

DIFFERENTIAL TITRATIONS WITH TUNGSTEN ELECTRODE.

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INTRODUCTION.

The classical method of determining the end point in potentiometric titrations consists of measuring the potential difference between an indicator and reference electrodes at suitable intervals during the progress of titration. The end point is usually observed by the sharp rise in E.M.F. c.c. curve, or by determining the maximum of the difference quotient $\Delta E/c.c.$

In usual practice the reference electrode used is the calomel half-cell, while the indicator electrode is either normal hydrogen or quinhydrone electrode. An electrode system consisting of two metallic electrodes has been used for determining the end points. The electrodes may be of the same metal, usually platinum, in which case a slight polarising current is used, or they may consist of two different metals preferably noble, for example, platinum and tungsten. The obvious advantage of such a system is the elimination of rather troublesome calomel half-cell and the prevention of the loss of solution by diffusion into the salt bridge.

Cox (*Jour. Amer. Chem. Soc.*, 1925, 47, 2138) was the first to use a differential method for finding out the end point in titrations. This method depends on the concentration-polarization of one of the two similar electrodes, by some mechanical device which prevents complete mixing of a small portion of liquid surrounding the electrode with the rest of the solution. The graph of E.M.F. observed in the above method, plotted against volume of the reagent added, resembles the $\Delta E/\Delta c.c.$ against c.c. graph obtained by the usual method, the value of the differential $\Delta E/\Delta c.c.$ for a small value of $\Delta c.c.$ being given by the equation $\frac{\Delta E}{\Delta c.c.} = \frac{RT}{F} \times \frac{1}{x}$ where x is the proportion of acid not yet neutralised. In Cox's first experiment, the solution to be titrated was divided into two equal parts, kept in two separate vessels and joined by a salt bridge and the standard solution was added from two burettes in such a way that the end point was reached in one vessel slightly before it was reached in the other.

The method of differential titrations has been extensively used by various workers [cf. MacInnes and his co-workers (*Jour. Amer. Chem. Soc.*, 1926, 48, 2831; 1928, 51, 1119; 1931, 53, 555; *Z. Physik. Chem.*, 1927, 130, 217) and Clarke and Woosten (*Jour. Phys. Chem.*, 1929, 33, 1468)].

Various kinds of cells have been used for differential titrations. Muller (*Z. Electrochem.*, 1925, **31**, 323; 1927, **33**, 182) has used two platinum wire electrodes, one kept in a capillary and the other wrapped round it. Hall, Jensen and Backstrom (quoted from *Ind. Eng. Chem. Anal. Ed.*, 1930, **2**, 213) have used a medicine dropper instead of a capillary.

MacInnes and Jones (*Jour. Amer. Chem. Soc.*, 1926, **48**, 2831) have used a cell with two platinum electrodes, one of which was surrounded by a glass cap to prevent the mixing of the surrounding solution with the rest of the liquid. They found it necessary to add a small quantity of quinhydrone in the solution, because it gave a strong oxidation-reduction potential which varied reversibly with hydrogen ion activity. In their subsequent work MacInnes and his co-workers have shown the utility of a hydrogen differential electrode for potentiometric titrations. They point out that, with such an electrode, the results are more nearly unambiguous than when some indicating substance is added.

The metallic electrodes can be used for differential titrations of acids and bases provided they show a linear relationship with pH, maximum sensitivity being obtained when the electrode gives a theoretical slope. The behaviour of a number of metallic electrodes with respect to pH has been studied previously (*This Journal*, 1938, **21A**, 345) and it has been found that both tungsten and antimony can be used for this purpose with advantage. The other metallic electrodes gave irregular curves and when used for the differential titrations gave spurious peaks.

In this investigation we have studied the utility of tungsten electrodes for differential titration of weak acids by using a thermionic valve arrangement.

EXPERIMENTAL.

The apparatus used for differential titrations is shown in Fig. 1. A pair of tungsten wires were used as electrodes, one of which was

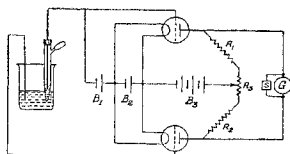


FIG. 1.

- B_1 = Grid Bias Battery 2 Volts
- B_2 = Filament Battery 2 Volts
- B_3 = High-tension Battery 60 Volts
- R_1 and R_2 = 5000 ohms Fixed Resistance
- R_3 = 400 ohms Potentiometer
- S = Universal shunt
- $V_1 V_2$ = Osram P·2 Valves

kept inside a medicine dropper, while the other dipped directly in the solution.

All the measurements were done on a thermionic valve circuit with two P₂ Osram valves in push pull as shown in the diagram. One of the valves was supplied with a grid bias of two volts, and the electrodes were joined to the respective grids of two valves. Sixty volts were used on the anode, when a mutual conductance of 1.5 milliams per volt was obtained.

Before the commencement of the operation, both the electrodes were polished and washed with distilled water. About 2 c.c. of the solution sufficient to dip the electrode, were then sucked in the medicine dropper. Standard alkali (prepared from sodium, with the usual precautions to avoid the formation of carbonate) was added to the solution in small lots, the dropper being pumped in and out at every step, when the galvanometer returned to zero within two to three divisions. The end point was indicated by the maximum deflection per c.c., on addition of small quantities of alkali.

In this way differential titrations of pure oxalic, malonic, succinic, adipic and formic acids were carried out. The results are shown in Figs. 2(a) and 2(b).

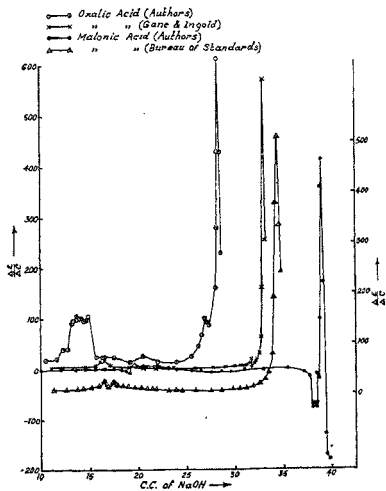


FIG. 2a.

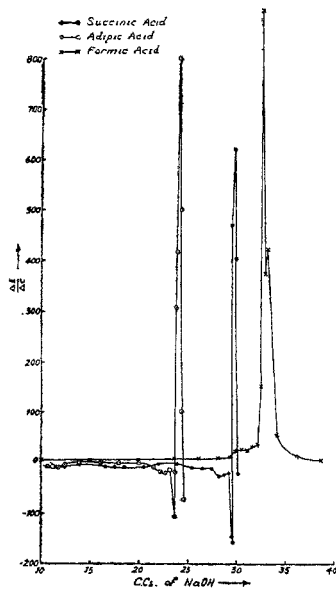


FIG. 2b.

DISCUSSION.

It is observed from the graphs showing $\Delta E/\Delta c.c.$ vs. c.c., that in the case of oxalic acid, a well defined double inflection is obtained when the first equivalent of alkali is added. This inflection is also present in the case of other acids, but it flattens out as the acids become weaker. By an approximate mathematical calculation, Auerbach and Smolezyk (*Z. Physik. Chem.*, 1924, 110, 65) have shown that the character of the titration curves of dibasic acids is determined by the ratio of their dissociation constants. Thus, when K_1 is greater than $16 K_2$, the curve will have an inflection in the middle, whereas when K_1 is less than $16 K_2$, the curve will be similar to that of a monobasic acid. The dissociation constants of various dibasic acids are given in the following table:—

Acid	K_1	K_2	K_1/K_2
Oxalic ¹ ..	5.90×10^{-2}	6.40×10^{-5}	922
Malonic ²	1.43×10^{-3}	2.20×10^{-6}	650
Succinic ² .. .	6.37×10^{-5}	2.54×10^{-6}	25
Adipic ¹	3.82×10^{-5}	3.87×10^{-6}	10

1. Gane and Ingold, *Jour. Chem. Soc.*, 1931, 2153

2. German and Vogel, *Jour. Amer. Chem. Soc.*, 1936, 58, 1546

In the case of oxalic acid, the ratio K_1/K_2 is maximum and consequently a maximum inflection is obtained at the half neutralization point. In other acids this inflection becomes less pronounced, being governed by the ratio K_1/K_2 .

The double inflection observed at half point is due to the formation of di-salt before half of the acid is neutralized. The graphs $\Delta E/\Delta c.c.$ vs. c.c. for oxalic and malonic acids obtained from the values of Gane and Ingold (*Jour. Chem. Soc.*, 1928, 1594) and Burton, Hammer and Acree (*Jour. Bureau of Standards*, 1936, 16, 575) are plotted side by side for comparison. The values of both the authors show an indication of double inflection at half points. The latter authors have observed that if the dissociation constants of malonic acid are calculated at these points on basis of mono-basic treatment of the acid, the values are abnormally high, while the values calculated by taking the di-salt formation into account, agree very well with the values calculated in the other regions of the titration curve. They mention that within 30% range, neutralization of both the acid groups occurs simultaneously. In the present investigation it was seen that distance between the two peaks at half neutralization point became greater and less sharp as the ratio K_1/K_2 became smaller and the

acid became weaker, indicating the widening of the range over which the two acid groups get neutralized simultaneously.

In the graphs it is shown that in malonic, succinic and adipic acids, the approach of the final end point is marked by an indication of negative inflection which becomes more pronounced as the acids become weaker. In strong acids like oxalic and formic acids two inflections are obtained at full neutralization. The occurrence of these double peaks has also been observed by MacInnes and Jones (*loc. cit.*) and Furman and Low (Jr.) (*Jour. Amer. Chem. Soc.*, 1933, **52**, 1310-15) while working with bimetallic systems. The former authors attribute this to the reaction of alkali with quinhydrone which they add to the solution, and the latter to the presence of small traces of carbon dioxide in the alkali. The presence of the double peaks in the present investigation can be due to neither of these causes, as all the precautions were taken to exclude carbon dioxide from alkali solution and no quinhydrone was added. The negative inflections and double peaks at the end point are obviously due to the hydrolysis of the salt formed.

SUMMARY.

The utility of tungsten wire electrodes for differential titrations of acids has been studied using a simple thermionic valve circuit for measurements. The graphs resemble very closely the graphs $\Delta E/\Delta c.c.$ vs. c.c. obtained from the direct potentiometric titrations. The method is found to be very sensitive for obtaining end points accurately and for indicating irregularities in the titration reaction, and has been used by the authors for the electrometric titrations of tannic acids from myrobalan (S. R. Sunthakar and S. K. K. Jatkar, *This Journal*, 1938, **21A**, 189-221) and yielded sharp end points in the regions where hydrogen electrode was sluggish and insensitive.

In the case of dibasic acids the differential method shows double peaks and negative inflections at half and full neutralization points respectively. The former are due to the formation of di-salt before half the acid is neutralized, and the latter is due to hydrolysis.

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