STATE OF OXIDATION-REDUCTION INDICATORS IN SOLUTION

B. P. Nikolsky and V. V. Palchevsky

(Paper read at General Meeting of the Division of Chemical Sciences of the Academy of Sciences of the USSR, March 29, 1956)

Various methods are used for determining the state of a substance in solution, and one of the most important of these is the potentiometric method. Potential measurements at metal and hydrogen electrodes are most frequently used for such purposes, and little use is made of oxidation potentials.

Clark [1, 2] showed that investigation of the relation between the oxidation potential \( \varphi \) of a reversible oxidation-reduction system and pH makes it possible to find acidic or basic dissociation constants of the oxidized and reduced forms of the system. The method consists in the determination of the relation between the oxidized potential of a half-reduced solution and pH. A typical curve for such a relation is shown in Fig. 1; it consists of linear sections joined by smooth curves. Clark formulated general rules for the analysis of these curves and used the graphical method for determining dissociation constants from the point of intersection of the continuations of two successive linear sections. A defect in the method developed by Clark is the indefinite value of the diffusion potential in the cell formed by the oxidation-reduction and calomel half-cells, which is used for the measurement of oxidation potentials. The determination of the dissociation constants of protolytic groups from the points of intersection of two successive linear sections gives good results only when the constants differ considerably in magnitude. The accuracy of the determination of constants by Clark's method is lowered when the linear sections have similar slopes. When two successive protolytic dissociation constants are close in value, the corresponding linear section of the curve disappears and appears only as a bend of more than usual length. In this case the determination of the constants simply amounts to a selection of the values for which the theoretical curve fits most satisfactorily to the graph. This process is very laborious and time-consuming and is associated with considerable errors. Moreover, the question of the effect of the ionic strength of the solution on the value of the oxidation potential of the system remains unresolved.

It was found that it is possible to improve Clark's method, both with respect to thermodynamic rigor, and also with respect to convenience of interpretation of experimental results and accuracy in the determination of protolytic dissociation constants of the oxidized and reduced forms of the system. This is attained by replacing the measurement of oxidation potentials, which was carried out in Clark's method with a cell operating with transference, by the measurement of the emf of a cell operating without transference:

\[
\text{Pt} \ | \ \text{dye, leuco dye + buffer solution} \ | \ H^+ \tag{1}
\]

The emf of such a cell does not include any indefinite contribution due to a diffusion potential and is given by the expression:

\[
E = \varphi - \vartheta \log a_{H^+}, \tag{2}
\]

in which \( \varphi \) is the oxidation potential of the system, \( a_{H^+} \) is the activity of hydrogen ions in the solution, and

\[
\vartheta = \frac{RT}{F} \cdot 2.303.
\]
The oxidation potential, and therefore the emf of the cell operating without transference, is related in a complex manner to the protolytic and oxidation-reduction equilibrium of the products of protolytic dissociation of the oxidized and reduced forms of the substance. The protolytic equilibrium greatly affects the value of the oxidation potential, and it itself depends on the pH of the solution. On the other hand, the protolytic equilibrium depends on the properties and structures of the substances forming the oxidation-reduction system and their abilities to combine with or yield a hydrogen or hydroxyl ion.

Fig. 1. Relation between $\varphi$ and pH. System formed by toluidine blue + leuco toluidine blue.

There will be a substantial difference in general character between the curves expressing the dependence of the emf $E$ of the cell (1) on pH and the dependence of the oxidation potential $\varphi$ on pH. It is most convenient to consider this difference for actual examples of oxidation-reduction systems. The examples we have selected are formed by thiazine dyes and their leuco forms, namely, methylene blue + leuco methylene blue and toluidine blue + leuco toluidine blue.

* These dyes have the general formulas;

a) for oxidized state

\[
\begin{align*}
\text{oxidized state:} & \quad X,N \quad \text{S} \quad \text{N} \quad \text{N} \quad \text{N} \\
\text{reduced state:} & \quad X,N \quad \text{S} \quad \text{N} \quad \text{N} \quad \text{N} \\
\end{align*}
\]

b) for reduced state

in which $X$ is a hydrogen atom or methyl group.