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Gd analytical curve has been corrected for a residual Gd content of 0.1 ppm, as determined by the graphical extrapolation method (27).

Precision and Accuracy. The coefficient of variation for the line pairs listed in Table II was calculated for the repetitive preparation of a standard sample on five different days,

(27) T. E. Beukelman and S. S. Lord, Jr., *Appl. Spectros.*, **14**, 12 (1960).

and ranged from 10 to 15%, with the Gd determination the least precise.

The accuracy of the method could only be assessed by the method of known additions, the data for which are listed in Table V.

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Bipolar Pulse Technique for Fast Conductance Measurements

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The applications and limitations of several ac bridge techniques and models are analyzed, especially with respect to polarization, the parallel (C_p) and series (C_s) cell capacitances, and the frequency required. In the case of using a phase-angle voltmeter as a null detector, the ideal frequency is shown to be proportional to $(C_p C_x)^{-1/2}$. A new technique, which is fast (40 μ sec), accurate (0.01%), wide ranged (100 Ω –1 M Ω), and independent of C_p and C_x , has been developed to overcome some of the limitations of ac methods. This technique consists of applying consecutive constant voltage pulses of equal magnitude but opposite polarity to a standard conductance cell. The current/voltage ratio is measured at the end of the second pulse. Theoretical and actual errors are discussed. The rate of ethanolysis of acetyl chloride is studied and compared to results by others. An EDTA titration of Zn^{2+} in a highly buffered medium is followed conductometrically and an end-point change of approximately 40 μ mhos out of a total conductance of 40,000 μ mhos is recorded.

RECENTLY, there has been wide interest in systems where conventional conductance techniques cannot be used, or can be used only with great difficulty. These systems include those with very high resistance (such as much non-aqueous work), with very low resistance (such as work in molten salts), or where platinized electrodes cannot be used (if surface adsorption is a problem). Furthermore, traditional bridge techniques are not readily applicable to systems which require continuous or instantaneous conductance measurements (such as in following reactions, titrations, flow systems, or ion exchange). The conductance techniques which are used today are quite limited in applications since each was developed for a particular model of the conductance cell. The conductance measurement is valid only as long as the model truly represents the cell. The most appropriate model, in turn, depends on the experimental conditions used, especially the cell design, resistance range, and frequency. The purpose of this paper is to show the limits of applicability of some of the models and methods which are commonly used for the measurement of conductance, and then to demonstrate a completely new technique which is not only less restricted in application than the traditional methods, but is also extremely fast (40 μ sec/measurement) and accurate (0.01 %).

AC MODELS AND METHODS

In 1893, Kohlrausch (1) developed the ac bridge technique shown in Figure 1. In his model, C_p (parallel cell capacitance)

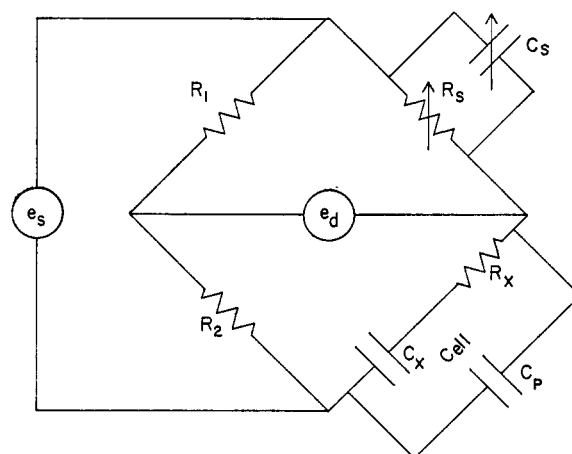


Figure 1. AC conductance bridge

Cell consists of C_x , R_x , and C_p

was not considered, and C_s was used only to obtain a null (not as a correction factor). This method is still the method most commonly used, as it works quite well on aqueous solutions whose resistance is between 200 Ω and 10 k Ω when platinized electrodes are used.

Jones and Josephs (2) extended this technique by using a modified Wagner ground to make meaningful measurements up to 60 k Ω . They demonstrated that for bridge balance, the reactance in any arm must be balanced in another arm, and that resistive balance occurs only if the phase angle between the current and voltage is the same in two adjacent pairs of arms of the bridge. They concluded that the Kohlrausch method was the best approximation to resistive balance. They discounted the method of Taylor and Acree (3) who used an inductor in series with the cell to compensate for C_x .

Adjusting C_s and R_s in Figure 1 until a null is obtained ideally causes an error of $(R_x C_x \omega)^{-2}$, where ω is the angular frequency ($2\pi f$). The equations for balance also require:

$$C_s = (R_x/R_s)[1 + (1 + K_x^2)C_p/C_x]C_x/K_x^2 \quad (1)$$

$$\text{or} \quad C_s R_s/R_x \approx C_p + C_x/K_x^2 \quad (2)$$

where

$$K_x = R_x C_x \omega.$$

Thus, knowing C_s and ω , it is possible to calculate the error term and compensate for it to obtain more accurate results.

- (2) G. Jones and R. Josephs, *J. Amer. Chem. Soc.*, **50**, 1049 (1928);
(3) W. Taylor and S. Acree, *ibid.*, **38**, 2403 (1916).

(1) F. Kohlrausch, *Wied. Ann.*, **69**, 249 (1893).

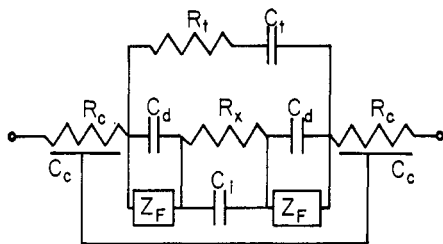


Figure 2. Complex equivalent circuit of conductance cell

Definition of symbols	Simplified circuit (Figure 1)
R_x solution resistance	remains the same
C_d double layer capacitance	forms C_x
Z_F Faradaic impedance	\gg impedance of C_d
R_c contact and lead resistance	reduced to zero
C_c contact and lead capacitance	} combine to form C_p
C_i inter-electrode capacitance	
C_t filling tube capacitance	} combine to form C_p
R_t filling tube resistance	
	low or non-existent

It is obvious from Equation 2 that two frequencies must be used in order to calculate both C_p and C_x , which would be necessary for highly accurate results. Usually C_p is ignored, which can lead to substantial errors for high R_x and/or high frequency. In any case, the frequency used should be high enough so that the correction term is very small, but not so high that C_p carries significant current. Whenever C_p carries substantial current, the balancing of its reactance becomes very tedious (if not totally impractical) since C_s must then be adjusted precisely in the pF rather than μ F capacitance range.

Jones and Bollinger (4) were first to realize that a conductance cell has a parallel capacitance associated with it. Their model consisted of a series resistance (R_t) and capacitance (C_t) across a cell of pure resistance (R_x). They were working with a capillary cell which had large filling tubes (the source of R_t and C_t), and by its nature, a large K_x , so that C_x can be ignored. They used R_t and C_t to explain the Parker effect which other authors (5-7) reported as a changing cell constant with increasing resistance. Their solution to this problem was to design the cell in such a way that close proximity of parts of opposite polarity is avoided.

When working with solutions of low resistance, one must be concerned not only with C_x and R_x , but also with the lead and contact resistance, R_c , and the Faradaic impedance, Z_F , if there is any possibility for a reaction taking place. A complete conductance cell can be represented by the equivalent circuit shown in Figure 2. Z_F consists of several terms, including a frequency dependent Warburg impedance (8) which varies inversely as the square root of the frequency. Winterhager and Werner (9) have used a high frequency (50 kHz) bridge to eliminate the importance of Z_F since at high frequency, the admittance of C_d is infinite with respect to that of Z_F . No technique has been used to compensate for Z_F : the experimental conditions are adjusted to minimize its effects (high frequency, low e_s , etc.). Feates, Ives, and Pryor (10) have devised a method to eliminate the effects of lead and contact resistance by using a special switching arrangement in their bridge. Probably the best method to date for the

measurement on low resistance solutions which have low C_d is that recently developed by Robbins and Braunstein (11). They use a specially designed bridge with a series (instead of parallel) R_s and C_s , and have obtained an accuracy of better than 0.5% ($R_x \approx 100 \Omega$).

All of the methods so far have ignored either C_p or C_x or both. Wershaw and Goldberg (12) used the equivalent circuit shown in Figure 1 for the cell model and devised a very ingenious technique using an inductive divider bridge to obtain very precise measurements of conductance changes. They have a variable capacitor in each of two bridge arms which is varied to balance the reactance of C_p or C_x . The frequency must be varied to ensure that each cell capacitance is balanced precisely. The main disadvantage of this method is the length of time required for a measurement (R_s and two capacitors must be balanced and the frequency varied). Strong support for the simple model is indicated as they were able to achieve resistive balance sensitive to 0.2 part per million.

One of the main problems of the ac bridge techniques, the tedious capacitance balancing, has been greatly reduced with the introduction of the phase-angle voltmeter to respond only to that portion of the difference signal which is in phase with the signal source. Klaus Schmidt (13) has shown that this technique can be used with a fair amount of success without C_s in the bridge circuit, leaving only R_s to be varied until the "in phase" signal is zero (a phase difference of 90° between e_d and e_s). The equations for the bridge can be solved, and for a 90° phase difference,

$$K_x^2(C_p/C_x)^2 + K_x^2\{(C_p/C_x)^2 + 2(C_p/C_x) - Q[1 + (1 + Q)R_2/R_1]\} - (1 + Q)^2R_2/R_1 = 0 \quad (3)$$

where $Q = R_x R_1 / R_s R_2 - 1$ = relative deviation from resistive balance.

At high frequencies, C_x acts as a nearly perfect shunt, so that the only error is the positive conductance deviation caused by the shunting capability of C_p . At low frequencies, C_p carries insignificant current and the only error is the negative deviation due to the impedance of C_x . Thus, to be within a desired error limit, $\pm Q_{\max}$, the frequency should be adjusted so that:

$$[Q_{\max}(1 + R_1/R_2)]^{-1/2}/(2\pi R_x C_x) < f < [Q_{\max}(1 + R_2/R_1)]^{1/2}/(2\pi R_s C_p R_2/R_1) \quad (4)$$

There is a frequency at which the two deviations exactly cancel ($Q = 0$), and at this frequency, true resistive balance occurs.

$$f_{\text{exact}} = [(1 + R_2/R_1)^{1/2} - 1]/[2\pi(R_2/R_1)(C_p C_x)^{1/2} R_s] \quad (5)$$

If C_p and C_x can be determined for a given cell with a given solvent, the square root of their product should be quite constant (1 to 2 orders of magnitude), regardless of the electrolyte present. The ideal frequency can then be calculated from R_s and R_2/R_1 using Equation 5. It should be noted that the frequency can normally be varied over 2 to 3 orders of magnitude (according to Equation 4) and not cause an intolerable ($<0.01\%$) error. It should also be noted that normally there is more room on the high side of f_{exact} than on the low side.

Thus, a phase-angle voltmeter can be used as a null detector in a conductance bridge network with the only capaci-

- (4) G. Jones and G. Bollinger, *J. Amer. Chem. Soc.*, **53**, 411 (1931).
- (5) H. Parker, *ibid.*, **45**, 1366, 2017 (1923).
- (6) M. Randall and G. Scott, *ibid.*, **49**, 636 (1927).
- (7) F. Smith, *ibid.*, p 2167.
- (8) H. Warburg, *Wied. Ann. Physik.*, **67**, 493 (1899).
- (9) H. Winterhager and L. Werner, *Forschungsber. Wirtschafts*, No. 341 (1956).
- (10) F. Feates, D. Ives, and J. Pryor, *J. Electrochem. Soc.*, **103**, 580 (1956).

- (11) G. D. Robbins and J. Braunstein, *J. Electrochem. Soc.*, **116**, 1218 (1969).
- (12) R. Wershaw and M. Goldberg, *ANAL. CHEM.*, **37**, 1180 (1965).
- (13) K. Schmidt, *Rev. Sci. Instr.*, **47**, 671 (1966).

tance balance being a rough frequency adjustment, which can be easily estimated. While this method is considerably faster than the other ac methods, it is still relatively slow. Because of the time required to make the necessary balance adjustments, none of the bridge techniques is conveniently applicable to timed measurements or measurements of continuously varying conductance. In most cases, some estimate of C_p and C_x must be made, and the frequency adjusted accordingly. If high frequencies are used, R_1 and R_2 can no longer be considered pure resistances, so that an additional error may be involved. Also, since the ac signal is applied continuously, heating of the solution will occur and temperature control may be a problem.

Thus, ac bridge techniques can be used accurately if, and only if, one carefully considers the accuracy required, the cell capacitances, the resistance range, the magnitude and frequency of the signal source, the power dissipation in the cell, and the null detector characteristics, and then designs his apparatus, cell, and experiment accordingly.

A NEW TECHNIQUE

The bipolar pulse technique involves the application of two successive constant voltage pulses of equal magnitude but opposite polarity to the conductance cell, and the measurement of the current passing through the cell at the end of the second pulse. Since the pulses can be as short as 20 μ sec, the effect on C_d and Z_F is the same as using a very high frequency, since C_d develops very little polarization. Assuming the lead and contact resistance can be reduced to a vanishingly small value, C_e and C_i (because of small polarization) will experience the same potential. Assuming the pulse width is much greater than $R_x C_i$, C_i may be considered in parallel with C_i and C_e , giving a total parallel capacitance of C_p . Thus, ignoring only R_e , when using the bipolar pulse technique, the cell can be accurately represented by the simplified equivalent circuit shown in Figure 3. The sequence of events in the measurement is described qualitatively as follows.

At the beginning of the first pulse, C_p will charge quickly causing a spike in the cell current. If $t_1 \ll R_x C_x$, the voltage, e_c , developed across C_x will be small and increase approximately linearly with time. Thus, the current flowing through R_x and C_x will drop slightly during t_1 due to the charging of C_x . When the polarity is reversed at the start of t_2 , C_p will again charge quickly to the new potential. The current through R_x and C_x will be enhanced by the potential, e_c , accumulated during t_1 . However, during t_2 , C_x will discharge the same number of coulombs that it charged during t_1 . This causes a decrease in current until, at the end of t_2 , the entire voltage drop across the cell is due to the voltage across R_x , since C_x is completely discharged. At the end of t_2 , $e_c = 0$ and no current is flowing through C_p since it is at constant potential. Therefore, the instantaneous current through the cell at the end of t_2 is simply $i = e_2/R_x$. Thus, the instantaneous current measured at this time is directly proportional to the conductance and independent of C_x and C_p .

THEORETICAL ERROR ANALYSIS

At this point it is fruitful to examine the circuit and measurement sequence more closely to get an idea of the theoretical error limits and the instrumental tolerances required. At the end of t_1 ,

$$(e_c)_1 = e_1[1 - \exp(-t_1/R_x C_x)] \quad (6)$$

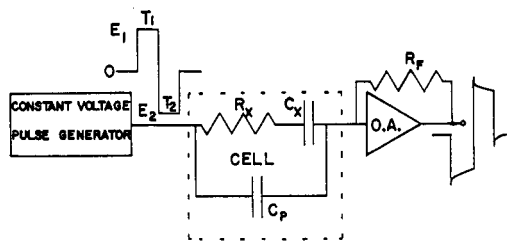


Figure 3. Bipolar pulse conductance device

and at the end of t_2 ,

$$(e_c)_2 = e_2[1 - \exp(-t_2/R_x C_x)] + e_1 \exp(-t_2/R_x C_x)[1 - \exp(-t_1/R_x C_x)] \quad (7)$$

Since the measured conductance is:

$$G = [e_2 - (e_c)_2]/R_x \quad (8)$$

and the conductance should be:

$$G_o = e_2/R_x \quad (9)$$

The relative error due to polarization is:

$$Q = (G - G_o)/G_o = -(e_c)_2/e_2 \quad (10)$$

A series of expansion of the exponentials in Equation 7 gives the following expression for Q in terms of dimensionless parameters:

$$Q = b(a - 1) - b^2[a(d + 2) - 1]/2 + b^3[a(d^2 + 3d + 3) - 1]/6 - \dots \quad (11)$$

where $a = -e_1 t_1 / e_2 t_2 \approx 1$ ($a = 1$ for truly complementary pulses)

$$b = t_2 / R_x C_x$$

and $d = t_1 / t_2 \approx 1$

If $a = 1$ and $d = 1$, then $Q \approx -b^2$. Even for the unfavorable case of $R_x = 200 \Omega$, $C_x = 10 \mu F$, and $t_2 = 20 \mu$ sec, $Q \approx -10^{-4}$ or -0.01% .

If in this example, there is a 1% deviation from having complementary pulses, i.e., $a = 1 \pm 0.01$,

$$Q \approx 10^{-4}(\pm 0.01) - 10^{-4}[3(1 \pm 0.01) - 1]/2$$

or $Q \approx -1.5 \times 10^{-6}$ if $a = 1.01$

and $Q \approx -1.99 \times 10^{-4}$ if $a = 0.99$

If, in addition, t_1 and t_2 differ by 10%, i.e., $d = 1 \pm 0.1$,

$$Q_{\max} \approx -10^{-4} - 10^{-4}[3.1 \times 0.99 - 1]/2 \approx -2.03 \times 10^{-4}$$

If C_x or R_x is increased, the resulting error is cut accordingly. For example, if $R_x = 2 \text{ k}\Omega$,

$$Q_{\max} \approx -10^{-5} - 10^{-6} \times 1.03 \approx -1.1 \times 10^{-5}$$

Theoretically, there is absolutely no dependence on C_p (as long as $C_p R_o < 5 t_2$, where R_o is the output impedance of the pulse generator) since at the end of the pulse, C_p has already charged to the constant voltage. Also, there is no theoretical limit on R_x if C_x and t_2 have appropriate values. Thus, if one can apply a complementary pulse pair matched to within 1%, and keep the time short enough so that the maximum double layer voltage, $(e_c)_1$ is less than 1% of the applied voltage, a measurement of the current at the end of the second pulse will give the conductance to within 0.02%, regardless of C_p and C_x .

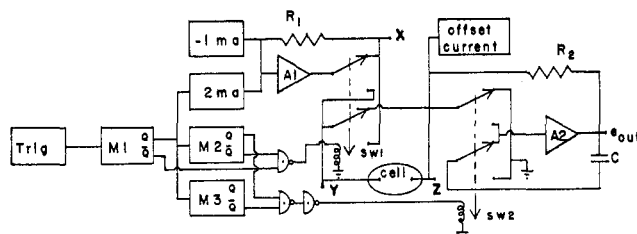


Figure 4. Bipolar pulse conductance instrument

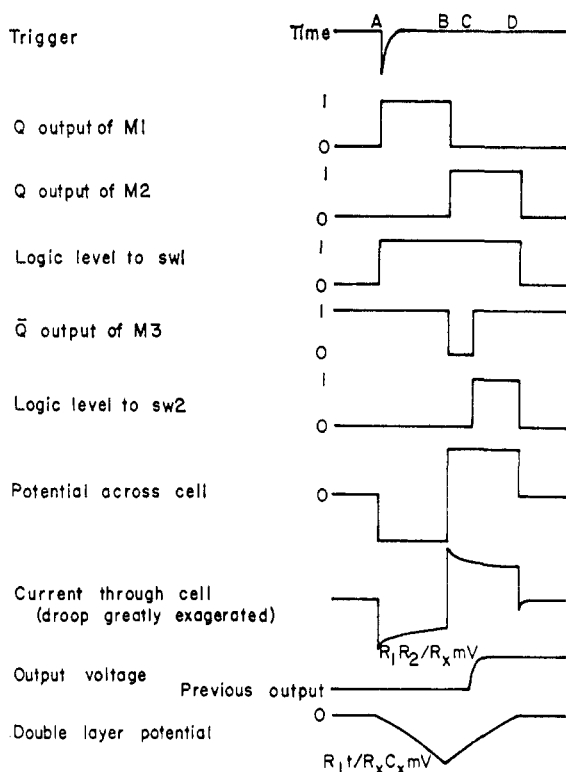


Figure 5. Timing sequence during measurement

EXPERIMENTAL

The Instrument. With these requirements in mind, the bipolar pulse conductance device shown in Figure 4 was built.

The time sequence of events is shown in Figure 5, with the important times labeled A, B, C, and D. Use Figures 4 and 5 along with the following explanation to understand the instrument functions during the measurement sequence.

TIME A. The trigger source can be the internal unijunction oscillator, line frequency *via* the unijunction, or some external trigger source. The repetition rate can be varied between 0.5–20,000 Hz, depending on the particular needs of the experiment. In any case, the trigger logic produces a negative-going pulse, which triggers monostable 1. M1 turns “on” the +2 mA going to A1, changing the voltage at point X from $+R_1 mV/\Omega$ to $-R_1 mV/\Omega$. M1 also causes sw1 to go “on” so that points X and Y are connected together. Point Z remains at ground (through sw2). A large instantaneous current flows as C_p is charged as fast as amplifier A1 can provide current. A voltage begins to develop across C_x as time progresses. The output voltage e_o is not affected as yet.

TIME B. M1 goes “off” (after 20, 200, or 2000 μ sec, depending on pulse width setting), triggering M2 and M3, and turning “off” the +2 mA going to A1 so that point X and point Y return to $+R_1 mV/\Omega$. Sw1 and sw2 remain in their previous states and the current that flows through C_p is again carried to ground through sw2.

TIME C. M3 goes “off,” turning sw2 “on,” putting A2 in the sampling mode. Point Z is connected to a virtual ground instead of ground, and A2 charges C to a new voltage, so that at time D, $e_o = -R_1 R_2 / R_x mV/\Omega$. It should be mentioned that M3 is used for the sole purpose of ensuring that C_p has been fully charged before A2 begins sampling (this prevents output spikes). This is especially necessary when both C_p and R_2 are large.

TIME D. M2 goes “off,” disconnecting point X from point Y as sw1 goes “off.” Also the cell leads are shorted together to equalize any slight polarization developed by the end of the second pulse. Sw2 also goes “off,” putting A2 in the holding mode and the output remains proportional to the current passing through the cell at the end of the second pulse (which has been shown to be e_2/R_x). Point Z is again connected to ground so that both sides of the conductance cell are at ground potential. This condition remains until the next trigger pulse starts another cycle.

It should be observed that the circuit was designed to minimize the effects of the switch resistances, since solid state analog switches had to be used. The constant potential of the pulses is not affected by the cell current since point Y is the controlled point, and the sampling accuracy is unaffected by switch resistances since point Z is controlled to be at virtual ground. In this prototype instrument, the switch resistance of sw2 can make the pulses noncomplementary, since

$$a = -(e_1 - R_{sw1}i_{cell})t_1/e_2t_2 \approx 1 + R_{sw}/R_x \text{ if } e_1t_1 = -e_2t_2 \quad (12)$$

This problem has been corrected and several other desirable features have been added in a new instrument which is currently being built.

Instrumental Tests. **LINEARITY OF e_o .** Using an ESI Potentiometric Voltmeter Bridge to measure the output voltage, e_o , and an ESI 0.01% decade resistance box for R_x , e_o was found to be within 1 mV (0.01% of full scale) of being exactly proportional to $1/R_x$. Thus, if absolute accuracy is needed, only one standardization (in each range) need be made by replacing the cell with a standard resistor, R_s . The absolute conductance would then be, $1/R_x = e_s/e_o R_s$, where e_s is e_o with R_x and e_s is e_o with R_s .

DEPENDENCE OF e_o ON C_p . C_p was varied between 0 and 1000 pF for resistances between 200 Ω and 10 M Ω . There was no observable dependence ($<0.004\%$) on the magnitude of e_o for any R_x and C_p combination. For very large R_x (≥ 1 M Ω), there was some scatter since C_p turned A2 into a high gain differentiator with 1 M Ω feedback resistor. For example, with $R_x = 1$ M Ω and $C_p = 1000$ pF, the relative scatter was 0.2%.

DEPENDENCE OF e_o ON C_x . A series combination of C_x (0.05–10 μ F) and R_x (1 k Ω –1 M Ω) was used as a dummy conductance cell. As expected from Equation 11, as R_x or C_x increased or as t_2 decreased, the error decreased. For a C_x of 10 μ F (which is much smaller than a real C_x would be), the error was under 0.01% for all $R_x > 1$ k Ω .

AC BRIDGE COMPARISON. The conductance of three solutions was measured using both this instrument and a modified Wien bridge (14). Below 10 k Ω the two methods agreed to better than 0.1%, but at 60 k Ω , the bridge could not be nulled and was about 2% high.

Instrument Tests on Chemical Systems. **REACTION RATE STUDIES.** The pseudo-first order reaction between ethanol and acetyl chloride was studied at three different temperatures. The ethanol was dried by the method of Lund and Bjerrum (15), and the acetyl chloride was used without further purification. Approximately 3 μ l of acetyl chloride was injected into 125 ml of ethanol for each experiment. Several experiments were run in the same solution, using the current

(14) H. Thompson and M. Rogers, *Rev. Sci. Instr.*, **27**, 1079 (1956).
(15) H. Lund and J. Bjerrum, *Ber. B64*, 210 (1931).

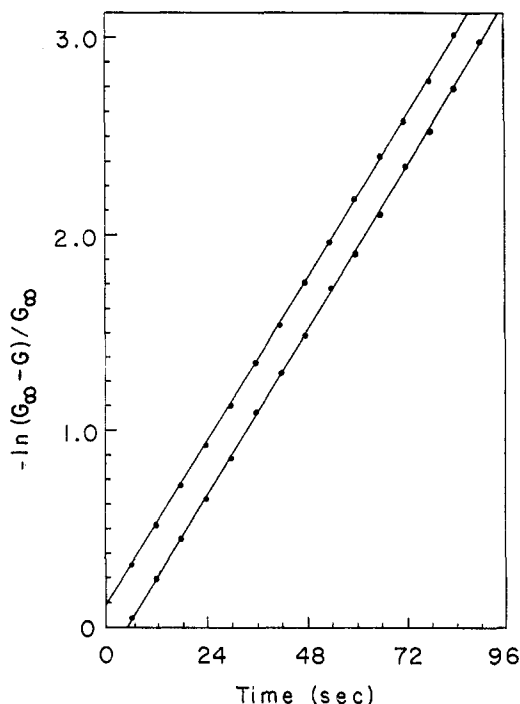


Figure 6. Reaction rate studies—acetyl chloride and ethanol

Consecutive reactions at 6.40 °C

Table I. Reaction Rate Studies—Acetyl Chloride and Ethanol

Temperature, °C	$K \text{ (sec}^{-1}) \pm \text{std dev}$	No. of runs
4.74	0.0306 ± 0.0002	7
6.40	0.0346 ± 0.0002	5
15.01	0.0700 ± 0.0007	15

offset to keep the same sensitivity, and no significant deviation was found between runs. The conductance change was measured using a Heath Universal Digital Instrument (UDI) in the digital voltmeter mode (0.1-sec aperture), with a period of 1,500 sec between measurements. Every fourth measurement was manually recorded (with another UDI keeping track of counts) so that a data point was obtained every six seconds. The rate constants were obtained using a three parameter least squares curve-fit computer program. The results are given in Table I.

Typical plots of $\ln(G_\infty - G)/G_\infty$ vs. time are shown in Figure 6. The standard scatter for a typical experiment is less than 0.1%. The data obtained agree very well with that obtained by Eurato and Leimu (16) by a rather complicated fast quenching titrimetric method. Their data and the data obtained conductometrically by us are shown in the Arrhenius plot in Figure 7.

It should be mentioned that the reactions were considered to take place at constant temperature although this is not strictly true. The temperature of the bath was constant, but the heat of reaction, and to some extent the original higher temperature of the acetyl chloride, caused the temperature to increase by about 0.01 °C during the reaction. A temperature profile is shown in Figure 8 for a 5 to 6 times greater concentration of acetyl chloride than was used to determine the reaction rate. These data were obtained by using the bipolar pulse conductance instrument to measure

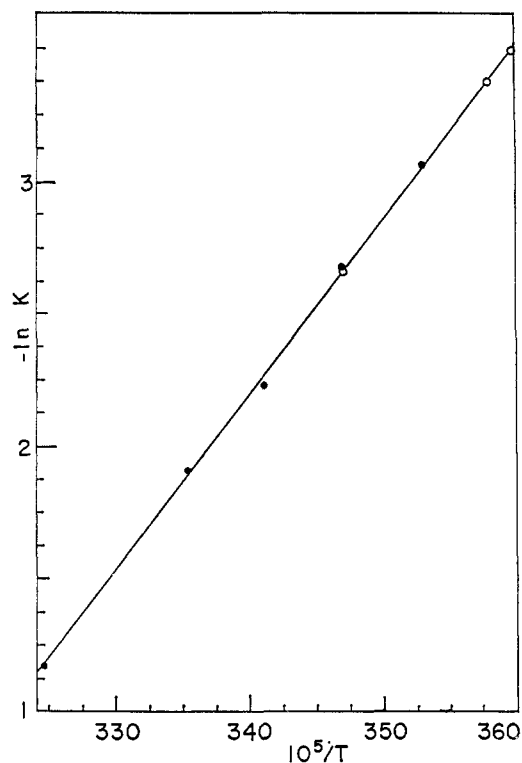


Figure 7. Temperature dependence of reaction rate

Circles obtained conductometrically, dots by another method

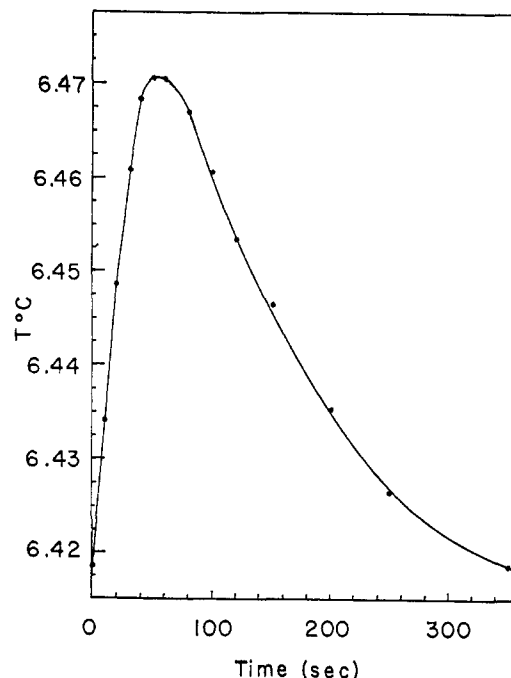


Figure 8. Temperature profile

18 μ l acetyl chloride into 125 ml ethanol at 6.42 °C

the conductance of a calibrated thermistor in place of the conductance cell. This instrument permits a rapid, accurate measurement of temperature with extremely little solution heating.

The half-lives of these reactions were between 10–20 seconds. Much faster reactions could be studied if appropriate readout and recording were used. Reactions with half-lives of less than 1 msec could easily be followed using

(16) E. Eurato and R. Leimu, *Acta Chem. Scand.*, **20**, 2029 (1966).

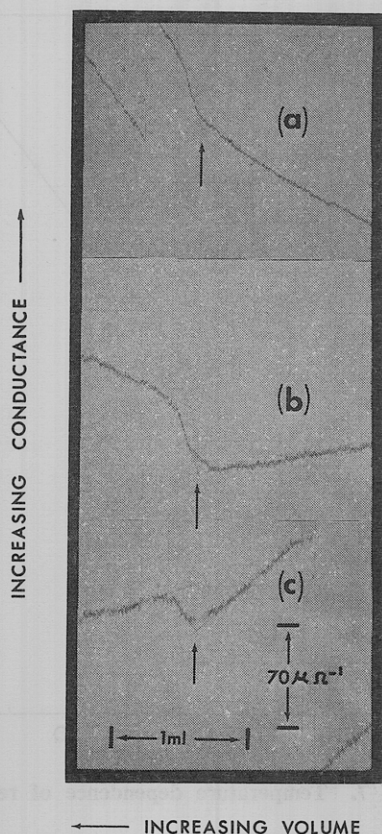


Figure 9. Conductometric EDTA titration of zinc

- (a) 10 ml buffer ($0.0281 \Omega^{-1}$)
 (b) 15 ml buffer ($0.0377 \Omega^{-1}$)
 (c) 20 ml buffer ($0.0476 \Omega^{-1}$)

Full scale = $175 \mu\Omega^{-1}$. Arrows indicate end point. Sharp breaks due to changing offset current

stopped-flow or other techniques. Since the output is proportional to concentration, the results are very easy to manipulate.

CONDUCTOMETRIC EDTA TITRATION OF ZINC. Known volumes of $0.04M$ $Zn(NO_3)_2$ and pH 10 buffer ($0.55M$ NH_3 and $0.10M$ NH_4Cl) were pipetted into a beaker and diluted to 125 ml. The resulting solution was titrated with a $0.1007M$ EDTA solution using a Sargent Automatic Burette (10 ml). The conductance cell consisted of two unplatinized platinum disks, 1 cm in diameter and 1 cm apart. The solution resistance varied between 21 and 35 ohms depending on initial concentrations of zinc and buffer, and the change at the end point was only about 0.02 ohm (0.1% of total). This is truly a worst case situation since the conductance instrument was not designed to operate below 200 ohms! The noise level was under 0.01% of the total conductance, even at this very high conductivity. The change in conductance was recorded on a strip chart recorder at 5 in./min with a full scale sensitivity of $175 \mu\text{mhos}$ (about 0.5% of the total conductance). The offset current source was used to "buck out" about 99.5% of the total cell current.

Typical end points are shown in Figure 9 for 10 ml of the zinc solution and varying amounts of buffer. Notice that this is not a typical conductance titration curve in that there are actually two breaks near the end point. The first break is taken as the end point for the following reasons:

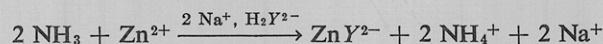
The first break is proportional to the amount of zinc added (whereas the second break is not); there is a sharp conductance increase which levels off to a more moderate increase even when no zinc solution is added (only 15 ml of pH 10 buffer); and the first break agrees within 0.2% with an Eriochrome Black T titration on the same system.

While it is not the purpose of this paper to go into a detailed study of equilibria, a few observations of the behavior near the end point should be mentioned. The pH is constant to within 0.001 pH unit throughout the titration, as recorded using a Heath expanded scale pH meter/recorder. It is not a slow, rate controlled process, but rather an equilibrium situation. The same type of end-point behavior is obtained when calcium is used instead of zinc. The difference between the initial and final slopes is inversely proportional to the buffer concentration. The difference between the initial and intermediate (between breaks 1 and 2) slopes is independent of both the zinc and buffer concentrations. This slope is:

$$3.2 \pm 0.2 \text{ ver div/hor div} \times 5 \text{ hor div/ml} \times$$

$$17.5 \mu\text{mhos/ver div} = 270 \mu\text{mhos/ml of EDTA}$$

Assume that the conductance is proportional to the total normality, then, $G = K \cdot N$ where K is a constant. Before the end point, the reaction is:



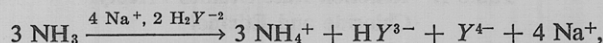
yielding an increase in ions of 0.4 meq/ml of EDTA. In the case of 15 ml of buffer, the conductance is practically constant before the end point, thus the increase in ions is almost exactly offset by the dilution with titrant. Thus, in this case,

$$N = 0.4 \text{ meq/ml,}$$

and

$$K = \frac{0.0377 \Omega^{-1}}{0.4 \text{ meq/ml}} = 0.1 \Omega^{-1} \text{ ml meq}^{-1}.$$

After the end point, the reaction (at pH 10) is:



yielding an increase of 0.7 meq/ml of EDTA. Of this, 0.4 meq/ml is needed to offset dilution and the remaining 0.3 meq/ml is used to increase the conductance of the entire solution. Thus, the slope after the end point should be:

$$\frac{0.3 \text{ meq/ml EDTA}}{129 \text{ ml}} \times 0.1 \text{ ml } \Omega^{-1} = 230 \mu\text{mhos/ml EDTA}$$

which is very nearly the experimental result.

These data tend to point toward the formation of a complex between EDTA and NH_4^+ after the EDTA concentration is built up following the end point.

The end point is easily detectable, even though it must be continuously recorded rather than obtained by making a few measurements and drawing intersecting lines.

The result of seven runs with different volumes of zinc and buffer solutions is:

$$2.132 \pm 0.003 \text{ inches/ml of } Zn^{2+}$$

A volume reading of 6095 on the buret was found to be 42.31 inches of chart paper. The experiment was repeated using 10 ml of Zn^{2+} and 15 ml of pH 10 buffer and 5 drops of Eriochrome Black T indicator. The result of four such titrations is:

$$\text{reading} = 3106 \pm 4$$

$$\text{blank} = 0029$$

$$\text{volume} = 3077 \pm 4$$

To correlate the results:

$$\frac{3077 \pm 4}{10 \text{ ml}} \times \frac{42.31 \text{ in.}}{6095} = 2.136 \pm 0.003 \text{ in./ml}$$

Thus, there is very good agreement between the two methods. Obviously since this method is capable of precisely

following very small changes in even highly conducting solutions, it opens the door to conductometric analysis in other systems (such as redox reactions and ion exchange monitoring) where it has previously been impossible or very impractical to make conductance measurements.

DISCUSSION

We have just shown two of the many possible applications for this conductance instrument. This instrument can be used anywhere that a conductance bridge apparatus can be used, including the accurate determination of equivalent conductance or cell constants. The absolute accuracy is limited to the accuracy of a reference resistor used for standardization, and the accuracy of the voltage measuring device. The precision and noise level is less than 0.002% over most of the resistance range (200 Ω –1 M Ω). With the present instrument, a precise measurement can be made every 50 μ sec if necessary,

and that value held with a drift of only 0.1% of full scale/sec. With a repetition rate of at least 100 Hz, a continuous analog output can be obtained. This method causes very little solution heating, as the power output is very low (0.2 μ watt/Hz maximum); thus, constant temperature is easy to obtain. And, most important, there is no capacitance balancing involved as this method is completely independent of the parallel cell capacitance and almost entirely independent of the double layer capacitance. Thus, this method should prove very useful for fast, accurate conductance measurements under a wide variety of experimental conditions.

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Direct Spectrophotometric Simultaneous Determination of Nitrite and Nitrate in the Ultraviolet

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The ratio of absorbance of aqueous sodium nitrite at 355 m μ to that at 302 m μ is 2.50 ± 0.02 . As nitrate does not absorb at 355 m μ but has a characteristic band at 302 m μ , absorbance due to nitrate can be calculated by dividing nitrate absorbance at 355 m μ by 2.50 and subtracting the quotient from total absorbance at 302 m μ . In 1-cm cells the lower detection limit for nitrite is 0.02 mg/ml and for nitrate, 0.09 mg/ml. Below pH 5, nitrite forms nitrous acid, with an absorbance maximum at 357 m μ which is twice as sensitive to concentration as the 355 m μ nitrite peak. Effects of heat, time, and reagents at various concentration levels are tabulated. Molar absorptivity of nitrite at 355 m μ is 23.3 ± 0.8 ; at 302, 9.12. At 302 m μ nitrate has a molar absorptivity of 7.24 ± 0.04 .

NITRITE AND NITRATE have been determined simultaneously in the ultraviolet by three methods. Hamaguchi, Kuroda, and Endo (1) resolved a simple two-component system of nitrite and nitrate at a pH greater than 5 by using two sets of standard curves of absorbance vs. concentration at their characteristic wavelength maximums. They found that at a pH less than 5, the characteristic peak of nitrite disappears and unique peaks of nitrous acid begin to develop. They did an interference study with hydrogen ion concentration and various salts. Recovery of nitrite and nitrate was good, and they were able to resolve interference due to aluminum by making the solutions basic. Meerman (2) found that nitrite in a mixture could be determined directly at 353 m μ ; after reducing the nitrite with sulfamic acid, the nitrate could be determined at 302 m μ . If the nitrite concentration was less than half the concentration of the nitrate, the step involving sulfamic acid was not necessary. Haddad and MacDonald (3) resolved a mixture of nitrite and nitrate in 4.9M potassium hydroxide, using a constant ratio of

3.37 ± 0.03 of molar absorptivities at 356 and 301 m μ for nitrite. They also found that the molar absorptivity of nitrate at 301 m μ and nitrite at 356 m μ decreased with increasing potassium hydroxide concentration. The value of ϵ for nitrite at 301 m μ increased with increased KOH concentration. They found ϵ for KNO₂ at 356 m μ to be 21.0 ± 0.3 and at 301 m μ , 6.17 ± 0.10 ; that for KNO₃ was 6.13 ± 0.35 . Vandenberg *et al.* (4) determined the molar absorptivity of KNO₃ to be 7.064.

The method of the present paper is based on the observation that the ratio of absorbance of aqueous sodium nitrite at 355 m μ to that at 302 m μ is constant at 2.50. Nitrate does not absorb at 355 but has a characteristic band at 302. This technique is more applicable to computer calculation than the methods of Hamaguchi and Meerman. A study was made of the effects of acids, bases, salts, reducing agents, and heat.

EXPERIMENTAL

Apparatus. A Cary 14 spectrophotometer with 1-cm quartz cells was used.

Reagents. Dilute nitric acid was prepared from concentrated, reagent grade nitric acid. Reagent grade sodium nitrite and sodium nitrate were used in preparing aqueous nitrite and nitrate solutions of different concentrations. Other concentrated acids, bases, and salts of various kinds were also of the highest quality available.

Procedure. The spectrum was scanned from 400 m μ downward at $\times 10$ speed to 290 m μ on solutions of nitrite and nitrate having absorbances between 0.1 and 1. Mixtures of nitrite and nitrate were also scanned in the same absorbance range. An interference study was conducted by making dilutions in the presence of various acids, bases, salts, and reductants in a concentration range from 10^{-4} to 1.0M. In each case the interference study was done with nitrite and nitrate by themselves and in mixtures, at the concentration of $2.14 \times 10^{-2}M$ sodium nitrite and $6.90 \times 10^{-2}M$ sodium nitrate. These concentrations were chosen to give an absorbance of 0.5 in 1.0-cm cells. These concentrations were obtained by diluting a 15.00-ml aliquot of a 0.357M sodium

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