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Short Communication

A GENERALIZED APPROACH FOR THE CALCULATION AND AUTOMATION OF POTENTIOMETRIC TITRATIONS
Part 2. Redox Titrations

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Summary. The very fast calculation procedure described earlier is applied to calculate the titration curves of complicated redox systems. The theory is extended slightly to cover inhomogeneous redox systems. Titrations of iodine or 2,6-dichloroindophenol with ascorbic acid are described. It is shown that correspondence between theory and practice is good as long as the relevant stability constants and redox potentials are known with sufficient accuracy.

In a previous paper [1], a generalized approach for the calculation of titration curves was presented. Based on the rapidity of the calculation, a sophisticated, automated titration procedure was introduced. The examples given in that paper were confined to pure acid-base reactions, although the calculation procedure was based essentially on the simultaneous change of both pH and redox potential of the system. The present paper deals with redox systems in which the pH also changes.

With respect to practical performance, redox titrations differ in some aspects from acid-base titrations. First, proton transfer is generally very fast, whereas many reactions involving electron transfer are slow. This can apply to the chemical reaction in the bulk of the solution as well as to the electrochemical reaction at the indicator electrode surface. It can be difficult to maintain the appropriate kinetic conditions and to control the reaction rates; moreover, if the solution is only moderately buffered, unstable signals will be observed and sometimes rather long waiting times have to be adopted. But it is in exactly such situations that automation can offer advantages. Secondly, most redox titrations show more pronounced end-points than acid-base titrations. This is partly due to the large difference in redox potentials between the substances in the sample solution and a properly selected titrant, but is also due to the fact that samples will normally contain fewer reducible or oxidizable substances than protolytes. Therefore, fewer potential jumps have to be accommodated on a larger voltage span. Further, the existence of different valency states in redox systems will mean that errors will be larger if activity coefficients are neglected.

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Although the previous treatment of redox equilibria [1] seems to be universal as far as protolytic reactions are concerned, it does not provide for situations where the coefficients for the oxidized and the reduced form are not equal for one of the substances participating in the reaction. Bishop [2] introduced the expression "inhomogeneous" for such reactions. This requires a short extension of the theory.

Theory

Two situations will be considered. First, a system is examined in which the coefficients of the oxidized (ox) and reduced (red) forms occur in the ratio 2:1; then, a system with the ratio 1:2 is considered.

Ratio 2:1. The redox reaction, e.g., $Hg_2^{2+} \rightleftharpoons 2Hg^{2+} + 2e^-$, has the following form

$$z_R Y_2^{red} + z_Y R^{ox} \rightleftharpoons 2z_R Y^{ox} + z_Y R^{red}$$

From the mass-balance equation, the concentration of Y^{ox} can be calculated

$$[Y^{ox}] = \tfrac{1}{4}\exp[\phi_Y]\ \{-1 + (1 + 8C_Y[V_0/(V_0 + V)]\ \exp[-\phi_Y])^{1/2}\} \qquad (1)$$

where $\phi_Y = z_Y F(E - E_Y^0)/RT$, $C_Y = 2[Y^{red}] + [Y^{ox}]$ (analytical concentration of Y), V_0 is the initial volume, and V is the volume of titrant added.

Further, the following implicit equation in V must be valid:

$$V = 1/8[(V_0 + V)/C_R]\,(1 + \exp[\phi_R])(z_Y/z_R)\exp[\phi_Y]$$
$$\times\ \{-1 + (1 + 8C_Y[V_0/(V_0 + V)]\exp[-\phi_Y])^{1/2}\} \qquad (2)$$

Ratio 1:2. The overall reaction, e.g., $2I^- \rightleftharpoons I_2 + 2e^-$ or sulfhydryl systems can be written as $2z_R Z^{red} + z_Z R^{ox} \rightleftharpoons z_R Z^{ox} + z_Z R^{red}$ and similarly to Eqn. 1 the concentration of Z^{ox} can be expressed as

$$[Z^{ox}] = 1/8\{4C_Z[V_0/(V_0 + V)] + \exp[-\phi_Z]$$
$$\times\ \{1 - (1 + 8C_Z[V_0/(V_0 + V)]\ \exp[\phi_Z])^{1/2}\}\} \qquad (3)$$

The implicit equation for V is

$$V = (V_0 + V)(1 + \exp[\phi_R])\,z_Z\{[4C_Z V_0/(V_0 + V)] + \exp[-\phi_Z]$$
$$\times\ \{1 - [1 + 8C_Z V_0 \exp[\phi_Z]/(V_0 + V)]^{1/2}\}\}/8C_R z_R \qquad (4)$$

It can be concluded that for solutions containing Y or Z systems, the extended redox equation can be presented in the form

$$V = \{(V_0 + V)(1 + \exp[\phi_R])/z_R C_R\}[\sum_{i=1}^{l} z_{Xi} C_{Xi} V_0/\{(1 + \exp[-\phi_{Xi}])(V_0 + V)\}$$
$$+ \sum_{i=1}^{m} 0.125\, z_{Yi} \exp[\phi_{Yi}]\,\{-1 + [1 + (8C_{Yi} V_0 \exp[-\phi_{Yi}])/(V_0 + V)]^{1/2}\}$$
$$+ \sum_{i=1}^{n} 0.125\, z_{Zi}\{4C_{Zi} V_0/(V_0 + V) + \exp[-\phi_{Zi}]$$

$$\times \{1 - (1 + 8C_{Zi}V_0 \exp[\phi_{Zi}]/(V_0 + V))^{1/2}\}] \quad (5)$$

where X indicates a redox substance that can be considered as a homogeneous system and l, m and n denote the total number of the three kinds of species, respectively.

Experimental

Chemicals. All chemicals were of analytical reagent-grade purity. Ascorbic acid solutions (0.1 M and 0.02 M) were prepared from the acid (Baker) in deionized-distilled water. The solution was standardized against the iodine solution [3]. Iodine solution (0.05 M) was prepared from Titrisol ampoules (Merck). 2,6-Dichloroindophenol solution (0.001 M) was prepared from the sodium salt (Merck) by dissolving the salt in deionized-distilled water, filtering through a Millipore filter (AAWP 02500) and diluting to the appropriate volume. This solution was standardized photometrically, as proposed by Armstrong [4].

Apparatus. The equipment, which was basically the same as described before [1], was extended with a platinum electrode, a silver/silver chloride reference electrode (Ingold C 373 M-NS) and a mV-meter (Knick Type DIN). The redox electrode system was tested simultaneously with the pH-measuring system by means of several buffers saturated with quinhydrone. All measurements were done under nitrogen. The solutions were usually deaerated by bubbling nitrogen; for the iodine-containing solutions, nitrogen was only passed over the solution.

Computer program. The extensions dealing with inhomogeneous redox reactions, as presented in the theoretical part, were incorporated in the program described in Part 1 [1]. Because the square-root terms in the equations can produce values that exceed the capacity of the computer, especially if the expressions $\exp[\pm\phi]$ have very small values, a value of 1 can be obtained for this square root which yields concentrations equal to zero. In order to circumvent this problem, the program switches automatically in such cases to the approximation $(1 + x)^{1/2} \simeq 1 + x/2$.

The program for the calculation of redox titrations is again presented as a choice of options for the selection of data input, correction and print out. Different kinds of calculation are possible. For instance, there is the option of faster calculation by omitting the iterative process for the calculation of activity coefficients. Although the variations of the differential quotients caused by changes in the activity coefficients are not taken into account, these variations are usually so small that the number of iterations needed to achieve the desired precision does not increase. The program offers the additional possibility of calculating the formal potentials of a system at each pH value by using the "absolute" standard potential as defined in Part 1.

Results and discussion

To illustrate the possibilities of the above approach, titrations of iodine and 2,6-dichloroindophenol with ascorbic acid were examined. In both cases, the pH drops during the titration, causing a slight change in the formal potential. However, there is a difference between the two systems. In titrations of iodine, a significant decrease in pH is observed at the beginning, whereas the pH remains approximately constant after the equivalence point. In titrations of 2,6-dichloroindophenol, a large drop in pH occurs just after the equivalence point, leading to an increase in the formal potential.

The results for the iodine titration are given in Fig. 1, which also shows the theoretical curves calculated with and without consideration of the inhomogeneity of the reaction. The large influence of this factor is clear. The titration proceeds quickly and reproducibility is very good.

The second example deals with 2,6-dichloroindophenol, which is used in its oxidized state as an indicator in titrations with ascorbic acid. When reduced in unbuffered solutions with ascorbic acid, the compound shows characteristic changes in both pH and redox potential (Fig. 2). For the theoretically calculated curves, the constants used first were those determined by Gibbs et al. [5] and summarized in Clark's classic work [6] and in a monograph [7] (see Table 1). The experimental values did not fit

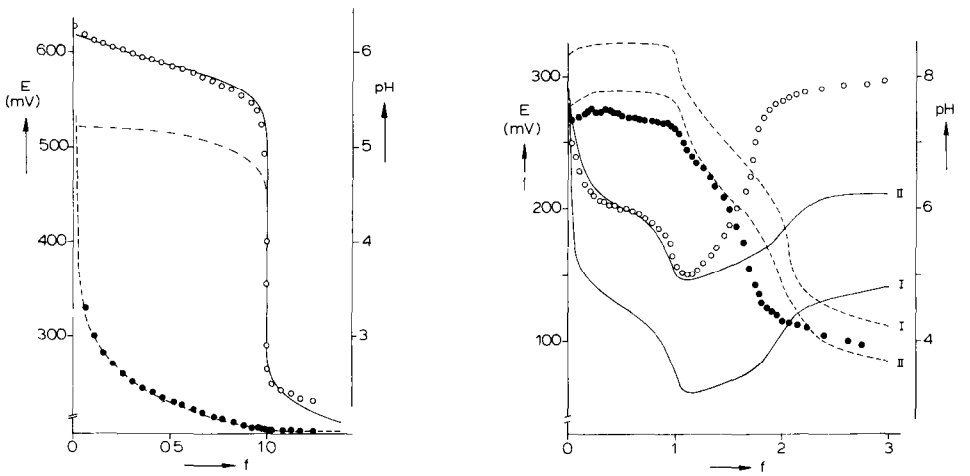

Fig. 1. Titration curves of iodine with ascorbic acid in unbuffered aqueous solution (C_{I_2} = 0.02 M; V_0 = 40 ml). pH change: (———) calculated; (•) measured. Potential change: (—·—) calculated without accounting for the inhomogeneity of the system; (——) calculated with inhomogeneity taken into account; (○) measured.

Fig. 2. Titration curves of 2,6-dichloroindophenol (sodium salt) with ascorbic acid in unbuffered aqueous solution (C_{DCIP} = 0.008 M; V_0 = 40 ml). pH change: (———) calculated with constants of Table 1; (•) experimental values. Potential change: (——) calculated; (○) experimental values. Curves: (I) calculated with constants in first row of Table 1; (II) calculated with constants in last row of Table 1.

TABLE 1

Relevant protonation constants and standard potentials for 2,6-dichloroindophenol and ascorbic acid

2,6-Dichloroindophenol					Ascorbic acid		
E_0 (V)	pK_{ox}	pK_{red1}	pK_{red2}	Ref.	E_0 (V)	pK_1	Ref.
0.669	5.7	7	10.1	5—7	0.3895	4.1	3
0.700	3.95	4.5	9.4	8			
—	6.02	—	—	4			
0.73	3.95	6.2	9.4	—	0.3895	3.1	—

the theoretical curves (Fig. 2; curves I); the experimental pH curve seems to be shifted to lower pH values, whereas the experimental potentials are shifted to higher values. However, for values of the titration parameter (f) lower than 1.2, the shapes of the theoretical and experimental curves agree fairly well. For larger values of f, the calculated pH values are too high leading to low redox potentials. With regard to these discrepancies, it has to be stressed that the relevant stability constants and redox potentials for many redox indicators in the literature are uncertain [7]. Table 1 gives some other, more recent values of some of the constants. No better correspondence was obtained with these values. Recalculation with the set of constants denoted by II yields a good fit in the first part of the titration curve. No set of constants could be found to improve the correspondence for $f > 1$. Probably this discrepancy has to be attributed to kinetic effects; the ascorbate/dehydroascorbate redox couple is irreversible [9].

It was not the goal of this work to verify or to determine values of the stability constants of this complicated system, but to show that in unbuffered redox systems such pH changes can occur during titrations that the change in potential can be inverted. Even for such complicated systems, the calculation of a complete titration curve takes only several minutes.

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