132. *The Accurate Measurement of Electrolytic Conductance in Ionic Melts.*

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A capillary cell is described for the measurement of a.c. conductance in molten-salt electrolytes at frequencies up to 100 kc./sec. and temperatures up to 1000°. The cell is constructed from transparent vitreous silica and has a cell constant of about 1000 cm.$^{-1}$. During measurements, the temperature along the capillary is kept steady and uniform to within $\pm 0{\cdot}1°$. The resistance and capacitance of the cell are measured with accuracies of $\pm 0{\cdot}05\%$ and $\pm 0{\cdot}1$—$0{\cdot}5\%$, respectively.

The performance of the equipment is reported for M-aqueous potassium chloride and molten potassium bromide. Resistance and capacitance show dispersion with frequency. The form of the dispersion is not adequately explained by Faradaic polarization, so that the usual extrapolation cannot be used to obtain the true resistance of the melt. Cell constants are independent of frequency, but except at the highest frequencies the values obtained by calibration are subject to dispersion errors. At 10—100 kc./sec. accurate data are obtained on the conductance of the melt.

The specific conductance of molten potassium bromide at 100 kc./sec. is given for a temperature t in the range 760—980° by $\kappa = -1{\cdot}327_1 + 5{\cdot}710_0 \times 10^{-3}t - 2{\cdot}313_9 \times 10^{-6}t^2$ (int. ohm)$^{-1}$ cm.$^{-1}$ (standard deviation $0{\cdot}002_2$). The results for κ and the curvature $d^2\kappa/dt^2$ differ substantially from those of Yaffe and Van Artsdalen. The poor agreement in published conductance data on melts is attributed to the lack of a suitable correction for dispersion. The difficulty is avoided in the technique now described.

Electrolytic conductivity and its temperature-dependence are important in the determination of the constitution of liquid electrolytes. It is usual, nowadays, to employ capillary cells in molten salts and other ionic melts, in view of the relatively high conductance in such liquids (typically, 1—10 ohm^{-1} cm.$^{-1}$). A problem in the design is the choice of suitable insulating material for working into complex shapes, which is also resistant to chemical attack by the corrosive melts.

To obtain very accurate measurements it is also necessary to eliminate effects such as polarization which cause dispersion of the cell resistance with frequency. This is usually attempted by making resistance measurements at a series of frequencies in the audio range, and extrapolating the results to infinite frequency with the aid of a dispersion formula. Extrapolation methods have also been used to correct for dispersion introduced by stray admittances in the cell connexions. Besides leading to confusion, these methods are of doubtful validity, and there are serious discrepancies in the conductance data of different investigators. It is shown in this Paper that provided special precautions are taken against stray reactive current paths the above uncertainties may be avoided by working at high frequencies.

EXPERIMENTAL

In the present apparatus, strays are avoided by the use of shielding in the measuring bridge as well as in the cell. The principle used is that of the guard circuit, in which a screen held at earth potential is interposed between the leads from the cell to the bridge. This ensures that outside the bridge there is only one path for the current, through the cell.

The Cell.—Transparent vitreous silica has been found to be satisfactory in chloride and bromide melts up to 1000°. The cell (Fig. 1) consists of a silica supporting tube, 50 cm. long, 8 mm. in outside diameter, 6 mm. in bore, fused to a capillary, 4 cm. long, 4 mm. in outside diameter, 0·8 mm. in bore. The capillary and its supporting tube are enclosed in another silica tube, of 10 mm. bore, which is sealed to the tip of the capillary. A tubular guard sheath of nickel foil, 0·002 in. thick, is inserted into the gap between the tubes. To ensure complete screening of the capillary, its external orifice is expanded into a bell and the outer tube is fused to the mouth of the bell. The guard sheath, which does not make contact with the melt, is pushed in until it reaches the seal.

The inner cell electrode is a piece of platinum foil, 0·5 cm. × 1 cm. × 0·1 mm., attached to a lead of 20 SWG platinum wire. The foil is inserted in the supporting tube so that it lies immediately opposite the internal capillary orifice. The outer electrode is a thimble of platinum foil, 1·5 cm. long. It is fitted over the end of the sheathed capillary. Connexion is made to this electrode by a lead of 20 SWG platinum wire outside the capillary assembly. Both electrodes are platinized in the usual way,[1] and are afterwards fired at about 1000° to convert the coating into platinum grey. Perforations in the thimble allow the melt to enter the capillary, while excluding any particles of solid impurity which might block it. Cell constants vary from 800 to 1200 cm.$^{-1}$ owing to slight differences in the lengths and bores of the capillaries selected. The air capacitance of the cell is about 10^{-4} p*F*.

The cell is connected to the bridge with a cable having two coaxial mesh screens and a multi-strand centre conductor. The three conductors are mutually insulated. Since the cell is lowered into a furnace during measurements on melts, it is necessary to use a long cable (6 ft.) to avoid heating the measuring equipment. The outer screen of the cable, which is earthed, is connected to the lead from the outer cell electrode. The inner screen, or guard, is connected to the guard sheath of the cell. The centre conductor of the cable is connected to the inner cell electrode. All these connexions are made with crocodile clips. A sliding metal sleeve with an insulating lining is used to provide continuity in the guard.

FIG. 1. Capillary cell and coaxial connector.

The Container for Melts.—The melt is contained in a transparent vitreous-silica test tube, 10 cm. long and 2·5 cm. in internal diameter. This forms the lining of a tube of pyrolytic carbon of the same length, and with a wall thickness of 1 mm. These tubes are held in a container consisting of a silica tube, 50 cm. long and of 31 mm. internal diameter. A B40 silica cone is fused to the top, and the container is closed with a bell fashioned from a B40 tapered socket. The bell is provided with orifices through which the cell and the thermo-couple are lowered into the melt. A slow stream of dry, oxygen-free nitrogen is admitted through a side-arm to blanket the anhydrous melt.

The cell is filled by immersion. As a precaution against blockage by gas bubbles, the melt is drawn past the inner electrode by means of a rubber suction bulb before the cable is joined to the cell leads. This operation is repeated at intervals during measurements to test the reproducibility of the cell resistance.

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[1] James, " Practical Physical Chemistry," Churchill, London, 1961.

The Furnace.—An electrical resistance furnace is used to heat the melt. This is of the pot type, with a cylindrical chamber, 2 ft. long, $2\frac{1}{4}$ in. in diameter. There are three coiled-coil windings of 21 SWG Kanthal A1 resistance wire, wound on a vitreous-silica former. Power from the mains is supplied independently to each winding through Variac transformers. Voltage fluctuations in the supply are compensated by an automatic motor-driven stabilizing transformer.

A lining of Inconel helps to give a smooth temperature distribution in the chamber. The lining is protected from corrosion by admitting a slow stream of nitrogen at the bottom of the furnace. Induction of current of mains frequency in the guard screen of the conductance cell is prevented by earthing the lining.

Heat insulation is provided by asbestos-fibre composition, 8 in. thick. The time lag between temperature changes in the laboratory and in the melt is considerable. Conductances are measured when the temperature in the melt is constant and uniform within ±0·1° along the outside of the capillary. In these conditions the uniformity inside is likely to be even greater. As the temperature coefficient of conductance in ionic melts is about 0·1% per degree, the uncertainty in temperature corresponds to an error of ±0·01% in conductance. This is less than the bridge error.

Calibration of Cells.—For calibration, cells are immersed in M-potassium chloride, controlled at ~25° in a water-bath. With the guarded capillary cell, measurements are entirely free from the effects of stray currents described by Jones and Josephs.[2] The temperature of the solution is read on a micro-Beckmann thermometer, calibrated within ±0·005° at a point close to 25°. Changes of ±0·002° are detectable on this thermometer, and during calibration the temperature of the solution is constant within these limits. The potassium chloride is weighed in air and the solutions are allowed to equilibrate with the atmosphere of the laboratory before the cell resistance is recorded. Although the solutions are saturated with atmospheric carbon dioxide, this does not affect calibration at the present level of accuracy. No drift in cell resistance is observed with time.

The results of Jones and Prendergast [3] for the conductance of M-potassium chloride are used to five significant figures. Since the temperature of the solution is known within ±0·005°, and the temperature coefficient of conductance is about 2% per degree, the cell resistance is constant within ±0·01%. Again, this is better than the bridge accuracy. The correction to the cell constant for expansion at the high temperature of the melt is less than −0·05% and is hardly significant in view of the bridge accuracy and the effects of dispersion (see below).

Bridge Measurements.—In making measurements on the specific conductances of melts, and in calibration, there are advantages in using a bridge which gives the parallel resistance and capacitance of the cell. Such measurements are less sensitive to errors due to shunt admittance and the skin effect at high frequencies. Also, wide variations in the series capacitance of the cell are brought within the scope of a single balancing capacitor.

A General Radio type 716-C capacitance bridge (10 c./sec. to 300 kc./sec.) is used (Fig. 2). This is modified for resistance measurements by using as the balancing resistor a General Radio type 1432-X decade resistor (six dials; 0—111, 111 Ω in steps of 0·1 Ω), R_N, connected in parallel with the internal balancing capacitor, C_N. Capacitance balance is obtained by using this capacitor in the normal way, C_D (the dissipation factor capacitor) being permanently set to zero. Earth admittances in the bridge network B–C–D–A–B (Fig. 2) are eliminated from the bridge balance by a General Radio type 716-P4 guard circuit (10 c./sec. to 300 kc./sec.). Shunt admittances between the cell leads A–F, D–E are also eliminated when the guard network (B–A–G–C–B) is balanced simultaneously with the bridge. Balancing of the bridge and guard networks is assisted by first balancing out the guard–earth capacitance in the coupling network B–G–D–C–B, with the coupling resistor R_C. The screening box of the decade resistor R_N is connected to the guard point, G, and is itself enclosed in another metal box connected to earth. This arrangement ensures that only the residuals of the decade units affect the parallel resistance and capacitance registered on the bridge. The errors due to these residuals can be calculated from the manufacturer's data.

Sinusoidal a.c. from a Waveforms 512 oscillator (1 c./sec. to 500 kc./sec.) is supplied *via* the built-in screened transformer connected to A and C (not shown in Fig. 2). Frequency-selective detectors are connected directly to B and D. In the range 100 c./sec. to 10 kc./sec. a Tinsley 5212-M tuned amplifier and a Telequipment S43 oscilloscope are used, above 30 kc./sec.

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[2] Jones and Josephs, *J. Amer. Chem. Soc.*, 1928, **50**, 1049.

[3] Jones and Prendergast, *J. Amer. Chem. Soc.*, 1937, **59**, 731.

an Airmec 853 wave analyser. The r.m.s. voltage across the conductance cell is normally set to 0·5 v. In experiments so far it has been found that the bridge readings are unaffected when the voltage is reduced to 1 mv, apart from a reduction in sensitivity which can be made good by adjusting the detector. The frequency is adjusted to ±1% as it is only of qualitative interest in the work now described.

Resistance is measured by the direct method. The guard and bridge balances converge rather slowly. At frequencies below 10 kc./sec. it is often speedier to balance the bridge network with the guard circuit controls, R_G, C_G, and the guard network with the bridge controls, R_N, C_N. Substitution methods are even more laborious, though potentially more accurate. Greater accuracy is not usually justifiable in the present application because of the limitations set by other factors, which are to be described.

A capacitance, C′, of at least 100 p*F* must be placed across D–A to ensure that the effective cell capacitance does not fall below the range of the balancing capacitor C_N (100—1150 p*F*) when the 1 : 1 ratio arms are in use.

Evaluation of Errors in Bridge Readings.—Resistance. Since it was desired to measure parallel resistances of 0·50—20 kΩ to ±0·1% (or better), it was necessary to examine the factors which might introduce errors of this order in the bridge readings. The following factors were considered: (*a*) Absolute accuracies of resistance windings in R_N, and their temperature coefficients. (*b*) Skin effect in the windings in R_N. (*c*) Resistance of internal connexions in R_N (" zero resistance "). (*d*) Resistance in leads and cable. (*e*) Dissipation in the cell walls. (*f*) Dissipation in the cable. (*g*) Dissipation in C′. (*h*) Dissipation in C_N. (*i*) Dissipation in the stray capacitative residuals of R_N. (*j*) Inductance in the bridge components and wiring, and dissipation in the stray coupling across the transformer. (*k*) Joule heating in the electrolyte. (*l*) Skin effect in the electrolyte. (*m*) Matching of ratio arm resistors. (*n*) Self-inductance in leads and cable. ' (*o*) Bridge sensitivity.

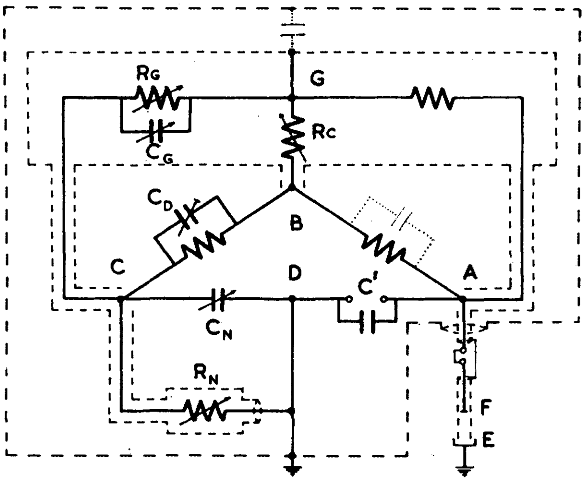

FIG. 2. Bridge and guard circuit.

Of these, the errors due to (*a*—*c*), (*h*), (*i*), and (*m*) were assessed from the manufacturer's data. Errors due to (*d*—*g*), (*n*), and (*o*) were calculated from trials on the equipment. The effects of (*k*) and (*l*) were investigated theoretically, but there were no data from which (*j*) could be arrived at directly.

Of the known errors, only those due to (*a*), (*e*), (*g*—*i*), and possibly (*n*) are important in deciding the accuracy of readings on R_N. The errors due to (*g*—*i*) cancel within 0·05% at all frequencies up to 500 kc./sec., provided the resistance does not exceed about 10 kΩ. Regarding (*n*), the inductance of the centre conductor and earth return of the cable was measured on a Wayne Kerr type B221 universal bridge. This inductance (1·8 μH) causes R_N to read 0·05% high when the resistance is 500 Ω and the frequency 1 Mc./sec., the error increasing as f^2. For higher resistances this error is only reached at higher frequencies. These conclusions are not materially altered by including the inductance of the cell leads.

Manufacturer's data on (*j*) are not available, but the performance of the equipment with a carbon resistor in place of the conductance cell throws some light on the influence of (*j*), and of (*m*) and (*o*) also. The resistor was inserted in the coaxial lead with the aid of a General Radio type 874-X shielded connector, the shield being joined to guard. The reading on R_N was constant at 1136·2 Ω within ±0·01% in the range 0·1—100 kc./sec., but was 0·2% lower at 300 kc./sec. The fall continued at higher frequencies. The observed constancy is in keeping with the maker's claim that the four pairs of resistors used in the ratio arms of the bridge in the frequency ranges 10—300 c./sec., 100—3000 c./sec., 1—30 kc./sec., and 10—300 kc./sec. are matched to better than ±0·1%. Evidently, (*m*) is not significant in producing errors in R_N. Apart from the evidence about (*o*) from the above test, experience with conductance cells has shown that the bridge sensitivity is at least ±0·05% in resistance. In view of the cancellation of the frequency-dependent errors due to (*g*—*i*), particularly above 100 kc./sec., it seems that the final fall in R_N is caused [4] by (*j*).

Consideration of error (*e*) is difficult. Trials with empty cells, or with filled cells sealed at one end,[5] are of dubious value on account of possible alterations in current distribution which change the wall conduction. Moreover, it is not obvious how to investigate wall dissipation without introducing further effects, such as contact potentials, which are absent under normal conditions. Conductance data on molten and vitreous silica [6] indicate that the parallel resistance of the wall of an empty cell is about 2 MΩ at 1000°. It is not known whether there is any contribution from dielectric dissipation, which would introduce dispersion. A wall resistance of 2 MΩ would cause an error of −0·05% in R_N at 1 kΩ, and this would be worse at higher settings. In ionic melts, which give resistances of 1 kΩ or less, a wall resistance of this level is tolerable. During calibration, where the temperature is only 25°, wall resistance may be ignored as it is many orders of magnitude higher than the electrolytic resistance.

On the above considerations a figure of ±0·05% is taken as the precision of resistance measurements with the bridge. As this is numerically equal to the absolute accuracy (*a*) of readings on R_N, it also represents the bridge accuracy. There is clearly no appreciable dispersion introduced by the bridge or cable in the resistance and frequency ranges of interest.

Capacitance. The capillary cell is not primarily intended for the measurement of capacitance, and would, on account of its geometry, be quite unsuitable for the determination of permittivities. Nevertheless, with the guard circuit described above, electrolytic capacitance can be measured with useful accuracy. The following affect the accuracy of cell capacitance readings on C_N: (*a*) Scale accuracy of C_N. (*b*) Residuals in C_N. (*c*) Capacitance of wiring in R_N. (*d*) Terminal capacitance in the bridge. (*e*) Lead inductance. (*f*) Residuals in the decade units of R_N. (*g*) Any cable and lead capacitance not removed by the guard circuit. (*h*) Bridge sensitivity.

Capacitance is measured by difference, since C′ is permanently connected. For such measurements (*a*) is ±0·1% or ±0·8 p*F*, whichever is the greater. The errors due to (*b*) depend on frequency, but at most amount to only +0·04% for 1000 p*F* at 500 kc./sec. In difference measurements, errors due to (*c*) and (*d*) are eliminated. Lead inductance causes C_N to read low by 8 p*F* at a cell resistance of 500 Ω. The error falls as R^{-2} and becomes negligible at 4 kΩ. It is not affected by frequency in the present range.

The effects of (*f*) are deduced from the manufacturer's data. The total series reactance of R_N is calculated from the residuals of the decade units at the appropriate settings. This reactance is then transformed to the equivalent parallel capacitance of R_N in the usual way. The result is not affected by frequency in the present range. For example, at 20 kΩ, R_N adds about 8 p*F* to the capacitance in the balance arm C–D, and C_N reads low by this amount. At 500 Ω, only 1·5 p*F* are added. Use of high settings on the low resistance dials causes R_N to become inductive when the total resistance is small. A setting of 499 Ω, for example, reduces the effective capacitance of C_N by 6 p*F*, so that it now reads high. The slow convergence of the guard and bridge balances at low resistances is due to these abrupt changes in the parallel capacitance of R_N.

The effectiveness of the guard circuit was tested as follows: The capacitance of the centre conductor and earth return of the cable was measured by substitution with the guard disconnected. The reading on C_N was 132·2 p*F* (the capacitance of C′ has been subtracted).

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[4] Field and Easton, *General Radio Experimenter*, 1947, **21**, No. 11, 1.

[5] Bloom and Heymann, *Proc. Roy. Soc.*, 1947, *A*, **188**, 392.

[6] Panish, *J. Phys. Chem.*, 1959, **63**, 1337.

When the leads and guard sheath of an empty capillary cell were connected to the cable, the reading rose to 413·7 p*F*. With the guard screen now connected to the guard point, C_N registered 0·8 p*F*. The same value was obtained with the cell disconnected from the cable. The stray capacitance is, therefore, reduced by the guard circuit to a level comparable with the scale accuracy of C_N.

With regard to (*h*), it is found that apart from measurements at low frequencies (100—500 c./sec.), where the cell capacitance may reach or even exceed the upper limit of C_N with uncertainties as much as $\pm 2\%$, the bridge balance is sensitive to changes well within the compass of error introduced by (*a*).

Materials.—Potassium bromide was of analytical grade. After being powdered and heated in air it was dried and stored under a high vacuum. Before conductance measurements, the melt was purged for several hours at the experimental temperature with anhydrous oxygen-free nitrogen.

Potassium chloride for calibrating solutions was also of " AnalaR " quality. It was dried by heating it in air, and stored in a desiccator.

RESULTS AND DISCUSSION

Preliminary work established that the cell was durable in alkali halide melts. Recalibration showed that cell constants changed by less than 0·05% during normal use. A detailed study of conductance in molten potassium bromide was then undertaken. Two runs were made. In both, the conductance was measured at a series of temperatures, with two or three cells at each temperature. A different set of cells was used in each run, and the temperatures were also different.

Dispersion.—In the melt and in the calibrating solution, the resistance and capacitance showed dispersion with frequency. The possibility that the cell constant might be affected by frequency, for example, through inhomogeneous current distributions near the electrodes (cf. the " Wenner effect," discussed by Jones and Bradshaw [7]), was tested in the following way. If the resistances R_A, R_B of two cells with cell constants K_A, K_B are measured in the same electrolyte, $R_A/R_B = K_A/K_B$. This ratio was obtained for several combinations of cells in potassium chloride solution, and in molten potassium bromide, at various temperatures. The same pair of electrodes was used throughout. It was found that, for any pair of cells, R_A/R_B was independent of the electrolyte and constant throughout the frequency range 0·5—100 kc./sec. This strongly suggests that the frequency-dependence of the cell resistance arises solely through the dispersion of conductance.

In Fig. 3 is shown the dispersion of resistance in a cell containing M-potassium chloride solution at 25° (curve A) and molten potassium bromide at several temperatures (curves B, C, and D). The excess of resistance, ΔR, is expressed relative to the resistance at 500 kc./sec. as zero. The sharp plunge above 100 kc./sec. is due to bridge errors of type (*j*) and should be disregarded. The curve for 919·0° lies close to that for 786·0°, and is omitted from Fig. 3 to avoid confusion. In the melt, there was no consistent trend of dispersion with temperature for any one cell. For the resistance data as a whole, however, there was a tendency for dispersion to be less serious at high temperatures.

Irregularities in the dispersion of resistance were reflected in the capacitance.* During the experiment at 761° the inner electrode was exchanged for one of roughly twice the usual apparent area, and at low frequencies the capacitance rose to larger values, as expected. In other cases, the electrodes were merely resurfaced between experiments without alteration in size, and the capacitance then varied unpredictably from melt to melt. This recalls dispersion behaviour in aqueous electrolytes discussed by Grahame.[8]

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* Since it has been customary to calculate conductance data from the series resistance, it should be mentioned that in the present case the difference between the series and the parallel resistance is negligible.

[7] Jones and Bradshaw, *J. Amer. Chem. Soc.*, 1933, **55**, 1780.

[8] Grahame, *J. Electrochem. Soc.*, 1952, **99**, 370 C.

An important point about all curves in Fig. 3 is the plateau between 10 and 100 kc./sec. In this region the dispersion falls to levels comparable with the bridge error.

Sources of Dispersion, and the Correction of Dispersion Errors.—Dispersion of resistance in ionic melts is usually attributed to electrode polarization.[9-14] In a.c. methods a polarization-free value of the electrolytic resistance is obtained by extrapolating the plot of the cell resistance against $f^{-\frac{1}{2}}$ to infinite frequency. According to the theory of Faradaic admittance in electrolytic cells [8,15] the excess of resistance and capacitance should be proportional to $f^{-\frac{1}{2}}$ if a Faradaic, or discharge, process is occurring in the cell. Such a process would not be expected during conductance measurements on pure melts, since the e.m.f. is kept at levels well below the decomposition voltage. Yet, in experiments specifically designed to test the properties of electrode impedance in molten salts,[9,12,13] dispersion has been observed under these conditions which is not sensitive to the polarization potential. Impurities, such as hydrolysis products in imperfectly dried halide melts, might lead to Faradaic currents.[9,12] In the present experiments, erratic variations in dispersion for different samples of melt may have been due to varying amounts of impurities. Thus, the constancy of the ratio R_A/R_B for any pair of cells in a given melt suggests that it is the electrolyte which controls dispersion. Further tests would be necessary to establish this point. The above explanation of dispersion is, however, complicated by the fact that the cell resistance to a.c. is not linear in $f^{-\frac{1}{2}}$ (sometimes called Warburg's law), nor is the capacitance. This is also the past experience.[9,10,12,13]

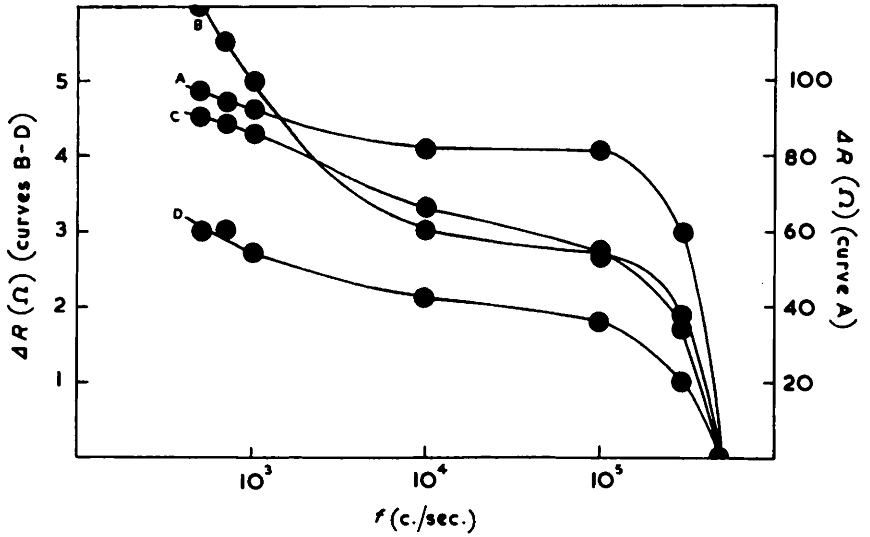

Fig. 3. Dispersion of resistance in electrolytes.

(A) M-Aqueous potassium chloride. (B—D) Molten potassium bromide at 716·6°, 786·0°, and 979·0°, respectively. Diameters of circles equals one-half max. error (±0·5%).

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[9] Laitinen and Osteryoung, *J. Electrochem. Soc.*, 1955, **102**, 598.

[10] Winterhager and Werner, *Forschungsber. Wirtschafts- u. Verkehrsministeriums Nordrhein-Westfalen*, 1956, No. 341.

[11] Winterhager and Werner, *Forschungsber. Wirtschafts- u. Verkehrsministeriums Nordrhein-Westfalen*, 1957, No. 438.

[12] Laitinen and Gaur, *J. Electrochem. Soc.*, 1957, **104**, 730.

[13] Hills and Johnson, *J. Electrochem. Soc.*, 1961, **108**, 1013.

[14] Ukshe and Bukun, *Russ. J. Phys. Chem.*, 1961, **35**, 1330.

[15] Randles, *Discuss. Faraday Soc.*, 1947, **1**, 11.

Space-charge polarization may play a role in dispersion in contaminated melts, particularly at frequencies below 10 kc./sec. The residual dispersion in the region of the plateau may represent the superposition of this on a Faradaic process.[16,17] A quantitative test would help to distinguish the various possibilities, but a comprehensive theory of polarization has not been given for melts. The usual extrapolation procedure for eliminating the polarization error, based only upon the theory of Faradaic admittance, would lead to erroneously low conductances. It is, therefore, preferable to use the cell resistance in the region of the plateau. A similar conclusion was reached by Winterhager and Werner,[10] who preferred to make measurements at 40—50 kc./sec.

Dispersion could also lead to error in the calibration of cells. To avoid this it is necessary, first, to use a value for the absolute conductance which is free of polarization errors and, secondly, to measure the cell resistance at a frequency which gives negligible dispersion. Where the cell design involves radical innovations, it may be advisable to study the dispersion in order to find this frequency. Jones and Prendergast's conductance data [3] for potassium chloride solutions are considered adequate for present purposes, as although they were not apparently corrected for dispersion the resistance varied by no more than 0·002% from 1 to 3 kc./sec. In the present cells, dispersion is not significant from 10 to 100 kc./sec. (Fig. 3, curve A), so that cell constants may be safely calculated from measurements in this range.

Conductance of Molten Potassium Bromide.—The specific conductance, κ, of molten potassium bromide was found in the first run to fit the equation:

$$\kappa = -1\cdot462_6 + 6\cdot006_2 \times 10^{-3}t - 2\cdot470_3 \times 10^{-6}t^2 \text{ (int. ohm)}^{-1} \text{ cm.}^{-1},$$

with a standard deviation of $0\cdot003_6$, at temperatures t in the range 780—980°. In the second run greater accuracy was achieved. Twelve measurements were made at five temperatures in the range 760—980°. These gave:

$$\kappa = -1\cdot327_1 + 5\cdot710_0 \times 10^{-3}t - 2\cdot313_9 \times 10^{-6}t^2 \text{ (int. ohm)}^{-1} \text{ cm.}^{-1}.$$

The deviations were:

Temp.	760·2	761·6	785·6	785·6	786·0	864·6
κ (int. ohm)$^{-1}$ cm.$^{-1}$	$-0\cdot002_2$	$-0\cdot000_1$	$+0\cdot001_6$	$-0\cdot000_4$ *	$+0\cdot002_4$	$+0\cdot001_6$
Temp.	864·6	865·0	918·0	919·0	979·0	981·1
κ (int. ohm)$^{-1}$ cm.$^{-1}$	$-0\cdot001_4$ *	$+0\cdot000_2$	$+0\cdot001_3$ *	$+0\cdot003_1$	$+0\cdot005_1$	$+0\cdot000_6$

The standard deviation was $0\cdot002_2$. The starred results were obtained with a cell of high cell constant. Here the resistance in the calibrating solution exceeded 20 kΩ, and bridge errors were high at 100 kc./sec. This cell was therefore calibrated at 10 kc./sec. The resistance of the melt was measured at 100 kc./sec. in every case.

Comparison with Previous Data.—The smooth rise in conductance with increase in temperature, and the fall in the temperature coefficient, confirm the observations of Yaffe and Van Artsdalen.[18] The present results for κ are lower than theirs, however, and the temperature dependence is different. They gave:

$$\kappa = -3\cdot226_1 + 1\cdot0124 \times 10^{-2}t - 4\cdot828 \times 10^{-6}t^2 \text{ ohm}^{-1} \text{ cm.}^{-1},$$

standard deviation 0·004. The two curves intersect at 980—990° (extrap.) and 760°, the maximum discrepancy being 0·04 (int. ohm)$^{-1}$ cm.$^{-1}$ (2%).† Their value for $d^2\kappa/dt^2$ is twice as large as ours.

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† As the cells of Yaffe and Van Artsdalen were calibrated by the method of Jones and Bradshaw [7] it is presumed that their data are based on the international ohm.

[16] Chang and Jaffé, *J. Chem. Phys.*, 1952, **20**, 1071.

[17] Jaffé and Rider, *J. Chem. Phys.*, 1952, **20**, 1077.

[18] Yaffe and Van Artsdalen, *J. Phys. Chem.*, 1956, **60**, 1125.

Earlier conductance data on molten potassium bromide include those of Biltz and Klemm,[19] which except near the melting point conform closely to the present equation. The agreement is possibly fortuitous since their cell had a cell constant of only 75 cm.$^{-1}$, and a single frequency of 500 c./sec. was used. Bloom *et al.*,[20] in a paper devoted mainly to molten salt mixtures, gave only an exponential equation for the conductance of potassium bromide. This gives values as much as 2% lower than ours.

Possible Connexion between Dispersion and Results for $d^2\kappa/dt^2$.—An unusual extrapolation was used by Van Artsdalen and Yaffe.[21] The cell resistance was measured over the range 2—20 kc./sec. and plotted against f^{-2}. The linear extrapolation to infinite frequency was said to have given a value of resistance free of errors due to lead inductance. Other possible contributions to the observed dispersion were not mentioned, but presumably they were supposed to have been eliminated also. The effect of temperature on dispersion was not described, and no assessment was given of the other factors affecting the accuracy.[18, 21]

Winterhager and Werner paid considerable attention to dispersion.[10, 11] Their values for sodium and potassium chlorides were about 1% lower than Van Artsdalen and Yaffe's. For potassium chloride the agreement in $d^2\kappa/dt^2$ was good, but Winterhager and Werner's curvature for sodium chloride was much smaller. The last authors claimed that their results for various chloride melts showed a linear dependence of conductance on temperature. They suggested that this was the true dependence, which was only disclosed by the successful elimination of polarization in their work.[10] On the other hand, Van Artsdalen and Yaffe attributed the curvature in their own plots to structural changes in the melt, and analysed it in terms of the temperature-dependence of the heat of activation in conduction.[18, 21]

Further discrepancies in published data are revealed in recent work by Bronstein and Bredig.[22] Their results for potassium iodide were as much as 5% lower than Yaffe and Van Artsdalen's, and showed a different dependence on temperature.

Although Winterhager and Werner's method has been criticized as liable to errors from lead inductance,[22] various lines of evidence suggest that their suspicion of a connexion between the apparent temperature-dependence of κ and polarization is actually correct. Any attempt at removing polarization dispersion by extrapolation of data depends for its success on the use of the correct dispersion formula. A formula such as that for Faradaic polarization, which only fitted the dispersion curve over a narrow range in the low frequency region, would cause κ to be underestimated. This is because the curvature is high in this region. If the dispersion decreased as the temperature of the melt increased, the error in κ would fall, affecting the values of $d\kappa/dt$ and possibly $d^2\kappa/dt^2$. This effect would be more serious with the dispersion formula of Van Artsdalen and Yaffe,[21] which assumes even greater curvature of resistance with frequency.

The possibility of a connexion between polarization dispersion and unsuspected impurities complicates matters still further. It could lead to different temperature-dependence in various experiments carried out under the same conditions. This would be likely to show more clearly in the discrepancies between the results of other workers. It may be significant, for example, that whereas Yaffe and Van Artsdalen gave 735° as the melting point of potassium bromide,[18] in the present work it was 740° (cf. Brewer,[23] and Kubaschewski and Evans [24]).

So far the main problem in accurate conductance work has been the elimination of

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[19] Biltz and Klemm, *Z. phys. Chem.*, 1924, **110**, 318.

[20] Bloom, Knaggs, Molloy, and Welch, *Trans. Faraday Soc.*, 1953, **49**, 1458.

[21] Van Artsdalen and Yaffe, *J. Phys. Chem.*, 1955, **59**, 118.

[22] Bronstein and Bredig, *J. Phys. Chem.*, 1961, **65**, 1220.

[23] Brewer, " The Chemistry and Metallurgy of Miscellaneous Materials. Thermodynamics," ed. Quill, McGraw-Hill, New York, 1950, Paper No. 7.

[24] Kubaschewski and Evans, " Metallurgical Thermochemistry," Pergamon, London, 3rd edn., 1958.

polarization errors. This may be attributed to the lack of a reproducible electrode with which dispersion could be studied reliably and interpreted correctly. It is believed that in the present research interference by polarization has been overcome by working at high frequencies with reliable equipment. Evidence in support of this is the close agreement of results in the two separate runs on potassium bromide.

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