

A Review of the Methods of Electrometric Determination of Hydrogen Ion Concentration

By D. McRae

At the outset, it should be pointed out that this paper is merely a compilation of some of the work already done in this branch of Physical Chemistry. It is not a complete compilation and is intended primarily to give the general principles underlying the methods for the electrometric measurement of hydrogen ion concentration. It contains no results of original research on the part of the author, practically all the facts having been gleaned from the papers listed on the appended bibliography. The original papers and standard text-books should be consulted, where further details are required regarding practical working, and the more detailed theoretical considerations.

Electrometric methods for the measurement of hydrogen ion concentration now occupy a place from which they cannot be displaced by any other known method. Those who have had experience with the colorimetric method will know of the difficulties experienced when working with turbid, dark-coloured and concentrated solutions. On the other hand, results with the electrometric methods are far from being infallible in every case. Precaution must be taken to ensure that all possible sources of errors are eliminated.

The electrometric methods are based upon the fact that when a metal is placed in a solution of its own ions, there is a difference of potential between the metal and the solution. This is best explained by Nernst's conception of electrolytic solution tension. He imagines each metal to have a definite tendency to go into solution as ions. The moment a metal, say zinc, sends positive ions into solution, it itself, becomes negatively electrified, and therefore an electrical double layer or a difference of potential between metal surface and solution comes into being, the resulting electrical force opposing the sending of more ions into solution. Owing to the enormous charges on the ions, equilibrium is reached at the metal surface with infinitesimal amounts of metal sent into solution.

The tendency for any particular metal to send ions into solution depends on the concentration of the ions of that metal in the solution. The lower the concentration of ions, that is, the weaker the solution, the greater will be the tendency for the metal to send ions into solution, that is, the bigger will be the potential difference between electrode and solution.

Theoretical considerations have established a relation between the concentration of metallic ions in a solution and the potential difference between the same metal and

the solution of metallic ions. This relation has been confirmed by practical results.

The application to the measurement of ion concentration is now obvious. The difference of potential between a metal and a solution of its ions will give a means of determining the metallic ion concentration of that solution. The metal or its equivalent, is usually called the electrode. The combination of electrode and solution is known as a "half-cell."

The electrometric methods for the determination of hydrogen ion concentration are therefore based on the measurement of the difference of potential between a hydrogen electrode and the given solution of hydrogen ions.

THE HYDROGEN ELECTRODE.

This electrode consists of a noble metal, on the surface of which is deposited a layer of platinum-iridium or palladium-black, which holds large quantities of hydrogen. When such an electrode is laden with hydrogen, and immersed in a solution, there is a difference of potential between the electrode and the solution which is dependent on the concentration of hydrogen ions.

The electrode usually consists of a piece of platinum foil, to which is joined a short length of platinum wire. This wire passes through the sealed end of a glass tube, in which contact is made with the lead from the potentiometer by means of mercury. Platinum gauze might be used in place of foil to give a larger surface, but the great difficulty of properly cleaning the gauze precludes its use in this connection.

The black deposit on the surface of the electrode may be either platinum, iridium or palladium. This deposit is made electrolytically, using 3% solutions of the chlorides and the current from a 4-volt accumulator. In making the deposits, it is essential to have a very high degree of cleanliness of the electrodes. The deposit must be even and of proper thickness; too thick a coating of the black metal produces a sluggish electrode. Best results are obtained using a thin deposit, just sufficient to mask the glint of the polished electrode.

When in use, the electrode should never be allowed to dry, and the black deposit should be renewed fairly often. The old deposit may be removed by electrolysis in hydrochloric acid.

The general method of operation is to immerse partially or wholly, the electrode in the solution to be measured, and then to bubble hydrogen through the vessel till constant potential is obtained. A large variety

of hydrogen electrode vessels have been used. In one type, the space above the liquid consists of pure hydrogen, and the electrode vessel of such a shape that when rocked, the electrode comes alternately into contact with the liquid and the hydrogen. Another method of obtaining similar results is to pass hydrogen into the solution and liberate it immediately below the electrode. Good results have also been obtained by bubbling a very finely divided spray of hydrogen into the solution through a disc of alundum fused in the enlarged end of a hard glass tube.

In this connection it is essential to have a good convenient supply of pure hydrogen. If the hydrogen is generated from zinc and sulphuric acid in a Kipp's Apparatus, it must be purified by passing in succession through caustic potash solution, mercuric chloride solution, phosphorous pentoxide, red-hot platinised asbestos and sodium thiosulphate solution. Such a supply, however, is not very convenient. The large volume of the apparatus employed, necessitates a long run before the hydrogen obtained is reasonably pure, while the necessity for periodically recharging with zinc and acid accentuates this difficulty. A much more convenient supply in every way is hydrogen obtained by the electrolytic process and stored under pressure in steel cylinders. Such a supply used in conjunction with a reducing valve, can be connected direct with the apparatus. It is necessary to first pass the hydrogen through a separate portion of the liquid under test before passing into the half-cell. This prevents any error being introduced due to evaporation of the test solution by the hydrogen.

With the hydrogen electrode, as with all gaseous electrodes, in accurate work, a correction is necessary, depending on the pressure of hydrogen. Tables have been prepared for correcting the potential, the actual pressure of the hydrogen being taken, for all ordinary cases, as the observed barometric pressure, less the vapour pressure of pure water at the working temperature. For instance, at 20°C. with a barometric pressure of 740 m.m., the correction is 0.64 millivolt.

The difference of potential (EH) between such a hydrogen electrode and a solution is related to the p H of that solution according to the following formula :

$$p H = \frac{E H}{0.00019837 T}$$

where T = absolute temperature

In actual practice, there are many factors which limit the general application of the hydrogen electrode. The need for a supply of pure hydrogen is a great drawback, and has done much to stimulate the research for other electrodes which could be used for the determination of hydrogen ion concentration. Equilibrium is not obtained immediately, anything from 5 to 60 minutes being necessary before a constant potential is obtained.

Probably owing to poisoning of the electrode, results obtained with industrial products are not always reproducible. The electrode cannot be used in the presence of sulphur dioxide, while the presence of platinum and palladium black catalyses the reduction of certain substances.

It is now necessary to consider methods for the measurement of the difference of potential between electrode and solution, i.e., methods for the measurement of the potential of individual half-cells.

It is impossible to measure the potential of a half-cell direct with any degree of accuracy. However, by establishing a contact between the solutions of any two half-cells, we obtain an ordinary galvanic cell, the potential of which will be the difference of potential between the two half cells, and which can be measured with a high degree of accuracy. As an example, one of the best known cells is the Daniels' cell, which consists of a copper electrode dipping into a solution of copper sulphate, connected through a porous pot with a solution of zinc sulphate into which dips a zinc electrode. If the potential of one of the half-cells is known, it is an easy matter to determine the potential of the other one.

The fact that the potentials of half-cells are all obtained by difference, necessitates the establishment of a zero, to which the potentials of all other half-cells may be referred. Thus arises the following definition :—

"The potential difference between a hydrogen electrode under one atmosphere pressure of hydrogen, and a hypothetical solution, normal with respect to the hydrogen ion shall be considered to be at zero at all temperatures."

The formula for the determination of p.H with the hydrogen electrode now becomes:—

$$p H = \frac{E - E(\text{ref})}{0.00019837 T}$$

where E = observed e.m.f. of combination

E (ref) = potential difference between the reference and the normal hydrogen electrode at t°C

STANDARD OR REFERENCE HALF-CELLS.

As stated above, it is impossible to measure direct the potential of an individual half-cell. As, however, it is essential to know the potential of individual half-cells the difficulty has been overcome by employing standard or reference half-cells. These are essentially half-cells, the potential of which, is a definite constant value. For hydrogen ion work, the normal hydrogen electrode with zero potential would be ideal. This, however, is not practicable.

In actual practice, the so-called calomel electrodes, or more correctly calomel-half-cells, have been found most convenient and are now almost universally used as reference half-cells.

These calomel half-cells consist essentially of mercury electrodes in contact with a solution containing a definite concentration of mercurous ions. In general construction, the cells consist of a layer of pure mercury, on top of which is a layer of pure calomel and over all a solution saturated with calomel and containing a definite concentration of potassium chloride. The potential of the half-cell depends on the concentration of the mercurous ions in solution, which in turn depends on the concentration of chlorine ions in solution; therefore, the higher the concentration of the potassium chloride, the higher will be the difference of potential in the calomel half-cell.

However, as a metal must of necessity be negative to a solution of ions, the higher the concentration of potassium chloride, the more negative will be the potential of the half-cell. The saturated calomel half-cell will therefore have a lower positive potential than the molar,

The potentials of these half-cells have been determined in various ways. The most commonly accepted values referred to the normal hydrogen electrode are as follows :

Saturated + 0.2488 volts at 20°C.
Tenth Molar + 0.3375 volts at 20°C.

The most commonly used is the saturated potassium chloride calomel half-cell ; tenth molar solution is also used.

The calomel (mercurous chloride) should be prepared from the purest obtainable chemicals. It may be prepared by dissolving mercury in nitric acid followed by precipitation of the calomel with hydrochloric acid. It can also be prepared electrolytically. Full details of the preparation of these half-cells are given in Clark's book on "The Determination of Hydrogen Ions."

Sometimes it is convenient to prepare standard half-cells using standard buffer solutions of known p H in conjunction with any of the electrodes used for the measurement of hydrogen ion concentration.

LIQUID JUNCTION POTENTIAL AND BRIDGE SOLUTION.

When the two solutions of the two half-cells are brought in contact as described above, there is the likelihood of an error being introduced in the measurement of the electromotive force of the combination due to the so-called liquid junction potential. This is due to the fact that a difference of electrical potential is produced when two unlike solutions of electrolytes are brought into contact with one another, principally, according to Nernst because of the unequal rates of diffusion of the ions at the junction.

A saturated solution of potassium chloride is commonly used as a bridge solution, to connect the two solutions of the half-cells. It practically eliminates the liquid junction potential when properly used.

The method of forming the bridge solution depends entirely on the type of electrodes and electrode vessels employed. A small porous pot or disc saturated with KCl has found fairly extensive use. Connection between the two half-cells has also been made through agar-agar containing potassium chloride. In more recent apparatus, connection is made through a ground glass stopper, moistened with saturated potassium chloride solution. Membranes should not be used.

The bridge should be of a reproducible form, easily renewable, and of low electrical resistance. For accurate work, the junction should be made immediately before taking the reading.

METHODS FOR THE MEASUREMENT OF THE ELECTROMOTIVE FORCE OF GALVANIC CELLS.

The most common method of measuring electromotive force is with the aid of a potentiometer. It consists essentially of a long wire of uniform resistance throughout, connected in series with an accumulator and variable resistance. A standard cell and a galvanometer are connected in series with a length of the potentiometer wire proportional to the e.m.f. of the standard cell ; the variable resistance is then altered until no difference of potential is indicated by the galvanometer, care being taken that the two e.m.fs. oppose one another. The fall in potential in the wire having been standardised in this way, it is now possible to measure the e.m.f. of any galvanic cell by putting it in place of the standard cell, and finding

the length of potentiometer wire along which the fall of potential exactly neutralises the e.m.f. of the cell.

There are other methods of determining the e.m.f. It may be determined by use of a quadrant electrometer connected directly to the electrodes. Still another method is to charge an electrical condenser from the cell and then to discharge the condenser through a ballistic galvanometer. In both these methods, thorough insulation of the wires is required. They do not give as accurate results as the potentiometer method.

Another method which finds use in continuous recording instruments is the use of electron tubes. The cell is connected with the grid and filament of the electron tube and the plate current measured either direct or after amplification.

In all measurements it is essential to take as little current from the galvanic cell as possible. If a fair quantity of electricity is taken from any cell, polarisation and other effects are produced, which change the electromotive force of the cell and so give erroneous results.

The accuracy of the measurements also depends on the resistance in the circuit. It is desirable to have all connections well made, and to have the internal resistance of the cell as low as possible.

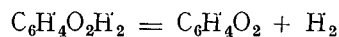
NON-GAS ELECTRODES FOR THE MEASUREMENT OF HYDROGEN ION CONCENTRATION.

Recently there have been developed, several so-called non-gas electrodes for the measurement of p H. As their name implies, no supply of hydrogen gas is required for their operation. The electrodes which have been used in this connection are the quinhydrone, tungsten and antimony electrodes.

QUINHYDRONE ELECTRODE.

Quinhydrone (benzo quinhydrone) is formed by the combination of one molecule of quinone ($C_6H_4O_2$) with the molecule of hydroquinone ($C_6H_4O_2H_2$). It is partially soluble in water and when dissolved, dissociates into its two compounds. Quinhydrone is prepared by pouring a solution of 100 gms. of ferric ammonium alum in 300 c.c. of water at 65°C. into a warm solution of hydroquinone in 300 c.c. of water. The quinhydrone precipitates as fine needles, and after cooling the liquid with ice, are removed by suction, washing three or four times with distilled water.

The action of this electrode depends on an equilibrium between the dissociation products of quinhydrone :—



The equilibrium is independent of the concentration of the quinhydrone.

The general method of operation, is to add 0.01 gms. of solid quinhydrone to 50 c.c. of the solution under test and then dip into the solution an electrode consisting of bright platinum foil or wire. Certain results obtained on buffer solutions and other solutions, have shown that gold-foil is preferable to platinum.

The potential of the half-cell so formed, is related to the hydrogen ion concentration according to the following formula :—

$$pH = \frac{At - E(\text{ref.}) - E_q}{.00019837 T}$$

where $At = 0.7175 - 0.00074t$

E (ref) = potential of reference electrode

E = potential of combination

$t^\circ\text{C.}$ = temperature of cell

T = absolute temperature ($273 + t^\circ$ centigrade)

This electrode is by no means a universal electrode. It has the great advantage over the hydrogen electrode in that no supply of pure hydrogen is required, and equilibrium is attained almost instantaneously. There are, however, other factors which limit the use of this electrode.

1.—Hydroquinone ionises as a weak acid ; this effect is negligible in well buffered solutions.

2.—Aside from errors which may occur at any pH due to oxidation or reduction by strong oxidising or reducing compounds in the solution, there is another which becomes important round pH 8.5 and higher, i.e., in alkaline solution. This is due to the oxidation of hydroquinone into quinone by molecular oxygen in the solution and present in the air in contact with the solution.

3.—High salt concentrations also cause errors. This error amounts to less than 0.1 pH with salt concentrations less than 0.2 M. The quinhydrone electrode cannot be used in the presence of sulphur dioxide which limits its use in the sugar-house control. It has, however, found fairly extensive use for hydrogen ion concentration measurement on soils.

TUNGSTEN ELECTRODE.

In general construction, this electrode consists of a glass tube coated at its lower end with manganese sesquioxide. Around the coating of sesquioxide tungsten wire is wound, terminating through the lower sealed end of the glass tube. Contact with the lead from the potentiometer is made with the aid of mercury.

The half-cell is formed merely by immersing the tungsten electrode in the solution, the pH of which is desired. Minute amounts of the sesquioxide are dissolved, and its partial reduction causes a potential difference to be produced between electrode and solution which depends on the hydrogen ion concentration of the solution.

This electrode has many advantages ; it is simple, sturdy and self-contained ; it requires no supply of pure hydrogen as does the hydrogen electrode ; it is not necessary to add any substance to the solution under test, as with the quinhydrone electrode, and the tungsten electrode may be used in solutions over the alkaline range of pH ; it is particularly free from poisoning.

H. C. Parker of the Leeds Northrup Company makes the following comment on this electrode :—

“The tungsten electrodes have invariably been found to indicate correctly, changes in the hydrogen ion concentration. In some solutions, however, they have been found to possess a slightly different pH voltage, characteristic from that determined with buffer solutions. In these cases, if an auxiliary method for checking is used and if the control setting or the pen is shifted accordingly, a quite satisfactory control or record may be obtained. Since some type of auxiliary check such as titration or a measurement with the quinhydrone electrode is generally in use already, this limitation is not serious. A check is usually necessary not more frequently than once a day.”

It will at once be realised that the tungsten electrode is admirably suited for the control and measurement of hydrogen ion concentration in industry.

A platinum manganese sesquioxide electrode has been used to a limited extent.

THE ANTIMONY ELECTRODE.

This electrode has been comparatively recently employed for the measurement of hydrogen ion concentration. It has been used by E. W. Todd in a reversing electric pH indicator on sugar juices, and more recently has been shown to be the most generally useful electrode in the pulp and paper mill.

The electrode consists simply of the ordinary stick preparation of a radially crystalline structure. The surface of the stick should be smoothed with a file and emery paper.

Like the tungsten electrode, the antimony electrode is self contained, no supply of pure hydrogen being required. The half cell consists merely of the test solution with the electrode dipping into it. The electrode is cheap and easy to secure, is unaffected by sulphites, gives a fairly quick response when placed in solutions, and is admirably suited for continuous reading on recording instruments. It seems to be a very promising electrode for use in the sugar industry. However, it is necessary that more work be done with this electrode before it can be safely recommended generally.

THE APPLICATION OF ELECTROMETRIC METHODS TO THE AUTOMATIC MEASUREMENT AND CONTROL OF pH IN THE SUGAR INDUSTRY.

It is probably unnecessary to dwell for any length of time on the importance of pH determinations in sugar house control. The importance of hydrogen ion concentration in every branch of sugar house work is gradually being realised, and every season, the literature on this subject is being increased. This paper is not intended to give a summary of the work done, but merely to indicate the general methods for affecting such a control.

Apparatus has been designed for the continuous recording of the hydrogen ion concentration of any suitable industrial liquid. If the quinhydrone electrode is used, the liquid is supplied with quinhydrone by passing through a vessel in which bags containing quinhydrone are suspended ; the tungsten and antimony electrodes, however, are more suitable for continuous recording apparatus. The reference cell is usually of the saturated potassium chloride calomel type, and the bridge formed by saturated potassium chloride in a porous disc or ground glass stopper. This apparatus is fairly expensive being listed by one well known firm at approximately £72.

The electrometric control of hydrogen ion concentration, however, is a much simpler matter. The half-cells are so arranged that the potential of the reference or standard half-cells is exactly equal to the potential of the other half-cell when the liquid under test is at the desired pH. The two electrodes are connected to a galvanometer. As soon as there is a change in the pH of the liquid under test, the potential of the half-cell becomes different from that of the standard, and a flow of current is indicated by the galvanometer. When the current flow is in one direction, the liquid is of too low pH, and when in the opposite direction the pH is too high.

Such an apparatus can be used for automatically con-

trolling the liming of juice, and the saturation of second Carbonatation juice. Experiments conducted in Porto Rico in a defecation factory showed that fluctuations in the pH of the limed juice were practically eliminated when electrometric control was used.

As stated above the colorimetric method is of limited application, and cannot be used for automatic control. Great strides have been made and are still being made in the application of the electrometric methods to factory control, and it may be safely predicted that in the near future, apparatus for the electrometric measurement and control of hydrogen ion concentration will form part of the equipment of every factory in which the control of pH is of any importance.

BIBLIOGRAPHY.

- "The Determination of Hydrogen Ions"—W. M. Clark.
 "Potentiometric Hydrogen Ion Measurements with Non-Gas Electrodes"—H. C. Parker, *Indus. & Eng. Chem.*, 17 (1925), 737.
 "Progress of Electrometric Control Methods in Industry"
 H. C. Parker, *Indus. & Eng. Chem.*, (1927), 660.
 "A Reversing pH Indicator"—E. W. Todd. *Facts About Sugar XXII* (1927), p. 14.
 "The pH with Quinhydrone Electrode"—L. E. Dawson. *Sugar* 28, (1926) 211-4, 262-4, 210-2, 369-70.
 "Measurement of Hydrogen Ion Concentration in the Control of Pulp and Paper Manufacture"—E. K. Frake and I. J. Willaman, *Indus. & Eng. Chem.*, 20 (1928), 87.
 "Practical Methods of pH Measurement, and Scheme for

Automatic Electrometric Control of Cane Juice Defecation"—R. G. Balch and H. S. Paine, *Planter and Sugar Manufacturer*, Vol. XXV, 347.

Chairman: I think this is a very lucid account of an apparatus which is rapidly becoming of very great importance in the sugar industry as in so many chemical industries. As Mr. McRae said, it will probably be only a matter of time before the potentiometer is a commonplace instrument in sugar house laboratories. So far as I know, there is only one potentiometer in the sugar industry in the country, the one recently obtained at the Experiment Station, but in Hawaii and especially in the Beet Sugar industry of America and Europe, the potentiometer is finding very important application.

Dr. Hedley: A continuous recording apparatus where you have a pH which can be adjusted to 7 or 7.2, is alright if your cane is the same all the time, but in a case like Felixton, where we have varying types of cane, a continuous record is not going to be as useful as a discontinuous one, because we cannot work definitely to any particular pH. It would have to be varied with the type of juice we are using. If you got, as you have in some of the mills, the same kind of cane coming in day after day then it is alright. Where we have different kinds of cane from hour to hour almost, we find the optimum point of liming is not the same with all canes. I would not like to give figures at present, but it certainly is not the same.

Mr. McRae: Quite a number of experiments have been done to determine the optimum pH, and I might say with regard to the work done so far, the results have not been concordant, which points to the fact that a different pH may be required with different qualities of cane.