decomposition may be different with different acids and different solvents. Nevertheless it is possible, as Hantzsch supposes, that the reaction velocity depends in any case upon salt formation by addition of hydrogen ion to the ester, and that the final steps of the reaction, leading to the different possible products, do not affect the velocity. This would account for the observed parallelism of reaction velocity and indicator acidity.

It should be of great importance to investigate other, less ambiguous reactions to see if this parallelism can be generalized.

Summary

A generalized theory of acidity is proposed and given mathematical expression. In this the effect of the basicity and of the dielectric constant of the solvent are both considered.

The predictions of the theory are in agreement with the available evidence on acidity in non-aqueous solutions, notably with the work of Hantzsch and with that of Hall and Conant.

NEW YORK CITY

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY, No. 583]

A BALLISTIC GALVANOMETER METHOD OF POTENTIOMETRIC MEASUREMENT FOR HIGH RESISTANCE CELLS

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Introduction

A recent publication by Jones and Kaplan[1] contains a description of a method of potentiometric measurement for high resistance cells which uses a condenser and ballistic galvanometer as a null point indicator. A deflection method for high resistance cells which used the condenser and ballistic galvanometer was used in this Laboratory by Beans and Oakes.[2] Since then we have developed a more exact method[3] which is in many respects similar to that of Jones and Kaplan but differs in that it is a semi-deflection method. We have experimentally demonstrated that our method may be used successfully with cell resistances as high as 50 megohms. The cells which Jones and Kaplan used had internal resistances no higher than 1.6 megohms. At higher resistances the null point method, while still possible, becomes very cumbersome due to the time required to charge the condenser sufficiently to cause a noticeable throw upon discharge. Our method overcomes this difficulty, at the same time retaining an accuracy of 0.1 to 0.5 millivolt.

[1] Jones and Kaplan, THIS JOURNAL, **50**, 1845 (1928).

[2] Beans and Oakes, *ibid.*, **42**, 2116 (1920).

[3] Walden, *Dissertation*, Columbia, **1924**.

Apparatus

A diagram of our apparatus is shown in Fig. 1. Our circuit is the same as that of Jones and Kaplan except in two particulars. We do not use a tapping key to discharge the condenser but a discharge switch, so that the ballistic galvanometer G_b receives the total discharge of the condenser, not the instantaneous discharge. Also the discharge switch has a third contact which automatically removes the damping shunt R_d at the moment of discharge. We also have a current galvanometer G_c for comparison purposes which may be substituted for the condenser-ballistic galvanometer system by means of a double pole double throw switch. G_b has a sensitivity of about 0.0007 microcoulomb per millimeter throw. C is a mica dielectric condenser of approximately 10 microfarads capacity. All switches have mercury contacts supported on hard rubber pedestals. Connections are made with wires supported by glass insulators or silk cord.

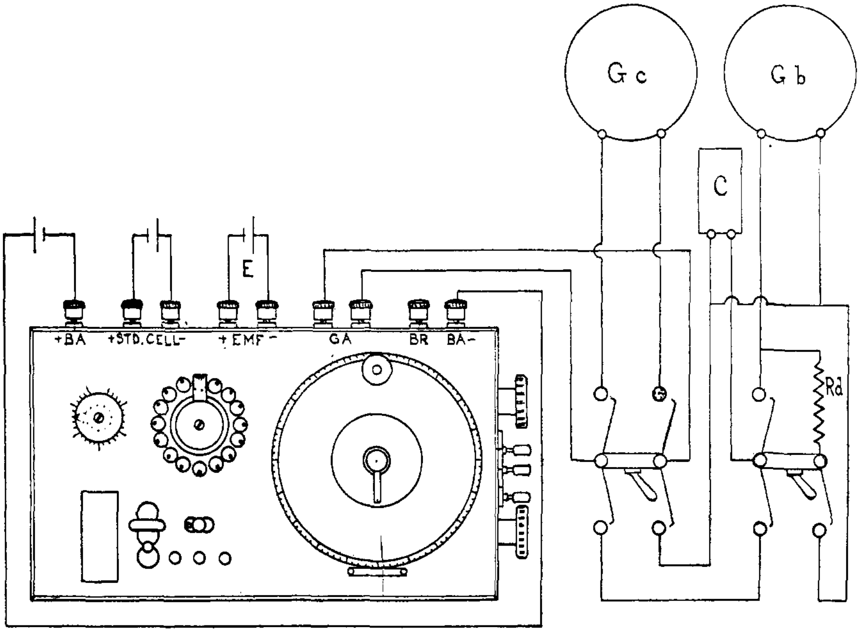

Fig. 1.—Working circuit diagram as used in connection with a Leeds and Northrup Type K potentiometer.

Method

Instead of locating the exact null point of the potentiometer by successive trials we locate it by this method within 10 millivolts. Then we measure the difference between the voltage of the potentiometer and the electromotive force of the cell by the throw of the galvanometer. To do this we need to determine the relationship between galvanometer throws and voltages between the condenser plates. This is accomplished as follows. We connect together the potentiometer binding posts marked "E.M.F." Then if the discharge switch is set to charge the condenser the applied potential difference will instantly be that of the potentiometer, since there is little resistance in the circuit. By charging and discharging with different settings of the potentiometer data are obtained with which to plot galvanometer throws against condenser voltages. Thus we empirically avoid all trouble due to a non-linear galvanometer characteristic and also from dielectric absorption. Data for this curve may be obtained in about fifteen minutes. It is necessary to check this curve occasionally since ballistic galvanometer constants change slowly. To measure the difference between the voltage of the potentiometer and the electromotive force of the cell, we may charge the condenser until it has attained its equilibrium charge nearly enough, discharge and observe the galvanometer throw, and read the difference directly from the curve. The required charging time becomes very long when cell resistances are high. For such cases we have devised a method of determining the equilibrium voltage by measuring the voltages between the condenser plates after two measured charging times. This cuts the time required to make a measurement about in half. When cell resistances are very high leakage through the dielectric of the condenser becomes a factor of importance. Our method considers this possibility and corrects for it where necessary.

Time Required to Charge a Condenser.—Let C = the capacity of the condenser; R = the resistance of the circuit; e = the charging electromotive force; v = the potential difference between the plates, of the condenser at any instant; q = the charge in the condenser at any instant; L = the resistance through the dielectric of the condenser and T = the elapsed time since the circuit was closed. As the condenser is charging

$$\mathrm{d}q = \left[\frac{e-v}{R} - \frac{v}{L}\right]\mathrm{d}T$$

$$T = RLC\int_0^q \frac{\mathrm{d}q}{eLC - q(L+R)} = RC\frac{L}{L+R}\ln\left[\frac{e}{e - v\dfrac{L+R}{L}}\right] \qquad (1)$$

If L is very much larger than R, Equation 1 reduces to

$$T = RC\ln\frac{e}{e-v} \qquad (2)$$

If $v = 0.99e$ (corresponding to an error of 0.1 millivolt in a measurement of 10 millivolts), it has been found that if the condenser is moderately well constructed Equation 2 is a sufficiently close approximation. When R = 50 megohms, C = 10 microfarads and $v = 0.99e$; T, by Equation 2, is equal to 38.4 minutes. This large charging time is very objectionable since in the absence of exact knowledge of the resistance of the cell the only way to tell when the charging time has been sufficiently long is to obtain the same result after a longer period. Therefore, when R is large we do not measure e directly but calculate it from two measurements of v obtained after different time intervals.

Method of Calculating e when T is Large.—If v is measured after two time intervals, we have from Equation 1

$$T_1 = RC\frac{L}{L+R}\ln\left[\frac{e}{e - v_1\dfrac{L+R}{L}}\right]$$

$$T_2 = RC\frac{L}{L+R}\ln\left[\frac{e}{e - v_2\dfrac{L+R}{L}}\right]$$

Solution of these equations leads to the expression

$$e = \frac{v_2^2}{2v_2 - v_1} \times \frac{L + R}{L} \tag{3}$$

if $T_1 = 2T_2$. If e is never greater than 10 millivolts, L can be as small as $100R$ before error from neglect of the leak correction factor $(L + R)/L$ becomes greater than 0.1 millivolt. We have found that leak resistances in a well constructed condenser are sufficiently high so that this correction need not be used.

Elimination of Error from Dielectric Leakage.—If it may be assumed that the dielectric resistance L is constant, the value of the factor $(L + R)/L$ may be experimentally determined by means of Equation 3. Two measurements of v are made after two time intervals, one twice as long as the other. Then the potentiometer setting is changed, changing e by a known amount to e', and two similar measurements of v' are made. Then

$$\frac{L + R}{L} = \frac{e - e'}{\dfrac{v_2^2}{2v_2 - v_1} - \dfrac{v_2'^2}{2v_2' - v_1'}} \tag{4}$$

from which it can be seen that if the difference between the values of e and e' calculated by Equation 3 neglecting the leak correction factor is equal to the difference between the potentiometer settings within the precision sought $(L + R)/L$ may be considered nearly enough equal to 1. If this is not the case it seems advisable to use another condenser with smaller leakage, since L may be expected to vary with the temperature and humidity. We have found that a sufficiently good condenser may be made by connecting 10 of the Western Electric Company's 1 microfarad condensers.

Error Introduced by Calculating e.—If v_1 and v_2 are measured after time intervals which are too short a very large error may be introduced. Since it is desirable to keep the charging times as short as possible in order to cut down the time required to make a measurement, some method of estimating this error is necessary. If Δv_1 and Δv_2 are the errors in the two measurements, the errors introduced by each into the calculation of e by Equation 3, neglecting the factor $(L + R)/L$, will be

$$\frac{\delta e}{\delta v_1}\,\Delta v_1 = \frac{v_2^2}{(2v_2 - v_1)^2}\,\Delta v_1 = \frac{1}{(2 - r)^2}\,\Delta v_1$$

and

$$\frac{\delta e}{\delta v_2}\,\Delta v_2 = \frac{2v_2(v_2 - v_1)}{(2v_2 - v_1)^2}\,\Delta v_2 = \frac{2(1 - r)^2}{(2 - r)^2}\,\Delta v_2$$

where

$$r = \frac{v_1}{v_2}$$

Since the two errors are of opposite sign, the maximum error which can be introduced by this calculation is

$$\Delta e_m = \pm \Delta v \left[\frac{1}{(2 - r)^2} - \frac{2(1 - r)^2}{(2 - r)^2}\right] = \pm \Delta v\,\frac{2r - 1}{(2 - r)^2} \tag{5}$$

where Δv is the maximum error expected in measuring v. This relationship may be plotted for any given apparatus, and the operator can then decide whether sufficiently long charging times have been taken by calculating r and finding Δe_m from the curve.

Error Caused by Leakage between the Poles of the Cell.—When electromotive force measurements are made on cells with large internal resistances very serious error may be caused by leakage between the poles of the cell. If R_L is the leakage resistance, R_I the internal resistance of the cell, E the electromotive force of the cell and ΔE the error caused by the leakage through R_L, it follows from Ohm's Law that $R_L = [(E-\Delta E)/E] R_I$. If the measurement of E is to be accurate to 0.1 millivolt and if E may be as large as 1 volt, it is evident that R_L must be 10,000 times R_I. If R_I is of the order of several megohms, great care must be exercised in the design of the cell and its connections to the measuring instrument.

Experimental

Since it is not easy to construct a high resistance cell of known electromotive force, an analogous system consisting of a low resistance standard cell in series with a high resistance was used for testing purposes. The high resistance and cell were placed side by side, connected together with a short lead, and connected to the potentiometer with the same leads which were afterwards used to connect the actual high resistance cell. The high resistance consisted of the requisite number of megohm resistance units connected in series. The units were made by spattering platinum on mica.[4] The resistance of each unit was measured and found to be correct within a few per cent.

Table I shows a series of measurements made on a cell in series with resistances from 1 to 10 megohms. Over this resistance range it is not

TABLE I

RESISTANCES OF 1 TO 10 MEGOHMS

R, megohms	T, min.	E.m.f., volts	Error, mv.
1	1	1.0154	0.0
2	2	1.0154	.0
3	2	1.0154	.0
4	3	1.0154	.0
5	3	1.0154	.0
6	4	1.0154	.0
7	4	1.0153	− .1
8	6	1.0154	.0
9	7	1.0155	+ .1
10	7	1.0154	.0

E.m.f. (measured without series resistance) = 1.0154 v.

TABLE II

RESISTANCES OF 10 TO 50 MEGOHMS

R, megohms	T, min.	E.m.f., volts	Error, mv.
10	1– 2	1.0188	−0.2
10	1– 2	1.0189	− .1
20	2– 4	1.0189	− .1
20	2– 4	1.0194	+ .4
30	3– 6	1.0184	− .6
30	3– 6	1.0193	+ .3
40	5–10	1.0192	+ .2
40	5–10	1.0188	− .2
50	5–10	1.0184	− .6
50	5–10	1.0188	− .2

E.m.f. (measured without series resistance) = 1.0190 v.

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[4] Furnished by the Prometheus Electric Company, New York City.

necessary to calculate e since the time required to approach equilibrium closely enough is never more than ten minutes.

Table II shows a series of measurements over a resistance range of 10 to 50 megohms. Here e was calculated by Equation 3, neglecting the correction factor for leakage through the condenser. Charging times were chosen so that Δe_m from Equation 5 was about 1 millivolt if Δv is 0.1 millivolt.

Summary

1. We have described a semi-deflection method of potentiometric measurement which may be used with cells having internal resistances as high as 50 megohms.

2. We have discussed the precautions necessary with work of this kind.

3. We have shown that when full precautions are taken measurements may be made with a precision of ±0.1 millivolt when cell resistances are as high as 10 megohms, and with a precision of ±0.5 millivolt with cell resistances as high as 50 megohms.

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[Contribution from the Chemical Laboratories of New York University]

TERNARY SYSTEMS. VII. THE PERIODATES OF THE ALKALI METALS

By Arthur E. Hill

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Following the discovery of periodic acid and the periodates, it was observed at an early date that the acid differed widely from the analogous perchloric acid in being distinctly polybasic and in the varying degrees of hydration of its hypothetical anhydride I_2O_7. The nomenclature most commonly adopted for classifying the various acids is, with slight modification, that of Blomstrand.[1] H_5IO_6, the hydrate of greatest water content, is known as para-periodic acid, $H_8I_2O_{11}$ as di-para-periodic acid, H_3IO_5 as meso-periodic acid, $H_4I_2O_9$ as di-meso-periodic acid and HIO_4 as meta-periodic acid. Although but two, or possibly three, of these acids are definitely known, salts derived from all of them have been reported; of these, the silver salts and the salts of the common alkali metals have been most thoroughly studied.[2] It does not appear, however, that the studies have been systematic in this nature; slight modifications in the conditions of preparation have given to the various investigators salts differing in their analyses and which were on that evidence assigned to the corresponding one of the five acids enumerated above. By such

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[1] Blomstrand, *J. prakt. Chem.*, **34**, 433 (1886).

[2] See Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans Green and Co., N. Y., **1922**, Vol. 2, p. 406.