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Electrolytic Conductance Measurements and Capacitive Balance

Reliable and meaningful measurements of electrolytic conductance require attention to design of cells, electrodes, and measuring circuitry.

Extraction of an Ohmic resistance from ac bridge measurements is a non-trivial procedure that requires a realistic model for the equivalent electrical circuit of a conductance cell. This entails an understanding of the electrochemical processes occurring when current is passed through a system consisting of electrolyte, electrodes, and bridge (*1*). However, electrode processes are seldom dealt with in the undergraduate chemistry curriculum—almost never in connection with conductance measurements. Furthermore, the principles of conductance measurements are unevenly covered in many standard physical chemistry textbooks, reference books, and laboratory manuals. For example, an aspect often dealt with either incompletely or erroneously is the physicochemical basis for capacitive balance and frequency dependence in conductance measurements with alternating current. Also, since the elements of bridge circuits and balance conditions tend to be compartmentalized into the physics curriculum, a unified treatment is rare.

Detailed consideration of all of electrochemistry undoubtedly is impossible in an undergraduate course, but there is no reason not to introduce some of the basic concepts in a qualitative manner; it is poor pedagogy to achieve simplicity by introducing erroneous concepts (it is not necessary, after all, to derive statistical mechanical equations for virial coefficients to discuss intermolecular forces in gases).

In this paper we review the principles of electrolytic conductance measurements, citing applications to molten salts and to solid electrolytes as well as to aqueous electrolytes. We discuss capacitive balance and the frequency dependence of ac measurements in the light of processes occurring in the bulk of the electrolyte and at the electrode surfaces in a conductance cell, as well as relevant properties of the Wheatstone bridge. Alternative methods of conductance measurement are pointed out, as are some aspects pertinent to the measurement of dielectric constant. The extent of coverage can easily be modified to suit the level of the course and the time available.

Phenomenology: Ohm's Law Applied to Electrolytes

Electrolytes conduct current by transport of ions, in contrast to electronic conductors or *n*-type semiconductors in which electrons are the charge carriers, or *p*-type semiconductors in which positive holes predominantly carry the current; both electronic and ionic conduction occur simultaneously in some substances (*2*). Since the mass of an ion is of the order of 10^4 times the electronic mass, quantum mechanical effects such as exchange, delocalization, and tunneling are much smaller for ions than for electrons. Electrolytic conduction often is accompanied by transfer of mass as well as charge across the electrode-electrolyte interface with the formation or discharge of ions at (usually metallic) electrodes. Massive ions, rather than delocalized electrons, drift through the bulk medium under the influence of an electric field, generally at velocities five orders of magnitude lower than electron velocities. These distinctions dictate differences in the methods of measurement. Thus the low inertia of electrons in a metal permits measurement of resistance with either direct or alternating current and ready demonstration of Ohm's law, $V = IR$. Extraction of an Ohmic resistance (reciprocal of conductance) for an electrolyte is more involved, since the variety of chemical as well as physical phenomena occurring at the electrodes must be separated from the voltage drop associated with the migration of ions through the bulk electrolyte (*3*). Although no physical principle requires the feasibility of extracting an Ohmic resistance, and, hence, conductivity of an electrolyte, it is experimentally possible to do so over an appreciable frequency range for a wide variety of electrolytes (*4*).

The conductivity (or specific conductance), κ, of a material may be thought of as the conductance (reciprocal of resistance) of a cube of 1 cm edge, assuming the current to be perpendicular to opposite faces of the cube. Since it depends partly on the number of charge carriers, a more useful indication of the nature of interactions of the constituents with the medium is the conductance per unit concentration of charge carrying constituent,[1] or equivalent conductance, $\Lambda = \kappa/c$; c is the concentration in equivalents per cm^3 (normality times 1000) (*4*). Combined with densities, molecular weights, and transference numbers (fractions of the current carried by the various constituents), the conductivity thus yields the relative velocities of the ionic constituents under the influence of an electric field.

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[1] The term *ionic constituent* refers to the ion-forming portion of an electrolyte, without specification of the extent of dissociation, association, solvation, etc. See, e.g., reference (*4*), p. 60. Thus the ionic constituents in an aqueous solution of CdI_2 are Cd^{2+} and I^-, regardless of the fact that the actual species in solution may include hydrated cadmium ions, anionic complexes such as CdI_4^{2-}, etc. Measurements of macroscopic properties yield information only on the *components* (CdI_2 and water) or the ionic constituents. Unusual values of these properties may *suggest* the microscopic nature of the species (e.g., ions). More detailed information on the nature of the *species* requires measurements sensitive to the species properties and distribution (e.g., spectra).

The *mobilities* (velocity per unit electric field, $cm^2\ sec^{-1}\ volt^{-1}$) vary with the nature of the constituents, their concentrations in mixtures, temperature, medium, and other factors. In dilute aqueous solutions of dissociated electrolytes, ionic mobilities vary little with concentration, and the equivalent conductance at vanishing electrolyte concentration may be expressed as the sum of independent equivalent conductances of the constituent ions. The limiting equivalent ionic conductance may be considered as the conductance of ions far removed from other ions so that solute-solute interactions are negligible. At finite concentrations, interionic forces generally lower the mobilities, and the concentration dependence of equivalent conductance has been a classical probe of the strength of ionic interactions (*1*). In dissociated solvents such as molten salts, the concept of independent ionic mobilities may be significant for dilute solute ions not common to the solvent, but not for solvent ions because of their mutual proximity. The equivalent conductance and (in mixtures) mobilities, and their temperature dependence, are important in testing theories of transport in liquids (*5*).

Some of the more important phenomena associated with the application of a voltage between electrodes immersed in a liquid electrolyte are indicated below, with reference to Figure 1, for an idealized system in which it is presumed possible to isolate the various phenomena.

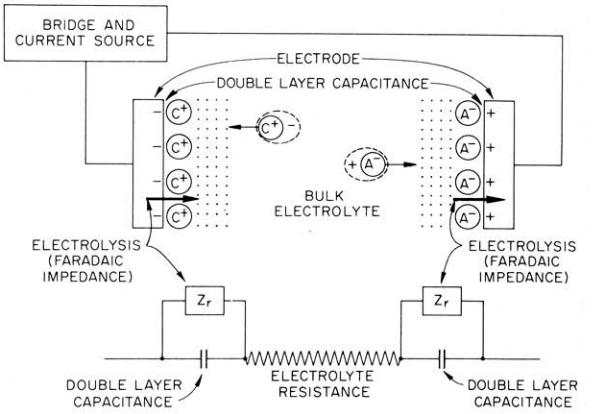

Figure 1. Electrolytic conductance cell—an oversimplified schematic representation of the double-layer at the electrodes, Faradaic processes, and migration of ions through bulk electrolyte.

Double-Layer Capacitance

A positively charged electrode will preferentially attract a layer of negative ions (and a negative electrode a layer of positive ions).[2] With increasing distance from a charged electrode, its orienting effect on ions in solution becomes rapidly more diffuse owing to thermal disordering (Brownian motion) (*6*). The double-layer, consisting of charges on the electrode and oppositely charged ions adjacent to it in solution (or separated from it by a layer of solvent molecules), constitutes an electrical capacitor, capable of storing charge. If a sufficiently low steady voltage is applied to the electrodes, virtually no current will flow beyond that required initially to charge the double-layer. The structure of the double-layer is considerably more complicated than the idealized version in Figure 1, and is greatly influenced also by the interactions of polar solvent molecules with the ions and with the electrode surfaces.

Electrolysis

As the voltage applied to the electrodes is increased, the charge accumulated in the double-layer increases until a decomposition voltage analogous to the breakdown voltage of a capacitor is exceeded;[3] current then flows across the electrode-solution interface, accompanied by oxidation at the positive electrode, reduction at the negative. This Faradaic (electrolytic) process partially short circuits the double-layer, behaving electrically somewhat like a resistor (although a voltage-dependent one) shunting a capacitor. Slow electron transfer processes at the electrodes may contribute a polarization resistance (*1*, *7*).

Ohmic Resistance

The current is carried though the bulk electrolyte by cations moving toward the cathode, anions toward the anode. Velocity-dependent retarding forces oppose the accelerating force of the electric field, and result in a constant drift velocity at a given field. Current flow is accompanied by dissipation of energy as heat, since the ions must overcome frictional forces in their motion through the medium, whereas the charging of the double-layer corresponds to storage rather than dissipation of electrical energy.

Concentration Polarization

On further increase of voltage, Faradaic removal of electroactive ions (i.e., ions reducible or oxidizable in the range of voltages applied to the electrodes) near the electrode may proceed faster than diffusion from the bulk electrolyte can replenish their supply. This can establish a concentration gradient between bulk electrolyte and the electrode surface, such that the current may reach a diffusion-limited value (*8*). The phenomenon of concentration polarization is exploited for analytical purposes in polarography (*9*).

Calculation of the Ohmic resistance of the electrolyte requires not only the (easily measured) current but also the voltage accelerating the ions—not the voltage applied at the electrodes. The latter voltage must also supply the driving force for the electrical work needed for the Faradaic processes, double-layer charging and concentration polarization. The problem of resolving electrolytic conductance (reciprocal of resistance) is that of eliminating the effects of the processes associated with the electrodes, and is generally accomplished by measurements with alternating current.

Alternating Current Effects

Reversal of the sign of the applied voltage reverses the direction of motion of the ions. With an alter-

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[2] Even without an external applied voltage, the surface of a metal immersed in an electrolyte will tend to become charged, owing to factors such as preferential adsorption of ions of one sign. Application of a voltage will modify the ionic distribution at the surface and the structure of the double-layer (*6*).

[3] In a real system it may not always be possible to separate exactly the double-layer and Faradaic processes (*3*). For example, the presence of traces of reducible or oxidizable species may permit current to flow at low voltages, before the double-layer is completely charged. The term decomposition voltage is used here in the phenomenological sense to indicate an experimentally observed voltage near which a reasonably sharp increase of current occurs whether the system be liquid, solid, or gaseous, single component or multicomponent. (See reference (*47*)).

nating (ac) rather than a steady (dc) voltage applied to the electrodes, the above processes reverse themselves with the period of the alternating voltage. But, having differing specific rates (or relaxation times), their relative contributions to energy dissipation vary with frequency. As the frequency is increased, concentration polarization can be greatly reduced or eliminated. The Faradaic effect can be eliminated in principle either by sufficiently reducing the applied voltage or by employing reversible (nonpolarizable) electrodes.

High-Frequency Effects

Although increased frequency of the applied voltage (to several thousand hertz) reduces many of the effects hindering accurate conductance measurements, indefinite increase of frequency leads to other problems. For example, the effects of stray capacitance in the measuring circuits increase. Also, the rearrangement of ions and solvent molecules in the vicinity of a moving ion may not be fast enough to keep up with the periodic reversal of the field. A moving ion will then essentially "see" a different environment than at a lower frequency. At frequencies comparable with the time required for an ion's oppositely charged ionic atmosphere to readjust to the reversal of motion of the ion, the conductivity increases because of the reduction of the dissymmetry of the ionic atmosphere. This is the Debye-Falkenhagen effect (*10*). The critical frequency is $\sim 10^7$ Hz, in a 0.001 M solution, and increases with increasing concentration. With still further increase of frequency, translational motion of the ions gradually ceases to respond to the rapid reversal of the electric field. Since dipole reorientation can still occur, dielectric properties of the material are measured; at still higher frequencies, e.g., optical, only electrons would respond to the oscillating electric field.

In spite of the necessity for sorting out many superimposed phenomena, conductance measurements have been developed to a very high art, primarily during the decades between 1920 and 1950, with precision of the order of 0.01% attainable (*1*). The techniques developed for dilute electrolytes were based to a considerable extent on the thorough investigations of Grinnell Jones and co-workers, who discussed Wheatstone bridge design (*11*), conductance cells and electrical leads (*12*), the electrode polarization resistance and its frequency dependence (*13*), the effect of high electric fields in increasing the conductance (the Wien effect) (*14*), and errors arising from the use of water rather than oil in constant temperature baths (*11*). It has become customary to adopt the *techniques* developed specifically for dilute aqueous electrolytes by Jones and co-workers even for studies of other media, e.g., molten salts, where modifications required for measurements of high accuracy follow from the *principles* enunciated by Jones (*15*).

Alternating Current Conductance Measurements: Equivalent Circuits

It should be recognized that, just as there are no perfect gases or ideal solutions, there are no perfect (i.e., frequency-independent) electrical components—pure resistances, pure capacitances, or pure inductances (*16*). Even if there were, it would not be possible to represent most electrochemical processes exactly in terms of such *linear* electrical components. Nevertheless, even an approximate representation facilitates analysis of electrochemical measurements in terms of ionic models (*1*). Electrical components representing electrochemical processes and stray current paths in a conductance cell are indicated schematically in the equivalent circuit in Figure 2 and are discussed below. Some of the high-frequency paths are primarily nuisances, to be eliminated when possible. The double-layer capacitance and Faradaic impedance, on the other hand, although difficult to evaluate, contain valuable information on surface properties and on rates of electrode processes.

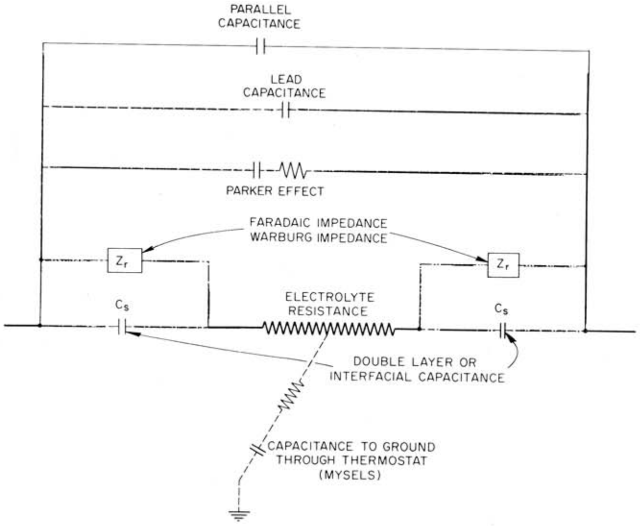

Figure 2. Electrical equivalent circuit of a conductance cell showing resistive and capacitive elements corresponding to circuit components and electrochemical processes.

Conductance Measurement

The evaluation of electrolytic conductivity generally is a comparative procedure. A conductance cell is calibrated by determining its *cell constant*, l/A, using a solution of known conductivity. l/A is the ratio of *effective* length and cross sectional area of the conducting path (rather than the geometric value). The conductivity, or specific conductance, is then calculated as $\kappa = (l/A)(1/R)$ where R is the measured resistance. The conductivity standards are aqueous KCl solutions measured by Jones and Bradshaw (*17*) and traceable back to the measured conductance of a mercury thread in a cell for which the geometric length and cross-sectional area give the cell constant. The Kohlrausch method employs a Wheatstone bridge, alternating current, and platinum electrodes which have been coated electrolytically with a deposit of platinum black to increase the surface area and reduce the polarization resistance (*18*). (In very dilute solutions, platinization may introduce errors through adsorption of solute.) The bridge circuit generally must contain not only resistance, but also capacitance (or inductance), to balance the capacitive effects in the conductance cell.

Capacitive Balance

A cursory examination of several widely used and highly regarded textbooks and laboratory manuals of physical chemistry reveals the following incomplete or inaccurate expositions of the origin of capacitive effects in the cell and the need for capacitance in the bridge

1. No discussion.
2. The capacitance is required simply to sharpen detection of the minimum in the imbalance potential but has no effect on the measured resistance.
3. The balancing capacitance is required to compensate the capacitance of a dielectric medium between the electrodes in parallel with the resistance of the electrolyte in the conductance cell.
4. The capacitance is required to balance stray capacitance in the bridge circuit components, connections, water bath, etc.

The third and fourth factors certainly introduce capacitance in the circuit, but the major capacitive contributions and source of frequency dependence under the usual conditions in conductance measurements arise from the electric double-layer at the electrode-electrolyte interface at applied voltages below the decomposition voltage,[3] and from the frequency-dependent resistance (impedance) associated with the Faradaic processes at voltages above the decomposition voltage.

Parallel Capacitance

The parallel capacitance of the medium between the electrodes is given by

$$C' = \frac{10^9 D}{4\pi c^2 (l/A)}$$

where D is the dielectric constant of the medium, c is the velocity of light (3×10^{10} cm/sec), and l/A is the cell constant (*19*). For a dilute aqueous electrolyte the dielectric constant may be taken as that of water, ~ 78. A cell constant of order 1 would thus yield a parallel capacitance of only $C' \cong 7$ picofarads. The corresponding magnitude of impedance (ac analog of resistance, i.e., ratio of voltage to current), $1/2\pi f C'$, is of the order of 2×10^7 ohms at 1000 Hz, in parallel with the electrolyte resistance, and therefore has little effect on measurements of electrolyte resistances below 10^4 ohms.

Series Capacitance: The Ideal Polarized Electrode

It has been pointed out above that the accumulation and dissipation of an excess of positive or negative ions at the electrode surfaces constitutes the charging and discharging of a condenser. This model of the electrolyte-electrode interface has been supported by extensive investigation, e.g., by Grahame (*20*) with mercury electrodes and highly purified electrolyte solutions. He showed that the current at dc voltages below the decomposition voltage is negligibly small (as expected for a "true" capacitor), and that with alternating current, the double-layer capacitance is essentially independent of frequency, behaving as a capacitance in *series*, not in *parallel*, with the solution resistance. An electrode such that no charge crosses the phase boundary when the potential is altered slightly is termed an ideal polarized electrode (*21*). It requires the absence of species capable of being oxidized or reduced at the voltage applied to the electrodes. Absence of frequency dependence of the capacitance indicates that the ionic distribution in the double-layer readjusts rapidly to changes of potential (at frequencies up to those corresponding to the Debye-Falkenhagen effect (*22*)).

Although electrodes in conductance cells generally do not satisfy all the criteria of the ideal polarized electrode, the model of a resistance in series with a capacitance appears to be a reasonable approximation. Thus extensive measurements with conductance cells have demonstrated that the series capacitance varies little with electrode separation but increases with increasing surface area (obtained by increased platinization of the electrodes) (*13*). An important physical implication of the series capacitance is that it derives from interactions at the electrode surfaces rather than from bulk effects, such as relaxation processes in the electrolyte, which would be manifested as a parallel capacitance (*23*).

The magnitude of the double-layer capacitance for many electrolyte-electrode systems including aqueous solutions and molten salts is of the order of 10–100 microfarads per cm^2 of electrode surface (*1, 13, 15*). This leads to a magnitude of impedance at 1000 Hz of the order of

$$\frac{1}{2\pi f C} = \frac{1}{6283C} \approx 1.6 - 16 \text{ ohms}$$

at a 1 cm^2 electrode. The impedance in series with the electrolyte decreases with increasing capacitance or increasing frequency, and a high double-layer capacitance greatly reduces errors in ac conductance measurements.

Hence for resistances of less than 10^4 ohms the model of a conductance cell as consisting of the electrolyte resistance in series with the double-layer capacitance, though not exact, is a more reasonable physical approximation than that of a parallel resistance-capacitance combination.

Faradaic Impedance

Conductance measurements are sometimes made with ac voltages as high as several volts, i.e., above the decomposition potential, and with electrodes platinized to reduce polarization (*13*). The use of such high voltages probably stems from the formerly low sensitivity of detectors, which is no longer a problem. At applied voltages above the decomposition voltage,[3] the double-layer capacity, C_s, in series with the electrolyte resistance, is shunted by an impedance, Z_r, associated with the transfer of charge through the electrolyte-electrode interface, as indicated in Figure 2. There is no simple representation of this Faradaic impedance in terms of frequency-independent resistances and capacitances. In conductance measurements, this impedance leads to high apparent values of the measured resistance, but decreases with increasing frequency. It is considered to have a resistive component attributed to a finite rate of electron transfer at the electrode surface (*7*). Warburg attributed the observed frequency dependence in conductance measurements to concentration polarization—the depletion of electroactive species at the electrode surface so that the current is limited by diffusion of such species to the electrode—resulting in an impedance proportional to the reciprocal of the square root of frequency, $\Delta R = k\,\omega^{-1/2}$ (*8, 13*). Linear extrapolation of measured resistances to infinite frequency by plotting against $\omega^{-1/2}$ eliminates this error. Grahame also found this form of frequency dependence for impedances associated with an electrochemical reaction, but under the restrictive assumption of vanishing sine wave amplitude, which limits its validity for conductance measurements (*20*). Many cases of frequency dependence other than $\omega^{-1/2}$ have been reported, however, and extrapolation to infinite frequency is best carried out with functions found empirically to be nearly linear unless a frequency independent range can be found (*24*).

The part of the polarization resistance resulting from electron transfer processes of finite rate is not eliminated by varying the frequency, and the extrapolated resistance then includes both the electrolyte resistance and a residual polarization resistance related to the specific rate of the electrochemical process (*7*, *13*). Detection and elimination of this source of error, which generally is only serious with very low electrolyte resistances, i.e., several ohms or less, would require measurements in cells with differing conductive path lengths, and hence electrolyte resistances, but with identical electrodes.

Parasitic Effects

High-frequency effects resulting from stray capacitances in leads, connections, and improper ground connections can be minimized by avoiding close placement of electrode leads and by the use of the Wagner ground (*1*, *16*). The "Parker effect" (Fig. 2) in high-resistance solutions may result when there is a resistive path through the electrolyte in series with, and capacitively coupled to, parallel (insulated) electrode leads passing through the solution; it can be eliminated with appropriate cell design (*12*, *25*).

Mysels *et al.* have analyzed an effect important with very high resistances, e.g., 10^5 ohms, resulting from capacitive coupling of the electrolyte in the conductance cell to ground through the high resistance in the cell and thermostat (*26*). This is difficult to avoid in measuring the conductance of solvent (necessary for obtaining electrolyte conductances in very dilute solutions). The effect leads to an apparent increase of resistance with increasing frequency, in contrast to the effects of polarization and capacitive shunts. The authors show that the anomalous excess resistance varies as the square of the frequency at low frequencies, and extrapolation to *zero* frequency is required to extract the Ohmic resistance.

Bridge Balance for Series or Parallel RC Circuits

At any one ac frequency it is possible to represent a resistance-capacitance combination in a "black box" equally well as a series or parallel combination, since ac measurements with sinusoidal applied voltages provide only an *absolute impedance* and a *phase shift*[4] (*16*, *27*). It is thus necessary to vary the frequency to distinguish between the two possibilities (or to use waveforms other than sinusoidal). Although many kinds of detectors may be used as null indicators for the Wheatstone bridge, an oscilloscope is recommended since it provides a visual display of both the phase shift and imbalance potential.

Balance of Pure Resistances

Figure 3 shows the circuit of a Wheatstone bridge and the conditions of bridge balance for the idealized case where all components are pure resistances. The unknown resistance is indicated by R_s, and R_B is a variable resistance for bringing the bridge to balance by adjusting the current, I, in the lower arm until the difference of potential between points C and D is zero. If the vertical deflection plates of an oscilloscope are used as the voltage null detector, and a sine-wave generator is connected to the horizontal plates, bridge imbalance is indicated by a sloping oscilloscope trace whose vertical projection is proportional to the voltage difference between C and D, and whose horizontal projection is proportional to the peak-to-peak voltage applied between A and B. A horizontal line indicates balance ($V_C - V_D = 0$, $R_s = R_B$), and this condition is independent of the frequency of the applied voltage. If the unknown resistance is a conductance cell, the oscilloscope trace generally is an ellipse rather than a straight line, because the cell is not a pure resistance. It is then impossible to bring the imbalance potential to zero at any frequency simply by adjusting R_B because the current is not in phase with the applied voltage. Introduction of a variable capacitance (or inductance) into the bridge permits compensation of the phase shift (time lag) and balance of the bridge.

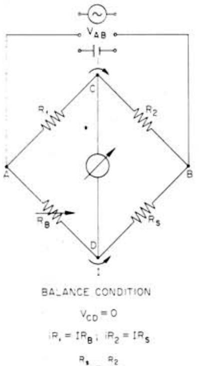

Figure 3. Balance conditions for a Wheatstone bridge with pure (frequency independent) resistances and either ac or dc voltage source.

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[4] The phase shift or time lag between current and voltage, caused by the capacitance follows from consideration of the application of a sinusoidal voltage, $V_0 \sin 2\pi ft = V_0 \sin \omega t$, across a capacitor, C. The charge stored by the capacitor at any instant is $q = CV$ and the current is $i = \mathrm{d}q/\mathrm{d}t = C\mathrm{d}V/\mathrm{d}t = \omega C\ V_0 \cos \omega t$. Hence the current leads the voltage by 90°, reaching its peak at $t = 0, 2\pi/\omega, \ldots$ while the voltage peak occurs at $t = \pi/\omega, 5\pi/2\omega \ldots$ For a series resistance-capacitance circuit (like that between points A and D in Fig. 4) the voltage drop v_c across the capacitor is the difference between the voltage v applied to the circuit and the iR drop through the resistor

$$V_C = V - iR$$

The current is given by the rate of change of charge of the capacitor

$$i = \frac{\mathrm{d}q}{\mathrm{d}t} = C\,\frac{\mathrm{d}(v - iR)}{\mathrm{d}t} = C\,\frac{\mathrm{d}v}{\mathrm{d}t} - RC\,\frac{\mathrm{d}i}{\mathrm{d}t}$$

$$RC\,\frac{\mathrm{d}i}{\mathrm{d}t} + i = C\,\frac{\mathrm{d}v}{\mathrm{d}t}$$

For sinusoidally varying voltage and current whose peak values are shifted in phase (displaced in time), the solutions are combinations of trigonometric functions. The algebra is much simpler if complex functions replace the trignometric functions, recalling that $e^{jx} = \cos x + j \sin x$, where $j = \sqrt{-1}$. Substituting $v = Ve^{j\omega t}$ and $i = Ie^{j\omega t}$ in the above differential equation, noting that V and I are independent of time but may be complex (e.g., $I = |I|e^{j\omega\tau'}$, $V = |V|\,e^{j\omega\tau''}$, $\omega\,(\tau' - \tau'')$ being the phase shift) yields

$$j\omega CRIe^{j\omega t} + \mathrm{I}e^{j\omega t} = j\omega CVe^{j\omega t}$$

$$(j\omega CR + 1)I = j\omega CV$$

$$V = I\,\frac{1 + j\omega CR}{j\omega C} = I\left(R + \frac{1}{j\omega C}\right)$$

$$= I\left(R - \frac{j}{\omega C}\right)$$

$$= IZ$$

$$|V| = |I|\,|Z| = |I|\,\sqrt{R^2 + \frac{1}{(\omega C)^2}}$$

$$= |I|\,R\,\sqrt{1 + 1/(\omega CR)^2}$$

Z is the total impedance, $|Z|$ its absolute value. $1/j\omega C$ is the capacitive reactance. See, e.g., reference (*28*).

Balance of Series RC Circuit

For cases where the conductance cell may be approximated as a series combination of a pure resistance and pure capacitance, the balance conditions for two bridge circuits are shown in Figure 4. (The resistances in the upper arms of the bridge have been set equal (R_1) to simplify the equations, but the equations can be derived similarly for unequal resistances.) The conditions are exact if the electrical components are those represented in Figure 4, i.e., if the cell is a true RC circuit. If it is not, the equivalent circuit must be known (or assumed) if a physically significant resistance is to be calculated from the resistance and capacitance readings of the balanced bridge (*1*).

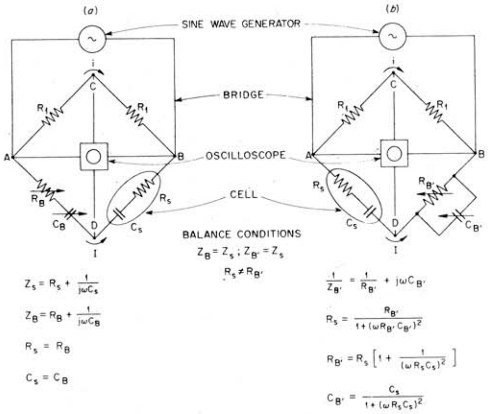

Figure 4. Balance conditions for a series RC circuit in bridges with series or parallel RC balancing arms.

The condition for zero potential difference between the vertical plates of the oscilloscope is, as in Figure 3, that the voltage drop between points A and C be equal to that between A and D; similarly, equality of the voltage drop from B to C and that from B to D is required. Now however, the phase shift, or lag between voltage and current peaks, resulting from the capacitance in the circuit, requires expression of the voltage drop in terms of the *impedance*, comprising a *reactive* component (here a capacitance) in addition to a *resistive* component.[5] The algebra describing the components of the impedance is handled most simply with complex notation (*27*, *28*). Thus the impedance of a series resistor and capacitor is the complex sum of impedances of the resistance, R, and of the capacitance, $1/j\omega C$, where $j = \sqrt{-1}$, and $\omega = 2\pi f$.

$$Z_{\text{Series}} = R + \left(\frac{1}{j\omega C}\right) = R + \frac{1}{j\omega C}\left(\frac{j}{j}\right) = R - j\left(\frac{1}{\omega C}\right)$$

Parallel impedances add like parallel resistances, but the complex notation must be retained, resulting in the equations for a parallel resistance-capacitance combination[6]

$$\frac{1}{Z_{\text{parallel}}} = \frac{1}{R} + \frac{1}{1/j\omega C} = \frac{1}{R} + j\omega C$$

$$= \frac{(1 + j\omega CR)}{R}$$

$$Z_{\text{parallel}} = \frac{R}{1 + j\omega CR} = \frac{R(1 - j\omega CR)}{1 + (\omega CR)^2}$$

$$= \frac{R}{1 + (\omega CR)^2} - j\,\frac{\omega CR^2}{1 + (\omega CR)^2}$$

Equating impedances at balance in Figure 4, it is seen that the balance condition for a series combination by another series combination (Fig. 4*a*) at any frequency is equality of both resistances and of both capacitances, since equality of two complex numbers requires equality of the real parts and of the imaginary parts independently. A similar result would obtain for balance of a parallel combination by another parallel combination. (It should be noted that complex numbers are not vectors, as is sometimes erroneously stated. Although they add vectorially, their products are not dot or cross products; i.e., $j^2 = -1$, not $+1$ or 0.)

In balancing a series RC combination with a parallel combination (Fig. 4*b*), however, the resistances in the two lower arms of the bridge (and the capacitances) will not be equal, and the balancing resistance (and capacity) will vary with frequency, i.e., show frequency dispersion. The balance conditions are those of the Wien bridge (a circuit formerly used to measure frequency with calibrated resistors and capacitors in the bridge circuit) (*16*). Thus the resistance reading on a parallel RC component bridge, when balancing a series RC circuit, will vary with frequency, and the true resistance must be calculated with the equations in Figure 4*b*. Often, in conductance measurements, this calculation is omitted. Rather it is assumed that $R_{B'} = R_s$, an approximation valid at small values of $\omega C_{B'}R_{B'}$ (or, correspondingly, at high values of $\omega R_s C_s$). The latter condition generally holds quite well for moderately dilute aqueous electrolytes under the usual conditions of measurement of resistances of the order of 10^3 ohms and greater. It is more difficult to attain for molten salts, owing to their much higher conductivities, unless capillary cells are used. Thus (Fig. 4)

$$R_{B'} = R_s\left[1 + \frac{1}{(\omega_s R_s C_s)^2}\right]$$

It may be seen that the factor in brackets differs little from unity for, say $R_s = 1000\Omega$, $f = 1000$ Hz, and $C_s = 100\ \mu$F (i.e., $1 + 3 \times 10^{-6}$), and the computation of R_s from $R_{B'}$

$$R_s = \frac{R_{B'}}{1 + (\omega C_{B'} R_{B'})^2}$$

is unnecessary. However for measurements in molten salts, with high conductivities, or in cells with low electrode capacitance, the term

$$\frac{1}{(\omega R_s C_s)^2} = (\omega R_{B'} C_{B'})^2$$

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[5] The balance conditions for Figures 4*a* and 4*b* are derived as follows

$$V_{AC} = V_{AD};\ iR_1 = IZ_B$$

$$V_{BC} = V_{BD};\ iR_1 = IZ_s$$

$$\therefore IZ_s = IZ_B;\ Z_s = Z_B$$

Similarly

$$Z_{B'} = Z_s$$

Also see footnote 4.

[6] These electrical equations are of analogous form to those for many mechanical, acoustic, or chemical systems in which the response to a sinusoidally varying perturbation is shifted in phase as a result of relaxation processes that can store (capacitive) or dissipate (resistive) energy (*48*, *49*).

may become quite large relative to unity, requiring the calculation of R_s from $R_{B'}$, $C_{B'}$ and ω (*7, 15, 29*). For a 10-ohm resistance, the error of assuming $R_s = R_{B'}$ would be 3%. The error $(R_{B'} - R_s)$ could exceed the value of R_s at still lower resistances, that might be observed in, e.g., crucible cells with small electrode separations. It may be convenient in some cases to eliminate the calculation by employing a bridge with a series RC balancing arm as in Figure 4*a*. The parallel combination is more frequently used because, as may be seen from the equations of Figure 4, the parallel capacitance required to compensate a series capacitance of 100 μF at 1000 Hz with a resistance $R_s = 1000\Omega$ is only $C_{B'} \cong 3 \times 10^{-4}\ \mu\text{F} = 300$ pF, and small capacitances can be obtained with higher accuracy and less frequency dependence than large ones.

With a conductance cell that is not a pure series RC combination, some frequency dependence of measured or calculated R_s still may be observed, and extrapolation to infinite frequency as a function of $\omega^{-1/2}$ or a more appropriate empirical function of frequency still may be required (*15, 24*). This extrapolation should not, however be based on an incorrect equivalent circuit of the cell. The fact that one does not know the exact equivalent circuit of the cell does not eliminate the necessity of a choice if a resistance is to be calculated from the measurable impedance and phase angle, and the series RC combination is the best approximation in many cases.

Application to Special Systems

Molten Salts

There has been increasing interest in molten salts, as models of ionic liquids including concentrated aqueous electrolytes (*30*), and for practical application in molten salt nuclear reactors (*31*), fuel cells (*32*), and metallurgical processes (*33*). Many molten salt electrochemical experiments are suitable for undergraduate laboratories (*34, 35*).

In molten salt conductance measurements the approximation $R_{B'} = R_s$ in Figure 4*b* frequently is not valid because of the low resistance, especially for corrosive melts which cannot be contained in capillary cells, but must be measured in crucible-type cells with low cell constants (*29*). Failure to make the appropriate calculation of R_s from $R_{B'}$ and $C_{B'}$ (or an erroneous correction resulting from flaws in the bridge) may lead to spurious frequency dispersion. Measurement with a series component bridge (Fig. 4*a*) has been employed to eliminate this error, and has yielded nearly frequency independent results at frequencies up to 20 khz, confirming the usefulness of the series RC representation of the conductance cell for molten salts (*15, 36*). Any bridge should of course be checked by measuring standard electrical components in the range of anticipated resistance and capacitance values. It would appear desirable to reduce the amplitude of the sinusoidal voltage below the decomposition potential,[3] if possible, to approach the frequency independent conditions at an ideal polarized electrode (*15*) and avoid electrolysis (*37*). Some very careful studies of molten zinc chloride by Bloom and Weeks, however, showed no frequency dispersion greater than 0.1–0.2% at frequencies between 0.5 and 100 khz and at voltages between 0.1 and 1.0 V (*38*). The polarization resistance can be further reduced by platinizing the electrodes (*13*), thereby increasing the surface area and reducing the current density.

Special Methods

Difficulties associated with frequency dispersion have encouraged attempts at other means of measuring conductance. King and Duke (*39*) measured dc conductance in molten alkali nitrates using silver electrodes in thin-walled glass compartments to sense the *iR* drop through the solution. Their cell contained four electrodes, two to carry current and two to measure the potential drop without carrying current. This method, however, requires reversible electrodes, frequently not available for systems of interest. A four-electrode ac potentiometric method also has been reported (*40*). One way to eliminate electrode polarization is to eliminate electrodes. Electrodeless conductance measurements have been accomplished by coupling a loop of electrolyte in an appropriate tube to a transformer circuit or a heterodyne circuit (*41*). These special methods, while useful in particular cases, lack the generality of the ac bridge method, and have not been widely adopted.

Solid Electrolytes

Interpretation of polarization effects at electrodes in solid ionic conductors is greatly simplified by recognizing the series representation of the resistance capacitance combination (*23*). Double-layer capacities in solid electrolytes are comparable to those of liquid electrolytes. A value of 200 μF/cm^2 has been reported for solid silver bromide.

Dielectric Constant

A realistic equivalent circuit must be employed also for the evaluation of dielectric constant from capacitance measurements in the presence of an ionic leakage current (*42*). Here it is the capacitance which is required; the parts of the impedance resulting from dissipation of energy, i.e., dielectric loss, inherent electrical conductivity, and impurity conduction, must be eliminated in order to obtain the part of the impedance associated with the storage of energy.

Summary

Conductance measurements are among the most accurate of the classical techniques available in physical chemistry, but attainment of high accuracy for systems of diverse properties requires an understanding of the electrochemical processes accompanying current flow through a conductance cell and its electrodes. Many commercial instruments operate at a fixed frequency and fixed voltage which make it difficult to assess possible errors associated with electrode polarization, bridge circuitry, parasitic effects, or unrealistic equivalent circuit. (The black box syndrome has been commented on also with regard to other areas of chemical instrumentation (*43*).)

With increasing interest in unusual materials and conditions (*5, 15, 44*), accompanied by the extension of conductance measurements to systems of very high (molten salts) or very low (solid electrolytes, organic solvents) conductance, it becomes necessary to modify standard techniques developed for aqueous electrolytes in accord with fundamental principles if serious error is to be avoided.

Conductance experiments in undergraduate laboratories, or as special projects, might well include studies of the effects of varying frequency, voltage, and electrode surfaces in various media. These could serve as an introduction to ideas on electrode processes important not only to conductance measurements, but to wide areas of physical chemistry (*45*) and electroanalytical chemistry (*46*, *47*).

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