[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE OHIO STATE UNIVERSITY]

The Asymmetry of the Ferrous Iron-Dichromate Titration Curve

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Introduction

Improvements on Cox's direct differential method of titration[1] have been described by various workers,[2-6] and MacInnes and Dole have shown that their modification yields results of high precision in the titration of ferrous iron with dichromate. These authors, however, did not report a peculiarity of the titration which is of considerable interest and significance, namely, that the curve obtained in such a titration is decidedly more unsymmetrical than is to be expected from theoretical considerations. Figure 1 shows a direct differential curve which is typical of those obtained in this Laboratory. The asymmetry to which we wish to call attention is the much greater steepness on the side where dichromate is in excess.

Experimental

Apparatus.—The behavior illustrated by the curve of Fig. 1 was first observed when the form of differential cell recommended by MacInnes and Dole was being used, but the effect was not very pronounced. The arrangement which has given greatest satisfaction in this Laboratory is a modification of that suggested by Hall, Jensen and Baeckström.[4] Our modification is to put the medicine dropper bulb on a side-arm and insert the inner electrode through a stopper in the top in such a way as to be readily removable. A fairly sensitive galvanometer connected directly across the electrodes serves to indicate the relative magnitudes of the potential differences due to each successive drop of standard solution. The end-point maximum can be observed readily without the necessity of constructing a curve or even of making close readings of the galvanometer. The galvanometer may be replaced by a potentiometer if one wishes to obtain specific data to illustrate the behavior.

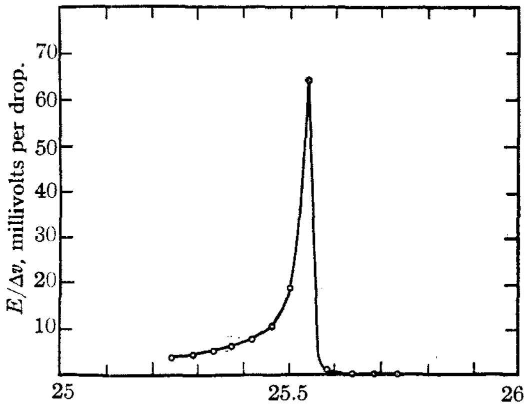

Fig. 1.—Direct differential curve.

Differential Titration of Iron with Dichromate.—The galvanometer deflection caused by the addition of one drop of dichromate solution is scarcely perceptible in the early stages of the titration, but as the equivalence point is approached more and more closely the deflections increase rapidly in size. The magnitude of the maximum deflection depends upon a number of factors such as sensitivity of the galvanometer, size of the electrodes, and concentration of the standard solution, but conditions can be adjusted so that the maximum deflection will be nearly the full length of the galvanometer scale. The striking feature of this titration is the abrupt cessation of galvanometer deflections immediately after the end-point maximum. Even with long waiting for equilibrium after the addition of each drop from the buret, no e. m. f. is developed in the differential cell when dichromate is in excess. This behavior may be observed by reference to Fig. 1, in which $E/\Delta v$ is plotted against the volume of solution added. In the reverse titration the curve is retraced in the reverse order, and in either case the end-point is very sharp and unmistakable.

Non-Differential Titration of Iron with Dichromate.—If the "direct differential" titration gives a truly differential curve (*i. e.*, $\Delta E/\Delta v$ against v), then it is reasonable to expect a differential curve constructed from data obtained by the conventional potentiometric method, using a standard half-cell against the indicator electrode, to exhibit the same peculiarity of shape. No such curves are to be found in the literature; the only asymmetry exhibited is that which is expected because of the difference in the valence changes of the iron and the dichromate (see Fig. 2). However, it is possible to titrate by the conventional potentiometric method and obtain a differential curve which resembles very closely the direct differential curve of Fig. 1. As long as ferrous iron is in excess a steady equilibrium potential is attained almost instantly, but as soon as dichromate is in excess the potential is not at all steady, and a relatively long time is required before it can be considered approximately constant. If, therefore, one allows a uniformly short time (the ten or fifteen seconds required to adjust and read the potentiometer) the results are as indicated by the experimental curve of Fig. 2, which in the differential form would be practically identical with Fig. 1. If one waits ten to fifteen minutes after each addition when dichromate is in excess the potential of the indicator electrode rises slowly and the shape of the curve approaches the theoretical. A comparison of the two curves of Fig. 2 makes it evident that the asymmetry under discussion is

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(1) Cox, THIS JOURNAL, **47**, 2138 (1925).

(2) Kolthoff and Furman, "Potentiometric Titrations," John Wiley and Sons, New York, 1931, p. 112–122.

(3) MacInnes and Jones, THIS JOURNAL, **48**, 2831 (1926).

(4) Hall, Jensen and Baeckström, *ibid.*, **50**, 2217 (1928).

(5) Clarke and Wooten, *J. Phys. Chem.*, **33**, 1468 (1929).

(6) MacInnes and Dole, THIS JOURNAL, **51**, 1119 (1929).

not due to the unequal valence changes of the iron and the dichromate.

Discussion

The ratio [Fe^{+++}]/[Fe^{++}] varies in a very definite way until the equivalence point is reached, after which the concentration of ferrous ions is practically zero and the concentration of ferric ions is constant. Since the ferric–ferrous potential is perfectly reversible, the behavior of the indicator electrode is normal until the equivalence point is reached. After that point the ferric–ferrous component of the potential remains (nearly) constant, and any variations on further addition of dichromate are due to the dichromate–chromic component. The potential of the dichromate–chromic electrode has been shown to be quite irregular and uncertain.[7,8] This is also the authors' experience. Since this equilibrium is established very slowly (if at all), the increasing concentration of dichromate ion after the equivalence point has been passed has but little immediate effect on the ratio [oxidant]/[reductant] and hence on the potential of the electrode.

It has been pointed out that when the course of the titration is followed in the conventional manner the potential of the indicator electrode, and hence the e. m. f. of the cell, increases slowly when an excess of dichromate is present. On the other hand, *long waiting after the addition of each drop of standard solution does not result in the development of an e. m. f. in the differential cell when dichromate is in excess.* This difference in behavior may be explained by the fact that in the former case the potential of the reference electrode remains constant while that of the indicator electrode changes, whereas in the latter case there are two dichromate–chromic electrodes both undergoing the same slow increase in potential, with the result that their potential difference does not change with time.

A number of other titrations have been made using the same direct differential procedure, but up to the present time only one other reaction, the reduction of iodine with thiosulfate, has been found to duplicate the behavior described above for the iron–dichromate reaction. Such titrations as iron with ceric sulfate and sodium hydroxide with hydrochloric acid give smooth, symmetrical curves. In the titration of ferrous iron with permanganate the behavior is anomalous: in the vicinity of the end-point the potential difference between the electrodes is not reduced to zero by mixing the two portions of solution, but the shielded electrode tends to remain less positive than the other one.

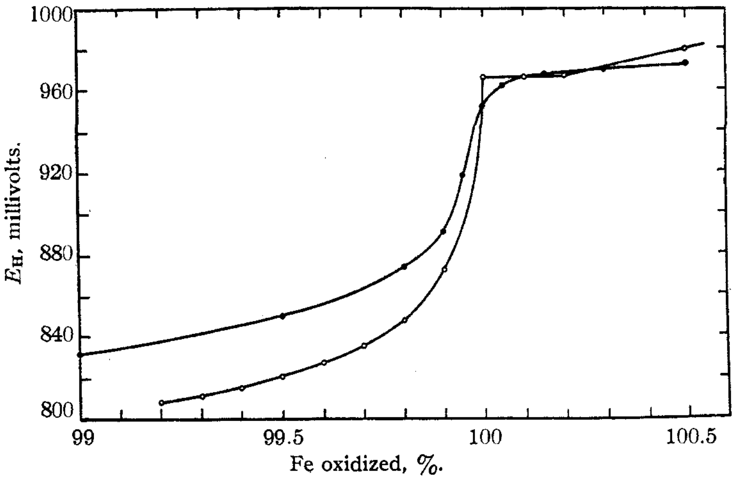

Fig. 2.—Titration of ferrous iron with dichromate: ●, theoretical curve (pH = 0); ○, experimental curve—readings taken rapidly.

Summary

The direct differential titration of ferrous iron with dichromate gives a titration curve which is decidedly unsymmetrical.

The conventional potentiometric titration using a standard half-cell will give an approximately symmetrical differential curve if a sufficiently long time is allowed for the potential to approach equilibrium after the end-point is passed, but the peculiar shape of the direct differential curve will be duplicated if the readings are taken rapidly.

The abnormal asymmetry of the direct differential titration curve is due to the fact that the dichromate–chromic electrode potential is not strictly reversible.

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[7] Luther, *Z. physik. Chem.*, **30**, 653 (1899).

[8] Kolthoff, *Chem. Weekblad*, **16**, 450 (1919).