SOME NOTES ON THE SIGNIFICANCE AND THE MEASUREMENT OF pH IN SUGAR FACTORIES

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Introduction
The general relationship between pH and the rate of inversion of sucrose is well known; the more acid the solution the faster sucrose decomposes.

Even if it was for this reason only, it would be one of the most important duties of every chief of fabrication to keep a close watch on the pH values of all the liquors in his factory. The pH, however, does not only affect the rate of sucrose inversion, it is also of primary importance in all chemical reactions which together are known as the clarification of our juices, and finally it has an important bearing on the rate of decomposition of the reducing sugars.

It is only by giving the fullest attention to the pH values in his factory (and incidentally also to temperatures) that a chief of fabrication can hope to attain maximum clarification effect and a minimum loss of sucrose.

pH measurement, or better pH recording, at a few strategically selected points in the factory is therefore a must wherever the highest efficiency is strived for. Yet, we have to admit that pH recording is not general practice in all factories, and that the factories endeavouring to operate pH recorders frequently run into difficulties. Electrical pH meters and recorders have not a very good name in our factories; the owners of the factories think that they are expensive gadgets, and the operating staff are often extremely doubtful about the practicability of operating them satisfactorily, i.e. with little interruption and with reliability.

As to the price, one has to realise that a pH recorder of say £350 pays for itself in one season if it succeeds in a factory of average size in reducing the loss of sucrose, either undetermined or in final molasses, by a few hundredths of one per cent.

As to the satisfactory operation of pH recorders the situation is more complicated and quite a number of factors could be indicated which may have contributed to the bad reputation of these instruments.

It is of course possible that the instruments used so far in our factories have not been built by their manufacturers to withstand adequately the rugged conditions of sugar factories. On the other hand manufacturers have the right to ask: Have our instruments always been operated as they should be? and finally there is the question of proper maintenance and repair when the instrument breaks down.

Obviously a solution to this problem can only be found by a close co-operation of pH meter manufacturers, who must have a well-founded knowledge of conditions in sugar factories and of reasonable requirements in regard to sugar pH meters, and of the sugar factory executives, who must at least have a working knowledge of the principles of pH meters, of the correct way to operate them and of minor repairs.

To stimulate such co-operation the S.A.S.T.A. Council has made arrangements for a full discussion of the subject at this Congress and I am happy to say that representatives of three pH meter manufacturing firms have agreed to give us their full co-operation. They will discuss the principal properties of their instruments, will tell us about correct maintenance, and finally, this afternoon, will demonstrate the instruments at the S.M.R.I. But before proceeding to the discussion of these industrial instruments, I thought it might be desirable to discuss pH and pH measurement in general terms.

The Definition of pH
We all know that positively-charged hydrogen ions are always present in aqueous solutions. They are formed either by the electrolytic dissociation of water molecules, or by the dissociations of acids.

\[ \text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^- \]

\[ \text{HA} \rightleftharpoons \text{H}^+ + \text{A}^- \]

Their concentration is one of the most important properties of the aqueous solution. In physical chemistry this concentration is usually expressed in gram ions per litre, and it was Sørensen who, in 1907, introduced a simple way of expressing the concentration by defining the pH of an aqueous solution as the negative logarithm of its concentration of hydrogen ions. \( \text{pH} = -\log [\text{H}^+] \).

In some simple cases it is possible to find the pH of a solution by calculation. Such a simple solution is, for example, N/100 HCl solution. Being a strong acid the HCl molecules are completely dissociated, which means that the concentration of the solution in respect of hydrogen ions is 0.01 gram ion per litre. Hence \([\text{H}^+] = 1/100\) and the pH of the solution is \( \text{pH} = -\log 1/100 = 2 \).

The pH of more complicated solutions cannot be found by calculation. We then have to measure the pH.

As said above, even pure water is slightly dissociated, the concentration of hydrogen ions at room
temperature being $10^{-7}$ gram ions per litre. The pH of pure water is 7, and as the number of negatively charged hydroxyl ions is equal to the number of positively charged hydrogen ions, one may also say that pH = 7. It is a property of all aqueous solutions at room temperature that the sum of pH and pOH is 14, independent of the acidity or alkalinity of the solution.

It is easy to see that the concentration of hydrogen ions in an aqueous solution has to be increased tenfold to reduce the pH by one unit. Also, to bring the pH of a solution from 3 to 2 requires 10,000 times the number of hydrogen ions required to bring the pH from 7 to 6. Generally when acid is added to an aqueous solution the hydrogen ion concentration increases and the pH drops. How much depends on the nature of the acid and on the original composition of the solution. In some cases, for example, when an organic acid is added to a solution of its salts, the drop is slight. In that case we speak of a strongly buffered solution.

This is all rather elementary, and can be illustrated by equations and figures for the so-called dissociation constants, but this does not seem necessary for our purpose at this stage.

For the moment we have to remember that the acidity of a solution as given by its hydrogen ion concentration, is commonly expressed by the term pH, and that since calculation is usually impracticable, measurement of the pH is our only recourse.

The Principles of pH Measurement

There are two methods of measuring the pH of a solution, viz. with so-called indicators and electrically. Indicators, i.e. organic compounds which change their colour according to the pH of the solution in which they are dissolved, have been used to a large extent in the sugar industry, and mainly as indicator papers, are still used. The main disadvantages of the use of indicators is the amount of labour required and the fact that it is impracticable to use them for pH registration. Otherwise indicators are quite satisfactory, particularly when their application has been properly standardised.

The electrometric method of determining the pH of a solution is based on the following phenomenon.

When an element, say a cylindrical rod of silver, 5" long and $\frac{1}{4}$" in diameter, is placed in a solution containing ions of this element—in this case a diluted silver nitrate solution—there is a tendency for the silver to push positive Ag-ions into solution. By doing so the silver tends to become negatively charged in respect of the solution. On the other hand the silver ions in the solution tend to give up their positive charge to the negative silver electrode and, having become atoms, to precipitate on the electrode. These opposing tendencies result when equilibrium has been attained in an electrical potential being set up between the element and the solution.

The pressure exerted by the electrode is independent of the concentration of the solution, but the pressure exerted by the ions depends on their concentration. Hence the potential difference between the electrode and the solution depends on the concentration of the ions.

The pressure exerted by the solution is not exactly proportional to the concentration of the ions. The solution pressure of the ions is usually defined as the "active concentration" of the ions, or their activity. Only in a few simple cases is the active concentration equal to the true concentration.

The relation between the active concentration of the ions and the potential at the surface of the electrode is given by the following equation:

$$E = \frac{RT}{nF} \ln \frac{a_o}{a_i}$$ (1)

where $E =$ the potential in volts

$R =$ the gas constant $= 8.313$ watt seconds

$T =$ the absolute temperature

$n =$ the valency of the ions

$F =$ 96494 coulombs

$a_o =$ a constant indicating the pressure exerted by the element

$a_i =$ the molar activity of the solution.

By substituting and converting to Napier's logarithms:

$$E = \frac{RT}{nF} \ln a_o - 0.0001984 \frac{T}{n} \log a_i \text{ volts}$$ (2)

Formula (2) gives us the relationship between the electrical potential difference at the electrode and the active concentration of the ions concerned. It clearly shows that this relationship if affected by temperature, i.e. even if the concentration of the ions at a higher temperature is equal to that at a lower temperature there will be a difference between the potentials measured. Later on we will come back to this point.

Since $a_o$, at least at constant temperature, is a constant, the first term of the right hand side of equation (2) is constant, and the equation can be written as:

$$E = E_o - 0.0001984 \frac{T}{n} \log a_i \text{ volts}$$ (3)

Formula (3), although explained here for a silver electrode in a solution of a silver salt, is also valid for the potential difference between a hydrogen electrode and a solution containing hydrogen ions. How a hydrogen electrode can be made will be explained later on, the main point at the moment is that it is possible to measure the concentration of hydrogen ions, i.e. the pH, electrometrically using equation (3).
Now in actual practice it is not feasible to measure the potential set up at a single electrode. A second electrode has always to be used to complete the circuit to the measuring instrument. This second electrode, usually called the reference electrode, is also placed in the solution to be tested, and normally also shows a potential difference against the solution. This potential difference is a function of temperature, but is independent of the pH of the test solution. Hence at constant temperature this potential difference is constant, and can be termed $E_1$.

Therefore the overall potential of a cell consisting of a hydrogen electrode and a reference electrode—now termed $E$—is given by the following formula:

$$ E = E_0 + E_1 - 0.0001984 \ T \ log a_1 \ \ (4) $$

In this equation $n$ has been left out since hydrogen ions are monovalent. If $E$ as measured on a solution for which $a_1 = 1$, e.g. $\ log a_1 = 0$, is termed $E_N$, then $E_N = E_0 + E_1$, and for any other solution the measured overall potential of the cell is

$$ E = E_N - 0.0001984 \ T \ log a_1 \ \ (5) $$

or in terms of pH, since $pH = -log a_1$

$$ pH = \frac{E - E_N}{0.0001984 \ T} \ \ (6) $$

Unfortunately $E_N$ is dependent on the temperature of the solution in a way which cannot be predicted or calculated and has to be found by experimental determination for each cell. This, however, is not too difficult and once the temperature dependency of $E_N$ is known, equation (6) can be used to convert millivolts into pH at all temperatures.

Many pH meters, however, are provided with a scale divided in terms of pH, instead of in millivolts. Obviously such a scale can only be correct for measurements carried out at one temperature, for example at 20°C. At all other temperatures a correction has to be applied. This is sometimes done automatically. The Speedomax instrument, for example, is provided with a "Thermohm temperature compensator which automatically changes its resistance with changes in solution temperature to compensate for the effect of the latter on the electrodes." A similar resistance thermometer automatic compensation is also found in electrodes made by other firms.

Some other pH meters are provided with a knob which has to be adjusted according to the temperature of the solution tested. This system is correct for ordinary laboratory determinations, but would be less suitable for pH recording purposes owing to the varying temperatures experienced in the factory.

Returning to equation (6) it will have been observed that although originally pH was defined in terms of the true concentration of the hydrogen ions, the new definition relates the pH to the active concentration of the ions. This is all to the good since the rate of inversion (and other chemical reactions) are more closely related to the active than to the true concentration of the hydrogen ions.

### Hydrogen Electrodes

Obviously we cannot make an electrode of solid hydrogen to be used for pH determination, but fortunately means have been found to overcome this difficulty. A true hydrogen electrode, for example, is a platinised platinum wire on which hydrogen is continuously absorbed during measurements. Such a hydrogen electrode is not suitable for industrial purposes but is still being used for accurate laboratory determinations.

The quinhydrone electrode is not of practical significance for the sugar industry, but the antimony electrode has been used in the cane and beet sugar industries with considerable success. However, it is the glass electrode which now, almost universally, has captured the field of industrial pH measurement and which is the only one used in the Natal sugar industry.

### Glass Electrodes

Theoretically the glass electrode is still imperfectly understood. It is sufficient to say that certain types of glass behave as though they were permeable to hydrogen ions, and if a thin membrane of such glass separates two solutions of different pH a potential difference is established between the two solutions which is a function of their difference in pH value. A glass electrode in its most primitive form is a thin glass tube closed at one end by a very thin membrane in the shape of a bulb, and open at the other end. The bulb and part of the tube are filled with a solution of a known pH, for example a N/10 HCl solution. The problem now is to establish the potential difference across the glass when the electrode is placed in a solution of unknown pH.

A suitable reference electrode has to be used, but to complete the circuit to the measuring instrument the N/10 HCl solution has also to be connected to this instrument. For this purpose a Ag/AgCl electrode is used and the complete cell may be represented as follows:

$$ Hg \ | Hg_2Cl_2 \ (s) _{KCl} ^{Sat} | Sample \ | Glass \ N/10 \ HCl, \ AgCl | Ag $$

At the interfaces a, b, c and d, potential differences may be expected, which, added up, constitute the overall potential difference $E$ which is measured. Since the potential differences at the interfaces a, b and d are constants at constant temperature, their sum is equal to $E_N$ in equation (6). Theoretically $E_N$ can be found by measuring the overall potential obtained when the active hydrogen ion concentration of the solution equals 1, but in actual practice the relationship between $E$ and pH is always found by measuring the potential of so-called buffer solutions of which the pH is accurately known at various temperatures.

Glass electrodes originally had one enormous drawback: the resistance of the glass membrane was...
so high that it was not possible to measure the overall potential difference on a normal potentiometer, and the glass membranes had to be made very thin. This made them extremely fragile which seriously reduced their usefulness.

At present more suitable types of glass are being used which allow the construction of robust glass electrodes. Moreover, although the cell potential is still balanced in the potentiometer against the potential of a battery which can be calibrated against a standard cell, suitable electronic amplifiers are now used in order to get adequate readings.

I will not go deeper into the problem of how exactly the overall potential difference is measured in the various commercial pH meters and recorders. I hope that the representatives of the manufacturing firms will spread some light on this subject, which in my opinion has now been solved satisfactorily in more ways than one.

In addition to fragility the glass electrode has also some minor drawbacks. The normal type of electrode which is most commonly used, is not suitable for high temperatures, i.e. temperatures above 50°C and not for high alkalinities, especially if the concentration of sodium is high. Fortunately special electrodes have been constructed which allow accurate measurements at extreme conditions.

The pH of Sugar Liquors at Elevated Temperatures

In many cases if it is desired to measure the pH of a juice, say clarified juice as it leaves the clarifiers, a sample of the juice is taken to the laboratory, and the pH is measured using a laboratory type pH meter. During the transport of the sample its temperature drops, and sometimes the sample is intentionally cooled down to room temperature before measurement. The interesting question now is: has the hydrogen ion concentration of the juice changed by reducing its temperature?

For quite a number of years we have tacitly assumed that the effect of temperature on the hydrogen ion concentration of sugar liquors was negligible, but more recently, particularly in connection with pH recording and the introduction of automatic pH control, more attention has been paid to this subject.

In the first place we know that when pure water is heated the concentration of hydrogen ions increases due to an increased dissociation of water molecules. The concentration of hydroxyions of course also increases at the same rate and hot water is still neutral, but its pH is lower than at room temperature.

The sum of pH and pOH which as we have seen is 14 at room temperature, drops to 12.32 at 100°C, i.e. the pH of pure boiling water is 6.16. If such a drop were also to occur in our juices, the determination of the pH at room temperature would give a completely wrong impression about the possibility of inversion at higher temperatures, since the rate of inversion is governed by the hydrogen ion concentration.

However, up till 1949 so little was known about the effect of temperature on sugar liquors that the referee for Subject 16—Determination of the Hydrogen-Ion Concentration of Sugar Factory Products, of the International Commission for Uniform Methods of Sugar Analysis, recommended that “for official reports, pH in sugar products shall be accepted as that obtained when using a set equipped with a suitable glass electrode at 20°C (or 28°C) standardised with N.B.S. buffers 4.005 and 9.20 pH, all products being tested at existing degrees Brix.”

But at the same meeting a report was submitted by D. Gross containing the results of pH determinations of sugar liquids at normal and elevated temperatures. In this report he discussed some previously published studies on the same subject and gave the results of his own determinations.

At the meeting of the Xth International Congress of Agricultural Industries in Madrid in 1954, Gross submitted new data over the range of 20-100°C. Although it had been known for some time that the pH of beet sugar products drops at higher temperatures, he found a positive temperature coefficient for 60° brix solutions of raw cane sugars of different origin. For example a B.W.I. raw sugar showed in a 60° brix solution at 20°C a pH of 5.77, and at 100°C a pH of 6.10. On the other hand, for various refinery products he found both positive and negative temperature coefficients. Carbonated and filtered brown liquor, for example, had at 20°C a pH of 9.10, and at 100°C at pH of 7.95.

The important conclusion for us to remember is that the determination of the pH in samples cooled down to laboratory temperature may give results which are different from the pH values actually existing at processing temperatures. The difference may be negative or positive. To determine the pH at elevated temperatures the pH meter has to be checked at the same temperatures with buffer solutions of which the pH is known at those temperatures.

This seems to be of importance firstly for the carbonatation process. At Tate & Lyle’s Plaistow refinery 0.6 is deducted as an “average correction” from the pH as determined at room temperature to calculate the pH value existing at the temperature of carbonatation (80°C), which factor, according to Gross, may even be somewhat too low.

It hardly needs stressing that the effect of the temperature on the hydrogen ion concentration of a solution is something quite different from the effect of temperature on the ratio between hydrogen ion concentration and the number of millivolts measured.
The latter effect is either automatically compensated for, or can be compensated for by turning a temperature regulator knob on the meter. Compensation is not feasible for the former effect since the temperature coefficient varies from liquid to liquid, may be positive, or may be negative.

The effect of temperature on the hydrogen ion concentration has also to be kept in mind when the pH of the boiler water is discussed. If a pH of say 7.5 is found when a sample of boiler water is tested in the laboratory at room temperature, it is a near certainty that the pH at the boiler temperature is under 7. The higher the temperature the larger the difference. That is why the pH of the contents of high-pressure boilers when tested—as usual—in the laboratory has to be higher than the pH of medium-pressure boilers. For sugar factories the measured pH should be between 9 and 10, but for high-pressure boilers a pH of 11 is recommended. At lower alkalinites corrosion of the construction material is likely to occur.

**The Application of pH Measurement in Sugar Factories**

In sulphitation factories the pH of the juice is intentionally altered in three places, i.e. in the pre-liming tanks, in the sulphur tower and in the tempering tanks. Further changes take place in the clarifiers and during evaporation, but they are largely independent of human interference and have to be regarded as "natural" properties of the juice. Hence the key position in respect of good work in the clarification department is the tempering tank and it is a primary requirement for the chief of fabrication to be continuously informed of the pH of the juice pumped to the heaters.

It is here that pH registration is required first. The objective of this registration is to inform him to what extent the pH of the tempered juice is equal to the pH value prescribed by him. The registration of the pH will not only inform him of the average difference between the expected and actual pH, but also—and this is very important—of the fluctuations occurring from tank to tank. A generous sample should continuously be taken from the pressure side of the pump to the heaters and run into the vessel into which the electrodes are placed, the excess of juice to be returned to the tempering tanks.

The exact pH to which the juice has to be tempered depends on two kinds of factors. In the first place this pH should be such that a maximum clarification effect is achieved, but on the other hand we should not forget that the loss of sucrose through decomposition during boiling, crystallization, etc., depends to a great extent on the pH of the syrup. It is true that normally little sucrose is lost through inversion, but we have to admit that it is not unlikely at all that if we had the means of adjusting the pH of syrup to exactly the correct value, our Undetermined Loss data would be reduced by a few hundredths of a per cent., which over a whole season is quite a lot of sugar.

Now, since it is at present not customary to adjust the pH of syrup, for example, by adding soda, the pH of the syrup is directly related to the pH of the tempered juice. Hence in fixing the pH of the tempered juice at say 7.4, the pH of the syrup is fixed, too, as long as the pH drop across clarifier and quad are normal, and the chief of fabrication when fixing the desired pH of tempered juice will in addition to the clarification effect, have to keep in mind what pH he desires in syrup.

This may seem to practical men rather academic, because normal factory data usually do not show any connection between pH of syrup and the Undetermined Loss figure, but one should not forget that so many factors influence the Undetermined Loss data that a reduction of the loss of sucrose through inversion at the pan stage by say 0.03 per cent. will hardly be discernible in them.

Yet, as apparent from the data published by Stadler, a loss of 0.03 per cent. or even more of sucrose due to syrup having a too low pH value, is a definite possibility. For maximum efficiency the pH of syrup is a factor which should not be neglected and has to be known in every factory with some accuracy. The same applies to clarified juice as it leaves the clarifiers. It would be a valuable contribution to a better understanding of the drops in pH occurring in clarifiers and evaporators if a couple of factories would register simultaneously the pH values of tempered juice, clarified juice and syrup.

For ordinary routine control purposes, however, it seems doubtful if the costs of pH recorders on clarified juice and syrup are justifiable. However much we are in favour of a pH recorder on tempered juice, it seems that a regular determination of the pH of catch samples of clarified juice and syrup in the laboratory will also serve our purpose.

In respect of the desirability of continuously recording the pH of pre-limed and of sulphured juice, I should like to make the following remarks. The general feeling amongst technologists about sulphitation clarification seems to be that the main purpose of pre-liming is to make the juice so alkaline that a sufficient quantity of SO₂ will be absorbed in the tower, this quantity, particularly in mill white factories, being of primary importance for the success of subsequent manufacturing operations. General experience, so far, has not indicated that the exact pH of the pre-limed and of the sulphured juice are of primary importance, provided sufficient SO₂ is absorbed in the available time in the tower.

One will have to admit that this opinion is at the best a very crude description of the effect of external conditions on the result of the clarification operation.
There is, however, sufficient evidence to presume that if it had been routine in Natal to register continuously the pH of pre-limed and of sulphured juice, general experience would have provided us with information about the correlation between these pH values and let us say factors like the destruction of reducing sugars, the calcium content of clarified juice, and even maybe the purity of final molasses. If we want to improve the effect of the clarification operation it is necessary to be informed of the pH values of pre-limed and of sulphured juice.

Therefore I should like to recommend sulphitation factories to install in addition to a pH recorder on tempered juice, arrangements for registration of the pH of pre-limed and of sulphured juice. Apparatus are available capable of recording simultaneously the pH as measured by separate cells at more than one place. Such an apparatus would admirably suit our needs.

Summarizing, if a sulphitation factory considers introducing or extending pH registration, the correct places, in order of urgency, are:

1. the tempered juice as pumped to the heaters;
2. pre-limed juice as pumped into the sulphur tower;
3. sulphured juice as emerging from the sulphur tower;
4. syrup as pumped to the pan stage;
5. clarified juice as pumped into the evaporator.

In a carbonatation factory the situation is different. It is still doubtful if pH is the correct criterion for the first carbonatation. But there is not the slightest doubt that it is the final pH of the second carbonatation which governs the soluble lime salts content of the second carbonatation filtrate. If the pH is either over or under the correct value the result is an unnecessarily high lime salts content, which means increased scaling, a higher viscosity and an unsatisfactory exhaustion of the final molasses. Here, I think, pH registration is a must in a modern carbonatation factory.

As to thin juice sulphitation, this of course is also important, since here is the last possibility for the factory operator to adjust the pH so that loss of sucrose through inversion further on in the factory will be at a minimum, and although I would like to see a pH recorder on thin juice as pumped into the quad in every carbonatation factory, if only one apparatus is available, its correct place is at the second carbonatation.

In defecation factories registration of the pH of the limed juice, particularly if liming is carried out as a continuous operation, is highly desirable. In respect of registration of the pH of the juice from the clarifiers, and of syrup, the same reasoning applies as set out for sulphitation factories.

**Final Remarks**

A pH meter, indicating or recording, is a delicate instrument and we have to realise, although manufacturers try to make them as rugged as possible, that satisfactory results can only be expected if proper care is given to electrodes and measuring unit.

Glass electrodes do not last for ever. On prolonged use there is a certain deterioration of the sensitive glass surface which may be aggravated by the need to clean the electrodes regularly. Glass electrodes have the unfortunate property that they are coated by a deposit when placed in our factory liquors. This makes it necessary to take them to the laboratory for cleaning, since the deposit affects the readings. It is difficult to give a general rule, but it certainly is recommendable to replace each glass electrode once every shift by a freshly-cleaned one. It is the task of the laboratory staff to change the electrodes at least once every eight hours, to take the coated electrodes to the laboratory, to clean them, for example, with diluted HCl, and to place them after washing in distilled water until the moment arrives that they will be commissioned again. Moreover, each glass electrode has to be tested in the laboratory once a week to check that the recordings are still correct. For every measuring cell in the factory three glass electrodes should be available for regular interchange. The calomel electrodes are more stable than the glass electrodes and it is not necessary to clean them as frequently as the glass electrodes. The care of the glass electrodes should be in the hands of the laboratory and the chief chemist will do well to see that proper care is always given.

If properly looked after glass electrodes can be expected to give satisfactory results for at least three to four months under normal factory conditions. The durability of glass electrodes of various makes is not necessarily the same. Gross, who in his investigation mentioned before, has used various makes of commercially available glass electrodes in his pH measurements at high temperatures, as well as home-made electrodes of “Corning 015” glass, reports that of these “the glass electrodes by G. Kent Ltd. proved to be superior with regard to pH response, durability and reproducibility.”

The recording unit is a rather complicated electrical device. I had hoped that time would have been available to discuss this morning the wiring diagrams of the older pH meters which have been developed by the Java Experiment Station and the Queensland Bureau of Experiment Stations, for this would have demonstrated the principles underlying the measurement of the minute voltages set up at the electrodes. Unfortunately this would have taken too much time. I hope, however, that we will be informed
later on in the morning of the principles of present commercial instruments. As said, they are delicate instruments, and in the first place attention should be given to the place where they are to be installed. Once installed they should be free from vibration and maybe more important, they should be protected from dust. But even then there is always a possibility of a breakdown. If this happens my advice is, unless there is somebody in the factory fully conversant with the wiring diagram, and interested in the subject, do not try to repair them. The Natal Sugar Millers' Association has appointed an instrument-maker at the S.M.R.I., who will gladly come to your assistance in such cases, and of course the firm who has provided the instrument should also be available for repairs.

The last point I should like to discuss is: should we have indicating or recording instruments? From what I have said before, it should be plain that the advantage of having records of the pH at some of the strategic points in the factory is difficult to underestimate. Hence recording instruments should be installed. But of course for proper adjustment of the desired pH values and for convenient supervision of processing, it is necessary to have indicating instruments of appropriate size. A combination of recording and indicating meters is thus the ideal.

Mr. Rault said that Dr. Douwes Dekker had not mentioned whether a high pH reaction favoured the absorption of SO₂ in the sulphitation tower.

At Natal Estates, where a very large quantity of lime was used for the vacuum filter station, the efficiency of CO₂ gas absorption was a constant problem, in order to deal with large juice capacities carbonated in a minimum period of time.

The easiest way out of the difficulty was to maintain a fairly high pH reaction during simultaneous liming and gassing, namely 10.8 to 11.0 pH. This high pH reaction in combination with a temperature of 70°C. was a cause of severe reducing sugar destruction and formation of soluble lime salts.

A pH control at this stage was extremely useful, but so far has not materialised, through the unreliability of control instruments and the non-existent servicing organisation.

pH control at the second stage was a much easier operation and could be made automatic.

He had found that the variation of lime salts content of second carbonatation juice was not so much a result of end point reaction, which was fairly stable at his factory, but was more of a legacy from the nature of the raw juice and the bad work done at the first carbonatation stage.

Dr. Douwes Dekker replied that he had not mentioned the rate of absorption of SO₂ gas in the sulphur tower in sulphitation factories. He had said that the total quantity of gas absorbed could be increased by adding more lime to the juice in the pre-liming tanks. The problem at Natal Estates on the other hand, owing to the limited capacity of the carbonatation tanks, was to achieve a faster absorption of CO₂ gas. The problems were different.

He was glad that Mr. Rault agreed that a pH recorder could be installed more usefully at the second than at the first carbonatation. It should be appreciated, however, that the correct final pH of the second carbonatation depended on certain properties of the juice and might fluctuate between, for example, 8.5 and 8.9. The pH of minimum lime salts content could, however, readily be established experimentally. The minimum lime salts content also depended on certain juice qualities.

Mr. de Kok enquired if there was any definite rule as to what the pH should be after the sulphur tower.

Dr. Douwes Dekker replied that the pH should be about seven, but usually, depending on various factors, the pH varied tremendously and he had even known it to go right down to three. On the average it should usually be just under seven, so that in the tempering tanks, lime could be added to bring it up to about 7.2.

Mr. de Kok asked at what pH should the juice be worked to prevent inversion.

Dr. Douwes Dekker replied that there was no such fixed point, but no serious inversion would occur at a pH of six or more.

Mr. de Kok said that as far as measurement of the pH of the juice going to the evaporator was concerned, if one found the pH to be too high or too low, what could be done to correct his?

Dr. Douwes Dekker said that the pH of the clarified juice was governed by the tempering of the juice.

Mr. Antonowitz said that he agreed that the pH at the tempering tanks was of vital importance, but to use a recorder here was difficult, because the electrodes kept on scaling up within a few hours.

Dr. Douwes Dekker said there was no method of keeping the electrodes clean, the only way was to change them. There was a possibility when antimony electrodes were used to brush them repeatedly during operations, but this could not be done with glass electrodes.

Mr. Phipson enquired if it were not possible to install electrodes in duplicate and keep them clean alternately by condensed water from the evaporator?
Dr. Douwes Dekker said he could not say if this would be effective; it would have to be tried out.

Mr. Harvey said that in his paper he would show that it is possible by using mechanical means to keep the electrodes clean.

Mr. Coignet enquired if the absorption of SO₂ and CO₂ would not be affected by differences in atmospheric pressure.

Dr. Douwes Dekker said he thought that although the rate of absorption was a function of pressure, the effect under actual working conditions could be slight.

Mr. Bax said he had done much work on after-products, especially molasses, but he had been informed that pH figures after dilution of these products were not reliable. He was referring to colorimetric methods. He wanted to know the extent of the error.

Dr. Douwes Dekker replied that it was almost impossible to measure the pH of coloured solutions colorimetrically, and measuring pH electrically was probably the only way for such products.

Mr. Bax said that in most cases colorimetric methods were used in Mauritius. Some electrical instruments were used, but generally gave so much trouble that they were not general.

Mr. Phipson enquired if the pH of syrup should be determined in its concentrated form, or after diluting down.

Dr. Douwes Dekker replied that diluting down was inadvisable.

Mr. Hardy enquired what would be the optimum pH which could be used without endangering the colour of the sugar in the case of a white sugar factory.

Dr. Douwes Dekker replied that a pH of 6.5 or thereabouts in syrup would not lead to large inversion or cause any poor coloration of sugar.

NOTE—The three papers which follow were presented by representatives of pH instrument makers, who were specially invited by the Association to describe the operation and points of interest pertaining to their firms' meters and recorders. This was done with a view to encouraging a more rigorous check on the clarification processes in the industry. The instruments were afterwards demonstrated at the Sugar Milling Research Institute.