THE MEASUREMENT OF OXIDATION POTENTIAL AND ITS SIGNIFICANCE IN THE STUDY OF OXIDASES

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(WITH TWO FIGURES)

In the course of a series of investigations on the rôle of plant oxidases, the writer has found it necessary to follow with accuracy the progress of various oxidation reactions. The best method of accomplishing this is found undoubtedly in the measurement of the oxidation potential of the solutions entering into the reactions. Since this method has never been employed in the study of biological processes, and has only a limited use in physical chemistry, a description of the apparatus as modified by the writer may be of interest.

According to electro-chemical conceptions, oxidation is the process of taking on positive charges of electricity or the giving up of negative charges of electricity. Hence if we have a measure of the tendency of a substance to take on or give up electrical charges, we may determine the oxidizability of that substance.

If we consider a hydrogen electrode, that is, a strip of indifferent metal, such as platinum, platinized to increase its surface and charged with hydrogen gas, dipping into a solution containing hydrogen ions, we see that there will be a potential difference between the electrode and the solution. The hydrogen on the electrode will give up to the solution positively charged hydrogen ions until equilibrium with osmotic pressure of the hydrogen ions in solution is reached. If two such electrodes dip into solutions containing hydrogen ions at different concentrations connected by a liquid (as through a siphon), the potential of the cell is equal to the algebraic sum of the two single potentials, and is expressed by the formula

$$E=\frac{RT}{2Q}ln\frac{P}{P_1},$$

where P and P_1 represent the concentrations of hydrogen ions in solution.[1] If the concentration of hydrogen ions in one solution is known, the concentration of the second may be calculated from the observed potential. In practice it is customary to substitute a standard half-cell (for example, a calomel electrode) for one of the hydrogen electrodes.

In a similar manner, when an oxygen electrode dips into a solution, the oxygen on the electrode tends to give up to the solution negatively charged oxygen ions until equilibrium is reached. The electrode, therefore, becomes positively electrified. If there be added to the solution an oxidizing agent (which, by definition, gives up positive charges), it will increase the positive charge on the electrode. In the case of potassium permanganate in acid solutions, the source of the positive charge may be represented by the equation

$$MnO_4^- + 4H^+ = Mn^{++} + 4OH^- + 5+,$$

and the potential may be calculated from the formula[2]

$$E = \frac{RT}{5F} ln\, K \frac{(MnO_4^-) \times (H^+)^4}{(Mn^{++}) \times (OH^-)^4}.$$

Experimental complications are met with in using platinum as an electrode, since it appears that oxygen combines with platinum to form oxides.[3] These complications are of theoretical interest, but for practical purposes they may be neglected, since the platinum electrode, when charged with oxygen, gives satisfactory comparative values of the oxidizing and reducing ability of different compounds. This is true even when the manner in which the compound ionizes is not known.

The measurements recorded in this paper, and in investigations to be reported on later, were made with the apparatus illustrated by fig. 1. The reaction cell A consisted of a 200 cc. beaker containing the solution to be tested, into which the two electrodes dipped. The electrode B was made from a platinum crucible of about 50 cc. capacity, platinized on both sides in the ordinary manner, and completely submerged in the solution. The other half of the cell was a standard calomel electrode (*C*) made up in a 150 cc. bottle with saturated KCl. To prevent contamination by diffusion of the reaction mixture into the electrode, connection was made by means of a siphon to a bottle (*D*) containing saturated KCl; and from this, by means of a second siphon, connection was made with the reaction cell *A*. To further prevent diffusion, this second siphon contained a cotton wick for a part of its length, and was kept closed by means of a pinchcock (on a rubber section of the siphon), and finally terminated in a fine capillary which dipped into the reaction mixture. The reservoir of saturated KCl at *E* allowed the capillary to be washed out frequently without disturbing the electrode.

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[1] LEBLANC, M., Electro-chemistry; translation by WHITNEY and GOWAN. New York. 1907 (p. 195).

[2] CROTOGINO, F., Zeit. Anorg. Chem. **24**:225. 1902.

[3] SCHOCH, E. P., Jour. Phys. Chem. **14**:665. 1910.

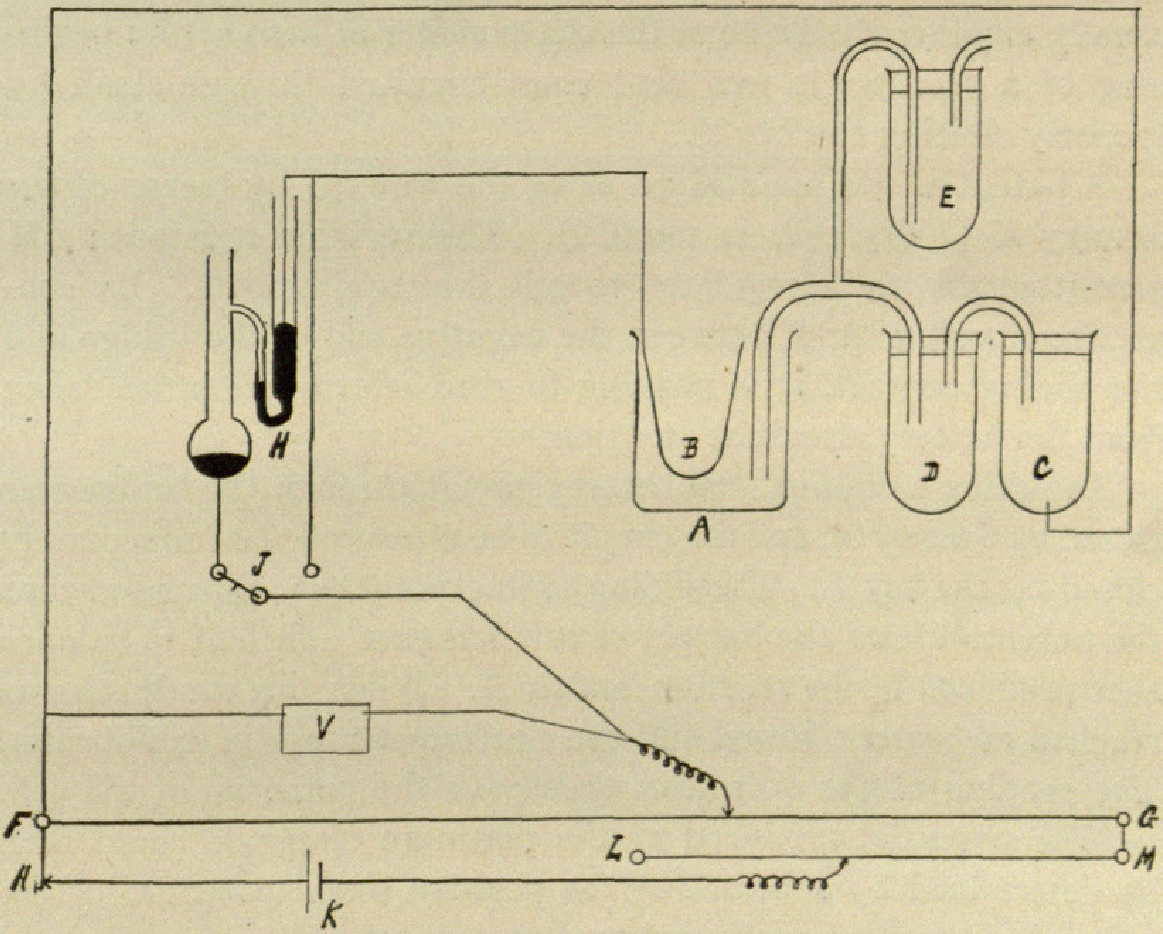

FIG. 1

Measurement of the total potential of the cell (that is, the potential at the platinum electrode plus the known potential of the calomel electrode as well as the exceedingly small contact potential between the KCl and the solution in *A*) was made by the Poggendorf compensation method, with the apparatus so arranged that the amount of current taken from the cell was reduced to a minimum.

The calomel electrode was connected with one end of a slide wire bridge (*FG*) and the platinum electrode was connected, through a zero instrument *H* with the sliding contact. A Lippman capillary electrometer (since it takes no current) was found more satisfactory as a zero instrument than a galvanometer, which is usually employed. To have the electrometer at zero at the beginning of a reading, it was kept short-circuited through itself by properly shifting the key *J*.

A potential was maintained along the wire *FG* by means of the battery *K* (3 dry cells in parallel). The variable resistance *LM* permitted this to be regulated to suit the requirements. By connecting a voltmeter *V* between the negative end of the bridge and the sliding contact, it is possible to read off the potential taken from the battery circuit at any time.[4]

In taking a reading, the battery circuit through the bridge was closed by the key *N*, and the circuit to be measured was immediately closed by the key *J*. The sliding contact was then adjusted so that the potential from the battery circuit was just sufficient to balance that produced in the reaction beaker *A*. When this condition was reached no current flowed and the electrometer was in equilibrium. The reading of the voltmeter then gave the potential of the cell.

The potential produced at the platinum electrode could then be determined by subtracting the positive single potential of the calomel electrode, usually referred to as 0.56 volt, from the total potential observed. For comparative purposes, however, since the potential of the calomel electrode was constant, the total potential of cell may often be used.

The curve of the oxidation of oxalic acid by acidified potassium permanganate, shown in fig. 2, illustrates the way in which a reaction may be followed by this method. On placing a platinized electrode, connected as previously described, in dilute oxalic acid, the potential quickly drops to very nearly the minimum value. The potential may continue to drop for some hours (this slow drop amounting to 0.1–0.2 volt) if the electrode has previously been subjected to an oxidizing agent; but if the electrode is previously subjected to a reducing agent, a constant potential is reached much more quickly. When standardized potassium permanganate (in this case 0.001 M) is added, the potential rises slowly until the concentration of positive ions becomes nearly equal to that of the negative ions, when a trace of permanganate causes a jump in the potential. The last trace of permanganate is sufficient to change the solution in contact with the electrode from a reducing agent to an oxidizing agent, that is, to one which gives up positive ions. It is evident that by this method the progress of an oxidation reaction may be followed with great accuracy.

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[4] This use of a voltmeter, to avoid the use of a standard cell and potentiometer calculations, was suggested by HILDEBRANT, Jour. Amer. Chem. Soc. **35**:869. 1913, in connection with measurements of H ion concentration.

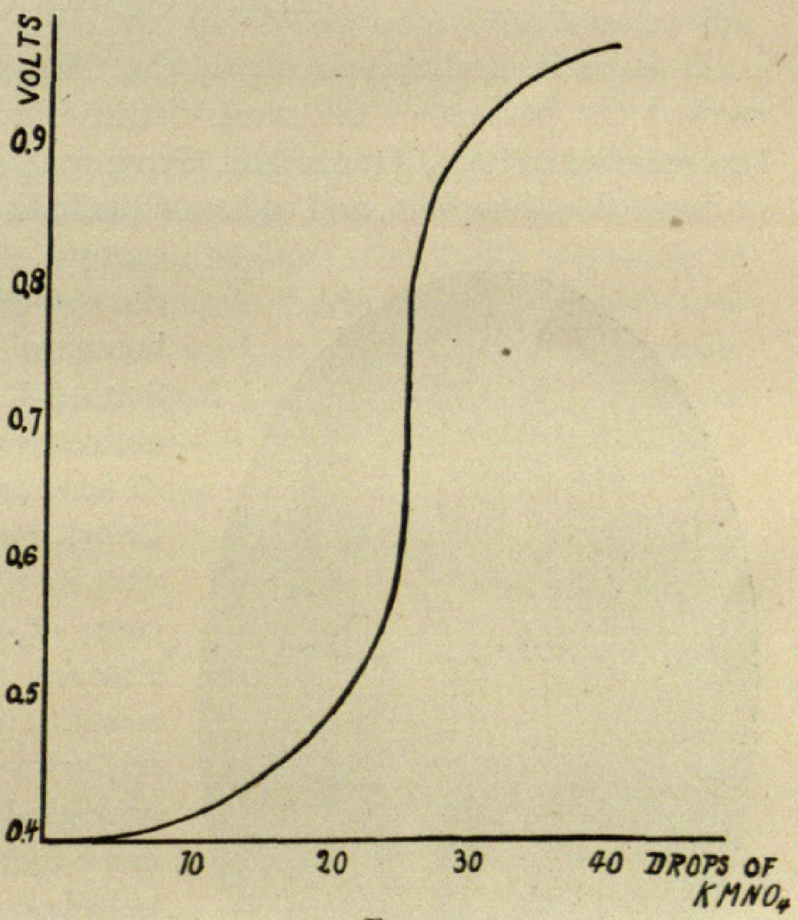

Fig. 2

The effect of a catalyzer in accelerating an oxidation reaction may be studied, in some cases at least, by this method with excellent results. The writer has begun some investigations of this character, in which various "inorganic ferments" have been used to catalyze the reaction with a view to utilizing the results in constructing a theory of oxidase action. These results will be described in subsequent papers.

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