the other hand, it is hopeful to notice the general agreement in the case of erbium. With ytterbium we again find two sets of values: the high reported by Meyer and Decker, and the lower one of 8300 given by Cabrera and the present authors. The negative value for yttrium, agreeing within the experimental error with R. J. Meyer's value, shows that our material is as pure as any yet prepared.

**Temperature Coefficient and Numbers of Magnetons.**—The qualitative values obtained by the authors check remarkably well with those given by Williams. Our value for erbium is perhaps a little low. These values do not allow any calculation of magnetons, but they clearly indicate that no value can be attached to the numbers calculated by Cabrera on the assumption that $\alpha = (1/293)$ $(\vartheta = 0)$.

In conclusion the junior author wishes to express his indebtedness to the Nederlandsch-Amerikaansche Fundatie and to the International Education Board, who enabled him to carry out this work.

## Summary

1. With the exception of europium, dysprosium and thulium, figures for the magnetic susceptibilities of rare earth preparations of known purity are given.

2. Qualitative values for the temperature coefficient of this property are reported.

3. These values are compared with those given by other authors, and discrepancies are briefly discussed.

4. It is pointed out that in the present state of our knowledge it is impossible to calculate magneton numbers, or to draw any conclusion as to the experimental existence of the magneton.

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# A METHOD FOR DIFFERENTIAL POTENTIOMETRIC TITRATION

BY D. A. MACINNES AND PAUL T. JONES

It has been repeatedly shown[1] that the data obtained from potentiometric titrations can be more readily interpreted if, instead of plotting the electromotive force, $E$, against the volume of reagent, $V$, as is the usual practice, the tangent to that curve, $\Delta E/\Delta V$, is plotted against $V$. The end of the titration appears in the first type of curve as a point of inflection which is not always clearly defined. In the second type of curve, the end of the titration is an unmistakable, sharp maximum. D. C. Cox,[2] in a recent

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[1] See especially Hostetter and Roberts, THIS JOURNAL, **41**, 1341 (1919).

[2] Cox, *ibid.*, **47**, 2138 (1925).

paper, has described an ingenious method for obtaining, by direct experiment, data which are related closely to $\Delta E/\Delta V$. Briefly, his method consists in titration from two burets into two beakers, each of which contains an electrode and half of the solution to be titrated. The beakers are connected electrically by means of a piece of wet filter paper. During the titration one of the burets is kept a small difference of titer, say 0.2 cc., behind the other. The potential readings are therefore those of concentration cells with liquid junctions. His method is restricted for practical use by the necessity of working with two burets in an unusual manner, and of dividing the solution into two equal portions. Furthermore, the accuracy of the method is greatly affected by slight inaccuracies in readings of, and calibrations of the two burets.

It has occurred to the authors that all the advantages of the method devised by Cox can be retained, and only one buret and beaker used, if a
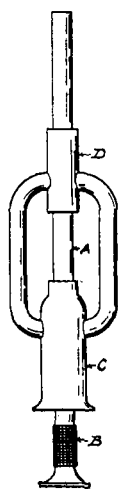


Fig. 1.

small amount of the solution surrounding one of the electrodes is temporarily kept from mixing with the rest of the solution until after each small increment of the titrating reagent is added. The device shown in Fig. 1 was constructed for that purpose after a number of less satisfactory forms had been tried. It consists of a central tube A carrying an electrode of platinum gauze B, which makes contact with mercury on the inside of the tube. The cap C is connected with the guide tube D by means of solid glass rods. C and D slide loosely on the inner tube A, a projection on which is ground to fit the lower edge of the cap C. When this
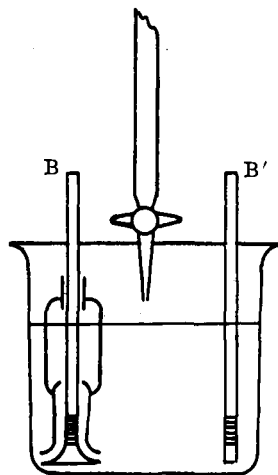


Fig. 2.

apparatus is placed in a solution and the cap lowered, the solution around the electrode B is held in place and is not disturbed by vigorous stirring. During a titration the cap is lowered before each addition of reagent and the potential, between Electrode B and Electrode B' placed in the body of the solution, is determined on a potentiometer.[3] The arrangement is shown diagrammatically in Fig. 2.

A curve for the titration of a strong acid with a strong base, which is

[3] The error due to holding a small portion of the solution temporarily from reacting can readily be shown to be very small. If the cap C is held 1 cc. from 100 cc. of solution the error would be 1% if the 1 cc. were not immediately mixed with the bulk of the solution. However. if the cap is finally lowered when the titration is 99% complete the error is 1% of this or 0.01%. The argument is the same as in the use of "outside" indicators except that in our case the error is not cumulative.

quite typical of the results obtained in our experiments, is shown in Fig. 3. In this case hydrochloric acid containing a small quantity of quinhydrone was titrated with sodium hydroxide solution. The addition of the quinhydrone was found to be desirable since it gives a strong oxidation-reduction potential, which has been shown by Biilmann[4] to vary reversibly with the hydrogen-ion activity. The points on the curve were obtained by adding 0.1 cc. to the external solution after the cap C had been lowered, and reading the resulting potential.
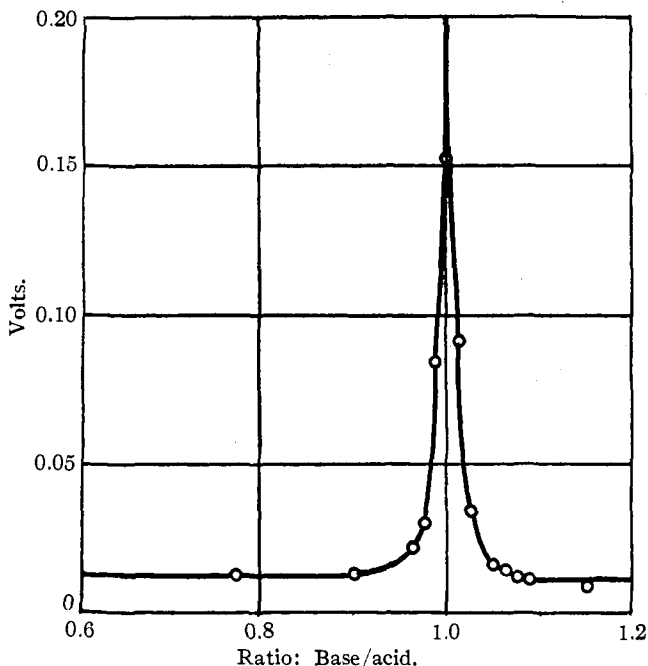


Fig. 3.

Neglecting for the moment the liquid-junction potentials which will be considered below, the theoretical form of the curve shown in Fig. 3 can be readily derived. Since a small amount of the sodium hydroxide solution is added to the much greater bulk of dilute acid, and the acid is steadily converted into salt, the total ion concentration does not change appreciably during the titration. Under these conditions the activity of the acid is proportional to its concentration, at least in reasonably dilute solution.[5] The potential $E$ at one of the electrodes will therefore be $E = E_0 - (RT/F)$-log $xC$, in which $E_0$ is a constant for the conditions obtaining in the solution, $C$ is the original concentration of the acid and $x$ is the proportion not

[4] Biilmann, *Trans. Faraday Soc.*, **19**, 676 (1923).

[5] Chow, THIS JOURNAL, **42**, 497 (1920). Harned, *ibid.*, **42**, 1808 (1920).

yet neutralized. The potential between two electrodes with a difference of the proportion of acid $dx$ will thus be $dE = (RT/F) \times (dx/x)$ or for a small finite difference $\Delta x$ the value of $\Delta E/\Delta x$ will be $(RT/F) \times (1/x)$. The descending portion of the curve, which is practically symmetrical with the ascending part can also, with but little error, be computed from the same formula, $x$, however, in this case being the excess of concentration of alkali. The smooth curve which passes through the experimental points has been obtained from the theory as given, allowance being made for initial difference of potential of the electrodes.

So far, we have neglected the liquid-junction potential between the two solutions. The type of liquid junction that occurs in these experiments is that of two solutions of the same total ion concentration but with various proportions of two different electrolytes. The formula for these liquid junctions, applicable to two electrolytes with the same degree of dissociation, is

$$E_l = \frac{RT}{F} \, ln \, \frac{x + c}{x' + c} \tag{1}$$

in which $x$ and $x'$ are the proportions of acid not neutralized on the two sides of the junction and $c = (1-N)/(N-N')$, $N'$ being the cation transference number of the pure acid and $N$ that of the salt resulting from the neutralization.[6] For the small differences of $x$ and $x'$ involved, the potentials

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[6] Equation 1 can be derived as follows. To be concrete we will assume that we are dealing with solutions of potassium chloride and hydrochloric acid mixed in various proportions. The differential equation is

$$F \, d \, E_l = RT(T_K \, d \, ln \, A_K + T_H \, d \, ln \, A_H - T_{Cl} \, d \, ln \, A_{Cl}) \tag{2}$$

in which $T_K$, $T_H$ and $T_{Cl}$ are the transference numbers and $A_K$, $A_H$ and $A_{Cl}$ are the activities, *in the mixture of solutions*, of the ions represented by the subscripts. Since $A_{Cl}$ is constant throughout the solution $d \, ln \, A_{Cl} = 0$. In such a mixture

$$T_K = \frac{N(1 - N')}{(N - N') + (1 - N)/x}$$

[see MacInnes, This Journal, **47**, 1922 (1925)] in which $N$ and $N'$ are, respectively, the cation transference numbers in pure potassium chloride and hydrochloric acid solutions, and $x$ is the proportion of potassium chloride in the electrolyte mixture. The corresponding value for $T_N$ is

$$T_N = \frac{N'(1 - N)}{(N' - N) + (1 - N')/(1 - x)}.$$

Since in these solutions the activities of the cations are proportional to the values of $x$ and $(1 - x)$, Equation 2 may now be written

$$F \, d \, E_l = RT \left[ \frac{N(1 - N')}{(N - N') + (1 - N)/x} \, d \, ln \, x + \frac{N'(1 - N)}{(N' - N) + (1 - N')/(1 - x)} \, d \, ln \, (1 - x) \right]$$

which may be simplified to

$$d \, E_l = \frac{RT}{F} \, \frac{dx}{x + \dfrac{1 - N}{N - N'}}$$

are negligible for our present purpose, since for the titration of hydrochloric acid with sodium hydroxide they vary from 0.3 to 0.9 millivolt on the acid side of the neutralization point, and are 0.3 mv. and less on the alkaline side.
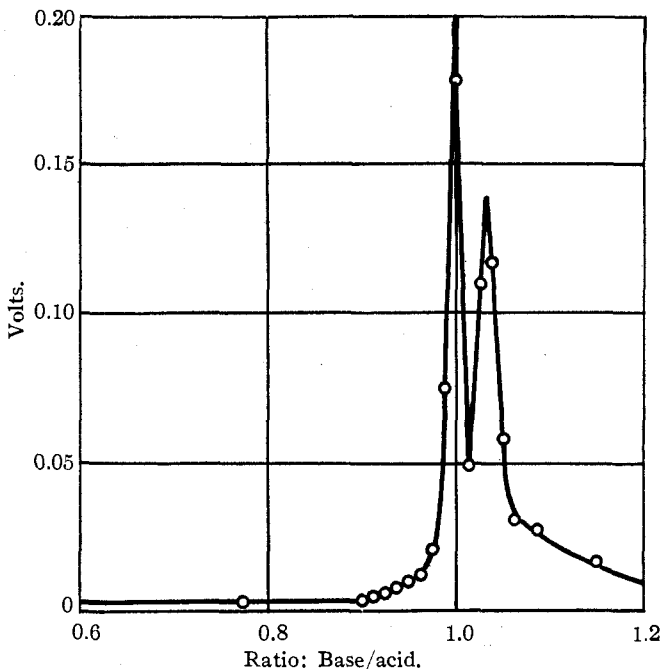


Fig. 4.

With larger quantities of quinhydrone than that used in the experiment whose results are plotted in Fig. 3, the curves take the form shown in Fig. 4, which is typical of many that we have obtained.    After the titration of the hydrochloric acid, yielding a sharp maximum identical with that in Fig. 3, another lower but equally sharp maximum is obtained due evidently to a reaction of the base with the hydroquinone.    A very similar curve is also obtained when phenolphthalein is substituted for quinhydrone.    It is interesting to note that the color change of this indicator occurs after the *second* maximum, showing graphically the need for a correction for the base

Footnote 6, cont.:   If now this is integrated between 0 and 1 we obtain

$$E_l = \frac{RT}{F} \ln \frac{1 - N}{1 - N'}$$

which is a form of the Lewis and Sargent equation.   Integrated between the limits $x$ and $x'$ we have

$$E_l = \frac{RT}{F} \ln \frac{x + \dfrac{1 - N}{N - N'}}{x' + \dfrac{1 - N}{N - N'}}$$

reacting with the indicator during such a titration. Phenolphthalein has the further similarity to quinhydrone in yielding an oxidation-reduction potential at the electrodes,

In all the experiments so far described the electrodes were unplatinized, since erratic values of the potentials were obtained unless the platinized electrodes were used in an atmosphere of hydrogen which was carefully kept free from oxygen, a procedure not easy to carry out in ordinary titrations, though worth while in cases having theoretical interest. Vigorous mechanical stirring was found necessary in all these experiments.

The method is especially applicable to oxidation-reduction reactions and is, indeed, serviceable in any case in which potentiometric methods are possible. The curves we have obtained for titrations of ferrous salts with permanganate and dichromate are nearly identical with those of Fig. 3. The end-points can apparently be established more accurately than can be judged by the usual color changes which appear, usually, one drop after the greatest rise of potential. Another paper will deal with this method as adapted to measurements of high precision.

For many practical titrations a potentiometer is unnecessary. The two electrodes shown in Fig. 2 can be connected directly to a galvanometer which remains undeflected, or nearly so, until near the end of the titration, when a slight swing announces the approaching end-point, and a larger one its arrival. In such titrations regular increments of reagent and lifting of the electrode cap after every addition were not found necessary. It is, however, necessary to lift the cap several times during the titration in order that the enclosed solution will have an opportunity to react. In the case of some oxidation-reduction reactions, resistances up to 20,000 ohms were needed in series with even low-sensitivity galvanometers.

## Summary

A method for potentiometric titrations is described, in which only one type of electrode is used, concentration cells being formed during the titration by temporarily isolating a portion of the solution around one of the electrodes. The measured potentials reach a sharp maximum at the end of the titration. The method is capable of high accuracy and is applicable in every case in which potentiometric technique is possible.

CAMBRIDGE, MASSACHUSETTS