

principle and equation of indirect catalysis are nothing else than the ordinary conception of solvent influence generalized and expressed mathematically.

If the equation here proposed is assumed to express generally the effect of indirect catalyzers, it furnishes important guidance in characterizing the type of catalysis involved in any given reaction and thus in deciphering the reaction mechanism itself. To mention a single example: we found that the retarding effect of water upon esterification follows the equation of indirect catalysis. From this we concluded that water, without itself taking part in the esterification, retards the reaction by its high dissociating power, and hence that esterification depends on the formation of complex molecules. This conclusion is in accord with a great deal of independent experimental evidence produced by several of my student-collaborators.

Further, having realized that the mechanism of a given reaction depends mainly on dissociation, or on the formation of complexes, as the case may be, one is enabled to foresee an indefinite number of substances that will act as positiv catalyzers and an indefinite number of other substances that will act as negativ catalyzers. Thus, having realized that esterification depends on the formation of complex molecules, we confidently expected that all substances of low dissociating power (and hence, presumably, high associating power) would greatly hasten that reaction. Experiment has strikingly confirmed this expectation in all cases tried.

These and similar practical services already rendered by the theory have encouraged me to bring it without further delay to the attention of other workers in chemical dynamics. A variety of experimental data supporting it will follow in a series of publications in course of the next few months.

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## AN IMPROVED APPARATUS FOR MEASURING THE CONDUCTIVITY OF ELECTROLYTES.

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### I. Introduction.

As a preliminary to an investigation of the electrical conductivity of aqueous solutions of strong electrolytes in the concentration range included between 0.001 and 0.000001 normal, it became necessary to examine some of the sources of error inherent in the Kohlrausch method when applied to solutions of such high specific resistances. As a result of this study, an apparatus has been evolved which permits the *easy* attainment of a

very high degree of precision, not only in the measurement of very large electrolytic resistances but of very small ones as well. In addition to the increased degree of precision attainable with the improved apparatus, it possesses the advantage of greater rapidity and convenience, and the sharp, perfect minima, obtained relieve the nerves of the operator of the strain imposed by the effort to find the correct bridge setting with a poor minimum. It seems desirable, therefore, to describe the improved apparatus at this time, especially as the completion of the investigation for which it was primarily devised may be considerably delayed.

The theory of conductance measurements with the alternating current has been so fully treated by Kohlrausch and Holborn in their standard work, "Das Leitvermögen der Elektrolyte," and in the later papers of Kohlrausch and his associates,<sup>1</sup> that it is unnecessary to enter into the subject in the present paper. The apparatus described below was designed to include all of the perfections of the most accurate apparatus employed by Kohlrausch<sup>2</sup> together with some additional improvements which permit the attainment of a degree of precision, about ten times that obtained by Kohlrausch in his most accurate investigations. This high degree of precision is, moreover, attained with the greatest ease and certainty as will be clear from the test experiments described below.

A consideration of the theory of conductance measurements with the alternating current made it appear very probable that the precision of the method could be increased by making the following changes in the customary apparatus:

1. Abandon the induction coil as a source of current and replace it by a high frequency generator giving a pure current of a single frequency, one which is entirely free from the overtones which are present in the complex wave system obtained with the induction coil

2. For measuring very *high* resistances (20,000 ohms or more) replace the ordinary resistance box by one in which the resistance units are free from both inductance and capacity.

3. Use a tuned telephone, and an "extended" bridge wire and make all measurements at the middle of the bridge. Take as much pains in balancing the capacities in the bridge arms as in balancing the resistances.

## 2. Description of the Apparatus.

*The High Frequency Generator.*—The only instrument on the market, as far as we were able to learn, which possessed most of the desired qualities was the "Small High-frequency Machine" manufactured by Siemens and Halske. This machine has a normal frequency of 1000 cycles per second but any desired frequency between 450 and 1800 cycles per second

<sup>1</sup> Especially the paper of Kohlrausch and Maltby, *Abhandl. Physik. Tech. Reichsanstalt*, 3, 157 (1900).

<sup>2</sup> As described in the paper of Kohlrausch and Maltby, *loc. cit.*

can be obtained by regulating the position of the eddy-current "brake" provided with the instrument. Our instrument is mounted upon a felt pad in a room some distance from the conductivity laboratory and is inclosed in a box to protect it from dust and to shut in the sound emitted by the rapidly moving toothed wheel.

All of the connections for the instrument are brought to the main electrical distribution board of the building, so that the high frequency current may be sent to any room in the building. The starting rheostat and the eddy-current brake are placed in the conductivity laboratory, the latter instrument being mounted near the conductivity bridge, so that the operator can vary the frequency of his current at pleasure. The normal frequency of the instrument, 1000 cycles per second, is the best frequency to employ in nearly all cases. Since, however, the frequency depends upon the rate at which the motor is driven, it is influenced by any sudden change in the load on the 110 volt circuit from which the motor is operated. Such changes, if they are not too frequent, can be readily neutralized by shifting the position of the eddy-current brake, but if they are liable to occur frequently they become a source of considerable annoyance. It is best, therefore, to operate the machine on a circuit of constant potential. In most of the experiments described below the machine was driven from a small 110 volt generator which was protected from a varying load. Under these conditions it has never been found necessary to vary the frequency.

The current obtained from the high frequency generator is regulated by means of a rheostat mounted beside the starting rheostat of the generator, and connected in series with the exciting coil of the electro-magnet. The exciting current employed during the conductance measurements was varied according to the resistance of the cell, from 0.2 amp. for low resistances to 2.3 amp. for high resistances. The heating effect of the induced current in the cell, during the time required by the measurements, is scarcely appreciable with a properly designed cell, if an accuracy no greater than 0.01% is sufficient.

*The Special "Film" Resistance Units.*—In order to prepare stable high resistances, practically free from either inductance or capacity, it is only necessary to seal two platinum wires into the ends of a glass rod and connect them by a thin film of platinum deposited upon the glass. For the preparation of thin metallic films of this character a number of different methods have been devised and published in recent years.<sup>1</sup>

One of the most convenient methods makes use of a colloidal solution of the metal in a suitable solvent. One of these solutions, under the name

<sup>1</sup> L. Houlevigüe, *Compt rend.*, 149, 1368; M. U. Schoop, *Electrochem. Z.*, 17, 53; *Met. Chem. Eng.*, 8, 404; H. G. Cannegieter, *Z. biol. Technik. Meth.*, 2, 21; J. K. A. U., Salomonson, *Z. biol. Tech. Meth.*, 1, 35-43; Leithäuser, *Engineering*, 86, 818.

of "platinum-glanz," is extensively employed in making gas electrodes. The procedure employed in making resistance units with this material is as follows:

Two lead wires of platinum are sealed into the ends of a U-shaped glass rod of suitable length. The joint between the glass and the platinum is then covered with a layer of the platinum-glanz and by means of a drawing pen a narrow line of the platinum-glanz is drawn along the surface of the rod so as to connect the two lead wires. After the layer of platinum-glanz is completely dry it is heated gradually to a dull red heat. This heating can, with care, be conducted in a flame, but it is safer to use an electric furnace. When the heating is completed the narrow line of platinum-glanz has been converted into a thin film of platinum which is fused into the glass so that it cannot be scratched with a knife. A resistance unit of 80,000 ohms can be obtained in this way upon a U-shaped, narrow, glass rod only 10 inches high.

When properly constructed and handled these resistances are very permanent. They have a temperature coefficient of 0.1% per degree between 25° and 50°, and hence where an accuracy of 0.01% is desired the temperature of the resistance box must be kept constant to 0.1° during the measurement. Our resistances of this type are mounted in regular resistance-box-form in an oil bath, provided with a thermometer, stirrer and heating coil. Since they are designed to serve as secondary standards only, they are checked at frequent intervals against a standard resistance box, using a galvanometer and direct current.

*The Telephone.*—Two telephones connected by a head piece constitute the most convenient arrangement. Both telephones should be tuned to respond to the frequency of the current employed. Those employed in the experiments described below were constructed especially for this work and were tuned to a frequency of 1000. Such an instrument is extremely sensitive when employed in a circuit of its own frequency.

*The Bridge.*—When a precision of more than 0.05% is desired in conductivity measurements it is necessary to lengthen the ordinary bridge wire. This is most conveniently accomplished by connecting to each end of the wire a resistance coil, having a resistance  $4\frac{1}{2}$  times that of the bridge wire, itself.<sup>1</sup> The bridge employed in the experiments described below was the Leeds and Northrup roller type, with two such coils mounted in the base so that by removing a couple of plugs the coils could be connected to the ends of the bridge wire. When these coils were so connected, the "extended" bridge wire thus obtained was equivalent to a wire 47 meters long. The smallest scale division was 3 mm. wide and corresponded to  $\frac{1}{20,000}$  of the total length of the extended wire. Since the bridge setting could be easily read to less than 0.1 of a scale division, the error in a con-

<sup>1</sup> Kohlrausch and Holborn, p. 43.

ductance measurement due to the error in *reading* the bridge setting could never amount to  $0.2 \times 0.0001$  or  $0.002\%$ , for a setting at the middle of the bridge.

A variable capacity was connected in parallel with the resistance box and was adjusted in each measurement until a maximum sensibility was attained.

### 3. The Test Experiments.

In order to obtain definite figures illustrating the degree of precision attainable with the new apparatus a series of test experiments were carried out, in which, solutions of various concentrations were measured in different forms of cells. The cells employed in most of these experiments will be referred to as Nos. 1, 2, 3, and 4, respectively. They were of the pipet type described in a previous paper.<sup>1</sup> The first three cells had platinized electrodes, 10 mm. in diameter and 75 mm., 15 mm., and 2 mm. apart, respectively. Cell 4 was fitted with two circular, unplatinized, platinum electrodes 30 mm. in diameter and 1.5 mm. apart. During the measurements the cells were submerged in a water thermostat maintained at room temperature to within  $0.003^\circ$  during the measurement of any cell.

The "extended" bridge wire was used in all the experiments and the high frequency machine was driven at its normal rate, giving a frequency of 1000 cycles per second. Except where otherwise specified the resistance boxes employed were standard, high grade boxes with manganin resistance coils. The special "film" resistance box described above was employed only in the measurement of very high resistances.

In order to eliminate the personal element as far as possible most of the measurements were made in triplicate, that is, the bridge setting for each cell was determined *independently* by three different observers.<sup>2</sup> In recording the results thus obtained, the value for the resistance of the cell (in ohms) obtained by each observer is given, together with a statement of the number of scale divisions through which it was necessary to swing the contact in deciding the proper setting. A "*perfect minimum*" means that *perfect silence* was obtained at one point and that a sound was heard if the contact was moved more than 0.1 scale division on either side of this point. In this connection it may be noted that the tones obtained on the two sides of the minimum were identical in all their properties and were perfectly clear and of uniform quality.

As a basis for comparison of the degrees of precision attained in the different experiments the mean of the three results is given, together with the maximum and the average deviations from this mean, expressed in per cent.

<sup>1</sup> Washburn and MacInnes, *THIS JOURNAL*, 33, 1688 (1911).

<sup>2</sup> We wish to acknowledge our obligations to Mr. G. Y. Williams for his efficient assistance in carrying out this series of test experiments.

*Experiment 1.*—The electrolyte was 0.1 N KCl and its resistance in cell No. 1 was determined. The results in ohms obtained by the three observers are as follows: 248.177, 248.172, 248.182; mean, 248.177; max. d., 0.002%; a. d., 0.0014%. Perfect minimum.

*Experiment 2.*—0.01 N KCl in cell 2. Resistance, 414.854, 414.862, 414.867; mean, 414.861; max. d., 0.0017%; a. d., 0.0012%. Perfect minimum.

*Experiment 3.*—0.001 N KCl in cell 2. Resistance, 4007.60, 4007.60, 4007.76; mean, 4007.65; max. d., 0.0027%; a. d., 0.0017%. Perfect minimum.

*Experiment 4.*—0.001 N KCl in cell 3. Resistance, 541.779, 541.774, 541.794; mean, 541.782; max. d., 0.0018%; a. d., 0.0015%. Perfect minimum. Owing to the small heat capacity of the thin film of liquid between the electrodes in this cell, the heating effect of the current made it necessary to make the final bridge setting very quickly. The time consumed in this operation varied from 6.4 sec. to 8.0 sec. with the different observers.

*Experiment 5.*—0.0001 KCl solution in cell 2. Resistance, 30,892, 30,894; mean, 30,893; dev., 0.003%. Minimum extended through 3 scale divisions.

*Experiment 6.*—Identical with experiment 5 except that the special "film" resistance box was substituted in place of the Hartman and Braun box used in experiment 5. Resistance, 28,895.8, 28,896.3; mean, 28,896.0; dev., 0.0011%. Perfect minimum. A comparison of the results of experiments 5 and 6 shows the improvement in the minimum effected by use of the film resistances.<sup>1</sup>

*Experiment 7.*—Conductivity water having a specific conductance of  $0.9 \cdot 10^{-6}$  mhos at the temperature of the experiment was measured in cell 4. Resistance, 33,185, 33,191; mean, 33,188; dev., 0.012%. Poor minimum. No point of complete silence could be found. A swing of 12 scale divisions was necessary in estimating the bridge setting.

*Experiment 8.*—The same as experiment 7 except that the special "film" resistance box was employed. Resistance, 32,857.9, 32,857.9, 32,857.9; mean, 32,857.9; dev., 0.0%. Minimum good, perfect silence being obtained. Range of swing 4 scale divisions, with sharp appearance of the sound at each end of the swing. The advantage of the "film" resistances is again evident from the results of experiments 7 and 8. The next three experiments deal with solutions of high specific conductance.

*Experiment 9.*—Normal KBr in cell 1. Resistance, 27.9293, 27.9296, 27.9296; mean, 27.9295; max. d., 0.0007%; a. d., 0.0005%. Perfect mini-

<sup>1</sup> The difference in the absolute values of the resistances given in experiments 5 and 6 is not significant, as the values used for the resistance units of the "film" resistance box are only approximate. No attempt was made to standardize these resistances for this set of experiments.

imum. This experiment shows that polarization has no influence upon the minimum at this concentration.

*Experiment 10.*—6 N  $\text{H}_2\text{SO}_4$  in an Arrhenius cell with the electrodes 10.2 cm. apart. Resistance, 1.5506, 1.5512, 1.5518; mean, 1.5512; max. d., 0.04%; a. d., 0.028%. Minimum very poor. Length of swing 40 scale divisions. The disturbing effect of polarization is evident in this experiment. It can be largely eliminated, however, by employing a properly designed cell, as is evident from the results of the next experiment.

*Experiment 11.*—6 N  $\text{H}_2\text{SO}_4$  in a special high resistance cell (Kohlrausch and Holborn, fig. 10, p. 16) fitted with platinized electrodes 3 cm. in diameter. Resistance, 149.401, 149.407, 149.425, 149.407; mean, 149.410; max. d., 0.010%; a. d., 0.005%. Minimum fair. Range of swing, 1 scale division. Complete silence was not obtained.

*Experiment 12.*—In measuring the resistance of very dilute solutions, fair results can also be obtained with a small induction coil, provided that "film" resistances are employed instead of the standard type of resistance box. The following results were obtained in this manner for a 0.0001 N KCl solution in cell 2. Resistance, 28,927.6, 28,928.9; mean, 28,928.2; dev., 0.003%. Minimum good. Perfect silence was obtained. Range of swing 3 scale divisions (cf. Exp. 6).

When the standard resistance box was used the following results were obtained. Resistance, 30,096, 30,102; mean, 30,099; dev., 0.01%. Minimum very poor. Silence could not be secured at any point. Range of swing, 20 scale divisions (cf. Exp. 5).

#### 4. Discussion of the Experiments.

The results obtained in the test experiments indicate very clearly that with the improved apparatus *the conductivity of any solution of an electrolyte from conductivity water itself up to a several-times-normal solution can be determined with a precision of 0.01% with the greatest of ease, and that by careful work this degree of precision can be raised to 0.001% in most cases.*

Although a *precision* of a few thousandths of 1% can be obtained with this apparatus, the attainment of an equal degree of *accuracy* is of course quite another story, involving as it does the elimination of all sources of constant error, amounting to 0.001% or more. The latter problem will not be considered here.

In cases where *changes* in conductance, *only*, are involved, however, constant sources of error are not necessarily objectionable. An example of this occurs in transference measurements by the Hittorf method. At the completion of such a transference experiment it is first necessary to discover whether the concentrations of the three middle portions are identical or not. This can be very quickly and accurately determined by finding successively the bridge settings for each solution in the same conductance cell. This method will usually result in the saving of a

considerable amount of time, since in exact work these concentrations must be determined with an accuracy of at least 0.01%. The new apparatus should prove of considerable value in all cases where a very exact analytical control of pure solutions of electrolytes is desired.

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## RECENT WORK IN INORGANIC CHEMISTRY.

BY JAS. LEWIS HOWE.

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*Elements.*—A very complete investigation of the precipitation of silver on glass in mirror form has been made by Kohlschütter (*Ann.*, **387**, 86). The solution used was ammoniacal silver nitrate with some reducing agent such as formaldehyde, grape sugar, milk sugar, tartaric acid, hydrazine, and others. In the solution very little silver is present as  $\text{Ag}^+$ , but there is a relatively large number of  $\text{OH}^-$  ions. The precipitation of silver in mirror form depends upon the very slow oxidation of the reducing agent, silver oxide being the oxidizing agent, and the concomitant formation of substances of high molecular weight or of colloidal form, everything which antagonizes sol-formation being unfavorable to mirror formation. The character of the mirror is greatly influenced by the composition of the silvering solution and also by the character of the glass upon which the mirror is precipitated. The reason for the precipitation of the silver on the glass is that the silver hydroxide is adsorbed by the glass (hence the influence of the kind of glass), and the reducing agent must also be adsorbed by the glass. Thus everything that affects the surface tension of the solution affects the mirror. Microscopic and ultramicroscopic examination shows that the silver is amorphous and homogeneous, and it may be considered to be in a state of colloidal division. Thus while the mirror is unchanged by alkalies, it is easily removed by very dilute acids, though not dissolved. The sudden appearance of electrical conductivity in the mirror and its rapid increase are explained by the precipitate being laid down in discrete particles which in time bridge over the intervening spaces. The increase in conductivity of the finished mirror corresponds to the spontaneous coagulation of a metal-sol, while the increase under the influence of acids corresponds to the electrolytic precipitation of the sol. The mirror formed by the cathodic dusting of silver in dilute gases varies in character with the gas used, as does the precipitated mirror with the solution.

The rapidly increasing use of many of the rarer metals has led to fuller investigation of their properties. Efforts to get a pure vanadium have been made by Ruff and Martin (*Z. angew. Chem.*, **25**, 49), but without complete success. Previous attempts to reduce the easily fusible  $\text{V}_2\text{O}_5$  to metal having been unsuccessful.  $\text{V}_2\text{O}_3$ , which fuses at  $2000^\circ$ , was reduced by aluminum, as well as by carbon and vanadium carbide. The best product obtained was nearly 99% pure. The difficulty of getting a pure metal lies in the fact that the vanadium dissolves the oxide  $\text{VO}$ , as well as aluminum and carbon, hence no latitude in proportion of reducing material is permissible, and the whole mass must react uniformly, conditions practically impossible of attainment. The melting point of the pure metal was calculated as  $1715^\circ$  and the density as 5.688. Brunck