$m_H^2/M - m_H$ in salt solutions up to 2 M and from 0 to 37.5° have been computed.

4. The ionization, k_A, was found to vary with the temperature in accordance with the equation of Harned and Embree.[7]

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[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Measurement of the Conductance of Electrolytes. IX.[1] The Use of the Cathode-Ray Oscillograph as a Detector

BY GRINNELL JONES, KAROL J. MYSELS[2] AND WALTER JUDA

A telephone has been almost universally used as the detector in making measurements of the conductance of solutions of electrolytes since Kohlrausch developed his alternating current technique. Recent advances in the science and art of electronics have made available two new tools as substitutes for the telephone. Hovorka and Mendenhall[3] have suggested the use of the "electric eye" (a 6E5 Cathode-Ray tube) as a detector for conductance measurements and give a wiring diagram for a combined amplifier and detector.

Lamson[4] has suggested the use of a Cathode-Ray Oscillograph as a detector for alternating current impedance bridges in general but without discussing specifically its use for the measurement of the conductance of the solutions of electrolytes. The Cathode-Ray Oscillograph converts complicated variable electric currents into visual form more successfully than the telephone converts them into audible form. We have found that the Cathode-Ray Oscillograph has important advantages over both the telephone and "electric eye" for conductance measurements and no disadvantages for a person having normal eyesight except greater cost.

The apparatus used in the experiments to be described below consists of the following parts assembled as a unit:

(1) A beat-frequency oscillator (General Radio Company Type 613-B) giving any desired frequency from 10 cycles to 13,500 cycles per sec.

(2) A Jones Conductivity Bridge provided with input and output transformers built by Leeds and Northrup and described by Dike.[5]

(3) A container filled with oil in which the cells are mounted, the temperature of which is automatically controlled by means of a thermoregulator.

(4) A tuned three-tube amplifier, General Radio Company GR-P-430, connected across the midpoint of the bridge through a shielded and grounded transformer. There was also provided an additional tuning device consisting of a variable capacitor of 0.2 μf capacitance and a variable inductor of 1 henry connected in parallel with the output of the amplifier.

(5) A RCA Stock No. 155 Cathode-Ray Oscillograph, whose vertical deflecting plates are connected to the output terminals of the amplifier and whose horizontal deflecting plates are connected to the oscillator. This instrument[6] has a three-inch fluorescent screen and gives an image which is bright enough for easy visual observation without darkening the room.

(6) All electrical connections between the parts are made by shielded wires with the shields grounded except the connections between the cell and the bridge, which are not shielded.

The screen of the oscillograph will show a horizontal straight line when the bridge is perfectly balanced so that there is no voltage coming from the midpoint of the bridge through the amplifier to the vertical plates, while the horizontal plates of the cathode-ray tube are con-

(1) The earlier papers of this series are: Grinnell Jones and Associates, THIS JOURNAL, **50**, 1049 (1928); **51**, 2407 (1929); **53**, 411, 1207 (1931); **55**, 1780 (1933); **57**, 272, 280 (1935); **59**, 731 (1937).

(2) Mr. K. J. Mysels' address is care of Shell Development Company, San Francisco, California.

(3) F. Hovorka and E. E. Mendenhall, *J. Chem. Education*, **16**, 239 (1939); Shuttleworth, *J. Intern. Soc. Leather Trades Chem.*, **23**, 326 (1939). Circuits involving an electric eye as a detector for inductance or capacitance measurements have also been described by the following: W. M. Breazeale, *Rev. Sci. Instruments*, **7**, 250 (1936); L. C. Waller, *R. C. A. Rev.*, **1**, no. 3, 121 (1937); R. L. Garman, *Rev. Sci. Instruments*, **8**, 327 (1937); J. F. Koehler, *ibid.*, **8**, 450 (1937).

(4) H. W. Lamson, *Rev. Sci. Instruments*, **9**, 272 (1938); General Radio Experimenter, **13**, No. 11 (1939).

(5) P. H. Dike, *Rev. Sci. Instruments*, **2**, 379 (1931).

(6) For a detailed description and wiring diagram of this instrument see a pamphlet entitled "Cathode-Ray Oscillograph, Stock No. 155" available on request from the RCA Manufacturing Company, Camden, New Jersey. Other models differing in size of screen, sensitivity, price and maker are commercially available. The list price of the "RCA No. 155 Cathode-Ray Oscillograph" is $63.95.

nected to the oscillator with the horizontal switch "on."

The screen will show a visual image of an ellipse when the bridge is out of balance with respect to both resistance and capacitance because there will be a variable voltage applied to the vertical plate which will have the same frequency but will be out of phase with the voltage applied to the horizontal plates directly from the oscillator (except in some special cases). This ellipse will have its axis inclined from the horizontal.

The tilted ellipse on the screen turns when the capacitance dial on the bridge is adjusted until at balance the major axis becomes horizontal.

Alternatively, the minor axis of the tilted ellipse can be decreased by adjusting the resistance balance leaving the capacitance unchanged until an inclined straight line only is visible. An unbalance of only 0.002% in the resistance is easily seen and the sensitivity permits an estimate to within 0.0005% under favorable conditions.

When both capacitance and resistance are adjusted to balance a horizontal straight line will appear.

This method permits independent adjustment of the resistance and capacitance balance which is a great convenience.[7] An approximate resistance balance can be obtained without bothering to adjust the capacitance balance. This is very important if speed in making measurements is required.

Another way to use the instrument is to turn the horizontal amplifier switch of the oscillograph to the position marked "timing" which has the effect of impressing a voltage varying linearly with time on the horizontal plates. The switch in this position disconnects the horizontal plates from the sine wave oscillator and connects them with a "saw-tooth" oscillator which is a part of the instrument. Then the saw-tooth oscillator is adjusted in frequency by means of the controls provided with the instrument so that its frequency is a submultiple of the frequency of the wave connected to the vertical plates. The true wave form of the oscillations on the vertical plate will be shown on the screen. If the oscillograph is used in this way as a detector for the bridge and the bridge is balanced, then a horizontal straight line will appear on the screen. If the bridge is unbalanced with respect to either resistance or capacitance, the screen will show a sine wave, provided the oscillator gives a pure sine wave and there are no pick-ups. An unbalance of 0.001% in the resistance is clearly apparent to the eye under favorable circumstances. The sensitivity permits an estimate to within 0.0002%. This corresponds to about 1.5 microvolts at the detector terminals of the bridge.

This method has the disadvantage that whenever either the resistance or capacitance, or both, are out of balance a sine wave will appear on the screen and repeated successive adjustments of both resistance and capacitance may be necessary to obtain a balance. However, it has the advantage over the ellipse method in being perhaps twice as sensitive to the resistance balance since it is easier to distinguish between a wave and a straight line than to observe a slight tilting or thickening of a line.

The following procedure for making measurements has been found convenient. When starting measurements on a cell whose resistance and capacitance are unknown or only very roughly known, set the oscillator at 2200 cycles and turn the horizontal switch "on" and then an approximate balance can be obtained quickly because the resistance balance and capacitance balance are independent of each other. This balance will be good enough unless the maximum possible precision is desired. Then throw the resistance in the bridge slightly out of balance and turn the switch to "timing" and adjust the frequency of the timing oscillator by turning the dials provided for this purpose until a stationary sine wave appears on the screen. Then adjust the resistance and capacitance on the bridge until the wave becomes a horizontal straight line.

Of course the use of a cathode-ray oscillograph instead of the telephone does not obviate the necessity of adjusting the ground balance of the bridge as usual, and checking the bridge balance after adjusting the ground balance. Similarly, after having completed the measurements at some one frequency (say 2200 cycles per second) the measurements should be repeated using at least one other frequency (say 1000 or 4000) and if any significant difference is found in the resistance something is wrong. The cause of the

(7) This statement needs some qualification. With our apparatus the resistance and capacitance balance seem to be substantially independent at 2200 cycles, yet when using other frequencies the phase relation progressively shifts and the two adjustments become less independent or even reversed, so that the resistance tilts and the capacitance opens or closes the ellipse. This difficulty could be overcome by the use of a phase shifting device as suggested by Lamson.

trouble should be ascertained and the error eliminated if necessary to obtain the accuracy desired.

For most persons, visual observations are easier and less tiresome than auditory observations, because the superior focusing and analyzing power of the eye permits more precise observations with less disturbance from extraneous sources. Furthermore, with the telephone it is necessary to follow the fading of a sound signal; in the oscillograph, on the other hand, changes in the shape of a signal of constant intensity are observed. An extreme unbalance causes a harmless movement of the image off the screen, instead of a deafening noise. Finally, if desired, the screen may be photographed, thereby giving a permanent objective record.[8]

A further and very important advantage of the cathode-ray oscillograph is that it can be used without serious sacrifice in precision or convenience over a wider range of frequency than the telephone. With our instruments, a sensitivity of 0.001% or better can be obtained from 500 to 5000 cycles per second, and a sensitivity of 0.002% or better up to 13,000 cycles per second. The limitations are, however, not in the oscillograph but in our oscillator and amplifier which were designed and built for use with a telephone. It would be possible to build an oscillator and amplifier which would extend the useful frequency range considerably. This good sensitivity over a wide range of frequencies is important if there is an apparent variation of resistance with frequency because errors due to polarization or to capacitative shunts are different functions of the frequency. Therefore, extending the range of frequencies used in the measurements facilitates the determination of the cause of the apparent variation of resistance with frequency and the calculations of the correction to be applied as is explained in detail in the third and sixth papers of this series.

Another important advantage in using the cathode-ray oscillograph instead of a telephone is that it is much easier to trace the sources of outside disturbances. When the cathode-ray oscillograph was first installed it soon became obvious that noises or mechanical vibrations near the amplifier appeared on the screen. Apparently the first tube acted as a microphone and the electric signals produced were amplified by the later stages of the amplifier. This microphone activity had a marked selectivity as regards pitch. Whistling at certain pitches showed clearly but at other pitches the response was feeble or missing. The simple device of mounting the amplifier on a sheet of air-foam rubber substantially eliminated this sensitivity to noises. The gears and bearings of the thermostat had become somewhat worn and noisy through years of use. It was easy to show by starting and stopping the motor that these vibrations were apparent on the screen. By overhauling this mechanism these disturbances were eliminated. Other disturbances were easily shown by the oscillograph to have a frequency of 60 cycles per second which clearly indicated that they were pick-ups from the lighting and power circuit of the laboratory. A little experimentation clearly showed that their chief cause was a mutual inductance between the heater in the thermostat and the cell. This was eliminated by using a direct current instead of alternating current in the heater.

Whenever the heater turns on or off there is a transient current shown on the screen. This momentary image is so weak and so different in character that it does not in the least obscure the main observation. Indeed it is an advantage because it may help to detect a cycle in the temperature of the thermostat. If, at the moment when the current goes on the bridge is balanced and the screen is watched, the straight line indicating a balance may change to a low wave and then again become straight periodically. If such a periodicity is observed and if the period corresponds to the period of the heater in the thermostat it indicates a temperature variation of the thermostat. By observing a change in the resistance balance necessary to obtain a new balance when the wave is at its maximum, it is easily possible to determine the significance of these temperature fluctuations in terms of observed resistance. If such a change is progressive it indicates that the cell has not yet attained the temperature of the bath or some other cause of inconstant resistance is operating.

When the telephone is used as a detector all of these disturbances are heard and spoil the minimum.

Every available oscillator gives some harmonics. They are negligible with our instruments under good conditions when the resistance is inde-

(8) We have obtained satisfactory photographs by the use of a Zeiss-Tessar f4.5 lens with one-fifth second exposure on Eastman Super Speed Ortho Portrait Film.

pendent of the frequency. When either polarization or the shunt effect are present and the bridge is balanced for the fundamental frequency it is not balanced for the first harmonic which will appear on the screen as a sine wave with twice the number of peaks as the fundamental. The harmonic can be made negligible by suitable tuning if desired. The precision of the balance is not affected by the appearance of the harmonic because even a slight unbalance of the fundamental frequency distorts the pure sine wave form of the harmonic and is therefore readily apparent. Since the harmonics cause less trouble when using the oscillograph than with a telephone it is less important to eliminate them by tuning. We do not know whether the harmonic comes solely from the oscillator or is also introduced as a result of the process of electrolysis in the cell, and therefore is one aspect of the complex phenomena called "polarization." At any rate it is clear that even if the harmonics are strong they will cause much less difficulty when using the oscillograph than with a telephone.

Summary

The utilization of the cathode-ray oscillograph instead of the telephone as a detector for precision measurements of conductance of electrolytes is described. The cathode-ray oscillograph has the following advantages over a telephone: (1) Visual observation is less tiresome and at least as precise as auditory observations. (2) The resistance and capacitance balance of the bridge can be made substantially independent. (3) Outside disturbances (pick-ups) are more readily traced to their source and eliminated, or more easily ignored if it is not feasible to eliminate them. (4) Measurements can be made over a greater range of frequency. (5) Harmonics and transients can be seen as such and are therefore less troublesome. (6) Progressive or periodic changes in conductance due to chemical reactions or variations in temperature can be followed more easily.

For the normal person the only advantage of the telephone is that it is less expensive than the oscillograph.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF DUKE UNIVERSITY]

The Vapor Pressures of Some Organic Compounds. I.[1]

BY JAMES M. STUCKEY[2] AND JOHN H. SAYLOR

A program of research on the solubilities of organic compounds has been in progress for several years in this Laboratory. The concept of vapor solubilities[3,4] has been of use in correlating the solubilities of various organic compounds.

The calculation of these vapor solubilities necessitates the knowledge of the vapor pressures of the organic compounds. Therefore it was decided to measure the vapor pressures of some of these compounds as there is considerable disagreement in the literature, particularly at low temperatures, and in some cases few or no measurements are to be found. The determinations were made between 0 and 75° because the solubilities determined in our laboratory have been within this temperature range.

Experimental

Method.—The method used was essentially the same as that devised by Ramsay and Young.[5] A diagram of the apparatus is shown in Fig. 1; it is very similar to that used by Linder.[6] The temperature was measured by means of a six-junction thermel constructed of no. 30 constantan wire and no. 36 copper wire and insulated with cellulose acetate. The e. m. f. measurements were made with a Leeds and Northrup type K-2 potentiometer and a Leeds and Northrup No. 2500-a galvanometer which had a sensitivity factor of 0.5 mmv./mm.

The thermel was calibrated in a well-stirred water-bath against a set of Goetze thermometers graduated in 0.02° which had been calibrated by the Physikalisch-Technische Reichsanstalt. The comparisons were made at intervals of about 5° ranging from 0 to 80°. In all measurements with the thermel the ice-bath was prepared in a manner similar to that described by Roper.[7] The data were fitted

(1) This work was supported in part by a grant from the Research Council of Duke University.

(2) This paper was taken from the thesis submitted by James M. Stuckey to the Graduate School of Duke University in partial fulfillment of the requirements for the Degree of Doctor of Philosophy, June, 1940.

(3) Saylor, Stuckey and Gross, THIS JOURNAL, **60**, 373 (1938).

(4) Gross, Rintelen and Saylor, *J. Phys. Chem.*, **43**, 197 (1939).

(5) Ramsay and Young, *J. Chem. Soc.*, **47**, 42 (1885).

(6) Linder, *J. Phys. Chem.*, **35**, 531 (1931).

(7) Roper, THIS JOURNAL, **60**, 866 (1938).