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AN ELECTROCHEMICAL INDICATOR FOR OXIDISING AGENTS.

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It is well known that small traces of oxidising agents exert a considerable depolarising action at an electrode, where, in their absence, hydrogen or a reducing agent would be formed. At high concentrations this depolarising action depends only to a small degree on the actual value of the concentration of the oxidiser, and often causes a decrease of as much as a volt in the amount of the electrode potential difference. A depolarising action of this kind is utilised in the bichromate battery. A zinc and copper couple immersed in a simple acid solution will give an E.M.F. of less than a volt, but if a soluble bichromate be added this can be increased to two volts. The increase is not greatly affected by small changes in the concentration of the bichromate. On the other hand, if the oxidising agent is present in minute quantity, then the depolarising effect varies considerably with the amount actually present, and can be used as a means of estimating as well as detecting the oxidiser. The depolarising action does not cease to be measurable until the amount is very small. It must, however, be remembered that the depolarising action of the oxidiser in a cell furnishing any appreciable current will involve a destruction of part of the oxidiser as such. Thus the E.M.F. of any such system will depend on the rate at which it is made to produce a current.

This principle may be made clear by a description of one of its applications—namely, the detection of minute traces of free or available chlorine.

The addition of chlorine, hypochlorites, and ozone is becoming general for sterilising waters intended for drinking, domestic, and trade purposes, and for the treatment of sewage effluents. A difficulty is found in judging the right quantity to add, for the liquor to be treated always varies in its power of consuming chlorine or other oxidising agent, while the sterilising solution, whatever its source, also fluctuates in its oxidising power. Hence it is often found that on some days the water flows out of the treatment-tank without any excess of oxidiser, and is therefore

incompletely sterilised ; on other occasions the water may contain an excess of chlorine and chlorine products, which are highly injurious to whatever use the water may be put.

To insure the addition of the correct quantity of steriliser it would be necessary to keep a continuous check upon the amount of free oxidising agent in the water leaving the waterworks. What is essential, therefore, is an analytical method of estimating small concentrations of unabsorbed steriliser. Such a method must be accurate for the dilutions met with in practice ; and, further, it is advisable that the whole procedure should be as automatic as possible.

It was found by us that the potassium iodide and starch reaction, usually employed in this connection, did not offer a practical basis for the solution of the

FIG. 1.

problem ; this is also true of the other chemical analytical methods, and we turned our attention to the physical and electrochemical changes produced by the presence of oxidising substances in water. We had to look for some property which water containing a powerful oxidising agent would possess, and which water containing no such agent would not possess. It was clear that any change which would be produced, for instance, in the density, colour, or refractive index of the water by the addition of a trace of an oxidising agent would be negligible compared to the fluctuation due to other causes. Nor would a measurement of the electrical conductivity be of use ; for, although this value varies enormously with the salinity of the water, the addition of oxidising agents as such will have no appreciable effect. On the other hand, the depolarising action of an oxidising substance, which does not depend substantially on the value of the conductivity or on the presence of neutral, non-oxidising salts, may very well be used as a means of detecting and determining oxidising agents.

Various forms of apparatus were considered, some being experimentally tested. In the end, the form (Figs. 1 and 2) which will now be described was adopted. It consists of a copper tube, (Fig. 1) *C*, 3.5 cm. long and 4 mm. internal diameter. Within this, running axially through it, is a platinum rod, *P* (diameter 1 mm.), which is insulated at the two ends from the copper tube by the ebonite caps *E*, *E*¹. Liquid is allowed to enter the tube at the lower end and flow out at the top. The copper and platinum are joined to the two poles of a sensitive current-detector of high resistance; in the particular case of the instrument used in most of our experiments this had a resistance of 200 ohms, and registered .000004 ampère per degree. If tap-water is

FIG. 2.

run through the cell approximately at a constant rate, there is practically no deflection so long as oxidising agents are absent. When, however, a trace of hypochlorite or chlorine is present, a movement of the pointer over the dial occurs, and the permanent deflection produced serves as a measure of the free chlorine-content of the water. Fig. 3 shows the relation between the concentration of free chlorine added as hypochlorite and the galvanometer-reading produced by it. It will be observed that the divisions of the ammeter used in obtaining Curve *A* roughly represents parts per 10,000,000 of chlorine with the conditions observed—namely, rate of flow 230 c.c. per minute, at a temperature of 13° C. Curve *B* shows the readings obtained at higher concentrations by the use of another less sensitive ammeter of 10 ohms resistance.

It is always observed that the pointer takes a short time to reach its maximum position; and after this, if tap-water containing chlorine is being used, a slow retrogressive movement takes place, showing that the chlorine is being absorbed by the free organic matter in the water, and that it is, therefore, diminishing in amount. This has been confirmed by titration. When tap-water free from chlorine is again allowed to pass the pointer sinks at once, although it takes some minutes to reach its exact zero position. The effect of adding to the tap-water all substances likely to occur therein, in the largest quantities likely to be found in practice, has been tried, and in no case has there been any appreciable deflection produced. The additions

FIG. 3.—FREE CHLORINE CONCENTRATION IN PARTS PER TEN MILLION.

tested include sodium chloride, sulphate, carbonate, nitrite, and nitrate, as well as ammonium salts. The effects of temperature and rate of flow have been investigated. Both these influences, as will be seen from Fig. 4, exert a considerable effect on the reading. It is, therefore, necessary to take the precaution of keeping the rate of flow sufficiently constant. In practice this is not difficult, since there will usually be the same head of water forcing the stream through the instrument. The temperature-coefficient is such that a rise of about 4 per cent. per 1° C. occurs in the reading, the head of water and other conditions being constant. There is no necessity to correct for this effect of temperature, for in warm weather the right quantity of chlorine (or other oxidising agent) which ought to be present in the water leaving a treatment station is smaller than in winter. For not only is a larger proportion of the

sterilisation done in the waterworks itself, but the oxidising agent is actually more active at the higher temperature.

Chlorine, ozone, and potassium permanganate, if present in tap-water, all cause a deflection in the apparatus. To the latter, as in the case of chlorine, the instrument is very sensitive. To ozone it is also extremely sensitive, and actually affords the best means of detecting and estimating that oxidiser, which has only a slow action on potassium iodide at the concentrations at which it gives a deflection of some degrees on the instrument. The weaker oxidising agents—*e.g.*, ferric chloride—cause no deflection. The appearance of a deflection on the latter may therefore be regarded as a sure proof that a powerful oxidising agent is present. On running a solution of hydrogen peroxide through the apparatus, a temporary deflection in the opposite direction is seen; this dies away gradually, and a low positive deflection appears. The phenomenon will serve to distinguish hydrogen peroxide and ozone at dilutions at which no other method will serve. The presence of mineral acids in the water causes a temporary positive jump. This initial deflection, appearing when an

FIG. 4.

acidified liquor is first run through, soon diminishes; but in the case of a liquid containing a mineral acid never quite disappears. The deflection remaining is, in the case of hydrochloric acid, only about $\frac{1}{150}$ of that obtained with an equivalent amount of free chlorine. Of course, free mineral acids do not occur in the class of liquors to be tested.

Although most reducing agents are without effect (unless they happen to be acids), phenylhydrazine hydrochloride gives a distinct negative reading, which is apparently permanent.

Finally, we may mention the fact that the current given out by the instrument is much less affected by large changes in the external resistance than would be expected from Ohm's law, assuming the E.M.F. to be constant. Although the external resistance is in both cases greater than the internal, the reading of the instrument under certain constant conditions was only changed from 7.2 to 6.7 divisions on altering the external resistance from 200 to 1,200 ohms (by the insertion of a 1,000-ohm coil).

Some of these statements may seem rather irregular, but the explanation will in most cases appear from the following discussion of the theory :

First, consider the action of the water containing a certain small amount of dissolved salts (as all waters do), but no free oxidising agent (*e.g.*, chlorine). When it flows through the tube between the copper walls and the central platinum rod a certain current will pass at first. Copper passes into solution at the one pole and turns out hydrogen at the other ; thus the copper tube will be left negatively charged, for the copper assumes a positive charge on entering the ionic condition, while the platinum rod will *receive* a positive charge from the discharging hydrogen ions. But this current can only continue as long as the hydrogen concentration in and around the platinum does not exceed a certain very low value. All *ordinary* hydrogen concentrations in the platinum—if caused by extraneous agency—would actually involve an E.M.F. in the opposite direction. It is well known that hydrogen at normal pressures can remove copper from its solutions. If, however, the hydrogen concentration at the platinum be below a certain value, there is an E.M.F. tending to produce a current through the liquid from the copper to the platinum, and this E.M.F. only vanishes when the hydrogen pressure at the platinum reaches that very low critical amount depending on the electrolytic solution pressure of the copper. Now, if there were no flow through the tube and no diffusion, this concentration would soon be arrived at, and current would cease to flow. But since the water flowing over the platinum surface is continually carrying off small quantities of hydrogen in solution, the concentration is kept slightly below this value, and there is thus a small E.M.F. produced ; a current therefore passes which, when a state of constancy has been set up, is exactly sufficient to replace the hydrogen carried off by the flowing liquid. With the apparatus used, which has the platinum surface small compared to that of the copper, the amount of current produced in the absence of chlorine is so small as to be barely detectable on the ammeter. It rarely exceeds 0.1 div., and can be allowed for in the zero adjustment of the instrument.

If, however, chlorine or some similar body which readily combines with hydrogen is present in the water, the case is different. The rapid attack of the chlorine keeps the concentration of hydrogen at the platinum pole permanently below the critical value, and thus there is always an E.M.F. acting from the copper to the platinum through the liquid. Therefore if these two electrodes are joined through a current measurer, a permanent current will be registered of a strength sufficient to replace the hydrogen carried off by the chlorine. It is immaterial whether the chlorine is regarded as a body which is continuously abstracting from the platinum electrode hydrogen which has already been discharged there, or whether we consider it as the active component of the electrode which attracts hydrogen ions which would not otherwise be discharged. The presence of chlorine implies that the hydrogen concentration in the platinum is kept low, although it may not reduce it, under the conditions in question, to the value demanded by the equilibrium :

Passage of the liquid through the tube is required only for the renewal of the chlorine which is used up in the production of the current. The current thus

becomes a measure of the amount of chlorine passing within striking distance of the platinum, and thus is not greatly dependent upon the resistance of the circuit. In other words, if the apparatus is required to furnish a current over a low resistance the E.M.F. automatically drops, whereas over a high resistance it yields nearly as great a current, but at a higher pressure.*

The reactions occurring at the two electrodes may be expressed by the following equations :

I. IN ABSENCE OF CHLORINE.

(a) At the copper pole the copper assumes the ionic condition :

(b) At the platinum pole hydrogen leaves the ionic condition. In solutions originally neutral this will clearly leave an excess of OH ions, and so confer alkalinity upon the solution :

As a whole, these equations can be summed up as :

an equation which involves the absorption of heat.

II. WHEN CHLORINE IS PRESENT AT THE PLATINUM SURFACE.

(a) At the copper pole the copper enters the ionic state as before, leaving the electrode negatively charged :

(b) At the platinum pole an equivalent amount of hydrogen ions are discharged :

which hydrogen is to a *large extent* taken up, as it is formed, by the chlorine :

When the chlorine is present in comparatively large amount this latter equation becomes practically complete, and we can now regard the platinum-pole equation as the sum of (b) 1 and (b) 2, thus :

which result is identical with that obtained by regarding the platinum pole as a

* The comparative independence of the current upon the total resistance is of no practical value. In any case, the external resistance would be kept constant, and would be made great enough to render negligible any changes in the internal resistance due to fluctuations in the conductivity of the water used. However, the case of a chemical cell which approximates more closely to a *constant current generator* than to a constant E.M.F. generator may be of interest. The case is an exaggeration of the "polarisation" of inefficient batteries, which drop their true E.M.F. when made to discharge too quickly.

chlorine electrode. It will be noticed that no excess of OH^- is left behind in *this* case.

By adding A and B together we get the equation for the total reaction :

or omitting 2H^+ :

Since the equation, $\text{Cu} + \text{Cl}_2 \longrightarrow \text{Cu}^{++} + 2\text{Cl}^-$, represents an exothermic reaction, the source of the electrical energy needed to produce the current is largely furnished without any cooling to the liquid.

Disturbances undoubtedly may occur, due to the fact that chlorine is present at the copper pole also, and may dissolve copper chemically ; it is possible, therefore, that a copper chloride concentration cell is thus set up. This effect, however, will undoubtedly be small compared to that of the main electro-chemical reaction.

Neglecting disturbances of this kind, one would imagine that the E.M.F. obtained by the cell discharging over a very high external resistance would be proportionate to

$$a + \log C_{\text{Cl}},$$

where a is a constant, and C_{Cl} is the chlorine concentration. Thus it will be almost independent of the free chlorine concentration at high concentrations of the latter. This is confirmed by experiment. The current-concentration curve becomes asymptotic at high concentrations of chlorine.

While elemental chlorine does not cause alkalinity during its depolarising action, oxidisers like sodium hypochlorite, ozone, and permanganate, presumably leave the liquid slightly alkaline.

What determines the sensitiveness of the indicator to different reagents is, however, the speed and completeness with which they reduce the concentration of hydrogen in the platinum.

The action of acids can now be readily understood. When neutral liquors have been running through the instrument for a short time, a state of constancy is arrived at in which the hydrogen contained in the platinum is practically in equilibrium with the hydrion of the liquid (it differs from the equilibrium amount only on account of the very small rate of removal due to the flow of the liquid, and replacement by the current produced). If, however, an acidified liquid with a vastly increased hydrion concentration be caused to run in, then the equilibrium relation will no longer hold ; a temporary current will pass, which will tend to raise the hydrogen-concentration in the platinum. As the concentration of liquid hydrogen in the platinum approaches a value which could balance the hydrion concentration of the liquid, the current will sink ; but it will never reach the minute value obtained for neutral solutions, since at its higher absolute concentrations in the platinum, the amount of hydrogen carried off by the flowing liquid will be increased. Thus acids give a high temporary, followed by a low permanent, deflection.

Again, after water free from oxidising agents or acids has been passing through the tube for some time, and has brought the hydrogen concentration in the platinum

to the constant value, and then water containing an oxidiser is run through the tube, it is always possible that the oxidiser may set up a cell of the type :

The oxidiser will be reduced at the copper surface, while the hydrogen will be oxidised from the platinum and re-enter the ionic condition. This will cause a current in the opposite direction to that usually experienced, but this current can only continue until the hydrogen in the platinum has been reduced to a certain very small value, after which any E.M.F. due to this cause must cease. Then the ordinary type of change must continue, and the oxidiser will act as a depolariser on the platinum (not the copper) surface, by attacking the hydrogen forced out by the solution of the copper ; this will involve a passage of a current in the normal

FIG. 5.

direction. This phenomenon of a *temporary current in the wrong direction* is to be expected from oxidisers, which exert a greater power of absorbing hydron at the copper surface than of attacking hydrogen occluded in the platinum. Undoubtedly the electrode material exerts a considerable catalytic action upon electrodic and chemical changes, and it is really impossible to say, on *a priori* grounds, as to which oxidisers, if any, will show this phenomenon. As a matter of fact, it has been observed in the case of hydrogen peroxide and sodium peroxide, and perhaps the comparative slowness with which the full positive deflection is shown in the case of hypochlorites may be due to a similar cause.

There remains to be mentioned the effect of passing reducing agents through the apparatus. Reducers sufficiently powerful to evolve hydrogen might conceivably act as a depolariser at one pole, absorbing $(\text{OH})'$ ions at that pole, and causing the discharge of H^+ ions at the other. As to which electrode would be the one at which

hydrogen was evolved—*i.e.*, as to which would become the positive pole—prophecy is difficult. One can only say that this will depend upon the relative catalytic action of the two metals. It is possible that the reducer, instead of forcing out hydrogen at the pole at which it is not oxidised, may cause the discharge of copper ions, which are the result of some chemical attack of the copper further up the tube. At all events, the only case of a reducing agent being responsible for a current, when run through the apparatus, is that of phenylhydrazine hydrochloride; this substance sends a current in the “negative” direction (*i.e.*, from platinum to copper, through the liquid). It is possible that the explanation given in this case is incorrect, but the experiment has been repeated and the result confirmed.

As an example of the use of the “chlorometer” as a laboratory instrument, we append curves obtained by its use showing the gradual “absorption” of free chlorine by typical potable waters (Fig. 5). A certain small amount of hypochlorite of sodium was added to the water at the commencement of the experiment, and the residual amount determined from time to time by means of the apparatus. It will be seen that a great deal of the chlorine initially added is quickly taken up by the quickly oxidisable matter; after this, a slow reduction of the chlorine occurs, due to the slow oxidation of the more stable organic compounds.

DISCUSSION.

Mr. A. CHASTON CHAPMAN asked whether, when the flow-rate was increased, the readings were increased in the same proportion; in other words, with the same water, would the readings be doubled if the flow-rate were doubled? He also asked what was the nature of the influence of temperature on the readings.

Dr. LESSING asked whether the results would be affected by differences in the dimensions of the apparatus. Would it be possible that discrepant results are obtained in different sets of apparatus in which the distance between the poles is varied? It seems conceivable that a polarising current might be set up which would counteract the main reaction to a greater or lesser extent, and so influence the reading.

Dr. STEVENS asked whether the authors' investigations as to chlorine absorption had gone far enough to enable them to say what connection there was between the chlorine absorption curve and any particular characteristic of the water—the proportion of nitrites, for example.

Dr. E. RIDEAL said that an increase in the flow-rate increased the readings in considerably less proportion. Changes in temperature affected the readings to the extent of about 4 per cent. for each degree Centigrade; so it was important to keep the temperature as constant as possible. At present they had only worked with two such instruments, and had found the results to be practically the same in both cases, though for extreme accuracy exact standardisation would certainly be necessary. If the distance between the poles were unduly large, small eddy currents would be formed, and something depended upon where the water was allowed to enter and leave the instrument. They had not done much work on the subject of chlorine absorption; but different kinds of organic matter would probably be attacked by

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chlorine at different rates, which could be ascertained by experiment. One advantage of determining the chlorine absorption in this way appeared to be that the observations could be made at very short intervals, and an infinite gradation obtained for the different substances attacked. They had investigated the effect of some of the salts usually present in water—sodium chloride, magnesium carbonate, potassium nitrate, potassium nitrite, etc.—in larger quantities than would be present even in badly polluted water, and had found no disturbance to be caused by these.

Dr. S. RIDEAL remarked that chlorine was now being used for the purification of public water-supplies in all parts of the world, the latest instance he had met with being that of British Guiana, where the water in the reservoirs was being treated by adding a little bleaching-powder once a month. That seemed a crude method; but even in that case an instrument of this sort would be useful for ascertaining exactly how much available chlorine was being added, and whether the quantity was sufficient or not.