

Conductance Measurements

Part 1: Theory

Lou Coury, Ph.D.

Bioanalytical Systems, Inc.
2701 Kent Avenue
West Lafayette, IN
47906-1382

coury@bioanalytical.com

Measurement of solution conductance is a classical electroanalytical technique that finds application in a variety of chemical and biochemical studies. For example, conductance can be used to assess solvent purity, determine relative ionic strengths of solutions (including functioning as a detector for ion chromatography), monitor dissolution kinetics and the approach to equilibrium for partially soluble salts, determine critical micelle concentrations, follow the course of some enzymatic reactions, as well as to provide basic thermodynamic data for electrolyte solutions. The first installment in this two-part article reviews the basic physicochemical concepts underlying ionic conductivity in solution and discusses the principles of two different approaches to the determination of conductance. Part 2 will present experimental details of conductance measurements and discuss a few representative applications of conductance measurements in chemical analysis.

A Review of Parameters Describing Electrolyte Solutions

When two electrodes are immersed in a solution and a potential is applied across them, a current will be produced in the external circuit that connects the two electrodes. The mechanism of electrical communication between the two electrodes in solution is the movement of ions in the solution. When no appreciable solution electrolysis occurs, the magnitude of the current observed generally obeys Ohm's Law:

$$E=iR \quad \text{EQ1}$$

where E is the applied potential, i is the current measured, and R is the resistance of the solution between the two electrodes.

Solution Resistance

It is the quantity R (in one form or another) that is of interest in the present discussion. The higher the

concentration of ions present in the solution, the lower R will be. Ostensibly "molecularly pure" water has a pH value of 7 and hence contains 1×10^{-7} Molar OH^- ions as well as 1×10^{-7} Molar H^+ ions (the latter present in the form of H_3O^+ , H_5O_2^+ , ...). If a strong electrolyte (i.e., fully dissociable salt) like KCl is dissolved in water, the number of ions per unit volume increases and the solution resistance R is lowered, thus increasing the instantaneous current measured for a particular applied potential. Therefore, current can be related to the concentration of ions in a particular solution. However, the distance between the electrodes, the surface area of the electrodes, and the identity of the ions also affect R .

Solution Conductance

The reciprocal of solution resistance is called *conductance*, symbolized by the letter S (or L). Conductance is expressed in S.I. units called *siemens* (S or Ω^{-1}), although older literature may refer to an equivalent unit called the *mho*

(Ω^{-1}). As discussed above in the context of resistance, the measured conductance for a solution is related to the distance between the electrodes (d) and the microscopic surface area (geometric area \times roughness factor) of each electrode (A ; assumed identical for the two electrodes), as well as the ionic concentration. These parameters are interrelated by (1):

$$S = \frac{1}{R} = \kappa \frac{A}{d} \quad \text{EQ2}$$

Conductivity

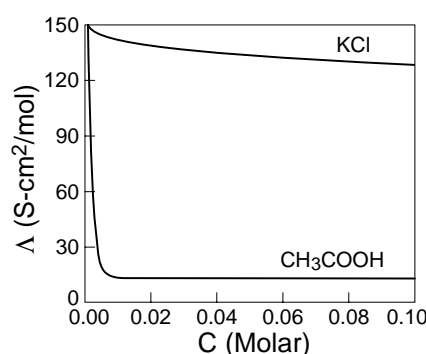
The quantity κ , above, is called *conductivity* and it contains all of the chemical information available from the measurement (e.g., concentrations and mobilities of the ions present). The ratio d/A is a constant for a particular measurement cell, and is hence referred to as the *cell constant*, θ (2). Therefore,

$$\kappa = S\theta \quad \text{EQ3}$$

The conductivity, κ , is an intrinsic property of a solution, rather than a

F1

A plot of concentration vs. molar conductivity measured for a typical strong electrolyte (KCl) and for a weak electrolyte (CH₃COOH). (Adapted from reference 3.)



property of the conductance cell used. However, for detection purposes in liquid chromatography or in determination of equivalence points during titrations, only relative changes are of interest (rather than absolute values); hence, the conductance, S , maybe be reported instead of κ .

Mobility

It is important to realize that conductance (and conductivity) values contain more information than simple ion concentrations. That is, the measured conductivity for a solution of 1 Molar HCl will be substantially different than for 1 Molar KCl. This fact arises because protons are much more mobile in solution than potassium ions. Such differences may be quantified by considering the parameter called the *mobility* (u) of an ion. The mobility is essentially that part of the conductivity that is independent of concentration. In an ideal case, the mobility of an ion " i " depends on the charge on the ion (z_i), its solvated radius (R_i), the viscosity of the solvent (η) and the elementary charge constant (e) according to (3):

$$u_i = \frac{|z_i| e}{6\pi\eta R_i} \quad \text{EQ4}$$

Conductivity and Concentration

The experimentally determined conductivity reflects contributions from all ions present in solution that are mobile and can support the current. Conductivity can be written in terms of the mobilities of all of the ions present (3):

$$\kappa = F \sum_i |z_i| u_i C_i = F \sum_i |z_i| \left(\frac{|z_i| e}{6\pi\eta R_i} \right) C_i$$

EQ5

where F is the Faraday constant (96,485 C/mol), and C_i is the concentration of ion " i " in mol/cm³. The significance of **EQ5** is that it shows that conductivity reflects the identity (charge and mobility) of all ions present in solution, as well as their concentrations. This is the principle that puts conductivity measurements in the realm of analytical chemistry, since there is a linear relationship between a measurable quantity (κ) and concentration.

Molar Conductivity

Since conductivity is concentration dependent, measured values for different solutions are not easy to compare directly. For this reason, a quantity called the *molar conductivity* (or sometimes *equivalent conductivity*) is used (2,3). The molar conductivity is symbolized by Λ , and it is defined as the solution conductivity (κ) normalized by the total ionic concentration (C):

$$\Lambda = \frac{\kappa}{C} \quad \text{EQ6}$$

In this context, total ionic concentration means "Molar concentration of positive charges" (or negative charges) in solution, expressed in units of mol/cm³.

Strong vs. Weak Electrolytes

In an ideal case, the molar conductivity experimentally determined for a compound would be the same,

regardless of the actual concentration of the solution used for the measurement. For example, although the values of κ for solutions prepared to be 0.1 Molar and 1.0 Molar in KCl would be different, Λ should be the same in each case, since κ has effectively been normalized for the difference in concentrations. In practice, however, most compounds that dissolve in water and undergo ionization behave differently in highly dilute solutions compared to even moderately concentrated solutions (3). Compounds that exhibit molar conductivities that do not change significantly with concentration are referred to as *strong electrolytes*, and include salts such as KCl. Other compounds such as acetic acid are nearly completely ionized at low concentrations, but are incompletely ionized at higher concentrations. This class of compounds is known as *weak electrolytes*. Experimental data (3) for KCl and acetic acid are plotted in **F1** to illustrate the severity of this effect.

Limiting Molar Conductivity

For comparison of conductivities of dissimilar compounds, the most useful quantity to consider is the *limiting molar conductivity*, Λ^0 . This parameter represents the molar conductivity for a compound that would hypothetically be measured in the limit of infinite dilution (i.e., the y-axis intercepts of plots like those in **F1**). In practice, such values are obtained by fitting experimental data to an equation known as *Kohlrausch's Law* (3):

$$\Lambda = \Lambda^0 - K\sqrt{C} \quad \text{EQ7}$$

The coefficient K depends primarily on the type of the electrolyte (e.g., 1:1 or MA, 2:1 or M₂A, etc.), rather than its specific chemical identity (3). In any event, experimental values of Λ have been carefully determined for many salts as a function of concentration in very dilute solutions, and the intercept values of the resulting plots obtained. In examining such data, it was discovered

T1

Limiting Molar Ionic Conductivities in Aqueous Solutions at 25°C

Data compiled from references 1, 2, 5, 6 and 9.

Cation	λ^0_+ (S-cm ² /mol)	Anion	λ^0_- (S-cm ² /mol)
H ⁺	349.6	OH ⁻	199.1
Li ⁺	38.7	F ⁻	55.4
Na ⁺	50.10	Cl ⁻	76.35
K ⁺	73.50	Br ⁻	78.1
Rb ⁺	77.8	I ⁻	76.8
Cs ⁺	77.2	NO ₂ ⁻	71.8
Ag ⁺	61.9	NO ₃ ⁻	71.46
NH ₄ ⁺	73.5	ClO ₃ ⁻	64.6
Ethylammonium	47.2	ClO ₄ ⁻	67.3
Diethylammonium	42.0	IO ₄ ⁻	54.5
Triethylammonium	34.3	HCO ₃ ⁻	44.5
Tetraethylammonium	32.6	H ₂ PO ₄ ⁻	57
Tetra- <i>n</i> -butylammonium	19.5	HSO ₃ ⁻	50
Dimethylammonium	51.8	HSO ₄ ⁻	50
Trimethylammonium	47.2	HC ₂ O ₄ ⁻	40.2
Tetramethylammonium	44.9	HCOO ⁻	54.6
Piperidinium	37.2	CH ₃ COO ⁻	40.9
		C ₆ H ₅ COO ⁻	32.4
Be ²⁺	90		
Mg ²⁺	106.0	CO ₃ ²⁻	138.6
Ca ²⁺	119.0	HPO ₄ ²⁻	66
Sr ²⁺	118.9	SO ₄ ²⁻	160.0
Ba ²⁺	127.2	C ₂ O ₄ ²⁻	148.2
Fe ²⁺	108.0		
Cu ²⁺	107.2	PO ₄ ³⁻	207
Zn ²⁺	105.6	Fe(CN) ₆ ³⁻	302.7
Pb ²⁺	142.0		
UO ₂ ²⁺	64	Fe(CN) ₆ ⁴⁻	442.0
Al ³⁺	183		
Fe ³⁺	204		
La ³⁺	209.1		
Ce ³⁺	209.4		

that Λ^0 for any electrolyte can be expressed as the sum of independent contributions from the constituent cations and anions present. This fact is now known as *Kohlrausch's Law of the Independent Migration of Ions* (3):

$$\Lambda^0 = \nu_+ \lambda^0_+ + \nu_- \lambda^0_-$$

EQ8

In **EQ8**, ν_+ and ν_- represent stoichiometric coefficients for the cation and anion in the electrolyte, respectively. For example, for K₄Fe(CN)₆, $\nu_+ = 4$ and $\nu_- = 1$, since there are 4 K⁺ ions present for each Fe(CN)₆⁴⁻ ion present in solution.

Limiting Ionic Molar Conductivities

Next, we must consider the meaning of the quantities denoted by λ^0_+ and λ^0_- in **EQ8**. These quantities are known as *limiting ionic molar conductivities*, since they represent the contributions to the total solution conductivity made per mole of each ion present in a dilute solution. It is these λ^0 values that are tabulated in reference books such as the CRC Handbook of Chemistry and Physics (4) and text books (2,3). Values for a few common ions are shown in **T1**. The data presented are for a temperature of 25 °C, and are limiting ionic *molar* conductivities, as opposed to the limiting ionic *equivalent* conductivities reported elsewhere (3). The molar and equivalent values are interconvertible through the stoichiometric coefficient ν defined above. (IUPAC has recommended discontinuation of the use of *equivalent* quantities.) Note that reference 4 tabulates data for a limited number of ions determined for a variety of other temperatures. Alternatively, a temperature coefficient (5):

$$\alpha = \frac{1}{\lambda^0_i} \left(\frac{d\lambda^0_i}{dT} \right) \cong 0.02 \text{ deg}^{-1}$$

EQ9

is customarily assumed (1) for all ions except H⁺ (0.0139 deg⁻¹) and OH⁻ (0.018 deg⁻¹). When λ^0_i at 25 °C and α are known, the value of λ^0_i at some other temperature, T , can be estimated by (5):

$$\lambda^0_{i,T} = \lambda^0_{i,25^\circ\text{C}} [1 + \alpha(T - 25^\circ\text{C})]$$

EQ10

Reference 6 includes data for many of the same ions listed in **T1** when dissolved in non-aqueous solvents.

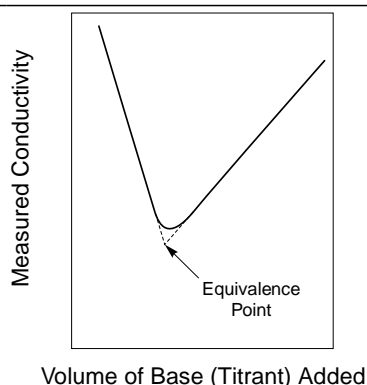
Examples of Use of Tabulated Values

To end this section, we present a few sample calculations to illustrate the use of data in **T1**.

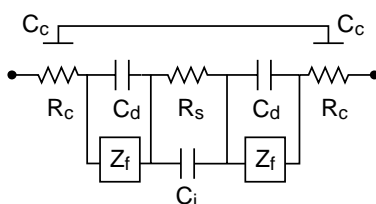
Λ^0 for Acetic Acid. We can calculate the limiting molar conductivity of a solution of acetic acid by

F2

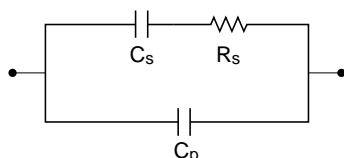
Example of a conductometric titration curve for the titration of a strong acid with a strong base. (Adapted from reference 1.)

**F3**

General equivalent circuit for a two-electrode conductance cell. (Redrawn from reference 8.)

**F4**

Simplified equivalent circuit for a two-electrode conductance cell. (Adapted from reference 8.)



using **EQ8** and data from the table. Both the cation ("H⁺") and anion (CH₃COO⁻) are singly charged; thus, $\nu_+ = \nu_- = 1$. From **T1**, $\lambda_+^0 = 349.6$ S-cm²/mol and $\lambda_-^0 = 40.9$ S-cm²/mol. Therefore, $\Lambda^0 = (349.6 + 40.9) = 390.5$ S-cm²/mol. It is interesting to compare this calculated value to the data plotted in **F1**. For milliMolar (or greater) concentrations of acetic acid, the *experimental* value of Λ^0 is less than 30 S-cm²/mol. This indicates that acetic acid is incompletely ionized under these solution conditions; i.e., it is a weak acid.

Λ^0 for KCl. Better agreement between the calculated limiting and measured values for Λ^0 could be expected in the case of the strong electrolyte KCl. Again using **EQ8** as above, we calculate Λ^0 to be 149.85 S-cm²/mol. The experimental data in **F1** are within about 10% to 13% agreement with the calculated value for dilute solutions.

Λ^0 for Ferric Oxalate. Fe₂(C₂O₄)₃ is an example of a 2:3 electrolyte. In this case,

$$\Lambda^0 = \nu_+ \lambda_+^0 + \nu_- \lambda_-^0 \\ (2 \times 204) + (3 \times 148.2) = \\ 852.6 \text{ S-cm}^2/\text{mole}$$

Comparison of Λ^0 for KOH, HCl and KCl. Last, we can compare values of Λ^0 for three electrolytes of interest in acid/base titrations. Calculated values for these 3 compounds are: 272.6 S-cm²/mol (KOH), 425.95 S-cm²/mol (HCl) and 149.85 S-cm²/mol (KCl). Now consider how the measured conductivity will change during the course of a titration in which HCl is the analyte and KOH is the titrant. Initially, the measured conductivity will have a relatively high value (undoubtedly not 425.95 S-cm²/mol in any real-life example, but "high" nonetheless). As KOH titrant is added, the conductivity decreases, since HCl is converted to KCl and water. At the equivalence point in the titration, all of the HCl has been neutralized to form KCl, and the conductivity will be at its lowest value. As KOH is added after reaching the equivalence point, the conductivity will begin to rise again, since KCl and unreacted KOH are both ionized in solution. The shape of the titration curve obtained is shown in **F2**. Examples of curves for other types of titrations are given in reference 1.

Conductance Measurements: Theory

The section above dealt with the chemical aspects of conductance and conductivity. In this section, we will examine the theory of conductance measurements from an electrochemical perspective.

A General Equivalent Circuit of a Conductance Cell

Most conductance measurements are made using two electrodes of the same geometric surface area. These electrodes are positioned parallel to and facing one another, separated by a gap of fixed dimensions. For this common configuration, the equivalent circuit drawn in **F3** applies (7,8).

In **F3**, the capacitance and resistance of the cell connectors and the contacts they make are shown as C_c and R_c , respectively. The double-layer capacitances of the two electrodes (C_d) are assumed to be equal, since the electrodes are constructed to have identical microscopic surface areas. The resistance of the solution between the two electrodes is symbolized by R_s . An interelectrode capacitance term, C_i , is included to account for the dielectric properties (9) of the bulk solvent (outside the diffuse layer). Last, a frequency-dependent Faradaic impedance, Z_f , which includes both charge-transfer resistance and Warburg impedance, is shown for each electrode.

A Simplified Equivalent Circuit

By making low impedance connections to the cell it is usually valid to ignore the influence of C_c and R_c . (However, for very low solution resistances, R_c may become important, since it is in series with R_s .) The complications imposed by the Faradaic impedance are minimized through experimental design. As we will see below, conductance measurements are often made by imposing a potential excursion (pulse or sinusoid) and measuring the resulting current. By using short pulse widths or high frequencies, the branch of the circuit containing Z_f can be neglected (Z_f varies as the reciprocal square-root of frequency, (3)). Therefore, the circuit shown in **F3** can be simplified to the three-component model drawn in **F4**.

In **F4**, R_s signifies the solution resistance, and the C_s and C_p denote combined series and parallel capacitances, respectively. Occasionally, other treatments of the above problem omit C_p and use a single resistor and capacitor in series. While valid for a range of experimental conditions, this assumption tends to break down for large solution resistances or when high frequencies are used in a.c. measurements (8,9).

Interrogation Waveforms

The experimental challenge in conductance measurements is to apply a waveform to a conductance cell represented by the circuit in **F4** and to accurately measure the response. The response must then be interpreted in order to separate the information due to capacitive elements from the solution resistance (i.e., the reciprocal conductance). The interrogation waveform used may involve an applied current (galvanostatic methods) or an applied potential (potentiostatic methods). Each of these broad categories may be further subdivided into frequency domain (a.c.) and time domain (pulse) experiments. Readers interested in frequency domain potentiostatic techniques should refer to a paper by Bott on a.c. impedance experiments (10) and to the information on the BAS-Zahner IM6/6e instruments available on our website (11). Controlled current techniques are discussed in several texts (3,9) and in the patent literature (12). BAS offers three instruments with galvanostatic capabilities: the IM6 (11), the IM6e (11) and the LG-50 (13). The remainder of this paper will focus on the theory of time domain potentiostatic techniques. The experimental implementation of these techniques for determining conductivity will be addressed in Part 2 of this paper, as will a planned series of BAS products named *ep-silon*[™].

Single-Pulse Measurements

When a potential pulse is applied to a conductance cell, the equivalent circuit drawn in **F4** can be simplified to a single capacitor (C_s) and a single resistor (R_s) placed in series for millisecond time scales (and longer). In this case, the applied potential (E) drops across the two circuit elements according to (3):

$$E_{app} = E_c + E_R = \frac{Q}{C_s} + iR_s \quad \text{EQ11}$$

where Q is the charge that accumulates on the capacitor, and i is the cell current. Since i is the time rate-of-change of charge (Q'), the above equation can be rewritten as:

$$Q' + \left(\frac{1}{R_s C_s}\right)Q = \frac{E}{R_s} \quad \text{EQ12}$$

The above ordinary differential equation can be solved by the method of Laplace transforms (14). The transform of **EQ12** is given by:

$$s\bar{Q}(s) - Q(0) + \left(\frac{1}{R_s C_s}\right)\bar{Q}(s) = \frac{1}{s} \left(\frac{E}{R_s}\right) \quad \text{EQ13}$$

In **EQ13**, s is the Laplace variable (not conductance!). A boundary condition for this experiment is that the charge accumulated on capacitor $C_s = 0$ until the potential is applied; i.e., $Q(0) = 0$. Making this substitution into **EQ13** and rearranging gives:

$$\bar{Q}(s) = \frac{\frac{E}{R_s}}{s \left(s + \frac{1}{R_s C_s}\right)} \quad \text{EQ14}$$

Taking the inverse Laplace transform ($s \rightarrow t$) of **EQ14** yields:

$$Q(t) = (EC_s) \left[1 - e^{-\left(\frac{t}{R_s C_s}\right)} \right] \quad \text{EQ15}$$

Thus, the magnitude of the charge that has accumulated at a given time, $Q(t)$, is given by **EQ15**. The corresponding current observed at any point in the circuit can be obtained by differentiating **EQ15** with respect to t :

$$i = \frac{dQ}{dt} = \left(\frac{E}{R_s}\right) e^{-\left(\frac{t}{R_s C_s}\right)} \quad \text{EQ16}$$

The above equation is identical in form to equation (1.2.6) in reference 3. However, C_s in **EQ16** is a function of the capacitances of both electrodes in the conductance cell, rather than the double-layer capacitance at a single (working) electrode.

That is, C_s equals $\frac{1}{2}C_{dl}$ if the two electrodes are perfectly matched in microscopic area (capacitances). In any case, **EQ16** can be linearized by taking the natural logarithm of both sides of the equation:

$$\ln(i) = \ln\left(\frac{E}{R_s}\right) - \left[\frac{t}{R_s C_s}\right] \quad \text{EQ17}$$

The solution conductance (S) can be obtained from the y-intercept of a plot of $\ln(i)$ vs. t :

$$\ln(i) = \ln(ES) - \left(\frac{S}{C_s}\right)t \quad \text{EQ18}$$

The advantage of the single-pulse technique is its simplicity. The disadvantage is that linearity in **EQ18** will only be obtained when the conductance cell can accurately be represented by an equivalent circuit with only two components (R_s and C_s) connected in series. As mentioned above, this assumption breaks down when the solution resistance is large and/or data are acquired at short times (high frequencies).

Bipolar Pulse Methods

A more robust approach is provided by the technique called bipolar pulse conductance (7-9). In this experiment, a potential pulse of magnitude $+E$ is applied for a period t_1 , followed by a pulse of opposite polarity, $-E$, for a period t_2 . There are two constraints placed on the pulse widths. First, t_1 should be sufficiently short such that no greater than 1% charging of the series capacitance (C_s) shown in **F4** occurs. Second, t_1 and t_2 should differ in duration by no more than 1% (i.e., they should be "identical"). No assumptions need to be made about the absence of a parallel capacitance in this case.

A single current measurement is made at time t_2 , when the current represents solely the resistive component of the cell impedance. That is, immediately after application of the first pulse, any parallel capacitance present charges quite rapidly.

The series capacitance also charges, but at a slower rate due to the impedance to charge flow imposed by the solution resistance. At time = t_1 a pulse of opposite polarity is imposed (total potential excursion = $2E$), and the parallel capacitance discharges. The series capacitance (which is only charged to about 1% of its capacity) also discharges. At time = t_2 , both capacitances are fully discharged, and the instantaneous current (i_2) is indicative only of R_s . The conductance is then determined in a straightforward manner (15) from the current at time = t_2 and the magnitude of the potential pulse, $|E|$:

$$S = \frac{i_2}{|E|}$$

EQ19

If t_1 and t_2 can be matched to 1% or better, and if the voltage dropped across the series capacitance does not exceed 1% of the applied voltage at t_1 , the conductance can be measured to within 0.01% of its value (9). In order to satisfy the latter constraint, pulse widths of no more than 10 ms are ordinarily allowable.

A Look Ahead

In Part 2 of this series, I will examine the experimental aspects of conductance measurements. In particular, I will discuss single and bipolar pulse experiments. Finally, a few representative applications of conductance measurements will be summarized.

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