SOME APPLICATIONS IN THE POTENTIOMETRIC TITRATIONS BY USING VACUUM TUBE.

By Kosaku **MASAKI** and Okiro **HIRABAYASHI**.

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Introduction.

During the process of work in analysis, it is very necessary to execute a titration securely and swiftly. The potentiometric titrations in oxidation and reduction reactions by using a vacuum tube were reported by many investigators.(1) In all of these investigations, a negative potential is put on the grid with respect to the filament and the indicator electrode is directly connected to the grid; for example the indicator electrode is platinum and the calomel electrode is connected to the battery impressing the negative potential to the grid. By this method it is necessary to plot $\Delta E / \Delta V$ to obtain the equivalence point, where ΔE is a small change of the e.m.f. of the cell during titration and ΔV is the volume of the titrating solution. The values of galvanometer or milliammeter defections may be used in place of ΔE. Recently J. L. Kassner, R. B. Hunze

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(1) Goode, *J. Amer. Chem. Soc.*, **44** (1922), 26; **47** (1925), 2483.
Calhane and Cushing, *J. Ind. Eng. Chem.*, **15** (1923), 1118.
Treadwell, *Hel. Chem. Acta.*, **8** (1925), 89.
Williams and Whitenack, *J. Physik. Chem.*, **31** (1927), 519.
Morton, *Pharm. J.*, **118** (1927), 761.
E. Beri, W. Herbert und W. Wohlig, „Die Chem. Fabrik,“ 1930, 445; 448.

and J. N. Chatfield⁽²⁾ studied the method to avoid the complication of plotting curves to obtain the equivalence point. It was reported that their method was preferable in the electrometric titrations of some oxidation-reduction reactions. The present investigation was started to find out the characteristics of the apparatus modified by the author, when it was applied on the electrometric titrations of many oxidation-reduction reactions.

Apparatus.

The circuit of the apparatus is shown in Fig. 1, in which the details of every parts are as follows. V in circle is voltmeter reading in units of 0.1 volt. D is potential divider of 10,000 ohms. C is 4-volt battery, A 6-volt storage battery and B 45-volt dry-battery. W is 30-ohm variable resistance. R is 10,000-ohm variable resistance. A in circle is milliammeter reading 500 milliamperes. T is Mazda vacuum tube, UX 201A, whose filament is operated normally with 5 volts, drawing 0.25 ampere. G is galvanometer, whose rating is as follows; made by Yokokawa, Type D_2, Class L, Sensibility 5×10^{-8}-Ampere, 6.8×10^{-5}-volt, Period 3 seconds, galvanometer resistance 300-ohm. C and c′ are platinum electrodes, 0.4 mm. in diameter and 40 cm. of length. P is shunt resistance, 5,000, 10,000, 20,000 and 30,000-ohms. K shown in Fig. 1 is the reaction vessel which is a beaker or an Erlenmeyer flask of about 200 c.c. But in accurate titrations, it is necessary to use the apparatus designed by Hostetter and Roberts.⁽³⁾ Ours is shown in Fig. 2. Reaction vessel is made of glass, 6 cm. in diameter and 13 cm. in length. From G carbon dioxide is passed into the vessel. S is a stirrer driven by a motor. Additions of a solution in a small quantity were carried out by the aid of slender glass rod L.

In potentiometric titrations, up to the present, a negative potential is impressed on the grid of the vacuum tube, while the apparatus shown in Fig. 1 differs from other's in that a positive potential is placed on the grid with respect to the filament of the vacuum tube. Accordingly, the grid current, which is very small due to the construction of the vacuum tube, flows through the titrating cell and has been employed to polarize bimetallic platinum electrodes which have been substituted for the monometallic system. The theory of polarized electrodes has been studied by

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(2) J. L. Kassner, R. B. Hunze and J. N. Chatfield, *J. Amer. Chem. Soc.*, **54** (1932), 2278.

(3) Hostetter and Roberts, *J. Amer. Chem. Soc.*, **41** (1919), 1337.

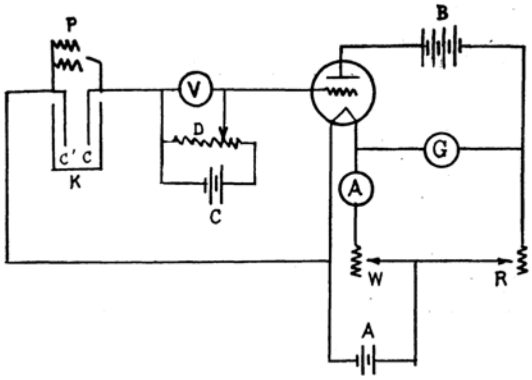

Fig. 1.

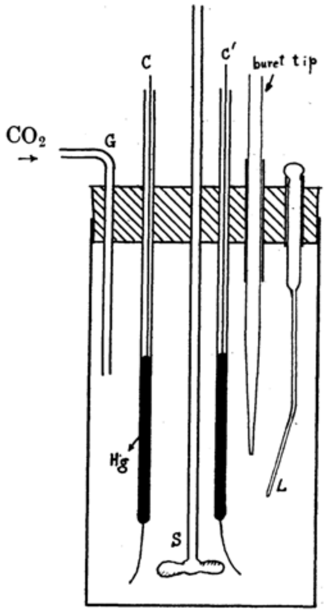

Fig. 2.

Willard and Fenwick⁽⁴⁾ and Van Name and Fenwick.⁽⁵⁾ They have shown that polarized electrodes owe their effect in electrometric titration to gas reaction taking place on the surface of the electrodes and that the potential difference between the electrodes remains practically constant up to the equivalence point. Moreover, a part of the grid current is shunted to the bimetallic electrodes with shunt resistance P as shown in Fig. 1 for the successful operation of this apparatus. It is very necessary that the potential difference between the electrodes remains constant up to the equivalence point in order to operate this apparatus, and this has been accomplished by shunting a part of the polarizing current to the electrodes. Thus shunted electrodes were first used by Foulk and Bawden.⁽⁶⁾ They stated no current flows through the solution when the drop in potential across the shunt is equal to the back e.m.f. due to polarization.

If the bimetallic platinum electrodes have been placed in the solution to be titrated and the resistance R adjusted so that the galvanometer reading is zero, then the potential at M and N would be the same. Electrons flow through the vacuum tube in three ciruits; namely, filament, filament to grid, and filament to plate. The electrons picked up

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(4) *J. Amer. Chem. Soc.,* **44** (1922), 2504.

(5) Van Name and Fenwick, *J. Amer. Chem. Soc.,* **47** (1925), 9; 19.

(6) Foulk and Bawden, *J. Amer. Chem. Soc.,* **48** (1926), 2045.

by the plate may be considered as flowing through the B-battery, R, and back to the A-battery. The strength of this current depends upon the temperature of the filament which is controlled by the filament current varied with W, the voltage of the B-battery, the value of R, and the potential impressed on the grid. The electrons picked up by the grid polarize the bimetallic platinum electrodes. The current in these three circuits will remain constant during the course of a titration as long as the potential difference between c and c′ remains constant if the other adjustments are not changed. A slight change in the potential between c and c′ will produce a corresponding change in the potential impressed on the grid, and this will produce a relatively large change in the plate current by the characteristics of the vacuum tube. Accordingly the balance at M and N is disturbed and it causes the deflection of the needle of the galvanometer.

Experimental.

The preparations of the solutions used were as follows. The reagents used were from Kahlbaum.

(1) Sodium thiosulphate is purified by recrystallization. About 26 gr. of it are weighed out and diluted to about 1 litre. The solution is standardized indirectly by titration with potassium bichromate. Dissolve 5 gr. KI and 4 gr. $NaHCO_3$ in 500 c.c. H_2O in an Erlenmeyer flask at room temperature and add HCl slowly, shaking the flask, until there is no more evolution of CO_2 and then add about 10 c.c. more of the acid, and 35 c.c. of 0.1 N. $K_2Cr_2O_7$. After mixing the solution, rinse the sides of the flask with a few c.c. of water, allowing it to form a layer over the solution without mixing; stopper the flask and allow to stand about 10 minutes. Then with thorough mixing run in thiosulphate until the solution is slightly yellow, add a few drops of starch solution and continue to add slowly the thiosulphate solution until the bright blue colour disappears and only the pale green colour of $CrCl_3$ remains.

(2) Potassium bichromate is purified by recrystallization and dried in an air oven, 4.9035 gr. of it are exactly weighed out and dissolved to 1 litre.

(3) Iodine. Dissolve about 13.5 gr. of pure iodine in a solution of 24 gr. of KI in 200 c.c. of H_2O and dilute to 1 litre. This solution is standardized by thiosulphate using starch as indicator.

(4) Ferrous sulphate. Weigh out exactly 39.214 gr. of ferrous sulphate and dissolve in dilute sulphuric acid (sp. gr. 1.2) to 1 litre.

(5) Potassium permanganate. Dissolve 3.3 gr. of $KMnO_4$ in 1 litre of distilled water and allow to stand a day. This is standardized by sodium oxalate extremely pure and dry.

(6) Potassium cyanide. Weigh out about 8 gr. and dissolve in 1 litre H_2O. This is standardized by 0.1 N. standard $AgNO_3$.

(7) Potassium bromate. Weigh out exactly 16.701 gr. and dilute to 1 litre exactly.

(8) Potassium iodide is purified by recrystallization and dried in air oven. Weigh out exactly 16.603 gr. and dilute to 1 litre.

(9) Potassium iodate. Weigh out exactly 4.2806 gr. and dissolve to 1 litre.

It was thought at first that it would be necessary to control the shunt to obtain good results with this apparatus, but in practice it was often not necessary. The results of the titrations using different shunts are shown in Table 1. The calculated value of c.c. of 0.1 N. sodium thiosulphate is the average of five determinations using starch as the indicator.

Table 1.

Titrations of approximately 0.1 N. iodine solution with sodium thiosulphate.(7)
V: 1.5 volts; A: 0.25 ampere; B: 45 volts.

Run	P:ohms	Sodium thiosulphate		
		c.c. calc.	c.c. found	c.c. dif.
1	5.000	10.45	10.45	0.00
2	10.000	10.45	10.43	0.02
3	20.000	10.45	10.43	0.02
4	30.000	10.45	10.45	0.00
5	50.000	10.45	10.44	0.01

When no shunt resistance was employed the needle of the galvanometer drifted off the scale after the addition of about 1 c.c. of thiosulphate, and under certain circumstances even after one drop. It is distinct that the end-point obtained by this apparatus is slightly in advance of the end-point obtained by the starch.(8) In many titrations described below, P shunt resistance was used in the range shown above.

The galvanometer deflections during titrations, for example, are shown in Table 2, but in many cases there are no great difference.

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(7) A. Schlfeichen, *Z. Anal. Chem.*, **65** (1925), 406.

(8) Foulk and Bawden, *J. Amer. Chem. Soc.*, **48** (1926), 2047.

Table 2.

Titration of approximately 0.1 N. iodine with sodium thiosulphate.

c.c. of 0.1 N.$Na_2S_2O_3$	Gal. def. (zero center)	c.c. of 0.1 N.$Na_2S_2O_3$	Gal. def. (zero center)
0.00	0.0	10.35	4.7 left
5.00	1.0 left	10.40	5.3 ,,
8.00	1.7 ,,	10.42	5.5 ,,
10.00	2.9 ,,	10.43	5.6 ,,
10.20	3.6 ,,	10.44	14.0 right
10.31	4.5 ,,		

Further, in order to show that it is not necessary to control the different variables in this apparatus within narrow limits the following data are presented (Table 3).

Table 3.

Titration of approximately 0.1 N. iodine with sodium thiosulphate.

Sodium thiosulphate				Filament Current ampere	V volts	P ohms
Run	c.c. calc.	c.c. found	c.c. dif.			
1	24.40	24.39	0.01	0.25	2.0	30.000
2	24.40	24.40	0.00	0.20	2.0	30.000
3	24.40	24.40	0.00	0.22	2.0	30.000
4	24.40	24.41	0.01	0.25	1.7	20.000
5	24.40	24.40	0.00	0.25	1.6	30.000
6	24.40	24.39	0.01	0.20	2.2	35.000
7	24.40	24.38	0.02	0.22	1.5	20.000
8	24.40	24.40	0.00	0.25	1.2	15.000
9	24.40	24.38	0.02	0.25	1.0	20.000
10	24.40	24.38	0.02	0.20	1.0	20.000
11	24.40	24.40	0.00	0.25	1.0	10.000
12	24.40	24.39	0.01	0.20	1.0	10.000

B-battery is 45 volts.

As is shown in Fig. 2, one of the platinum electrodes is placed close under the burette, so that there will be temporarily a slight difference in the composition of the solution when the drops of a titrating solution is added. And the deflection of the needle of the galvanometer will be also temporarily unstable and great. But it again becomes stable if the addition of the titrating solution is interrupted. Thus the approach of the end-point is indicated.

Results of some applications in oxidation-reduction reactions using this apparatus are given in the following tables.

As an additional characteristic in this apparatus, there is the indication of the approach of the end point.

Table 4.

Titration of ferrous sulphate with potassium permanganate.

V: 1.5 volts; A: 0.20 ampere; P: 20.000 ohms; B: 45.0 volts.

Run	c.c. calc.	c.c. found	c.c. dif.
1	22.94	22.89	0.05
2	22.94	22.89	0.05
3	22.94	22.90	0.04
4	22.94	22.88	0.06
5	22.94	22.89	0.05

V: 1.0 volt; A: 0.25 ampere; P: 25.000 ohms; B: 45 volts.

1	22.94	22.89	0.05
2	22.94	22.88	0.06
3	22.94	22.89	0.05

The calculated values are the average of five determinations when the solution to be titrated is coloured pink.

Table 5.

Titration of iodine with potassium cyanide.

V: 0.7 volt; A: 0.21 ampere; P: 20.000 ohms; B: 45 volts.

Run	c.c. calc.	c.c. found	c.c. dif.
1	12.84	12.75	0.09
2	12.84	12.76	0.08
3	12.84	12.76	0.08
4	12.84	12.76	0.08
5	12.84	12,76	0.08

The c.c. calculated is the average of five determinations using starch as indicator.

The following experiments were carried out to test the possibility of the titrations of some oxidation-reduction reactions, though the c.c. calculated is not so accurate as the value obtained from the weight of reagents.

Table 6.

Titration of ferrous sulphate with 0.1 N. potassium bichromate.

V: 0.8 volt; A: 0.20 ampere; P: 20.000 ohms; B: 22.5 volts.

Run	c.c. calc.	c.c. found	c.c. dif.
1	23.12	23.10	0.02
2	23.12	23.11	0.01
3	23.12	23.11	0.01

Table 7.

Titration of ferrous sulphate with 0.1 N. potassium bromate.

V: 1.4 volts; A: 0.20 ampere; P: 10.000 ohms; B: 45 volts.

Run	c.c. calc.	c.c. found	c.c. dif.
1	8.17	8.18	0.01
2	8.17	8.17	0.00
3	8.17	8.18	0.01

Table 8.

Titration of potassium iodide with 0.1 N. potassium bichromate.

V: 0.8 volt; A: 0.20 ampere; P: 10.000 ohms; B: 22.5 volts.

Run	c.c. calc.	c.c. found	c.c. dif.
1	25.00	24.96	0.04
2	25.00	24.95	0.05
3	25.00	24.95	0.05

In this case, the galvanometer deflection is very unstable and the titration becomes difficult. Above data are only the most likely results selected among many titrations.

Table 9.

Titration of potassium iodide with 0.1 N. potassium bromate.

V: 1.0 volt; A: 0.25 ampere; P: 20.000 ohms; B: 45 volts.

Run	c.c. calc.	c.c. found	c.c. dif.
1	25.00	25.05	0.05
2	25.00	25.07	0.07
3	25.00	25.06	0.06

Table 10.

Titration of potassium iodide with potassium permanganate.

V: 2.0 volts; A: 0.25 ampere; P: 25.000 ohms; B: 45 volts.

Run	c.c. calc.	c.c. found	c.c. dif.
1	23.30	23.27	0.03
2	23.30	23.25	0.05
3	23.30	23.25	0.05

In this case, the galvanometer deflection is exceptional and the end-point is very apparent.

Table 11.

c.c. of $KMnO_4$	gal. deflection	c.c. of $KMnO_4$	gal. deflection
0.00	0.0	23.10	18.1 left
10.00	10.4 left	23.20	18.1 ,,
20.00	17.7 ,,	23.23	18.0 ,,
22.00	18.1 ,,	23.24	18.1 ,,
23.00	18.1 ,,	23.25	to right extremely

Table 12.

Titration of potassium iodide with 0.1 N. potassium iodate.

V: 1.5 volts; A: 0.20 ampere; P: 20.000 ohms; B: 45 volts.

Run	c.c. calc.	c.c. found	c.c. dif.
1	25.00	24.89	0.11
2	25.00	24.80	0.20
3	25.00	24.80	0.20

Table 13.

Titration of potassium permanganate with potassium ferrocyanide.

V: 0.6 volt; A: 0.20 ampere; P: 10.000 ohms; B: 45 volts.

Run	c.c. calc.	c.c. found	c.c. dif.
1	23.19	23.00	0.19
2	23.19	22.99	0.20
3	23.19	22.99	0.20

Author wishes to express his thanks to Prof. K. Kido who gave him the reagents.

Summary.

In the above investigation, the polarized platinum electrodes by means of grid current, which is obtained by impressing a positive potential on the grid, were used in the potentiometric titrations. In this apparatus, the approach of the end point is indicated, thus the neither plotting or recording nor adjustments is necessary during the titration; but it is necessary to control the positive potential impressed on the grid at the beginning of the titration lest the needle of galvanometer will kick off. The agreement between the calculated and found values is very good in each case.

Yokohama Higher Technical School,
Yokohama.