of the ions from one electrode to the other under the impulse of impressed voltage. Future work has indicated many of the details of Arrhenius' original theory were in error, but the general concept of ionization and ionic conduction is still accepted as correct.

The electrical properties of solutions, particularly those properties involving the flow of current, are indications of the ions present in solution, their conditions, and their concentrations, all in response to an externally applied stress, voltage. The measure of the capability of a solution to carry current is the electrical resistance of the solution, better expressed for our purposes as the conductance, the reciprocal of the resistance.

14.1 CONDUCTION OF CURRENT

The process by which current is transported through matter varies greatly as one considers the various states of matter from solids to solutions. Solid conductors in general have the lower resistances, while temperature has a greater effect on the resistance of solutions. The effect of temperature on the conductance of solids and solutions best illustrates the basic differences in the manner and mechanism of electrical conductance in these two materials.

Raising the temperature of a solid normally increases its resistance. Because the charge carriers are electrons and higher temperatures increase the state of kinetic motion of all the atomic elements of the solid, the passage of these electrons is made more difficult, so that the resistance increases. Solutions, however, show very marked decreases in resistance with increasing temperature. The charge carriers are often molecular in size, though always much larger than subatomic elements, and their passage depends heavily on the viscosity properties of the bulk solvent. As the viscosity of most solvent systems decreases markedly with temperature, such a change produces a corresponding drop in solution resistance.

The conductance of a solid therefore is then considered to be a property of the material (although "doping" or alloying very pure metals will produce effects characteristic of the "solution"), while the resistance of a solution is to a large extent a property of the dissolved ions. It is this basic idea that makes conductance useful as an analytical procedure, and it is the methods and ideas underlying the use of conductance as a tool to study these dissolved ions we wish to develop.

14.2 SOME BASIC ELECTRICAL CONCEPTS AND DEFINITIONS

Although our purpose is to consider the electrical properties of solutions, the definitions of terms and the systems used in the measurement of these properties are perfectly general for all conducting solids, and may be best introduced in terms of solid conductors. Only the briefest of reviews will be presented. The student is referred to any elementary physics text for general discussion.²

A. OHM'S LAW

Ohm's law is the basic equation describing the relationship between the three common electrical parameters, current, voltage, and resistance. It is an equation having the identical structure of the equations of motion in mechanical systems,

$$\frac{\text{Force applied}}{\text{Resistance to motion}} = \text{resulting motion}$$

$$\frac{\text{Potential difference}}{\text{Resistance}} = \text{current}$$

(Ohm's law)

$$\frac{PD}{R} = i \quad (14.1)$$

"Potential difference" (PD) is, in precise terms, a force term related to the work required to move a unit charge under its influence, but for the purposes of measurement, a less precise, more accessible potential difference unit is used, voltage. Voltage is defined as the potential difference required to produce a flow of 1 standard ampere through a standard 1 ohm resistance.

A useful analogy to Ohm's law and the relationship it describes involves a water system with hydrodynamic pressure at the input, flow resistance in the form of pipes in the system, and a flow meter to indicate water delivered per unit time (terms corresponding to PD, R , and i). The relationship between these three physical factors is precisely that described by the equations, and the intuitive effect of changes in hydrodynamic pressure or pipe constriction on the flow is precisely that predicted by the equation. Analogous intuitive reasoning with regard to PD, R , and i in the electrical system produces similarly correct predictions.

B. RESISTANCE MEASUREMENT

It is apparent that the resistance is a constant of proportionality between voltage and current leaving units of volts per ampere or ohms (Ω). To

put the measured resistance of materials on some standard basis, a correction for the size and/or shape of the sample measured is made to produce a standardized measure, the specific resistance. By definition, the resistance of a cube 1 cm long with 1-cm² faces, the specific resistance (R_s) is related to the measured resistance (R) by

$$R_s = \frac{A}{l} R \quad (14.2)$$

where A and l are the measured sample's cross-sectional area and length, respectively.

For the purpose of describing the flow of current in a system, the inverse of the resistance and specific resistance, the conductance L and specific conductance L_s , are used. These terms are directly related to current flowing and can be related to voltage, current, specific resistance, and resistance in simple ways.

$$L = 1/R \quad L_s = 1/R_s \quad (14.3)$$

$$i = VL \quad (14.4)$$

$$L_s = \frac{l}{A} L \quad (14.5)$$

Several basic ideas must be kept in mind in accurately measuring values of resistance. Because the resistance is normally measured from the effect it produces on the flow of current, the measured value is the sum of all such effects present. If the connecting leads or the points of attachment possess significant resistances, these will be included in the measured value; for low resistance measurements this phenomenon is of considerable importance. As the resistance increases, these contributions become negligible; except for very poor design, the resistances measured in solutions are too high to be affected by this factor.

Measurements of the resistance of solutions possess a unique and particularly troublesome difficulty, the effect of the electrode reactions on the solution properties. Aside from the changes flowing current produces in the solution by ions moving, the largest single problem is the collection of electrode reaction products (notably hydrogen or oxygen) on the electrode surface itself. These products then oppose the desired electrode reaction with a potential difference of their own, markedly diminishing or totally cancelling the effect of the externally applied voltage. This effect, referred to as "polarization," is of particular concern in direct current methods, where because the current always passes in the same direction, the effects of polarization continuously increase until measurement becomes impossible. This phenomenon is overcome to some extent by coating the electrodes with "platinum black," but the use of alternating current is much more successful. By reversing the field rapidly, the products are not allowed to accumulate and true polarization-free readings are obtained.

C. MEASUREMENT CIRCUITS

The use of Ohm's law to measure resistance involves a so-called series circuit as shown in Fig. 14.1. By applying a known voltage as the battery, a measured current would permit calculation of the resistance using Eq. (14.1). The problem that the precision of such measurements depends on the calibration of the meter and the battery, as well as their constancy, has led to the use of the bridge principle rather than this series circuit for such measurements, so that no such calibrations or constancy are required. In general terms, the principle involves balancing the current's effects on the unknown resistor against the same current's effects on a calibrated, known

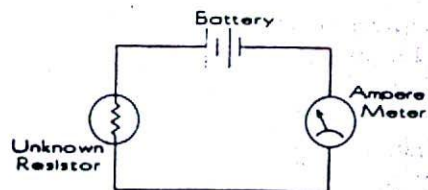


FIGURE 14.1: A simple series circuit suitable for measuring resistance using Ohm's law.

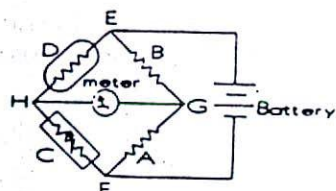


FIGURE 14.2: The Wheatstone bridge for measuring the unknown resistance D by comparing it with the calibration resistance C .

resistor, resistance standards being much easier to maintain than voltage standards. The design normally used is the Wheatstone bridge (Fig. 14.2). The unknown resistor (or solution D) is being balanced against the adjustable standard C using the "ratio arms" A and B to determine the relationship between C and D . When "balanced" so that no current is indicated by the ammeter between G and H , the resistance indicated on C is uniquely related to D . The theory is straightforward and instructive.

In practice, the unknown is placed at D and the resistance of C then adjusted until no current flow is indicated in the meter. At this point, the voltage at H and G are equal (no current is flowing in the ammeter). Designating voltage at a point by V with that point's letter as a subscript, the voltage at F (V_F) is distributed over the parallel circuits A , G , B , and C , H , D , dropping to zero at E , and the voltages for each segment can be calculated using Ohm's law,

$$\begin{aligned}
 V_F - V_G &= i_A R_A \\
 V_F - V_H &= i_C R_C \\
 V_H - V_E &= i_D R_D = V_H \\
 V_G - V_E &= i_B R_B = V_G \\
 V_E &= 0
 \end{aligned}
 \tag{14.6}$$

where i_A is the current through the resistor A , whose resistance is R_A . Because $V_G = V_H$ at balance, the same current passes through both resistors in any one arm, $i_A = i_H$ and $i_C = i_D$; with this in mind,

$$\begin{aligned} i_A R_A &= i_C R_C \\ i_A R_B &= i_C R_D \end{aligned} \quad (14.7)$$

or, eliminating i_A ,

$$\frac{R_C}{R_A} = \frac{R_D}{R_B} \quad R_D = \left[\frac{R_B}{R_A} \right] R_C \quad (14.8)$$

The value in the Wheatstone bridge lies in the fact that neither the actual value of the current flowing in either arm i_A or i_C nor the voltage of the

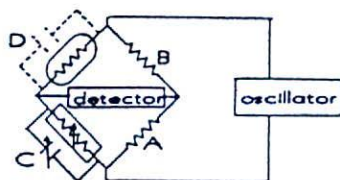


FIGURE 14.3: The simplest form of the low frequency alternating-current bridge. The oscillator is normally audiofrequency, about 1000 Hz, and the detector is often an earphone.

battery V_F is required for the calculation. Although it is not explicit in the equations, variations in V_F play no part either, these having the same effect on both arms. A variable, calibrated resistor R_C can be used to measure very wide resistance ranges by using variable pairs of ratio arms R_A and R_B . Accurate measurements of their resistances are not required, only their ratio R_B/R_A .

As described before, overcoming polarization requires the use of alternating current for the best results, and alternating current presents special problems in measurement and circuitry. There are two general frequency ranges of alternating current devices in use, so-called low frequency (i.e., up to 1–2000 Hz, and high frequency, usually in the range of 1–10 mHz).

Because alternating current is affected by capacitance as well as by resistance, alternating current bridges require adjustment for these capacitance links in various parts of the circuit in order to balance the bridge. Thus both resistance and capacitance balances must be made. In its simplest form low frequency alternating current measurement requires the use of a circuit as shown (Fig. 14.3). The adjustable resistance at C still measures the resistive component of the unknown resistance D the adjustable, non-calibrated, variable capacitor now balances the capacitance present in the electrodes and leads of the unknown resistor, or solution, D . Because it is alternating current power we are using, an electronic oscillator is used as

the power source, and an alternating current receiver such as an earphone as a detector. To eliminate as much extraneous alternating current as possible, the oscillator and detector are normally tuned to generate and detect only a particular frequency, usually 1000 or 2000 Hz. Thus noise from the overhead lights and other electric devices does not interfere. Considerably more complex, but also more useful, circuits are available to balance the capacitance of the measuring system to the earth. The best known of these is the Wagner Earthing circuit,³ as illustrated in Fig. 14.4.

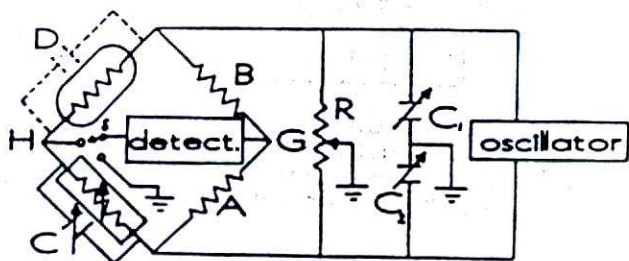


FIGURE 14.4: The Wagner Earthing circuit for eliminating extraneous currents caused by capacitance links to the earth.

The additional "balancing" resistor and capacitors (R , C_1 , and C_2) are used to bring point G to ground potential when the detector is switched to ground. At balance then, not only are the resistance and capacitance factors of unknown and standard (C and D) matched, but the detector inputs (G and H) are grounded, preventing stray ground capacitance effects from producing detector currents.

High frequency alternating current measurement (1–10 MHz) requires quite a different system. The unknown resistance, or solution is placed into an oscillating circuit, where its inductance (a function of its resistance and capacitance) influences the frequency at which the circuit involving it oscillates. Several of the circuits used in this way are shown in Fig. 14.5.

A measurement of the change in oscillation frequency or power drawn from the oscillator system by the cell and solution, or a measurement of the adjustment required to bring the system back to its original state are the measurement factors. In the former circuit, changes in values of plate or grid current measured on a sensitive meter are made.

Although several commercial instruments are available, a number of relatively simple devices have been described in the literature. In Fig. 14.5a and 14.5b are two of these showing one with the cell in the feedback loop and one with the cell in the plate circuit. Both are used by reading plate current directly on the meters as functions of added titrant current. The block schematic in Fig. 14.5c represents the concept behind the substitution

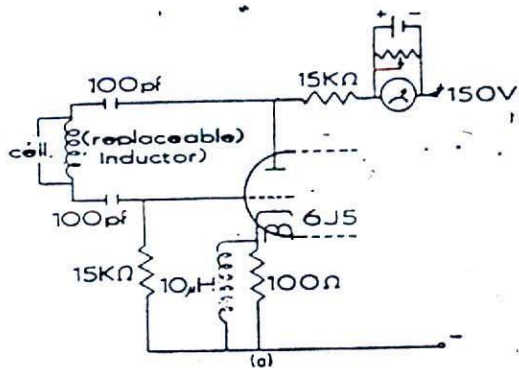


FIGURE 14.5a: High frequency triode oscillation circuit where the conductance cell is part of the feedback loop. The replaceable inductor is used to vary the frequency of oscillation and the meter shunt circuit serves to "zero" the meter at the start of titration. Reprinted from Ref. 4, p. 99, through the courtesy of the publisher.

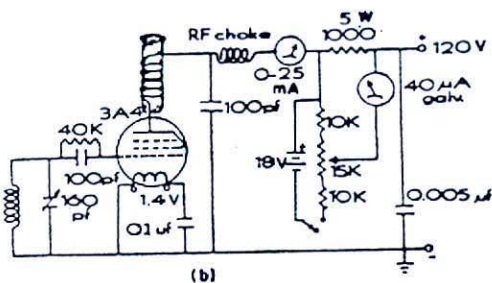


FIGURE 14.5b: A battery-operated high frequency oscillator circuit where the conductance is part of the plate circuit. The adjustable grid capacitor is used to set the starting current, read on the 0-25 mA meter. The galvanometer is biased to allow precise readings of the plate current during titration. Reprinted from Ref. 5, p. 492, through the courtesy of the publisher.

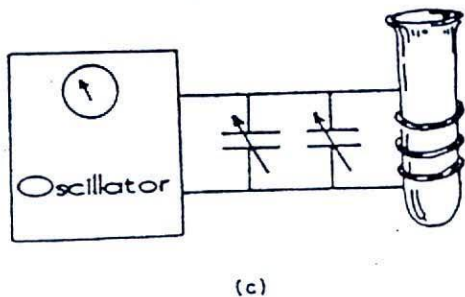


FIGURE 14.5c: Block diagram of the substitution method for high frequency titration. During titration, the adjustment in the two calibrated variable capacitors, required to return the system to its prior state, is noted.

method. After the oscillator frequency is noted, titrant is added and the change in the variable capacitors required to return the oscillator to its former condition is noted as a function of the added titrant.

Systems involving high frequency have not reached the high precision of low frequency measurements and are customarily used only for measuring changes, such as detecting an end point during titration, so that meter readings alone are normally used in making the required graphs.

14.3 PROPERTIES OF SOLUTIONS AS THEY AFFECT ELECTRICAL RESISTANCE MEASUREMENT

Solutions, the prime concern in pharmaceutical analysis, present some very real differences and problems in comparison to solids when the meaning and measurement of their conductance is considered.

A. ELECTRODE REACTIONS

As mentioned earlier, when current flows in a solid no real change occurs in the circuit through which the current flows; in a solution, however, an important but not always appreciated phenomenon occurs; a reaction occurs at *both* electrodes whenever current flows.* As a corollary, some reaction must occur (albeit small) for a voltage to be generated also, but the initial concept is the one of concern in conductimetry. The importance of this idea lies in the fact that no current flows without producing some change in the solution, and in some cases in the electrodes, through which it flows. It behooves the analytical chemist, therefore, to keep such change-producing current flow negligible or in some way cancelled, to prevent his measuring tool from interfering with the measurement he wishes to make.

B. CHARGE CARRIERS

Unlike current flow in a solid, current in a solution is carried by a variety of carriers (ions) derived from the solvent or from entities dissolved in the solvent; these carriers have either positive or negative and single or multiple charges. In addition, because we are most often concerned analytically with dissolved entities, the additional influence of their number and physical state will influence their ability to carry current. The latter factors, concerned with the effects of concentration and physical state, make the analytical prospects of solution conductance great.

* As earlier, the general discussion involved dc aspects. The high frequency units and systems described do *not* require reactions at each electrode as in truth they measure inductance, a combination of factors including resistance, not resistance alone and with proper frequencies, the electrodes do not contact the solution. For our purposes, as dc (and low frequency ac) systems will be considered here, the current flow-reaction idea is correct.

C. MEASURING CELL

The solution being measured must be contained in a conductance "cell," a chamber made of high resistance and heat conducting material in which the "electrodes" are relatively rigidly placed, roughly as shown in Fig. 14.6.

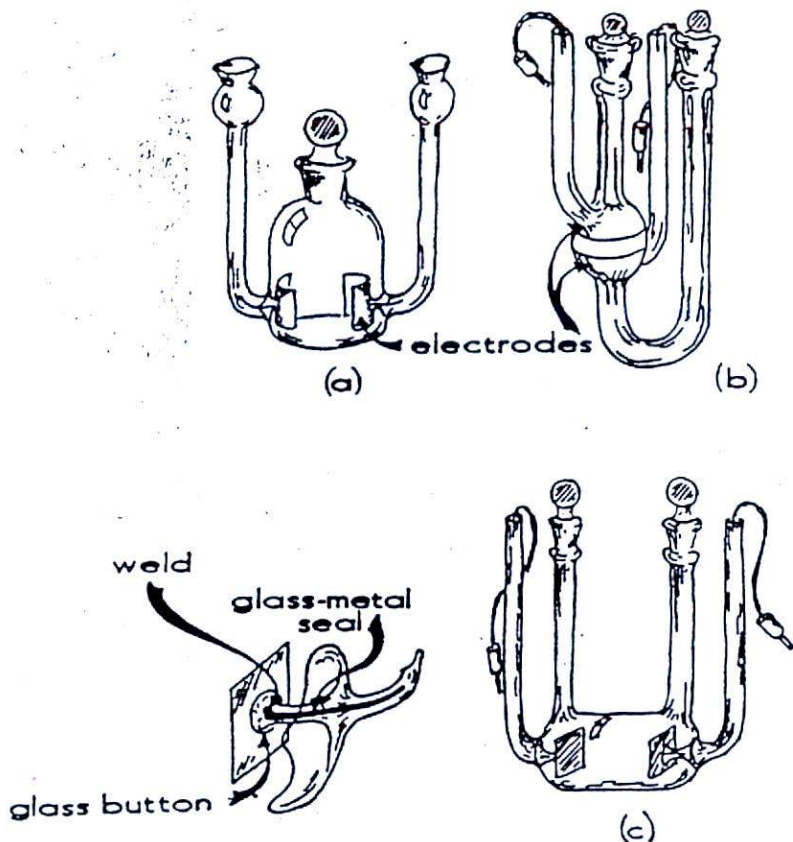


FIGURE 14.6: Several representative conductance cells for titration (a), small volume (b), and high-precision work (c). The detail of a rigid mounting for an electrode is also shown.

The precise dimensions and the design used will depend greatly on the type of analytical work being done and the conductance of the solutions being measured, but some general points may be made.

Glass is the usual external container material because of its easy workability, high electrical resistance at temperatures satisfactory for solution measurements, structural rigidity, and ease of cleaning. The placement of

filling tubes depends on the purpose of the experiment. For titrations and experiments where frequent additions are to be made to the cell, one with a large single opening as shown in Fig. 14.6a is often used. Smaller volumes of solution are more simply filled if the tubes are in a vertical plane as in Fig. 14.6b. Platinum is the customary electrode material; because of its inertness and high oxidation-potential, the conductance of most solutions can be studied without affecting the electrodes. By proper design of the glass-to-metal joint and the use of heavy gauge lead-in wires, the cell electrodes may be made rigid (see Fig. 14.6) as is required for precise, absolute measurements. The placement of the lead insulation tubes is critical only for ac measurements; because the liquid of the temperature bath intervenes between the leads, the closer these leads are together, the higher the capacitance that must be allowed for in balancing. While rigidity is actually all that is required, measurements are much simpler to make if the leads are kept as far apart as possible. External connections are made either through a drop of mercury in the insulation tubes or by soft-soldering the leads permanently, directly in the insulation tubes, with a small torch.

The platinum electrode plates are usually coated with platinum black after assembly to make the bridge system easier to balance. This may be accomplished by filling the cell with a dilute solution of platinum chloride and passing current through the cell for several minutes in both directions. In cases where platinum black will create catalytic problems, it may be omitted, but an increase in bridge balancing difficulties may be expected.

Cleaning and aging cells after manufacture is of concern in all accurate work. The cell constant will be observed to change slowly for several months after manufacture, after which it will remain stable indefinitely. This process can be hastened at the time of initial cleaning of a new cell by boiling for an hour in concentrated HCl then, after rinsing, boiling in distilled water.

D. SPECIFIC CONDUCTANCE

A solution in a cell has a specific resistance and conductance, defined precisely as discussed previously: it is not normally found by exactly measuring the resistance of a precisely measured gap between the electrodes as is usually done with solids, but by measuring the resistance of the cell filled with a carefully prepared standard solution whose specific resistance and conductance (L_s) is precisely known (Demal solutions, Jones and Bradshaw*). From this measured resistance R , the cell constant K is, when required, calculated from the equation

$$K = RL_s \quad (14.9)$$

The constant K is roughly related to the dimensions of the electrode gap by the equation

$$K = \frac{\text{length}}{\text{electrode area}} \quad (14.10)$$

This constant is then used to convert the measured R for an unknown solution to specific conductance L_s , again using Eq. (14.9).

E. EQUIVALENT CONDUCTANCE

To completely describe the electrical properties of a dissolved salt, the conductance of 1 equivalent of the salt at the concentration in question (Λ at concentration c , equivalents per liter) is defined.

In a diagrammatic sense this is the conductance of a cell with electrodes 1 cm apart, but large enough to hold 1 equivalent of the solution. The volume of this cell is $(1000/c)$ ml, and the conductance of this cell per square surface of electrode area is the equivalent conductance Λ ,

$$\Lambda = \frac{1000L_s}{c} \quad (14.11)$$

Most analytical conductimetry data may be used without conversion to these more basic terms, resistance alone being adequate for the plotting required.

F. DISSOCIATION AND ASSOCIATION

The development shown in the last section, of the parameter dependent on concentration, implies in light of our earlier discussion of the relationships between ions and conductance, that all of any dissolved material dissociate upon dissolution into its constituent ions. If this does not occur, the value of specific conductance L_s , and thus the equivalent conductance Λ will depend on the ions actually present, i.e., on the completeness of this dissociation. In truth, as discussed when the background of solution conductance was being presented, the development of the present theory of dissociation began with efforts to explain the data obtained from conductance measurements. The equivalent conductance of a completely dissociated solute in solution is normally referred to as the equivalent conductance at infinite dilution Λ_0 . As the solution becomes more concentrated, the equivalent conductance is observed to decrease so that the degree of dissociation, or ionization, α was early defined by Arrhenius¹ as

$$\alpha = \frac{\Lambda}{\Lambda_0} \quad (14.12)$$

This equation appears intuitively correct, but ignores the differences in the solute ions at the two concentrations implied by Λ and Λ_0 .

At infinite dilution, it is apparent that all molecules that can dissociate will have done so and the ions so produced will have become as independent of each other as it is possible for them to be; at this concentration each ion will contribute its own intrinsic equivalent conductance to the measured

equivalent conductance; these are designated as λ_0^+ or λ_0^- , for cations and anions. These "limiting ionic conductances" can be intuitively seen to depend on the particular speed with which the ion in question moves through the solvent used under a standard potential difference, called "mobility" (μ), and the number of current units (coulombs) the ion carries in 1 equivalent ξ ,

$$\lambda_0^{\pm} = \xi \mu_{\pm} \quad (14.13)$$

Once determined, these individual limiting ionic conductances could be combined in any stoichiometric way to deduce (when required) the equivalent ionic conductance at infinite dilution of any salt. As a first approximation, at other concentrations, similar relationships are assumed to hold for that fraction of the salt that is ionized, so that the measured equivalent conductance at infinite and finite dilution is the sum of the contributions of all ions present (see any physical chemistry text for a table of limiting ionic conductances, i.e., Ref. 7). As an example, at infinite dilution, for a salt $A_n B_m$,

$$\Lambda_0 = n\lambda_0^+ + m\lambda_0^- = \xi(n\mu_+ + m\mu_-) \quad (14.14)$$

$$\Lambda = \alpha \xi(n\mu_+ + m\mu_-) \quad (14.15)$$

where α is the fraction of molecules dissociated. Some of the assumptions inherent in Arrhenius' intuitive equation [Eq. (14.12)] can then be seen,

$$\alpha = \frac{\Lambda(n\mu_+ + m\mu_-) \text{ at infinite dilution}}{\Lambda_0(n\mu_+ + m\mu_-) \text{ at concentration } c} \quad (14.16)$$

and $\alpha = \Lambda/\Lambda_0$ only when μ_+ and μ_- are the same at all concentrations. This factor is often assumed true in analytical work.

G. DEBYE, HUCKEL, AND ONSAGER

The final assumption of the last section was the culprit at whose door a number of strange anomalies were laid as the ionic theory was being developed. Several "strong salts," sodium chloride, etc., even when relatively dilute, seemed to possess a finite α , suggesting that they were not completely ionized in solution (despite other evidence to the contrary). Through the work of Debye, Huckel,⁸ and Onsager,⁹ these anomalies were corrected on both a theoretical and practical level by theorizing and correcting for the interactions between the ionized molecules in solution, that affect the effect of the external field on those same molecules. At the concentrations normally involved in analytical work these equations permit nearly complete explanation of the anomalies in conductance caused by concentration that are observed in solution of completely ionized salts. The corrections take the form of a simple equation relating measured equivalent conductance and concentration:

$$\Lambda = \Lambda_0 - (\theta\Lambda_0 + \sigma)\sqrt{c} \quad (14.17)$$

indicating that for solutions of finite concentration plots of equivalent conductance vs. the square root of concentration are straight lines. Of passing interest to us here is the fact that the constants θ and σ are theoretically calculable from nonconductance data. Great studies have been made in increasing our knowledge of solution conductance and the serious student is referred to the work of Fuoss and co-workers.¹⁰

14.4 ANALYTICAL ASPECTS OF SOLUTION RESISTANCE

To the foregoing general discussions, the special problems of the various types of conductimetric analyses must be appended. The more precise problems of the use of conductimetry as a tool for the probing of the nature of ions in solution are rather complex subjects in and of themselves and will be dealt with only briefly. We are concerned mainly with the concentration aspects of conductimetry and the use of that tool in measuring changes in the solution concentrations of ions.

A. CELL AND TEMPERATURE CONTROL

As mentioned before, the conductivity cell is usually made of glass, with platinum electrodes. In high-precision direct current or low frequency work, seeking Λ_0 for instance, exact knowledge of the cell constant is required and rigidly positioned electrodes are essential so that the cell constant, once determined, remains constant. The dimensions of such cells are made such that measured resistance of the solution-containing cell is in the most sensitive region of the bridge system, normally, 1000–10,000 Ω .

As viscosity of the solvent is a prime effector of the velocity of the ions and viscosity is very sensitive to temperature, the temperature of cells whose resistance is being measured must be accurately known and controlled. The viscosity of water varies at a rate of about 2%/deg near room temperature, so that to make measurements of aqueous solutions with a precision of the order of 0.1% requires that the cell temperature be maintained constant to at least $\pm 0.05^\circ\text{C}$.

The problems associated with ac measurements have been discussed in general, but an additional point arises in these systems when the measurement cell is placed in a bath liquid. The capacitance contributed to the system by the electrode leads into the cell depends, of course, on the lead insulator positions and the dielectric constant of the intervening material. For precise work a low dielectric constant bath oil is preferred, but with proper and rigid design, precise low frequency ac measurements can be obtained using cells of the general shape shown in Fig. 14.6c, in a water bath where the leads are separated as much as possible.

Titration and other low accuracy measurements can be made with much simpler cells; often simply two pieces of wire mesh or foil clamped into a

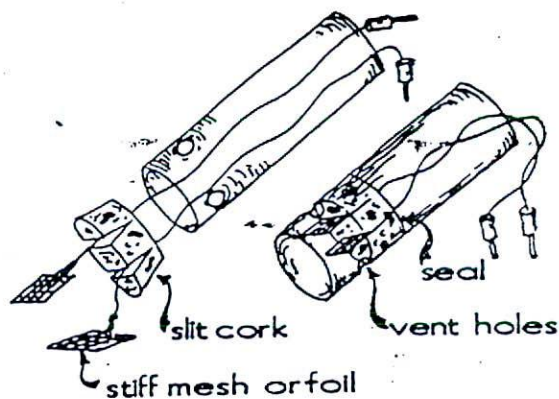


FIGURE 14.7: A "dipping" conductance cell, made of cork and glass tubing. The dimensions may be adjusted to provide any suitable cell constant.

beaker will suffice. The homemade "dip" cell shown in Fig. 14.7 functions well, and can be conveniently varied for any resistance solution by adjusting the area of mesh showing. It is fashioned from a stopper sliced, reassembled with electrodes in the slices, then pushed completely into the glass tubing. A bit of de Kohtinsky cement on top of the stopper completes the seal.

The only requirement for titration cells is that sufficient electrode area be accessible to the solution to permit the bridge system used to be read in its most accurate region and that the electrodes remain in their relative position throughout the one titration.

Higher frequency titrations require (or permit) quite different electrode placement methods. The electrodes are usually *outside* the vessel and rigidly mounted directly to the vessel walls. High frequency conductance cells are normally variations of types shown in Fig. 14.8.

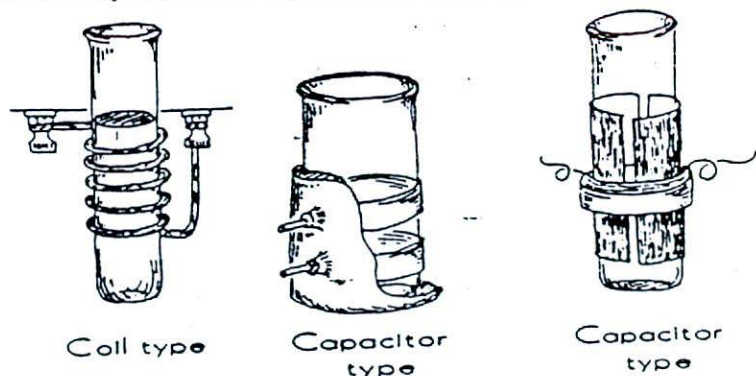


FIGURE 14.8: Three general types of high frequency conductance cell.

In the capacitive cell, the electrodes are cylindrical metal foil rings or plates with the glass solution chamber between. Because glass is a dielectric in itself, the glass wall is kept thin, to contribute as little as possible to the overall capacitance. The coil-type cell usually uses a test-tube-shaped cell made to fit snugly into heavy gauge, self-supporting coils.

14.5 EXPERIMENTAL METHODS

A. PRECISE MEASUREMENT OF LIMITING IONIC CONDUCTANCE

Studies of the physical properties of ions in solution most often require estimates of Λ_0 and/or measurements of the limiting slope of the Onsager plot of Λ vs. \sqrt{c} .

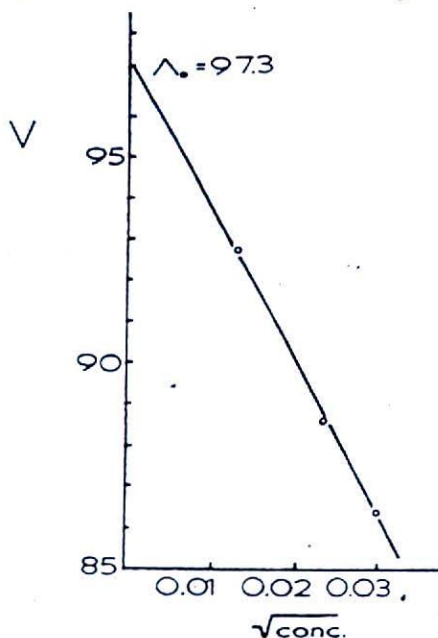


FIGURE 14.9: The plot of the data for Example 1 using Eq. (14.17).

The cell constant for the cell used must be precisely determined using an appropriate one of the standard solutions of Jones and Bradshaw⁶; then, using all the precautions outlined earlier, solutions of decreasing concentration are measured. The contribution of the solvent to the conductance is subtracted from the measured conductance using the equation

$$L_s(\text{solute}) = L_s(\text{solution}) - L_s(\text{solvent}) \quad (14.18)$$

and plots of the Onsager equation or some variation of it used to determine Λ_0 and the slope from the solute data so obtained. An example of such data and its handling are shown below:

EXAMPLE 1: Conductance of tetra-*n*-hexylammonium iodide in methanol at 25°:

a. Cell constant

L_{25} , (0.001 Demal KCl) = 0.0001479 mho (corrected for solvent)

R (0.001 Demal solution) = 5557 Ω , 5524 Ω , 5552 Ω

b. Methanol solutions ($L_{\text{methanol}}(25^\circ) = 3.4 \times 10^{-7}$ mho)

Concentration, $\times 10^{-4} M$	(Mean R value), $\times 10^4$	L_s , $\times 10^{-6}$ mho	L_s (corrected for solvent), $\times 10^{-6}$ mho	Λ
8.991	1.051	7.79	7.76	86.4
5.464	1.685	4.861	4.827	88.6
1.633	5.295	1.548	1.514	92.7

c. Cell constant $k = 5.544 \times 1.479 \times 10^{-3} = 0.8199 M$

d. A plot of Λ vs. \sqrt{c} yields Fig. 14.9, suggesting $\Lambda_0 = 97.3$

References to any of the newer texts on electrochemistry,¹¹ or even one of the older ones,¹² should be made for specifics on high precision work and in particular for aid in the interpretation of the data.

B. LOW FREQUENCY CONDUCTANCE TITRATION

Conductance measurements are most often used for end-point detection in titrations; in this instance, a cell of the simplest type should be used, often only a beaker with clamped electrodes or a dipping cell such as shown in Fig. 14.7. Most titration-curve shapes may be theoretically deduced, and even a brief discussion of the curve shapes for several common titrations and the methods used for deducing them will be sufficiently instructive to permit the student to deduce nearly any others of concern.

The basic assumption underlying conductance titrations is that the conductance will vary linearly with concentration, so that as the ion titrated decreases in concentration to zero during titration, the conductance changes in a similar fashion. It is comforting that although the conductance of an ion in solution by itself decreases linearly with the square root of the concentration, in the usual conductance system used for titration, the relatively constant ionic strength of the solution permits strong electrolytes to change conductance quite linearly with concentration. The association-dissociation phenomena exhibited by weaker electrolytes are then included as corrections on this basic assumption.

Titrations of strong acids and with strong bases are the simplest systems; all ions concerned can be accounted for easily, and their individual conductances allowed for in assembling the theoretical curve. The steps involved in theorizing this basic curve shape are shown in Fig. 14.10. All ions present in the initial solution sample are accounted for in ratio to their limiting ionic conductances (note, we actually desire the accounting to be in ratio to their ionic concentrations and their limiting ionic conductances $m\alpha\lambda_0$, where m is

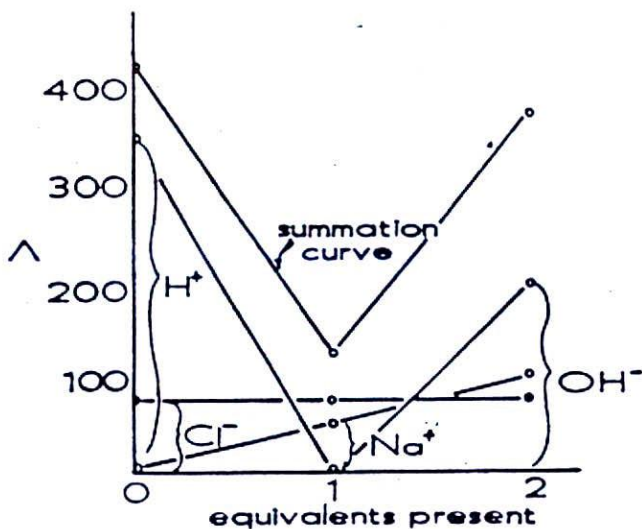
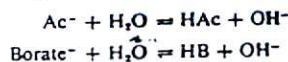


FIGURE 14.10: A hypothetical titration of HCl with NaOH from the start to 1 equivalent beyond the end point. It is assumed that each ion present exerts its own limiting ionic conductance. At each point, the total conductance is represented by the "summation curve."

total equivalents present and α the degree of ionization, but in drawing theoretical curves λ_0 alone will suffice). The same accounting should be done at the end point and at 1 equivalent beyond the end point, assuming ideality. These individual points are shown in Fig. 14.10.

When beyond the end point, it is of real concern to note we are using $n\lambda_0$ for the titrant, where n is the equivalents of titrant present. One assumes, in Fig. 14.10, that all of the H^+ is used with all of the OH^- to reach the end point; the Na^+ added rises with the slope $n\lambda_{(Na^+)}$ and the Cl^- is constant throughout. Connecting all these basic points with straight lines produces a rather good approximation of the conductance curve for this titration as it is obtained. For weaker acids, corrections for variations in the degree of ionization α , occurring during the titration, can be estimated from knowledge of the acid being titrated or the base used.

In effect two alterations are being made when correcting for dissociation: at and near the end point the occurrence of hydrolysis of the salt titration product produces an "apparent non-end point" in that more titrant is present than one would expect, producing a pronounced rounding of the sharp break expected at the end point. For example, at the end point of acetic and boric acid titrations, solvent equilibrium produces the situations,



so that a sharp end point is not achieved. The same result is produced by titrating a weak base with a strong acid.

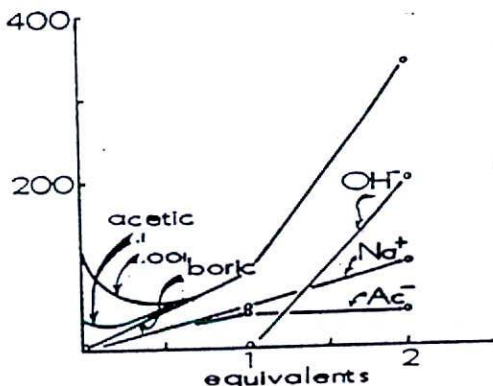


FIGURE 14.11: Hypothetical titration curves for boric and acetic acid. Boric acid, being very weak, contributes no conductance until the borate ion is produced as titration proceeds. Acetic acid shows the effect of initial weakness followed by common-ion suppression of ionization. The degree of ionization is a function of initial concentration.

The amount of curvature to be included in deducing the curve for a weak titrant is in direct proportion to the weakness of the acid or base being titrated. This problem can be diminished somewhat by adding a miscible solvent with a low dielectric constant, such as ethanol or acetone, to decrease hydrolysis. Most often the end point can be satisfactorily determined by extrapolating the straight line portions before and after the end point to their intersection at the actual end point.

The effects of the degree of dissociation are allowed for at the point where the weak solute is in highest concentration: at the beginning of the titration for a weak titrant. The extremes at the end for a weak titrant are shown with hydrochloric acid (for our purposes completely dissociated), Fig. 14.10, and with boric acid (for our purposes completely undissociated), Fig. 14.11. The first shows the completely additive effects of all constituent ions; the second shows the effect of the very low dissociation of the acid, a slow,

proportionate rise in all ions present: the borate ion is produced as the hydrogen ion is titrated to the end point.

The titration of acid such as acetic, intermediate between these two extremes, shows a low but finite dissociation and conductance initially, Fig. 14.11 (the dissociation dependent on the concentration being titrated) followed by a suppression of their initial dissociation by the common ion produced in the titration as evidenced by a decrease in conductance, which then rises slowly to the end point. All curves are essentially identical after the end point, in essence, being due to addition of the titrant alone.

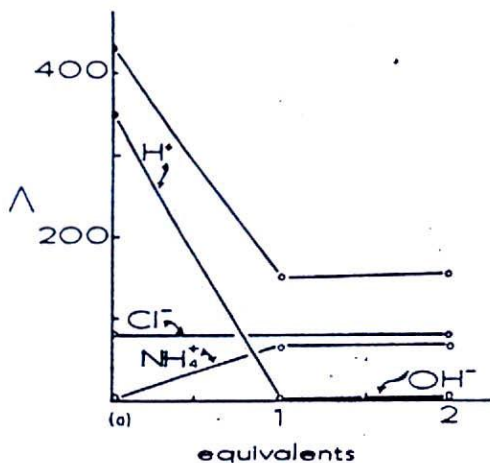


FIGURE 14.12a: A hypothetical titration curve of a strong acid titrated with a weak base. The overall measured curve is shown at the top.

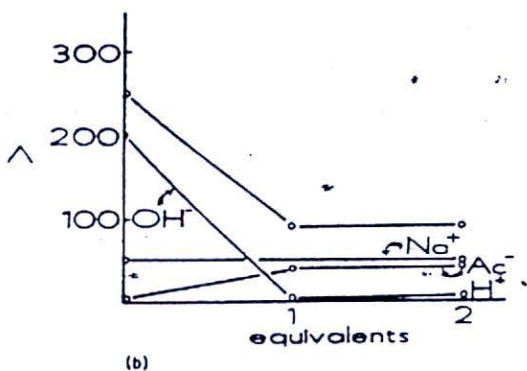


FIGURE 14.12b: A hypothetical titration curve of a strong base titrated with a weak acid. The overall measured curve is shown at the top.

The effects of titration on a strong titrant with a weak base or a weak acid are handled similarly, but produce one interesting variation, as shown in Figs. 14.12a and 14.12b. In passing the end point, little increase in constituent ions is produced by weak titrants both because of their weakness and because ionization is further suppressed by the high concentration of counterion present as the product of the titration; the curve flattens almost immediately after the end point.

As an example of the handling of titration data, consider the following titration of a mixture of acids with a strong base.

EXAMPLE 2: Titration of sulfuric and acetic acids: 3 ml of sulfuric and 5 ml of acetic acid solutions of unknown strengths added to 200 ml of water and titrated with 0.2541 *N* NaOH, produced the following results:

Titrant, ml	$L_{\text{read}}, \times 10^{-4}$ mho
0	17.7
1	14.9
2	11.7
3	9.26
4	8.40
5	8.71
6	9.15
7	9.50
8	9.94
9	11.20
10	12.50

Note that the stronger acid is titrated first and provided the strengths differ by at least 2–3 *pK* units, the two end points can be easily detected. (See Fig. 14.13.)

Titration involving other types of systems such as oxidation-reductions and precipitations are handled in a similar manner, i.e., considering the ions present at the three stages of the titration and correcting for the completeness of the reactions involved; curves of generally the same shape are obtained.

The theory just developed has made some very basic assumptions that should be considered: that the conductance system being used is capable of accurate measurements of the solutions involved, that an increase in concentration can be obtained without increasing the volume (the abscissa on these plots is concentration in equivalents, not milliliters added). The first of these can usually be solved by proper concentrations and/or electrode placement, spacing, and bridge design. The second is solved by using titrant at least 10 times as concentrated as the titrand, and/or by correcting for volume changes using the equation,

$$L_{\text{corr}} = L_{\text{measured}} \left(\frac{V + v}{V} \right) \quad (14.19)$$

In this equation V is the initial sample volume and v the total titrant volume added up to that reading. This correction will normally eliminate the slight bending toward the abscissa that volume changes during titration produce.

Conductance titrations are most often performed in aqueous solvents, but the system is not limited to water. Any solvent in which the compound to be analyzed is soluble and in which the ionic concentration changes during titration is acceptable. The advantages of increased solubility for organic compounds in organic solvents may be outweighed by the complications

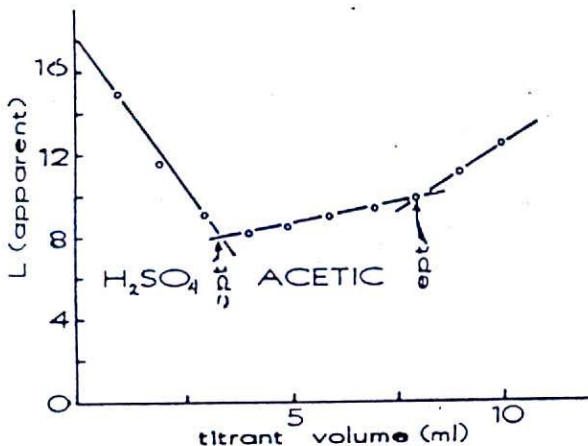


FIGURE 14.13: The plot of data from Example 2, titration of sulfuric and acetic acids with sodium hydroxide.

of ion association that occur in low dielectric media, but the advantages of increasing the ionization of weak acids and bases by dissolving them in strongly basic or acid solvents should not be overlooked. For example, weak acids such as hindered phenols can be titrated successfully in pyridine and toluene.¹³

Combinations of solvent have value as mentioned before, the addition of up to 10 or 20% of water-miscible, low dielectric constant liquids such as methanol, acetone, or ethanol to aqueous solutions, to suppress hydrolysis and sharpen the end points of weak acids and bases is a particularly valuable procedure of this type.

C. HIGH FREQUENCY CONDUCTANCE TITRATION

All of the foregoing portion of this section was presented from the standpoint of dc or low frequency ac systems. The behavior, operation, and results obtained from high frequency ac methods are sufficiently different to warrant separate discussion.

High frequency titrations can involve either coil or capacitor systems with the cell design differences discussed earlier. As the latter are much better developed in the available literature, they will be the only ones considered in detail. Without concerning ourselves with the analysis of the equivalent circuits of the cell-solution system, the high frequency conductance (G_p) of a solution in a capacitance system is related to the low frequency conductance (L) by the equation,

$$G_p = \frac{L\omega^2 C_c^2}{L^2 + \omega^2(C_c + C_s)^2} \quad (14.20)$$

an equation which also involves ω , the frequency, C_c , the capacitance of the cell walls, and C_s the capacity of the solution. It is of concern to note that G_p is linearly related to L , the low frequency conductance, when L is very small (resistance high), with a slope at most equal to 1 but most often less than 1. For example, a plot of the high frequency conductance of a specific system and cell as a function of L is shown in Fig. 14.14 for two frequencies;

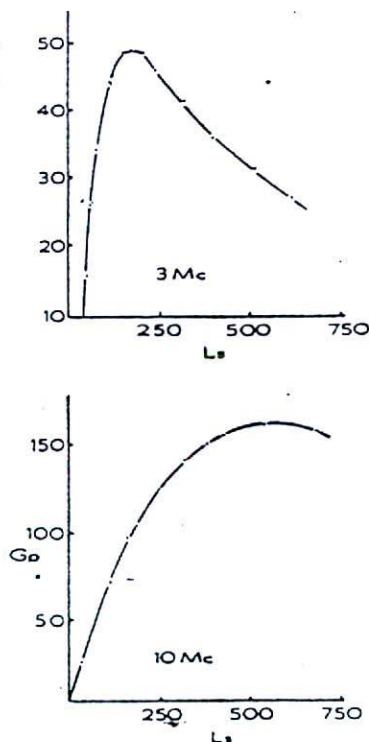


FIGURE 14.14: High frequency transfer curves for a capacitance cell showing the relationship between the high frequency (G_p) and the low frequency conductance (L_s). Reprinted from Ref. 14, p. 89, through the courtesy of the publisher.

as one might surmise by studying the equation, the height and the value of L at which the maximum G_p occurs is a function of the frequency used for analysis.

These so called "transfer curves" are of concern, as the result obtained from a high frequency titration depends heavily on them. Let us consider

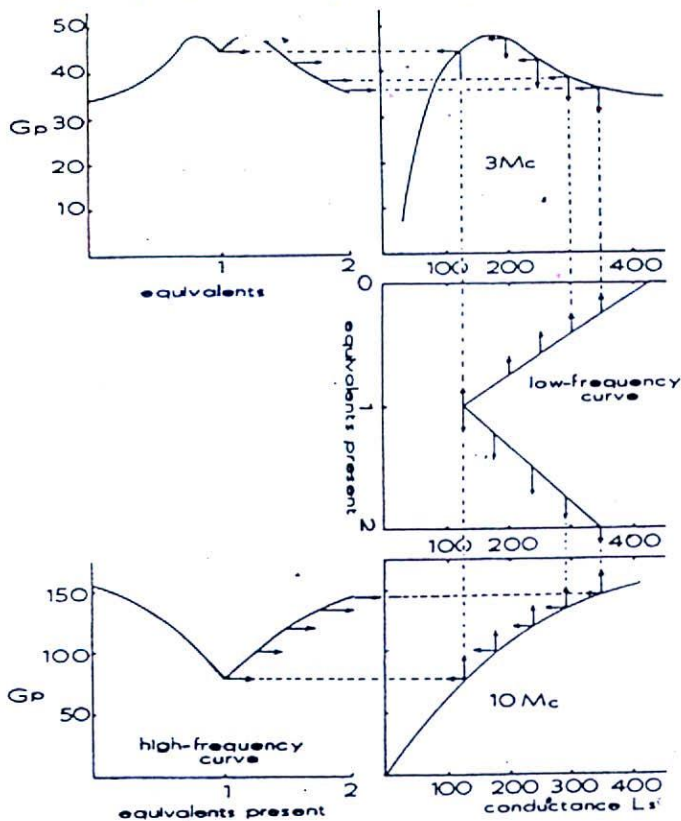


FIGURE 14.15: The use of high-low frequency transfer curves to deduce the shape of a high frequency titration curve from one obtained at low frequency.

the low frequency (or dc) conductance titration shown in Fig. 14.10 and use the transfer curves shown in Fig. 14.14 to predict the shape of the high frequency titration curves we would expect for that simple titration system.

The variations in L as observed on the low frequency titration curve may be transformed by replotting the corresponding G_p points read from the 3- or 10-mc curves, into the V - and inverted W -type curves shown. It is an interesting exercise to reduce the other general types of titration curves to

high frequency curves using some standard transfer curves, for example, that in Fig. 14.14.

EXAMPLE 3: Using the transfer curves in Fig. 14.14, predict the shape of the following low frequency titrations at 3 and 10 mc:

A weak and a strong acid		A weak acid with a strong base	
ml	L	ml	L
0	277	0	200.0
1	249	1	210.0
2	217	2	217.5
3	192.6	3	225.6
4	184.0	4	233.9
5	187.1	5	244.0
6	191.5	6	258.6
7	195.0	7	275.4
8	199.4	8	292.8
9	212	9	209.3
10	225	10	212.0

It is of concern here that the shape of the high frequency curve is directly dependent on the position of the transfer curve peak and the absolute value of the low frequency conductance readings. Small amounts of added salts, which produce only a vertical shift in the titration curves made at low frequencies, may well move the high frequency to a much less sensitive region (put the end point at or just near the G/L peak) so that experimentation with concentrations, while desirable in low frequency titration, must always be considered with high frequency titration. It is also apparent from Eq. (14.20) and Fig. 14.14 that as the sharpness of the end point is dependent of the slope of the G_p/L plot and this slope is essentially independent of frequency at low values of L (where sensitivity is highest), variations in frequency will not enhance end-point sensitivity once an appropriate concentration is selected.

In practice, the transfer curve is not required, though it can be deduced with known solutions by measuring L and G_p . In practice, the concentration of the sample is simply adjusted in the titration until appropriately sharp end-point curves are obtained.

Systems involving use of measurements of capacitance change in the cell during titration produce similar results. The relationship between the high frequency capacitance C and the low frequency conductance L is

$$C = \frac{L^2 C_c + \omega^2 C_c C_i^2 + \omega^2 C_c C_s}{L^2 + \omega^2 (C_c + C_s)^2} \quad (14.21)$$

and plots of the change in capacitance during titration ΔC vs. L produce transfer plots of the shape shown in Fig. 14.16.

These plots may be used to deduce the high frequency plots from low frequency titration data precisely as described for high frequency conductance. Again, however, these transfer plots are not required; adjustment of concentrations to produce sharp end points being all that is needed.

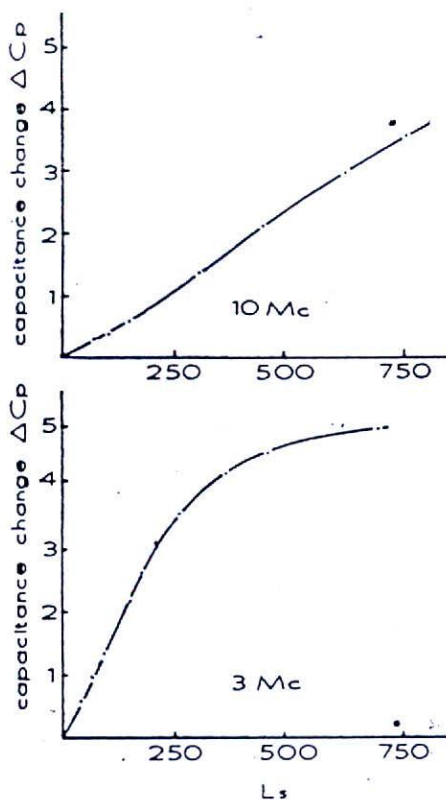


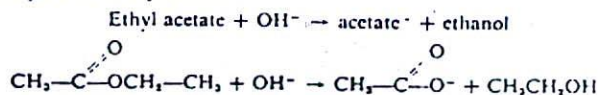
FIGURE 14.16. Transfer curves for high frequency capacitance change as a function of low frequency conductance. Reprinted from Ref. 14, p. 91, through the courtesy of the publisher.

Titration systems using coil-type cells produce similar results. The versatility and suitability of high frequency titrations for pharmaceutical analysis are shown in the paper of Allen et al.,¹⁵ who found high frequency conductance titrations suitable for a variety of titrants, including sulfa drugs in anhydrous acetic acid.

D. CONCENTRATIONS AND KINETIC ANALYSES

Analytic procedures aimed at determining changes in concentration are, from the conductance viewpoint, often the most interesting as well as the easiest, as one uses changes in conductance rather than absolute values. Absolute calibration is not required, therefore, only structural rigidity. As an example, we will be concerned with studies in which kinetic constants are sought.

In any reaction in which ions are produced, used up, or exchanged, conductimetry may often be used to perform an "analysis" and to produce the kinetic data desired without the customary methods of sampling and analysis, using only the conductance change. This is of particular concern in sealed systems, but is often of use in rapid reactions and those carried out in small volumes. The classic ester hydrolysis serves as a good example for the analysis of the problem:



If performed in a solution of suitable concentration for conductance measurements, the exchange of the relatively immobile acetate ion for the very mobile OH^- ion can easily be followed conductimetrically. The total conductance is due initially only to the base added; during the reaction to the residual base plus acetate product; and at the conclusion, to excess base and total acetate (or acetate alone if the base is the limiting reactant). If, as we did with our titration assumptions, we assume that the conductance varies linearly with concentration of all ions, then for each ion:

$$\begin{aligned} L_A &= f_A(A^-) \\ L_{\text{OH}} &= f_H(\text{OH}^-) \end{aligned} \quad (14.22)$$

and taking as initial concentrations, E and B , for ester and base, respectively, the conductance at anytime can be described as,

$$L_{\text{total}} = f_H(B - x) + f_A(x) + f_R \quad (14.23)$$

where x is the extent of the reaction and f_R the contribution of any constant, blank and/or solvent. Initial and final conditions may be similarly defined for the usual case, where the ester is the limiting reagent:

$$L_0 = f_H(B) + f_R \quad (14.24)$$

$$L_\infty = f_H(B - E) + f_A(E) + f_R \quad (14.25)$$

Algebraic manipulation produces the result for L at time $t(L_t)$,

$$(x) = (E) \frac{L_0 - L_t}{L_0 - L_\infty} \quad (14.26)$$

and,

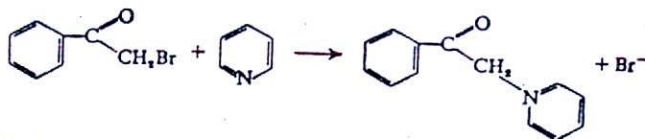
$$\frac{E}{(E - x)} = \frac{L_0 - L_t}{L_0 - L_\infty} \quad (14.27)$$

which, along with knowledge of initial concentrations of base and ester, will produce the required information for plotting the second-order equation.

$$\log \frac{E(B-x)}{B(E-x)} = \frac{(B-E)kt}{2.303} \quad (14.28)$$

Simplifications such as using equal initial concentrations can produce the desired plots directly from the conductance readings, without the necessity of separate determination of initial concentrations.

EXAMPLE 4: McGuire¹⁶ has studied the conductance change of the following reaction:



If phenacyl bromide and pyridine are mixed at the same initial concentration (A_0), kinetics predict that their concentrations at any time a will change according to the equation:

$$\frac{1}{a} = kt + \frac{1}{A_0} \quad (14.29)$$

or, if expressed in terms of the amount of products produced x , the equation becomes:

$$1/(A_0 - x) = kt + 1/A_0 \quad (14.30)$$

As the products of the reactions are ions, and assuming the conductance to vary linearly with concentration, the following data reported by that author may be plotted according to Eq. (14.30), using Eqs. (14.22) through (14.27).

$A_0 = 0.0385 M$, Cell constant 1.000

Time, min	Resistance, ohms
7	45000
28	11620
53	9200
68	7490
84	6310
99	5537
110	5100
127	4560
153	3958
203	3220
368	2182
∞	801

E. ION ASSOCIATION AND CRITICAL MICELLE FORMATION

One of the most pharmaceutically useful, nonquantitative uses of conductimetry is certainly in the determination of critical micelle concentrations (CMC), those concentrations above which the solubilization properties of a micelle-forming ion may be expected, and below which it has been convenient

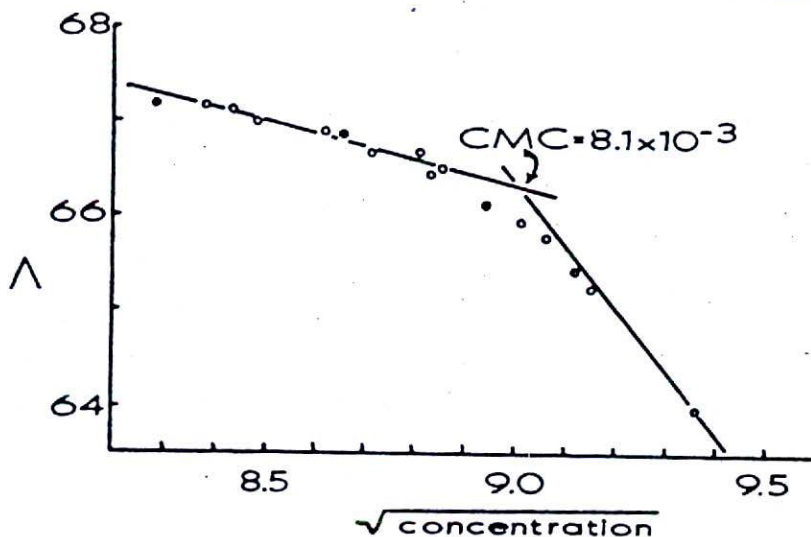


FIGURE 14.17: Onsager plots indicating the determination of critical micelle concentration from conductance data. Reprinted from Ref. 17, p. 1392, through the courtesy of the publisher.

to postulate no association occurs.* The equilibrium being described by this idea is



Evidence for micelle formation and an example of how the concentration at which it occurs may be determined conductimetrically as shown in Fig. 14.17. Although the lines are curved at the precise point of intersection, extrapolation of the straight portions of the lines produces rather precise and reproducible critical micelle concentrations.

The shape of the plots obtained may be explained (though with some doubt as to their complete correctness*) by considering the conductance

* Although it does not affect the interpretation of the curves that are obtained for micelle-forming ions, it should be pointed out that rather convincing evidence has been obtained suggesting that at concentrations considerably below the CMC, dimerization occurs (Mukerjee et al., Ref. 17).

one would postulate for the micelle-forming ion in the concentration regions surrounding the CMC. If Λ_m^- represents the conductance of the anion monomer, and Λ_p^- that of the micelle, the contribution of the former is decreased and of the latter increased as monomer is transferred to micelle. If α is defined as the fraction of the total solute in micelle form, $C(1 - \alpha)$ and αC represent the relative concentrations of monomer and micelle at a particular monomer concentration, respectively, the total conductance then is

$$\Lambda = \Lambda_m^-(1 - \alpha) + \Lambda_p^-\alpha \quad (14.32)$$

As the concentration is raised, the equivalent ionic conductance varies linearly with \sqrt{c} approximating a straight line with a slightly negative slope due to ionic interactions, as one would expect. After the CMC is reached and passed the additional monomer is forced into the highly charged but relatively immobile micelles ($\Lambda_p^- \ll \Lambda_m^-$); α and αC both rise. The rise in the solution conductance decreases, while the value of Λ drops sharply.

EXAMPLE 5: Mukerjee et al.¹⁷ measured the resistance of dilute aqueous solutions of sodium lauryl sulfates and reported the following results:

Temperature = 25°C Cell constant = 0.7492 cm ⁻¹	
Concentration, $\times 10^3 M$	Resistance
6.455	1725
6.859	1626
7.029	1587
7.111	1588
7.185	1556
7.430	1508
7.485	1497
7.579	1483
7.752	1449
7.796	1447
7.835	1438
7.995	1418
8.111	1401
8.140	1396
8.212	1387
8.322	1376
8.370	1372
8.456	1352
8.770	1336
9.287	1299

Determine the critical micelle concentration from these data.

Estimation of ion association and association or dissociation constants from conductance data is based upon the Arrhenius' observation discussed.

that for solutes at a concentration of n molecules/liter,

$$\alpha = \frac{\Lambda}{\Lambda_0} \quad \text{where} \quad K = \frac{n\alpha^2}{(1-\alpha)} \quad (14.33)$$

The equation is not precisely correct, as mentioned before, but the full effect of the imprecisions involved is often not large and for many determinations α may be estimated directly from Eq. (14.33).

EXAMPLE 6: Shedlovsky and McInnes¹⁸ measured the conductance of acetic acid solutions with the following results (data reprinted through the courtesy of the publishers).

Concentration, $\times 10^3 M$	Λ
0.028014	210.32
0.11135	127.71
0.15321	112.02
0.21844	96.466
1.02831	48.133
1.36340	42.215
2.41400	32.208
3.44065	27.191
5.91153	20.956
9.8421	16.367
12.829	14.371
20.000	11.563
50.000	7.356
52.303	7.200
100.000	5.200
119.447	4.759
200.000	3.650

Estimate α and the dissociation constant for acetic acid over this concentration range.

REFERENCES

1. S. A. Arrhenius, *Z. Physik. Chem.*, **1**, 631 (1887).
2. H. E. White, *Modern College Physics*, Van Nostrand, Princeton, N.J., 1948.
3. G. Jones and R. C. Josephs, *J. Am. Chem. Soc.*, **50**, 1049 (1930).
4. M. F. C. Ladd and W. H. Lee, *Lab. Pract.*, **9**, (2), 98 (1960).
5. J. P. Dowdall, D. V. Sinkinson, and H. Stretch, *Analyst*, **80**, 491 (1955).
6. G. Jones and B. C. Bradshaw, *J. Am. Chem. Soc.*, **55**, 1780 (1933).
7. S. H. Maron and C. F. Prutton, *Principles of Physical Chemistry*, Macmillan, New York, 1965, p. 423.
8. P. Debye and E. Hückel, *Physik. Z.*, **24**, 185, 305 (1923).
9. L. Onsager, *Physik. Z.*, **27**, 388 (1926); **28**, 277 (1927).
10. For example, see R. A. Fuoss, *J. Am. Chem. Soc.*, **81**, 2659 (1959).
11. J. J. Lingane, *Electroanalytical Chemistry*, Academic Press, New York, 2nd ed., 1958.

12. D. A. MacInnes, *The Principles of Electrochemistry*, Reinhold, New York, 1939; Dover, New York, 1961.
13. D. B. Bruss and G. A. Harlow, *Anal. Chem.*, **30**, 1836 (1958).
14. C. N. Reilly and W. H. McCurdy, *Anal. Chem.*, **25**, 86 (1953).
15. J. Allen, E. T. Geddes, and R. E. Stuckey, *J. Pharm. Pharmacol.*, **8** (11), 956 (1956).
16. W. J. McGuire, M.S. thesis, Northwestern University, Evanston, Ill., 1947.
17. P. Mukergee, K. J. Mysels, and C. I. Dulin, *J. Phys. Chem.*, **63**, 1390 (1958).
18. T. Shedlovsky and D. A. MacInnes, *J. Am. Chem. Soc.*, **54**, 1429 (1932).