[CONTRIBUTION FROM THE PITTSFIELD WORKS LABORATORY OF THE GENERAL ELECTRIC COMPANY]

DIFFERENTIAL ELECTRO-TITRATION

BY D. C. COX

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Electrometric titration is rapidly taking its place among the standard methods of analysis, not only for the estimation of acidity and alkalinity[1] but also in the titration of oxidizing and reducing agents.[2] The great precision of which this method is often capable, together with the entire absence of the personal equation so troublesome with colored indicators, has assured the method of a field of usefulness wherever positive, accurate results are worth a little care.

In all such titrations measurements are made of the potential difference between a standard electrode (calomel half-cell) and an electrode immersed in the solution to be titrated. As portions of the titrating solution are added this potential difference changes, gradually at first, rapidly at the end-point, then slowly beyond the end-point. If these points be plotted a characteristic curve will be obtained similar to the one shown in Fig. 1. As P. A. van der Meulen and Frank Wilcoxon have pointed out,[3] the rather delicate hydrogen electrode usually employed in these tests may be replaced in many cases by a simple polished platinum wire operating in the natural atmosphere. Tests carried out in this Laboratory have confirmed that claim. In fact, the titration graphed in Fig. 1 was conducted in that manner. Twenty-five cc. of an acetic acid solution (0.1012 N) was titrated with sodium hydroxide solution (0.1215 N). A calomel half-cell was used as a reference standard of potential. Differences between this potential and that of an ordinary clean platinum wire immersed in the acetic acid solution were measured in the ordinary manner with a potentiometer. These values are plotted as ordinates against the amounts of sodium hydroxide solution added as abscissas. The point of inflexion (20.8 cc. of sodium hydroxide solution) is recorded as the end-point.

From the mathematical equations of curves, points of inflexion may be discovered by equating the second derivative to zero. This is, of course, equivalent to finding more directly the extreme value of the first derivative. In electro-titration this is simply the point at which the potential difference changes most with a given small increment of titrating solution. The method offered below and referred to as "differential titration" gives this directly as the potentiometer or millivoltmeter reading. The highest

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[1] Böttger, *Z. physik. Chem.*, **24**, 253 (1897). Hildebrand, THIS JOURNAL, **35**, 847 (1913).

[2] Jones and Lee, *J. Ind. Eng. Chem.*, **14**, 46 (1922).

[3] Van der Meulen and Wilcoxon, *Ind. Eng. Chem.*, **15**, 62 (1923). See also Furman, THIS JOURNAL, **44**, 2685 (1922).

reading is recorded as the end-point and the necessity of plotting and estimating the point of inflexion is eliminated. The rather troublesome calomel half-cell is done away with entirely. Whereas in the regular electro-titration a "drifting" with resultant slight errors is occasionally encountered, in titrating by the differential method, these errors are compensated by the arrangement opposing the potentials of two almost identical systems. Until one has actually tried this method it is difficult to realize how simple and definite it is despite the fact that it involves handling two burets.

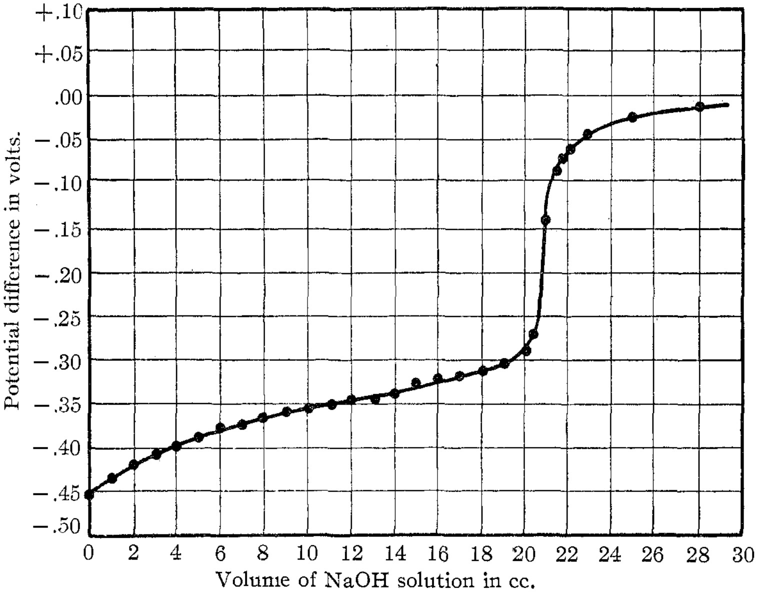

Fig. 1.—25 Cc. of 0.1012 *N* acetic acid titrated with 0.1215 *N* NaOH, using calomel and air electrodes.

Explanation of the Differential Method

Let us assume that two identical titrations are carried on side by side by the regular method using calomel half-cells and "air electrodes" (polished platinum wires). As the titrations proceed let the right buret be kept always 0.2 cc. ahead of the left one. Instead of recording and plotting the potentials from the two cells, let us note only their difference from time to time. When this is maximum the end-point has been reached.

This scheme involves much more trouble than a single titration and is given only for its explanatory value.

Simplified Differential Titration

The solution to be titrated is poured into a 200cc. volumetric flask which is then filled to the mark with distilled water, and the contents are thoroughly mixed. From this supply a 100cc. flask is filled. The two halves of the whole solution are then poured into two 150cc. beakers and placed side by side under a pair of matched burets both filled with the titrating solution. Into each beaker is placed a coiled platinum wire to serve as an electrode.[4] These wires are connected to a potentiometer or millivoltmeter so that any differences of potential may be estimated.[5] A strip of filter paper serves as a conducting bridge between the two beakers.

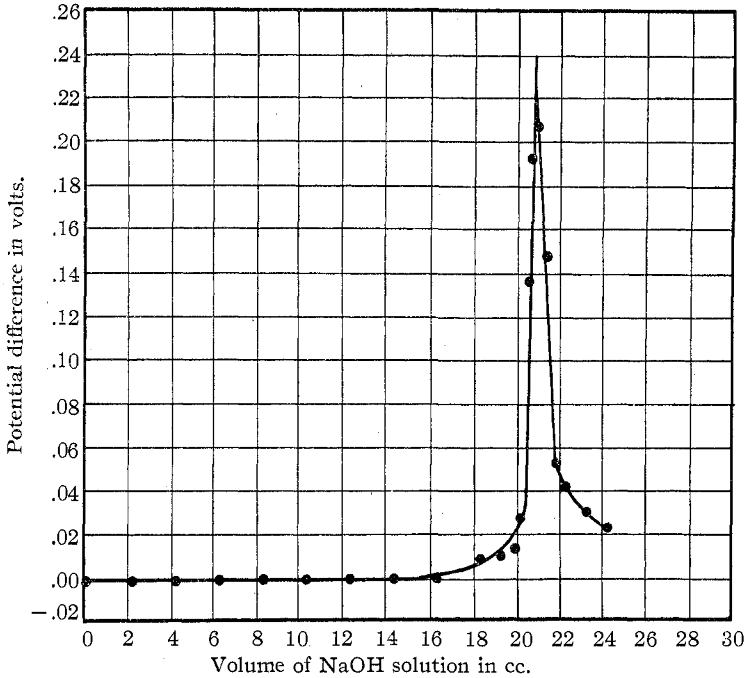

Fig. 2.—25 Cc. of 0.1012 *N* acetic acid titrated with 0.1215 *N* NaOH, using two "Air Electrodes." Differential titration.

The titration is now allowed to proceed, the right buret being kept 0.2 cc. in advance of the left. The first readings of potential difference will be nearly zero. As the end-point is approached, the readings will increase in value, exhibiting a sudden great rise at the end-point, then rapidly dropping practically to zero again. The desired point, being a simple maxi-

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[4] Apparently the shape and size of the wire is of no importance except in providing reasonably good contact with the solution. The electrodes we used were made from 12.5cm. lengths of 0.75 mm. in. platinum wire, 5 cm. being left straight and the remaining 7.5 cm. being coiled about a rod 0.6 cm. in diameter. It is well to use new platinum wires and to keep them in concd. hydrochloric acid when not in use. The acid is washed off readily with a little distilled water before use.

[5] As the potentials measured are only relative there is absolutely no advantage in using a standard cell and carefully calibrating the potentiometer.

mum, does not require plotting for its estimation. The sum of the buret readings is recorded as the titer of the sample.

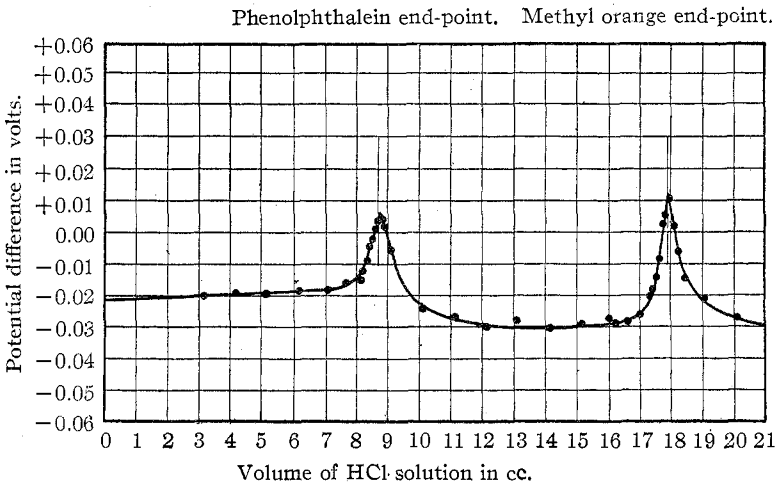

Fig. 3.—Differential titration of Na_2CO_3 solution with 0.1 *N* HCl.

The curves given below show the clear end-points obtainable by differential titration and give an indication of the precision of which this method is capable.

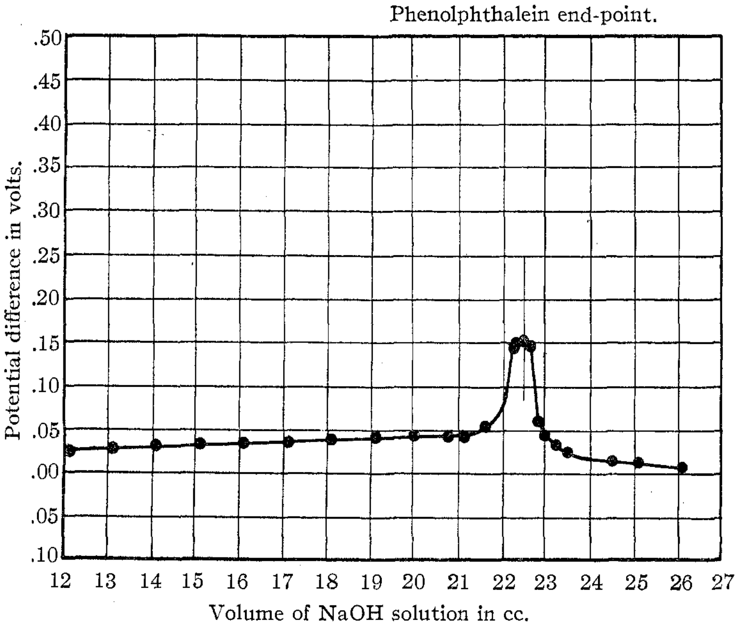

Fig. 4.—Differential titration of butyric acid with NaOH. Offset: 0.6 cc.

Fig. 2 has been plotted from a differential titration employing the same acid and alkali as those used in Fig. 1. Note that even though the acid is comparatively weak the end-point is quite sharp.

In titrating soluble carbonates, bicuspid curves will be obtained. Such a curve is shown in Fig. 3. This was obtained by titrating a solution of a sample of commercial sodium carbonate with approximately 0.1 *N* hydrochloric acid. The first cusp is 0.1 cc. beyond the phenolphthalein end-point. This is not due to experimental error, for both of the high potential readings were obtained after phenolphthalein had bleached in this same solution. The discrepancy may be explained as follows. Upon passing an end-point the hydrogen-ion (or hydroxyl-ion) concentration as registered by the electric potential changes rapidly from one level to another. Any indicator that registers between these values will give an approximate indication. Only such an indicator as changes exactly at the point of inflexion will give a highly accurate result.

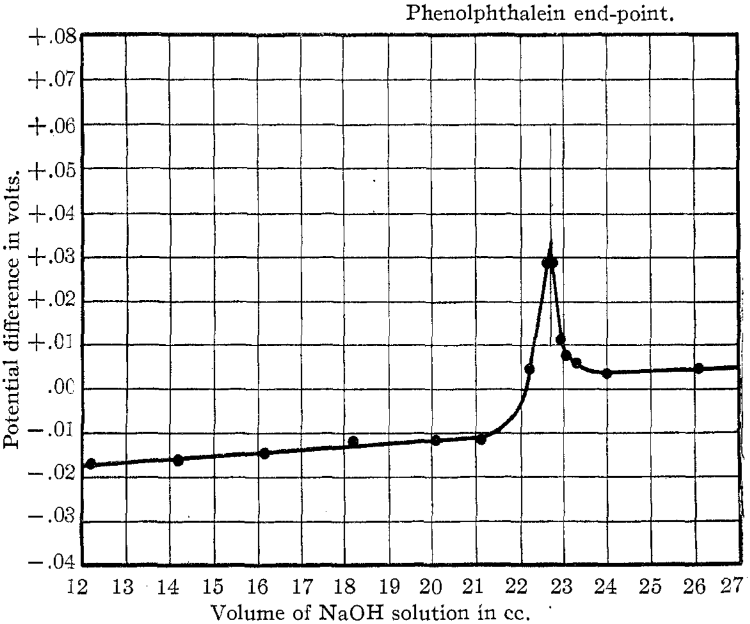

Fig. 5.—Differential titration of butyric acid with NaOH. Offset: 2 cc.

The methyl orange end-point agrees very well with the second electric end-point. In this manner a differential titration with a colorimetric indicator present may be used to determine the suitability of an indicator for a specific titration. Fig. 4 shows the effect of keeping one buret 0.6 cc. ahead of the other instead of 0.2 cc. as in the previous cases. Naturally, the end-point is rendered less sharp. Approximately 0.1 *N* butyric acid was used and, being a rather weak acid, this exaggerated the effect. The same titration using a 0.2cc. offset gave the curve shown in Fig. 5. It is quite possible to decrease the offset further if great care be observed to ascertain that the burets are quite accurate. If such care be not observed small and irregular potential readings may be obtained or else the cusps may turn downward indicating that the wrong buret is in the lead. For ordinary use with 0.1 *N* or 0.05 *N* solutions an offset of 0.2 cc. has been found to be most satisfactory.

Summary

It has been found that in many cases the method described above and referred to as "differential titration" is simpler and more accurate than electro-titration as usually practised. The reasons for this are summarized as follows.

1. The necessity of plotting curves is eliminated.
2. The use of the troublesome calomel half-cell is avoided.
3. Slight errors due to "drifting" (very slow change of potential at an electrode upon standing) are compensated.
4. By the use of solutions almost identical in composition all trouble from diffusion is avoided.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF CALIFORNIA]

A NEW OXIDE OF NITROGEN, NITROSO-NITROGEN TRIOXIDE, AND ITS BEARING ON THE OXIDATION OF NITRIC OXIDE

BY R. LEONARD HASCHE[1]

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In an earlier paper,[2] the negative temperature coefficient of the rate of reaction between nitric oxide and oxygen was attributed to the formation of an unstable intermediate compound which is more stable at low temperatures than at high. It was the purpose of this investigation to discover whether such an intermediate would be sufficiently stable at liquid-air temperatures to be isolated. Two previous attempts have been made to prepare and identify the compound formed from the interaction of nitric oxide and liquid air or liquid oxygen. Helbig[3] in 1903 by passing an electric discharge through liquid air obtained a light green solid which was very unstable. He pumped off the liquid air and a light blue, amorphous solid remained which by his analysis corresponded to the formula N_2O_3. Raschig[4] prepared a compound by passing nitric oxide through liquid air

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[1] National Research Fellow in Chemistry.

[2] Patrick and Hasche, THIS JOURNAL, **47**, 1207 (1925).

[3] Helbig, *Atti accad. Lincei*, **5**, 166 (1903).

[4] Raschig, *Chem.-Ztg.*, **35**, 1096 (1911).