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STUDIES OF HYDROGEN ION CONCENTRATION MEASUREMENTS. I. METHODS OF MEASUREMENTS

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Introduction

Beans and Oakes[1] state that their investigation undertaken for the purpose of developing a method of measuring the hydrogen ion concentration of pure water as directly as possible became a problem of developing and applying a new method of measuring potential differences in which the resistance of the circuit would not affect the accuracy of the results, and which at the same time would not require an excessive amount of current for operation. In other words, this new method was to have all the advantages of the potentiometer arrangement with the additional advantage of being independent of the internal resistance of the cell.

It is also stated that the application of such a method would not be limited to the cell mentioned above. This same method could be applied to all concentration cells, finding its greatest use, however, in connection with the measurement of the electromotive force of cells having such a high internal resistance as to render them impossible of measurement so long as the potentiometer method is the only one available. The method so developed consisted of the employment of a high grade condenser, standard cell and ballistic galvanometer. The diagram of the connections is shown in Fig. 1.

A similar method was described by Carhart;[2] Potter,[3] also, describes the condenser method of determining the conductivity of cells of high internal resistance.

Considerable data have been accumulated on acids and bases by Davis, Oakes and Salisbury,[4] where a standard procedure was employed throughout, using the apparatus described by Beans and Oakes.[1]

[1] Beans and Oakes, This Journal, **42**, 2116 (1920).

[2] Carhart and Patterson, "Electrical Measurements," Allyn and Bacon, Boston, 1900, pp. 188–189.

[3] Potter, *Proc. Roy. Soc. London*, **84B**, 260–275 (1911–1912).

[4] Davis, Oakes and Salisbury, *Ind. Eng. Chem.*, **15**, 182 (1923).

In consideration of the moderate cost of the apparatus as pointed out by Beans and Oakes,[1] a standard Leeds and Northrup condenser, capacity of one microfarad, subdivided into five sections was used by Davis, Oakes and Salisbury.[4] Several anomalies in the data as obtained by Davis, Oakes and Salisbury[4] were noted and reasons suggested for such discrepancies; however, it seemed there were experimental errors in the general ballistic method outlined by Beans and Oakes[1] which have hitherto been overlooked.

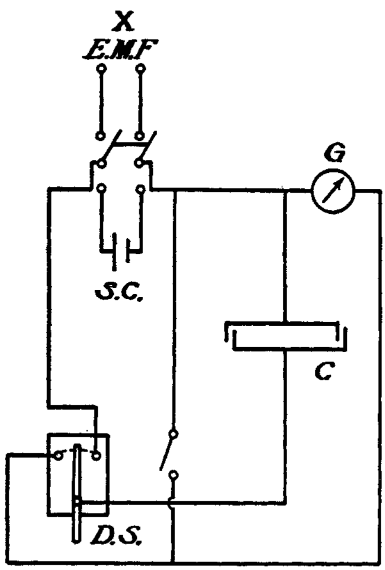

Fig. 1.

The primary purpose, therefore, of this investigation was to test the effectiveness and technique required in electrometrically determining hydrogen ion concentration of a solution by means of the condenser arrangement. It was also our purpose to determine the significance of the individual data obtained by the condenser arrangement and the precision necessary to secure a given accuracy for the resultant electromotive force. In order to secure accuracy of final results, it was necessary to compare directly measurements of electromotive force by the condenser method with those obtained by the standard potentiometer method.

Apparatus and Method of Measurement

The investigation was divided into three major parts: (1) the measurement of the inherent errors in the ballistic galvanometer method of hydrogen-ion determinations; (2) the titration of typical acids with sodium hydroxide to point out the significance of such errors as was noted in part one; (3) a mathematical discussion of the formula used in calculating the unknown electromotive force as determined by the ballistic galvanometer method.

Part (1) of this experiment was conducted in the following manner. The condenser was charged with a definite electromotive force obtained from the potentiometer. This charge was then released through the ballistic galvanometer and the swing accurately noted to plus or minus 0.1 mm. A swing as nearly equal as possible was then made with the standard cell using the proper condenser capacity. The agreement of the swings in most cases could be obtained within 2 to 10 mm. Knowing the ratio of the plates used and the voltage of the standard cell, the electromotive force equivalent to this swing can then be calculated. The difference between the calculated electromotive force and the charging electromotive force from the potentiometer was considered an inherent error in the ballistic galvanometer method. The diagram of the connections is shown in Fig. 2.

The apparatus used consisted of a Leeds and Northrup Type K Precision Potentiometer with Leeds and Northrup Type H highly sensitive galvanometer, Leeds and Northrup standard mica condenser of one microfarad capacity subdivided into five sections having values of 0.5, 0.2 and 0.05 microfarads' capacity, respectively, Type R highly sensitive galvanometer and two Weston Standard cells.

The standard cells used were checked against two Eppley cells, standardized by the U. S. Bureau of Standards, as well as calibrated by means of a Wolff potentiometer in the Ernest Kempton Adams Laboratory, Department of Physics, Columbia University.

Discussion of the Galvanometer and Condenser

Many precautions are to be observed and possible errors guarded against in the operation of the general ballistic galvanometer method.

The individual errors of leakage and inequality of swings have been pointed out to a certain extent while many inherent errors of the ballistic galvanometer and condenser have been omitted. These errors are many in number and may be neutralized one by the other or may be additive. In this respect, Zeleny[5] and White[6] have noted several precautions and possible errors which apply to the ballistic galvanometer method.

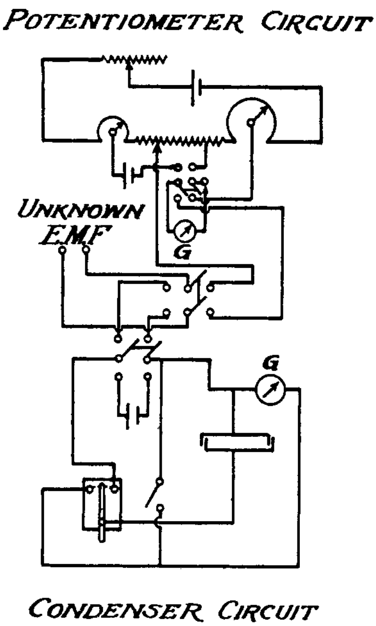

Fig. 2.

In ballistic work the throw that is equal at least to the maximum that is to be used is given to the coil so that a set is affected in the direction of the throw that is to follow.

The coil on returning to the null point must not be allowed to move past, as otherwise part of the set is removed. Subsequent throws in the same direction cause little or no addition to the set.

Hysteresis Effects.—The first throw of the galvanometer is generally at least 0.3% more than the following ones and should be discarded.

When a ballistic throw is to be taken while the coil is not entirely at rest, the discharge must be made when the coil is at either turning point of its motion. The throw in either case must be computed from the natural zero point and not from the point at which the throw originated, as is sometimes stated.

In all cases the galvanometer should be used on an open circuit; it is

[5] Zeleny, *Phys. Rev.*, **23**, 399 (1906).

[6] White, *ibid.*, **23**, 382 (1906).

then more sensitive and the quantities more nearly proportional to the throws. When the circuit is closed an error may be introduced by the thermo-electric current that usually exists in a closed circuit, which itself produces an appreciable deflection.

The ballistic galvanometers for use in the condenser method have a relatively short period and the possibility of reading the throw accurately is very difficult and is generally taken as plus or minus 0.1 millimeter. Calculations show that amount of error in the resultant electromotive force due to this personal error in reading cannot be overlooked.

The zero shift of the ballistic galvanometer amounts to 3.0 to 7.0 mm. during the usual period required in titration work. This effect is due to such factors as change in temperature, lengthening and shortening of the suspensions, hysteresis in the suspensions from magnetic foreign material, possible set in the suspension fiber and other mechanical disturbances in the system.

With this knowledge of the working peculiarities of a ballistic galvanometer, it would be difficult to calibrate the galvanometer deflections and construct a graph so as to read electromotive forces directly. As will be noted, the zero point will change from time to time, and shifting the zero point on the scale to equal the original zero will now create a possible variation in the angular deflection of the galvanometer and thus change its calibration, as the relationship between the electromotive force and deflection of the galvanometer for a given capacity is not a straight line function but curvilinear. It will be seen that such a precaution is eliminated in using the galvanometer as a null instrument because in such a case the deflections when in service are small and do not disturb the zero position.

In the operation of the ballistic galvanometer method, it is necessary to select by trial a set of plates of one capacity for the standard cell and a set of plates of another capacity for the unknown electromotive force in order to secure proper equality of ballistic deflections. The arrangement of the plates in either case to secure the proper capacity may have been either in series or parallel. The guaranteed accuracy as stated by the manufacturers is plus or minus 0.1 to 0.25% for each individual set of plates. With this idea in mind, it is very probable and possible that in such an arrangement of the plates, to secure proper agreement in swings, this error is additive, for instance, positive error for the standard cell and negative error for the unknown electromotive force. Calculations will show these errors to be of primary importance in the resultant electromotive force.

It was noted in a previous paragraph that the errors due to inaccuracy in reading the galvanometer deflections plus or minus 0.1 mm. were of like magnitude, as pointed out above, thus making the total error of significant value. From this standpoint of errors originating from the use of several sets of plates, it would seem only logical to use a fixed condenser of suitable capacity, that is, 0.3 or 0.6 microfarad. This particular idea was pointed out by Beans and Oakes[1] where they suggest the use of a single unit condenser, thus eliminating the capacity factor in the equation $E_1/E_2 = d_1C_2/d_2C_1$. With such an arrangement it is obvious that the capacity value would not appear in the calculations for the unknown electromotive force and the calibrated value of such a fixed condenser need not be accurately known. This method, however, could not be used with any degree of accuracy, as the equality of the swings in such a case would never be possible and errors of such magnitude as shown in Fig. 4 would be encountered.

There is also a serious objection to the condenser method inasmuch as the condenser will maintain with uncertainty the same capacity from time to time. This would invalidate calibration data being used over various periods of time. The condenser plates are held together by the insulating materials only, usually the paraffin in which they are imbedded. If the temperature of the room varies to any great extent, or in case the condenser were placed in such a manner so as to be subjected to external heating, the plates would change their relative positions and thus raise or lower their stated capacity. It is obvious from this consideration that great care should be exercised in preventing such temperature variations and the condenser should be tested from time to time for its accuracy.

In the selection of a condenser for such electromotive force measurements as herein discussed, it is of great importance to secure an instrument which has a very small absorbed charge. The absorption charge in good mica condensers will vary from 0.1 to 1.5%; each condenser or set of plates will have its own characteristic property as to absorption.

Furthermore, and of greater importance, is the adoption of a condenser which can be properly calibrated. Condensers designed for precision measurements are of two general types, namely, fixed single-unit condensers and condensers subdivided into several sections so as to provide various parallel and series combinations.

When considering the use of a condenser subdivided into several sections so as to eliminate errors in the swing of the galvanometer, such as would be encountered when using a fixed condenser, we find there are two general classes of this type of condenser. The first class consists of those with binding posts fastened to the terminals of the condenser and the second class is those of the plug switch type.

With condensers of the latter type the leakage across the exposed metal bars for holding the plugs will be of an appreciable value. Also, it will be noted that each plug switch affords a small air condenser, which will play an important part when calibrating this type of condenser. The value of the error arising from these small air condensers will be directly proportional to the frequency used for calibration.

Experimental

In the discussion of the condenser method by Beans and Oakes,[1] practically no emphasis was placed on the importance of adjusting the swing of the galvanometer for the unknown electromotive force to an equal value as obtained with the standard cell.

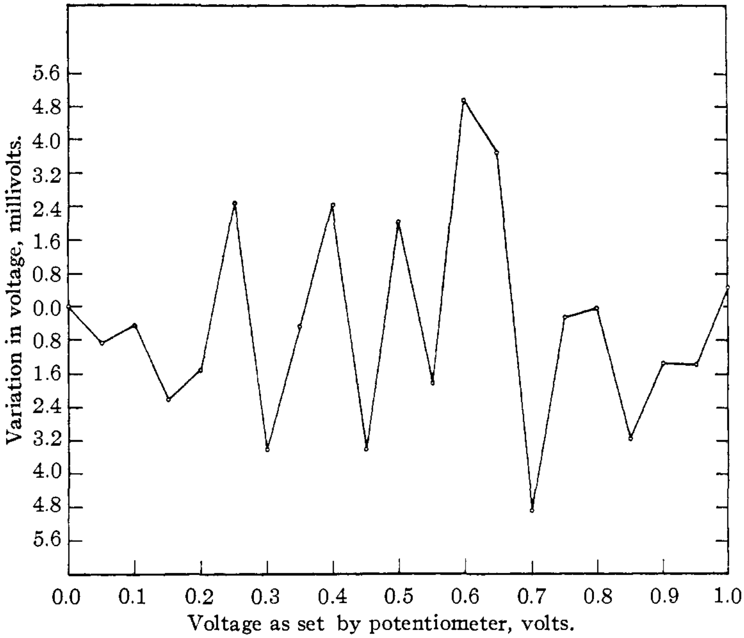

Fig. 3.

"The average deflection for this cell after reaching maximum voltage is 25.0 mm. for one microfarad capacity. Since the standard cell of 1.01823 volts gave a deflection of 50.0 mm. when used with a capacity of one microfarad, the voltage of this cell is 25/50 $\times$ 1.01823 volts or 0.5091 volt." Such a method of disregarding the equality of swings leads to extremely large errors in the final calculated electromotive force. With this precaution in mind variations in the resultant electromotive forces were determined with the swing of the galvanometer for the unknown electromotive force adjusted by trial as nearly equal as was possible to that obtained with the standard cell as a source of potential. These results are shown graphically in Fig. 3.

The average of these observations was plus or minus 2.0 millivolts, the error being plus or minus depending on whether the swing of the galvanometer for the unknown electromotive force was greater than the swing obtained with the standard cell. Actually, when the swing of the galvanometer for the unknown electromotive force was greater, the error was in all cases minus, and *vice versa*.

It will be noted from Fig. 3 that the error in 0.50000 volt was plus 2.0 millivolts. Fig. 3 was plotted from data obtained by using a Leeds and Northrup Type 1058 condenser where there are 57 possible direct series and parallel plate combinations, thus affording 57 possible variations of capacity. Actual readings of the galvanometer swings for the above point were 227.0 millimeters for the unknown electromotive force and 229.0 millimeters for the standard cell.

This is a variation of 2.0 millimeters in approximately 230.0 millimeters, the result of which is a difference of less than 0.9%. Even with this small variation in galvanometer swings, the resultant error was large, namely, 2.0 millivolts. This error might have been slightly reduced in case the use was made of a high grade precision condenser where a greater number of plate combinations is possible. It will be readily seen that such a means of decreasing this error as noted above, by a cut and try method of finding the exact combination of plates which would give a swing for the unknown electromotive force more nearly approximating that of the standard cell, would result in an excessive waste of time when compared with the potentiometer method for obtaining the same result.

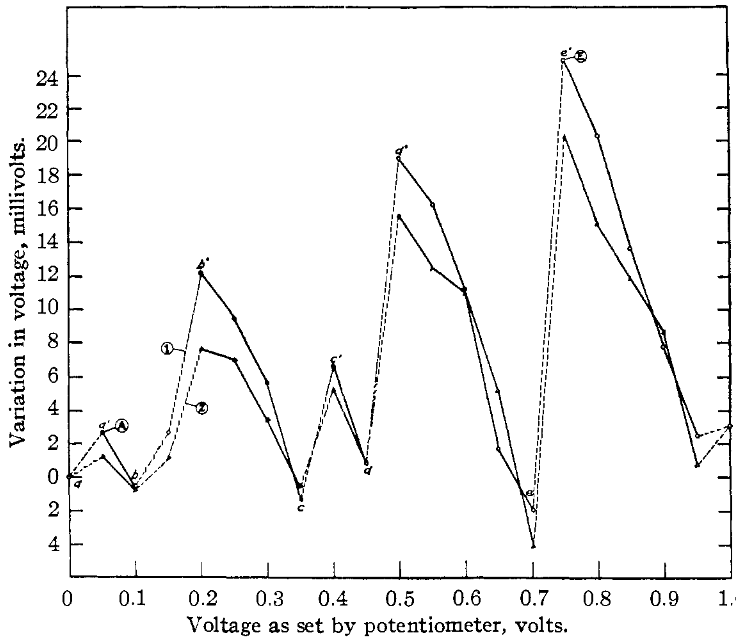

Fig. 4.

Fig. 4 shows several possible sources of error: first, the large error obtained when no account is taken of the equality of the galvanometer swings for the unknown electromotive force and the standard cell. This error is not a fixed one and depends largely on the differences between these two values of swing. This error is also a factor of the voltage, that is, point (A) was obtained with a difference in the swings of 67.0 millimeters, while with point (E) there was 25.0 millimeters' variation. This points out that large differences at low voltages will give less error than small differences at higher voltages. In other words, the best range at which to operate the swing on the galvanometer would be below 100 millimeters' rather than around 200 millimeters' deflection, as is generally assumed. In the next case, the slopes a-a′, b-b′ and c-c′ are significant because they show a decrease in the error with the increase in voltage for each particular slope. The points on the slope a-a′ were taken with one definite combination of plates; likewise for b-b′ and c-c′. In each case it will be seen that as the voltage increases the deflection differences decrease and the error between the electromotive force for the potentiometer and that calculated from the standard cell with the condenser approaches a small value.

Finally, the error due to a high humidity condition surrounding the apparatus was considered. Curves 1 and 2 of Fig. 4 were plotted from data obtained with relative humidities 39.0 and 66.0%, respectively. Although these observations were made on separate days, care was exercised in order to have approximately all conditions except the humidity the same in each case. In other words, the combination of the plates of the condenser arranged for the proper capacity at each point was made

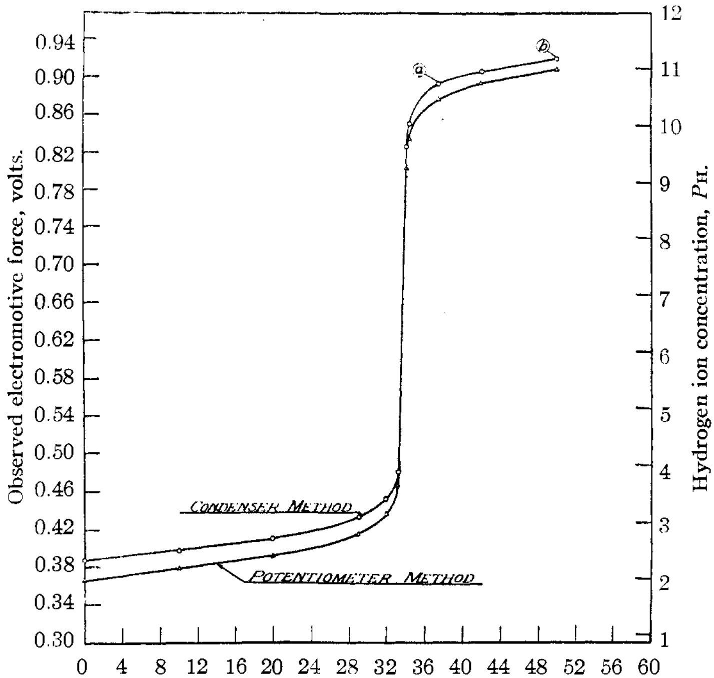

Fig. 5.—Titration of sulfuric acid with 0.1 M sodium hydroxide.

identical, thus eliminating any possible error due to a change in plates or an error which might arise due to a marked difference in the deflection of the galvanometer. It will be seen from these two graphs that with a high humidity the error is apparently decreased; this is no doubt due to a leakage of the charges from the plates and from the system comprising the condenser apparatus. Humidity will cause a difference in the insulation resistance of the condenser arrangement and consequently a variation in the leakage. This would include leakage across the terminals of the galvanometer, leakage across the terminals of the charge and discharge key and leakage between the leads to and from the various instruments. It will be noted that this is an important factor which might easily be overlooked and give conflicting results in case the atmospheric conditions were disregarded.

Fig. 5 represents a change in voltage when sulfuric acid was titrated with sodium hydroxide and shows typically the displacement which occurs when the condenser method is used to determine this electromotive force. Considering the irregularities of the errors obtained on different readings, one might assume that the curve obtained with the condenser would be somewhat jagged and not smooth in character. The lower section of the curve up to the beginning of the break does not agree with this view but is quite regular and is a very smooth curve. The reason for this is no doubt the fact that over this region one set of plates was used on the condenser. The accumulated errors on the plates were apparently greater than the errors set up by the inequality of the swings on the ballistic galvanometer. Therefore the displacement was practically constant throughout this region.

It will be seen that the curve obtained with the potentiometer and that with the condenser coincide at the inflection point. This must be so since the points are vertically displaced and the inflections here have assumed a perpendicular touching all the points of the two systems. Where the upper part flattens out again we have another disagreement between the two systems. The amount of this difference is slightly less than in the lower section of the curve. This again is no doubt due to the accumulated errors on the combination of the plates used on the condenser. Another consideration which seems to indicate that the plate error is considerably greater than the error of unequal swings is shown at points (a) and (b). At (a) the difference in the swing between the unknown and the standard electromotive force on the galvanometer was 7.5 mm., and at (b) this difference was practically zero. Even with this equality of swings the displacement for both points is nearly equal, which points out strongly that the error of displacement is from some other source which might well be due to the errors in the calibration of the plates of the condenser.

An important point which must be emphasized here is that the center of the break in the curve as obtained with the potentiometer is equivalent to a P_H of 6.9, while with the condenser the center is equivalent to 7.2 in P_H value. Although this difference may not have significance in a curve of one deflection, it is of vital importance when two deflections occur, such as in the titration of orthophosphoric acid.

What was said of the sulfuric acid curve regarding the displacement of the two systems as being due primarily to the summation of the plate errors, may also apply in the phosphoric acid titration curve. It can readily be appreciated that if the two breaks in the phosphoric acid curve are displaced due to the errors mentioned above, that difficulty might be encountered in showing the true relationship for the first and second end-points.

The purpose of the curve in Fig. 6 is to show the variation in the trend of the curve with a change in the combination of plates of the condenser. The section a-b was obtained by titrating orthophosphoric acid with sodium hydroxide and with the use of one combination of plates arranged for the most suitable capacity. The displacement is in accordance with that found in titrating sulfuric acid. Section b-c was obtained with a second combination of plates. It will be seen that the slope of the curve breaks very sharply at point b-b′ due to the difference in the accumulated errors in the two sets of combinations. The smoothness of the curve when using the condenser method depends, therefore, upon the number of times the combinations of plates are changed. If any changes are made, a jagged curve is certain to arise. This is seen in Fig. 3, where for each point a different set of plates was used.

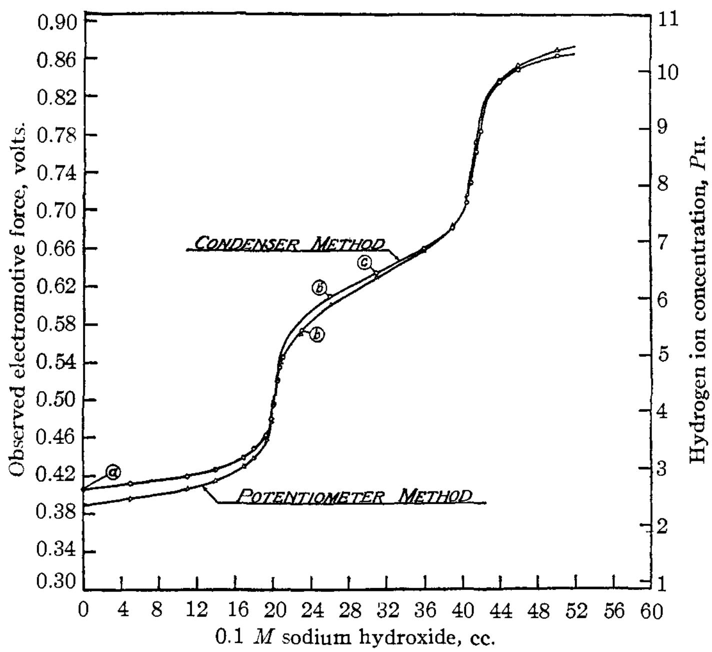

Fig. 6.—Titration of orthophosphoric acid with 0.1 *M* sodium hydroxide.

Mathematical Discussion of Errors

Since the galvanometer cannot be read to a value closer than plus or minus 0.1 mm., the following calculations will show the magnitude of such errors in the resultant electromotive force due to the personal error in reading the swing of the galvanometer.

$$\text{Electromotive force of the standard cell} \times \frac{\text{Gal. Swing Unknown}}{\text{Gal. Swing Known}} \times \frac{\text{Con. Cap. Known}}{\text{Con. Cap. Unknown}}$$

is equal to the Unknown Electromotive Force.

The following figures are taken from actual data as obtained during these experiments, the condenser arrangement being identical with that used by Davis, Oakes and Salisbury.[4]

$$1.01850 \times \frac{230.3}{229.0} \times \frac{0.183}{0.250} = 0.74979$$

Assuming a plus or minus 0.1 mm. difference of the two readings of the galvanometer, we have

$$1.01850 \times \frac{230.5}{228.8} \times \frac{0.183}{0.250} = 0.75106$$

This gives us an error of 0.00127 volt or 1.27 millivolts.

Since each plate of the standard mica condenser used is only accurate to plus or minus 0.25% and the manipulation to obtain equality of swing necessitates the arrangement of as many as five plates in parallel and series, one can easily see that an extremely large error may result from this cause. Calculating the resultant error due to the percentage variation on the average of three plates used for this point, we have

$$1.01850 \times \frac{230.3}{229.0} \times \frac{0.18346}{0.24937} = 0.75357.$$

Here the difference between this value and the original value of 0.74979 volts gives an error of 0.00378 volt or 3.78 millivolts.

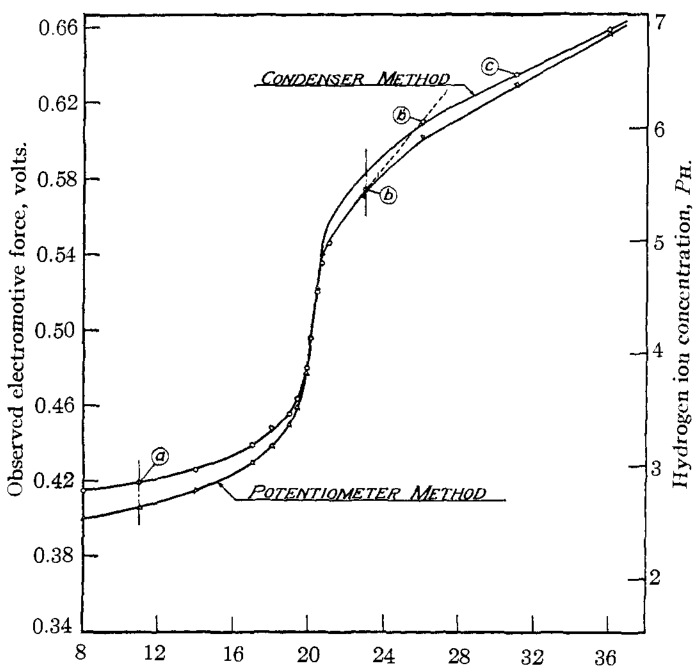

Fig. 7.—Section from Fig. 6 enlarged.

Since it is quite possible that the plate errors and errors due to the reading of the galvanometer swings might occur at the determination of the particular electromotive force stated above, we have a maximum possible error equal to the sum of these two errors, which is 5.05 millivolts.

When considering the use of a precision condenser similar to the type employed by Beans and Oakes[1] (Plug Type Precision Standard Mica Condenser, manufactured by Jas. G. Biddle), we have the values of capacitance accurate to approximately 0.1%. Calculating the resultant error due to this particular percentage variation in capacitance, for the above point in question, we have

$$1.01850 \times \frac{230.3}{229.0} \times \frac{0.18318}{0.24975} = 0.75128 \text{ volt}$$

With this added accuracy in capacitance values, we have still a noticeable error amounting to 0.00149 volt or 1.49 millivolts. Now we will have as a maximum possible error occurring at the determination of the particular electromotive force indicated above, a value equal to 0.00276 volt or 2.76 millivolts. These calculated maximum errors of 5.05 and 2.76 millivolts are equal to more than ten and five times, respectively, that quantity given by Beans and Oakes,[1] which states a precision of plus or minus 0.5 millivolt for the condenser system of measuring potentials.

It might be well to mention here that with small deflections amounting to approximately 70.0 mm., the above errors are greatly reduced because the multiplying factor is of a smaller quantity.

Although this may theoretically give a smaller error it will be apparent to those who have used a ballistic galvanometer that, for small deflections the time period is so much shorter than in higher ranges, it is doubtful whether the readings can be made to as close a value as plus or minus 0.1 mm. as assumed above. It would not be at all surprising if this error approached a value of approximately plus or minus 0.2 mm. It can be seen therefore that it is almost impossible to judge the accuracy of any electromotive force measurement as obtained by the use of the condenser system, and further it seems almost impossible to eliminate one or many of these sources of error.

The above formula as used for these calculations of the unknown electromotive force and, as recommended by Beans and Oakes,[1] requires the use of the electromotive force of the standard cell, which is assumed to be accurate to one or two in the fifth decimal place and multiplies this value by a factor, condenser capacity, which is accurate to only one in the third place.

When several independent sources of error conspire to produce a resultant error, we find that if any term in the operation is in doubt by say 1.0%, the product or quotient will be in doubt by 1.0% on account of that term alone. In other words, the product or quotient cannot therefore be more precise than the percentage precision of the least precise factor entering into the computation.[7] In the case of the example mentioned above, we can calculate the probable resultant error as follows.

[7] F. W. Mellor, "Higher Mathematics for Students of Chemistry and Physics," Longmans, Green and Co., London, 1919.

$$Q = \frac{q^1 q^2 q^3}{q^4 q^5}$$

where q^1 = electromotive force of the standard cell; q^2 = ballistic swing of the unknown electromotive force; q^3 = condenser capacity of the known electromotive force; q^4 = ballistic swing of the known electromotive force; q^5 = condenser capacity of the unknown electromotive force.

The percentage deviations are used in these calculations, for in such a function as above the percentage error in any component factor produces the same percentage error in the final quantity, that is

$$100 \frac{\Delta q_n}{q_n} = 100 \frac{\frac{\delta Q}{\delta q_n} (\Delta q_n)}{Q}$$

The value of Q was found to be equal to 0.74979 volt. Consequently, if E is the actual error in Q caused by errors e_1, e_2, e_3, e_4 and e_5, which arise from errors in the components, the percentage error in Q will be given by

$$100 \frac{E}{Q} = \sqrt{\left(\frac{100\,\Delta q^1}{q^1}\right)^2 + \left(\frac{100\,\Delta q^2}{q^2}\right)^2 + \left(\frac{100\,\Delta q^3}{q^3}\right)^2 + \left(\frac{100\,\Delta q^4}{q^4}\right)^2 + \left(\frac{100\,\Delta q^5}{q^5}\right)^2}$$

from which the actual error E can be computed.

Using the data of the foregoing calculations, the percentage precision of Q becomes $\pm 0.35\%$. The actual error E is then 0.74979×0.0035, which is 0.00252 volt or 2.52 millivolts.

The percentage precision of Q when using a precision condenser similar to the one employed by Beans and Oakes[1] becomes 0.15%. The actual error E would then be 0.74979×0.0015, which is 0.00112 volt or 1.12 millivolts. Here the value of the error is reduced somewhat as the accuracy of the condenser plates is plus or minus 0.1%.

General Summary and Conclusions

1. The use of the condenser and ballistic galvanometer in determining electromotive forces of solutions was employed by Carhart[2] and by Potter.[3]

2. The important errors in this method are due to the accumulation of errors on the plates of the condenser, the throw of the galvanometer, humidity and the formula used in the calculation of the unknown electromotive force.

3. The important errors have been calculated and graphs drawn to show the significance of such errors in the titration of sulfuric acid and orthophosphoric acid.

4. The accumulative error may sometimes reach a value approximating plus or minus 3.0 to 4.0 millivolts.

5. Results seem to indicate that the condenser system of electromotive force measurements cannot be used where precise work is required, such as in the titration of solutions or in the determination of equilibrium constants.

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