[Contribution from the Geophysical Laboratory of the Carnegie Institution of Washington.]

ELECTRICAL APPARATUS FOR USE IN ELECTROMETRIC TITRATION.

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The increasing use of the electrometric method of locating end-points in certain titrations has made it seem pertinent to discuss and describe suitable electrical apparatus for the purpose. The choice of apparatus is rendered very different from that of potentiometric apparatus for other purposes because of the following facts: (1) We are interested here in relative rather than absolute values of the electromotive force developed during the titration; (2) the electromotive force frequently changes sign;[1] and (3) the apparatus must often be used in an atmosphere charged with acid fumes.

The end-point of the titration is located at a point of inflection of the curve obtained by plotting, against the volume of titrating solution added, the electromotive force developed between an electrode immersed in the solution being titrated, and another, whose potential remains constant.[2] The latter is generally a calomel half-cell, connected through a capillary to the solution being titrated.

The potentiometer used by Hildebrand[3] consisted of a millivoltmeter shunting a variable resistance. Except for the fact that the electromotive force of the potentiometer battery is uncertain and variable, the variable rheostat might well be calibrated directly in millivolts, and the millivoltmeter omitted. It will be shown later that the variation of the battery is unimportant and that the rheostat may be calibrated in any unit whatever, provided the indications of its scale are practically proportional to the potential drop across it.

The change of voltage at the end-point is so great, under appropriate conditions, that the potentiometer may merely be balanced at the beginning of the titration, and the end-point located by the large, permanent galvanometer deflection that accompanies this change.[4] Apparatus for use with this method as applied to the determination of chromium, manganese and vanadium has been designed by G. L. Kelley and others[5] and has been put on the market.[6]

For more precise work, the end-point of the titration can always be

[1] When titrating with $SnCl_2$, for example.

[2] J. Hildebrand, This Journal, **35**, 847–871 (1913).

[3] *Loc. cit.*, p. 851.

[4] G. S. Forbes and E. P. Bartlett, This Journal, **35**, 1527 (1913); G. L. Kelley, *J. Ind. Eng. Chem.*, **9**, 780 (1917).

[5] *J. Ind. Eng. Chem.*, **9**, 780 (1917).

[6] Leeds and Northrup Co., *Bull.* 498.

located much more closely by plotting. Moreover, many substances likely to be present in the solution cause the change of the electromotive force at the end-point to be so slow that plotting is absolutely essential.[1] Thus the usefulness of the Kelley apparatus would be greatly extended by the presence of a scale of equal parts on the potentiometer proper.

If we plot electromotive forces as ordinates against amounts of titrating solution as abscissas it is obvious that the whole curve may be shifted up or down without changing the abscissa of the point of inflection. Moreover, since the coördinates of the point of inflection are independent of the scale chosen in plotting the curve, the electromotive force may be measured in any unit whatever, whose actual value need not even be known.

From these conditions we see that our potentiometer may be provided with a scale, of an arbitrarily chosen unit, whose zero is so placed that the scale readings are always positive although the electromotive force developed by the potentiometer changes from negative to positive as the

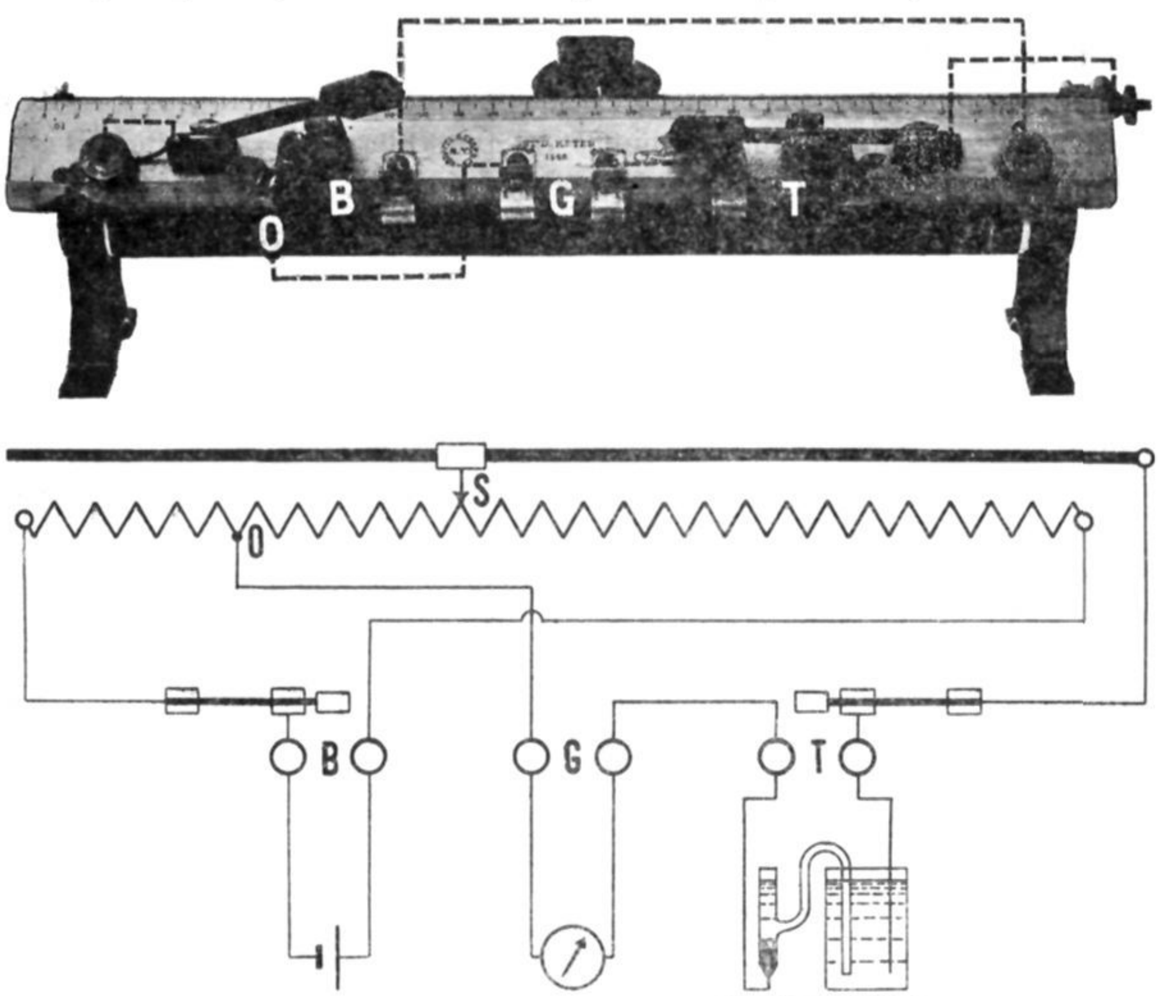

Fig. 1.—Photograph and diagram of simplified potentiometer for use in electrometric titration.

[1] Hostetter and Roberts, THIS JOURNAL, 41, 1337 (1919).

slider is moved along the scale. This condition can be attained by taking off a tap at a suitable point along the potentiometer winding, as at O in Fig. 1. This method has the very distinct advantage of making it unnecessary to use a reversing switch when the electromotive force being measured changes sign. It also does away with the necessity of writing (or forgetting) the minus sign before some of the readings.

Experience has shown that the electromotive force developed by the potentiometer may vary 5% from being proportional to the scale reading, provided the variation does not change abruptly by an amount greater than 1%. The voltage of the potentiometer battery may be permitted to change even more than this during the course of a titration without causing trouble, because this change, being the result of polarization, is gradual and will therefore have very little effect on the shape of the curve. Thus an ordinary dry cell may be used, though the resistance of the potentiometer should in this case be 50 ohms or more in order that the dry cell may have a long life. A single storage cell gives a much more constant electromotive force, but is not essential.

The potentiometer shown in Fig. 1 was made by fitting a boxwood ruler to a well known type of rheostat,[1] and mounting the battery switch, galvanometer switch and terminals on the ruler. Its resistance is 325 ohms. The tap at the point O is made with a fine, stranded wire soldered to one turn of the rheostat winding and reinforced with a drop of De Khotinsky cement over the solder. All of the connections are on the under side of the ruler and are indicated by dotted lines in the photograph. This particular rheostat, when used with a single dry cell, will measure electromotive forces between about—0.3 volt at a scale reading of 25 mm. and +1.0 volts at a scale reading of 275 mm.

While several of these potentiometers have been in use for over two years and have proven entirely satisfactory, it has seemed desirable to find an alternative style of rheostat for them. This has been found, in the form of a "tuning coil" for amateur wireless work. It is shown diagrammatically in Fig. 2, and its connections are indicated. This rheostat has two sliders, each of which may be provided with a scale. The scale readings may all be made positive by numbering the two scales in opposite directions, and arranging them so that when the two sliders are set on the last turn of wire to the left the reading on both the scales will be alike. Stops of some sort may be provided to stop the sliders at this turn. One or the other slider is always left at this point, and a balance obtained by shifting the second, one slider being used for positive electromotive forces and the other for negative. If the near slider, S′ in Fig. 2, is placed at the extreme left as shown in the figure and the far slider S then moved from the position in Fig. 2 to the extreme left, the

[1] "Jagabi," purchased from J. G. Biddle, Philadelphia.

potential difference between the two sliders will increase from its original negative value to zero, while the scale reading will increase to 100, and the readings on both scales now will be 100. If the far slider S is now left at 100, and the near one S′ moved to the right, the potential difference will increase from zero to some positive value, while the scale reading will increase from 100 to some higher value.

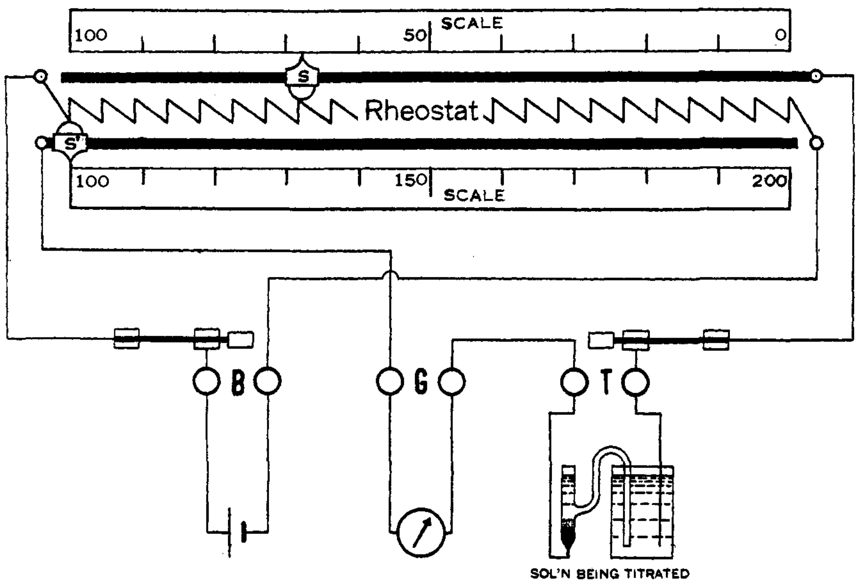

Fig. 2.—Diagram of common wireless tuning coil used as a potentiometer for electrometric titration.

The disadvantage of this rheostat lies in the fact that it is wound with copper wire. The coil not only corrodes readily, but the resistance, a very few ohms, is so low that the dry cell used with it does not last very long. However, it may readily be rewound with resistance wire which will correct both of these defects. Some such wire as chromel, nichrome, etc., is best for this purpose because the coating of oxide on the wire provides ample insulation between the turns. An approximate calibration curve can readily be constructed for either of these potentiometers. The voltage in millivolts of the battery, divided by the length in scale divisions of the rheostat winding, gives the value of one scale division in millivolts. The voltage represented by any point on the scale is then the product of this value by the distance to the zero point of the scale, *i. e.*, the point at which the slider and tap-off, or the two sliders, as the case may be, make contact with the same turn of wire.

A millivoltmeter may be connected to the slider and tap-off, or to the two sliders, as in Hildebrand's potentiometer; but it must be borne in mind that a calibration of the potentiometer can not be made in this way because of the shunting effect of the millivoltmeter.

The Galvanometer.

As the resistance through the solution and capillary is often several thousand ohms, the galvanometer should have a rather high resistance—so high as to make it impracticable to substitute an ordinary millivoltmeter. It need not be very sensitive; 1 to 2 megohms is sufficient. A much greater sensitivity than this is to be avoided because of the tendency for the pointer to be deflected off the scale and to follow the insignificant changes of electromotive force due to stirring, etc. It should have a short period to facilitate rapid work. The other considerations are dictated by resistance to acid fumes, convenience, and cost.

A capillary electrometer may be used in place of the galvanometer. It is a cheap, simple instrument to make, but not an easy instrument to use, for the movements of the mercury meniscus are very small and it is readily put out of commission by a relatively small electromotive force applied to it in the wrong direction. Where it is used, it should be connected in such a way as to make the mercury side of the electrometer become more positive as the voltage changes during titration. This will reduce the danger of its becoming deranged.

The inexpensive, portable "flip-flop" galvanometer,[1] though sensitive enough, is not always easy to use in a poorly lighted hood. A reflecting galvanometer placed outside the hood and arranged to throw a spot of light over the top of the operator's head onto a scale, or an index line on a white surface, behind the burets, makes an ideal arrangement. The box-type, lamp-and-scale galvanometers on the market[2] are also good; for, being entirely enclosed in a wooden box, they can be placed in the hood behind the burets with little danger that acid fumes will cause much damage.

Cost.

The material for either of the potentiometers of Fig. 1 and Fig. 2 can be bought for about $12. A portable galvanometer can be had for $18 or $20, and the reflecting type of galvanometer should not cost more than $50.

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[1] Such as the Leeds and Northrup Company's Type 2320 or the Weston Model 324.

[2] Such as the Leeds and Northrup Company's Type 2420.