

the sample, 100 ml. of 3 *N* sodium hydroxide solution was added, the mixture shaken and then transferred to a separatory funnel, where the shaking was continued for several minutes. By this process the selenium and iodine are both quite completely transferred to the aqueous layer, the selenium being oxidized mainly to selenite, with perhaps some selenate. After separating the two layers, the aqueous phase was saturated with sulfur dioxide and an equal volume of concentrated hydrochloric acid was added. More sulfur dioxide was then passed in and the solution was boiled to coagulate the elementary selenium, a process which required several hours. Near the end of the precipitation process a small quantity of hydrazine hydrochloride was added to precipitate any of the element left in the form of selenate. The selenium was collected in a sintered glass crucible, washed with water, then with alcohol, dried for several hours at 105° and then weighed.

The results of these experiments are shown in Table I. It is seen that there is a linear relationship between the quantity of selenium dissolved and the concentration of iodine. This is what would be expected for an equilibrium of the type:



This is evidence that the compound has two atoms of iodine per molecule but leaves the number of selenium atoms undetermined.

TABLE I  
SELENIUM-IODINE EQUILIBRIUM IN CARBON  
TETRACHLORIDE

Moles I <sub>2</sub> per 1000 g. solvent	Gram atoms Se per 1000 g. solvent	Moles I <sub>2</sub> C atoms Se
0.04236	0.00106	40.0
.05622	.00140	40.1
.07620	.00191	39.9

The author wishes to acknowledge his indebtedness to Dr. Arnold O. Beckman, in whose laboratory this work was done, for suggesting the study of selenium and for his interest in the problem.

### Summary

1. Absorption spectra give strong evidence in favor of compound formation between selenium and iodine in carbon bisulfide.

2. Quantitative measurements of the equilibrium between selenium and iodine in carbon tetrachloride show the presence of a compound having the formula  $\text{Se}_n\text{I}_2$  with  $n$  undetermined.

LOS ANGELES, CALIF.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE INSTITUTE OF TECHNOLOGY OF THE UNIVERSITY OF MINNESOTA]

## Amperometric (Polarometric) Titrations. I. The Amperometric Titration of Lead with Dichromate or Chromate

BY I. M. KOLTHOFF AND YU-DJAI PAN

The classical methods of electrometric titrations are the potentiometric and conductometric titrations. In potentiometric titrations the potential of a suitable indicator electrode is measured during the titration and the end-point is characterized by a more or less pronounced change of the potential upon addition of a small amount of reagent. In conductometric titrations the electrical conductance of the titration mixture is measured during the titration and the end-point is found graphically as the point of intersection of the lines giving the changes of conductance before and after the equivalence point. To these two methods may be added another which we propose to call "*amperometric titrations*." In amperometric titrations the current which passes between two suitable electrodes at a constant applied e. m. f. is measured. Depending upon the conditions one or

both electrodes are placed in the titration medium. Quite generally, the end-point is found as the point of intersection of two lines giving the change of the current before and after the equivalence point.

The principle underlying amperometric titrations was mentioned as early as 1897 by Salomon<sup>1</sup> and later by Nernst and Merriam.<sup>2</sup> It is peculiar that these papers have escaped the attention of analytical chemists. It was shown by the above authors that the so-called "diffusion current"<sup>3</sup> is proportional to the concentration of the electro-reduced substance. In a paper entitled "On a Galvanometric Titration Method"

(1) E. Salomon, *Z. physik. Chem.*, (a) **24**, 55 (1897); (b) **25**, 366 (1898); (c) *Z. Elektrochem.*, **4**, 71 (1897).

(2) W. Nernst and E. S. Merriam, *Z. physik. Chem.*, **53**, 235 (1905).

(3) For terminology compare I. M. Kolthoff and J. J. Lingane, *Chem. Rev.*, **24**, 1 (1939).

Salomon<sup>1c</sup> described the amperometric titration of chloride with silver nitrate. He placed two silver electrodes in dilute potassium chloride, applied an e. m. f. of 0.1 v. and titrated with silver nitrate. Until the equivalence point the "residual current" was very small, but after the equivalence point both electrodes became depolarized, resulting in a sudden, large deflection of the galvanometer which was placed in the circuit. Nernst and Merriam<sup>2</sup> placed two palladium electrodes, saturated with hydrogen, in solutions of various acidities and alkalinities and determined the current which passed through upon application of a small e. m. f. Both electrodes adopted the hydrogen potential and the e. m. f. of the cell was zero. The current passing through upon application of a small e. m. f. was determined approximately by Ohm's law ( $E = iR$ ). When the solution contained an excess of acid, the hydrogen ion concentration at the cathode decreased and at the anode increased during the electrolysis. This caused concentration polarization which remained small as long as the current which passed through was small and the excess of acid was great. Similarly, the concentration polarization was found to be small in alkaline medium. However, in neutral medium, when the hydrogen ion concentration is only of the order of  $10^{-7}$ , a slight electrolysis gives rise to a considerable concentration polarization and the setting up of an appreciable back e. m. f. Under ideal conditions the current should quickly drop to zero. Thus, the current passing between two hydrogen electrodes at a small applied e. m. f. during the titration of an acid with a base, or *vice versa*, decreases continuously until the equivalence point is reached and then increases again. Fresenius<sup>4</sup> has investigated the possibility of the determination of small hydrogen ion concentrations by making use of the above principle, but in this particular instance the method is of little importance.

The method proposed by Salomon<sup>1</sup> in 1897 resembles very closely the so-called "dead stop end-point method" of Foulk and Bawden.<sup>5</sup> In their application of this method to various oxidation-reduction titrations, Guzman and Rancano<sup>6</sup> proposed the name "depolarimetry," as the end-point usually is characterized by a sudden de-

polarization or polarization of one or of both of the electrodes. Heyrovsky and Berezicky<sup>7</sup> used a depolarized anode and the dropping mercury electrode as indicator electrode in the titration of barium with sulfate and suggested the name "polarographic titration." Majer,<sup>8</sup> discussing the titration of lead with sulfate and the fundamentals of the method, coined the term "*polarometric titrations*." As it is the current which is measured during the titration, we prefer to call this type of titration "*amperometric* (or galvanometric, [Salomon]) titration," corresponding to the use of the words potentiometric and conductometric titrations.

So far, no systematic studies have been made of the possibilities and limitations of amperometric titration methods. At present, we are engaged with such studies, using the dropping mercury electrode or a platinum wire microelectrode as the indicator electrode. It is expected that this type of titration will find at least as extensive an application as potentiometric titrations experience now. We find the amperometric method especially useful in the titration of very dilute solutions. For the sake of brevity we will not discuss the general characteristics of amperometric titrations, their possibilities and limitations, but will postpone such a discussion until more experimental data have been made available.

In the present paper the amperometric titration of lead with chromate or dichromate is discussed, using the dropping mercury electrode as indicator electrode.

### Experimental

**Apparatus.**—The set-up used is given in Fig. 1. A is a battery composed of three dry cells with a total voltage of 4.5 v. R is a potential divider composed of two rheostats, one with 1000 and the other with 10 ohms resistance.  $R_s$  is a four dial standard resistance box of 9999 ohms, connected in series with the cell. The potential drop across the resistance box is measured with a student's potentiometer P, using a portable galvanometer as a null point instrument. The magnitude of the current which passes through is calculated with the aid of Ohm's law.<sup>9</sup> S. C. is a standard cell of known e. m. f. G. S. is a gang switch which makes the various connections with the potentiometer. By the proper adjustment of the potential divider a known e. m. f.  $E_0$  is applied between the dropping cathode

(4) L. R. Fresenius, *Z. physik. Chem.*, **80**, 481 (1912).

(5) C. W. Foulk and A. T. Bawden, *THIS JOURNAL*, **48**, 2045 (1926).

(6) J. Guzman and A. Rancano, *Anales soc. españ. fis. quim.*, **32**, 590 (1934); Guzman, *ibid.*, **33**, 109 (1935); see also *Z. anal. Chem.*, **103**, 445 (1935).

(7) J. Heyrovsky and S. Berezicky, *Coll. Czech. Chem. Commun.*, **1**, 19 (1929).

(8) V. Majer, *Z. Elektrochem.*, **42**, 120, 122 (1936).

(9) For details and also for the use of a shunted d'Arsonval galvanometer see J. J. Lingane and I. M. Kolthoff, *THIS JOURNAL*, **61**, 825 (1939).

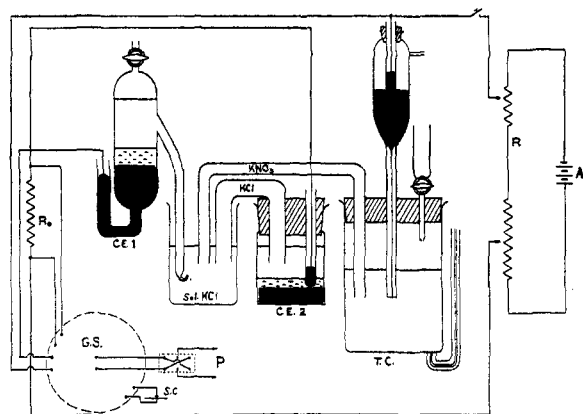


Fig. 1.—Diagram of the set-up.

and a standard saturated calomel electrode (C. E. 1). Another saturated calomel electrode (C. E. 2) was used as a practically depolarizable anode in the electrolysis cell, electrolytic contact with the catholyte in the titration cell being made by two salt bridges. One siphon filled with a 3% agar gel saturated with potassium chloride made electrolytic contact between the anode and a saturated solution of potassium chloride in a beaker, and a second siphon filled with a gel saturated with potassium nitrate made electrolytic contact between the saturated potassium chloride solution and the catholyte in the titration cell. In ordinary work the use of two calomel electrodes is not necessary, as a slight polarization of the anode does not affect the results. In the present work it was preferred to use the C. E. 1 as a reference electrode in order to measure or adjust at any desired time the potential of the dropping electrode against an unpolarized electrode. The use of the outside anode (C. E. 2) can also be dispensed with, as a large layer of pure mercury on the bottom of the titration cell can serve as an internal anode. This involves the practical disadvantage of the use of much mercury, as the cell has to be cleaned after each titration, and a new layer of pure mercury must be added for the next titration. In many titrations a large silver-silver chloride electrode can serve as an internal anode. However, since the use of the external anode does not involve any difficulties and such a saturated calomel electrode can be used for a long period of time, we have not made a special study of the use of suitable unpolarizable internal anodes.

The titration cell T. C. of the model given in Fig. 1 had a capacity of about 100 ml. It was provided with an inlet tube for nitrogen (or hydrogen for the removal of dissolved oxygen before and during the titration. Since oxygen is reducible at the dropping mercury electrode, giving one wave due to reduction to hydrogen peroxide at a relatively small applied e. m. f., and a second drawn out wave due to reduction to hydroxyl ions at higher voltages, the removal of oxygen is recommended, especially in the titration of very dilute solutions. The titration cell was closed with a four-hole rubber stopper; one hole served for the introduction of the salt bridge, the second for the introduction of the buret, the third for the introduction of the mercury capillary and the fourth for the outlet of the gas (not shown in the figure). In most cases the reagent was added from a calibrated senti-microburet of 5 or 10 ml.

capacity and with scale divisions of 0.01 ml. The concentration of the reagent was at least 10 times greater than the solution to be titrated. The drop time of the capillary was of the order of three seconds. As in the following work the temperature of the solution remained sensibly constant during the titration, the titration cell was not placed in a thermostat.

**Performance of the Titration.**—When the characteristics of the substance to be titrated and of the reagent are not known, it is always necessary to determine the current voltage curve of both in the medium in which the titration is being carried out. In order to eliminate the migration current<sup>10</sup> and to reduce the resistance, it is always advisable to have a sufficient excess of indifferent electrolyte present. When the current-voltage curves of the substance to be titrated and of the reagent have been determined, the potential of the dropping electrode is adjusted at the beginning of the titration to such a value that the diffusion current of one or of both of them is obtained. In the case of the titration of dilute lead solutions in the presence of an excess of indifferent electrolyte the diffusion current of lead (after suppression of the maximum with methyl red) was obtained at cathode potentials (against the satd. calomel electrode) between  $-0.7$  and  $-1.4$  v. The shape of the current-voltage curves of potassium chromate and dichromate depend greatly upon the pH of the solution. When the pH of the solution is smaller than 6, the reduction begins immediately upon short circuiting without an applied e. m. f. The reduction proceeds from the hexavalent to the trivalent state. With increasing applied e. m. f., another wave occurs corresponding to the reduction of the trivalent to the divalent chromium and at still greater negative potential a third wave occurs corresponding to the reduction to metallic chromium. The interpretation of the polarograms of chromate is involved and will be discussed in a subsequent paper with Dr. J. J. Lingane. In the present work the cathode potential as a rule was adjusted to a value at which the diffusion currents of lead and of chromate (to  $\text{Cr}^{+++}$ ) were obtained. When at the proper cathode potential,  $E_0$ , lead is titrated with chromate or dichromate, the diffusion current of the lead decreases during the titration and becomes equal to the residual current of the medium at the cathode potential at the equivalence point. If the solubility of the precipitate at the equivalence point is negligible and the medium does not contain electroreducible substances at the applied cathode potential, the residual current at the equivalence point is almost equal to zero. Upon addition of an excess of reagent, the diffusion current of chromate is obtained which increases with increasing excess added. When the values of the current (corrected for volume change) are plotted against the amounts of reagent added, two straight lines are obtained which intersect at the end-point (see Fig. 2). In order to obtain straight lines it is necessary to correct for the volume changes during the titration. When the original volume of the solution to be titrated is  $V$  ml., the amount of reagent added is  $X$  ml. and the current measured is  $i$ , then

$$i_{\text{corr.}} = \frac{V + X}{V} i$$

(10) Cf. J. J. Lingane and I. M. Kolthoff, *THIS JOURNAL*, **61**, 1045 (1939); see also Ref. 3.

In all of the figures  $i_{corr}$  is plotted against the volume of reagent added. In all of the titrations of lead with chromate or dichromate it was necessary to make only a few (three or four) readings before and after the end-point. However, in order to obtain a greater accuracy a large number of measurements has been made.

The titrations were performed in the following way. A measured volume (usually 50 ml.) of the lead solution was introduced with the aid of a calibrated pipet into the titration cell, and the latter covered with the rubber stopper. Nitrogen (or hydrogen) was passed through for about ten minutes. In the meantime the potentiometer system was adjusted against the Weston standard cell. After passage of the nitrogen the dropping electrode and the reference electrode (Fig. 1) were connected and the desired value of  $E_0$  was applied. The dropping electrode was then connected with the saturated calomel electrode which served as anode and by a change of the switch the current measuring device was introduced in the circuit. A measured volume of the reagent was added from the microburet, nitrogen was passed through for one minute to remove any oxygen and to effect a good mixing and the current was measured again. If necessary, the cathode potential was readjusted to its original value. This process was repeated after successive additions of reagent. If necessary, the constancy of the current was checked before a new addition of reagent. If no other reducible substances are present in the solution, the approach of the end-point is indicated by the current, which becomes smaller and smaller. When the solubility of the precipitate is negligibly small it is desirable to make a greater number of measurements in the vicinity of the end-point in order to find the location of the minimum with a greater degree of accuracy. On the other hand, if the solubility is appreciable, there is no practical advantage in making many readings near the end-point. In such a case the minimum current does not necessarily correspond to the location of the equivalence point (e. g., in the titration of lead with dichromate, see Fig. 2). In such cases points are required only at that distance from the end-point where the (corrected) current-reagent line has become straight.

At the end of the titration the values of the current are corrected for the volume effect and plotted against the volume of reagent added. The point of intersection of the two straight lines marks the end-point.

**Materials Used.**—All chemicals used were of reagent quality. The lead nitrate was recrystallized twice from water and dried at 120°. A standard solution was prepared and the concentration determined by precipitation as chromate and iodometric titration of the precipitate. The potassium dichromate was a standard substance. The c. p. potassium chromate was recrystallized from water and dried at 120°. Its stock solution was standardized iodometrically and compared with a standard dichromate solution.

### Experimental Results

In Fig. 2 are represented the results obtained in the titration of 50 ml. of 0.01 *M* lead nitrate which was 0.1 *N* in potassium nitrate with 0.05 *M* potassium dichromate at a cathode potential  $E_c$  of

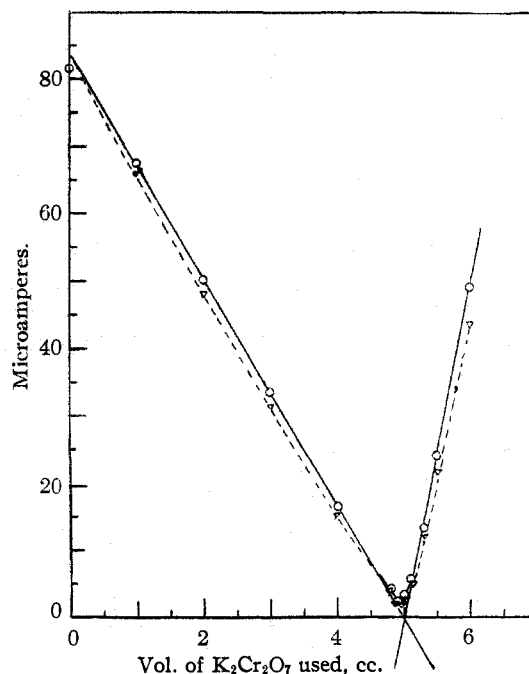
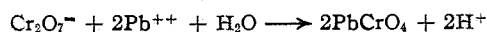


Fig. 2.—Titration of 50 cc. of 0.01 *M*  $Pb(NO_3)_2$  in 0.1 *N*  $KNO_3$  with 0.05 *M*  $K_2Cr_2O_7$  at  $E_c = -1.0$  v.

—1.0 v. vs. S. C. E. The dotted lines give the values of the current as actually determined; the drawn lines give the values after volume correction. It is seen that after correction two straight lines were obtained which intersected exactly at the equivalence point. The reproducibility and accuracy were excellent; the end-point was found in four different titrations after addition of  $5.00 \pm 0.01$  ml. of dichromate. From Fig. 2 it is seen that the residual current at the equivalence point was relatively great, and that both the precipitation and the reagent lines were curved in the neighborhood of the end-point. The large residual current at the end-point is to be attributed to dissolved lead chromate while the straight lines intersect at a point where the residual current is smaller than 1 microampere. The relatively large solubility of the lead chromate under the above experimental conditions is due to the free acid which is formed during the titration



When neutral lead nitrate solutions were titrated with potassium chromate solutions in 0.1 to 1 *N* potassium nitrate the residual current at the point of intersection of the two lines was always found to be less than 1 microampere. However, under the latter conditions the end-point was always found 0.8 to 1% before the equivalence

point, the deviation undoubtedly being due to coprecipitation of basic lead chromate with the neutral lead chromate. For this reason we prefer to carry out the titration with potassium dichromate in neutral or slightly acid medium or with potassium chromate in a buffered or acid solution.

As experimental details of amperometric titrations are not described in the literature, some values of the current measured during a titration and the same data corrected for the volume effect are given in Table I.

TABLE I  
TITRATION OF 50 ML. 0.01  $M$   $Pb(NO_3)_2$  (IN 0.1  $M$   $KNO_3$ )  
WITH 0.05  $M$   $K_2Cr_2O_7$ :  $E_0 = -1.0$  v.

Ml. of $K_2Cr_2O_7$ added	$i$ determined, microamp.	$i$ corr. for dilution, microamp.
0	81.56	81.56
1.0	66.22	67.50
2.0	48.34	50.20
3.0	31.66	33.60
4.0	15.25	16.45
4.8	3.79	4.15
4.9	2.09	2.30
5.0	2.9	3.19
5.1	5.1	5.62
5.3	12.03	13.3
5.5	21.86	24.0
6.0	43.86	49.1

As the slope of the reagent line is steeper than that of the lead (precipitation) line, the actual

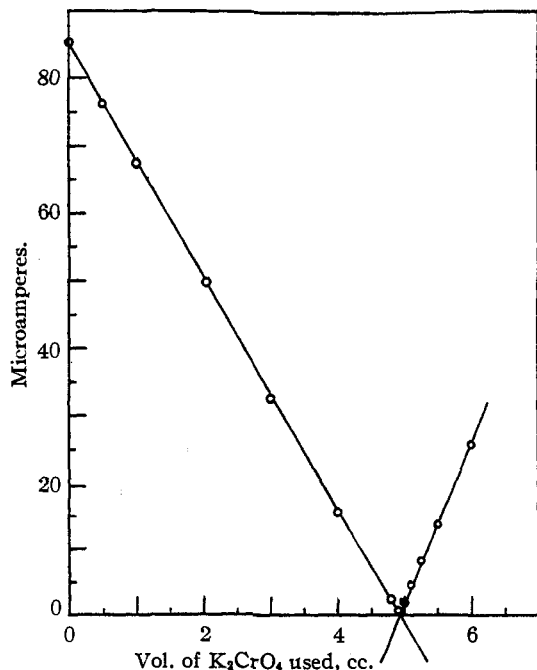


Fig. 3.—Titration of 50 cc. of 0.01  $M$   $Pb(NO_3)_2$  in 0.1  $N$   $KNO_3$  with 0.1  $M$   $K_2CrO_4$  at  $E_0 = -1.2$  v.

minimum is not found at but before the equivalence point (Fig. 2).

The amount of potassium nitrate present in the lead solution was found to be without effect upon the results, if enough was added to eliminate the migration current. Titrations were carried out in 1  $M$  potassium nitrate instead of in 0.1  $M$  nitrate, the end-point being found again after addition of 5.00 ml. of dichromate.

A straight precipitation line was not obtained in the absence of potassium nitrate. The current at the beginning of the titration is much greater than the diffusion current of lead, as the initial current is the sum of the diffusion current and the migration current. During the titration the amount of dissolved lead decreases, while the concentration of the soluble reaction products potassium nitrate and nitric acid increases. Consequently, the contribution of the migration current becomes less and less the nearer the end-point is approached and during the precipitation of the last 20% of the lead the currents practically correspond to the diffusion current of the dissolved lead. An example of the titration of 0.01  $M$  lead nitrate with 0.05  $M$  dichromate in the absence of added salt is given in Fig. 4.

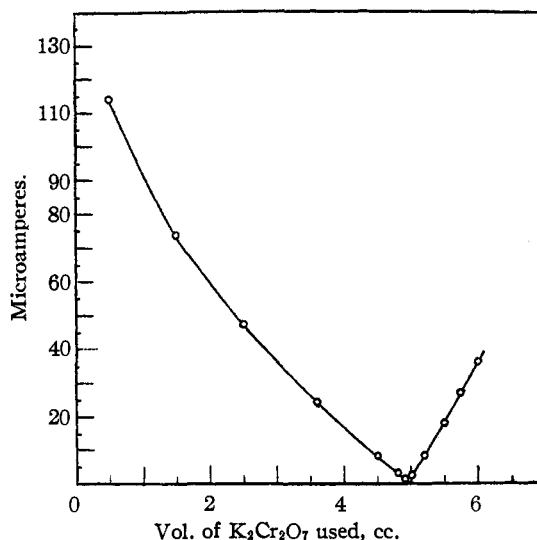


Fig. 4.—Titration of 50 cc. of 0.01  $M$   $Pb(NO_3)_2$  with 0.05  $M$   $K_2Cr_2O_7$  at  $E_0 = -1.0$  v.

As the solubility of lead chromate in dilute nitric or perchloric acids is small, titrations of lead could be carried out at relatively high acidities. Three titrations of 50 ml. of 0.01  $M$  lead nitrate in 0.01  $N$  perchloric acid and 0.1  $N$  potassium nitrate and three titrations in 0.1  $N$  per-

chloric acid were carried out. Again, the results were perfectly reproducible and accurate within 0.2%. Results obtained in 0.01 and 0.1 *N* acid are given graphically in Fig. 5 in which only the corrected values of the current are plotted. The solubility of the lead chromate and therefore the residual current near and at the equivalence point increase with increasing acidity. In the titration in 0.01 *N* perchloric acid the residual current at the equivalence point was found to be 7.0 microamperes, and in 0.1 *N* perchloric acid 10.1 microamperes. In all these titrations the cathode potential need not be adjusted very accurately; it may vary between -0.8 and -1.2 v., and in neutral solutions it even may be -1.5 v.

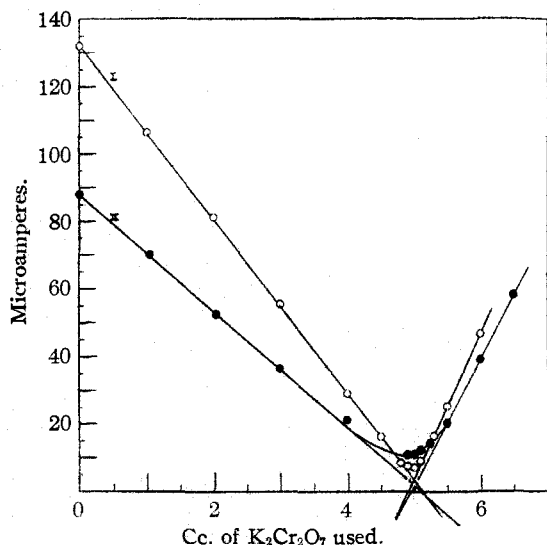


Fig. 5.—Titration of 50 cc. of 0.01 *M*  $\text{Pb}(\text{NO}_3)_2$  in 0.1 *N*  $\text{KNO}_3$ : (I) in 0.01 *N*  $\text{HClO}_4$ , at  $E_0 = -1.2$  v.; (II) in 0.1 *N*  $\text{HClO}_4$ , at  $E_0 = -1.15$  v.; with 0.05 *M*  $\text{K}_2\text{Cr}_2\text{O}_7$ .

Titration also have been carried out with dichromate and chromate in an acetate buffer with a *pH* of 4.2 at cathode potentials varying between -0.8 and -1.4 v. and accurate results again were obtained. Acetate increases the solubility of the lead chromate and also the residual current at the equivalence point.

The polarogram of 0.001 *M* potassium dichromate in the acetate buffer of *pH* of 4.2 is given in Fig. 6. Evidently the dichromate is already reduced without applying any external e. m. f. The same, of course, is true when the solution is more acidic. Thus, it is possible to carry out the titration without application of an external e. m. f. Under such conditions, which are very

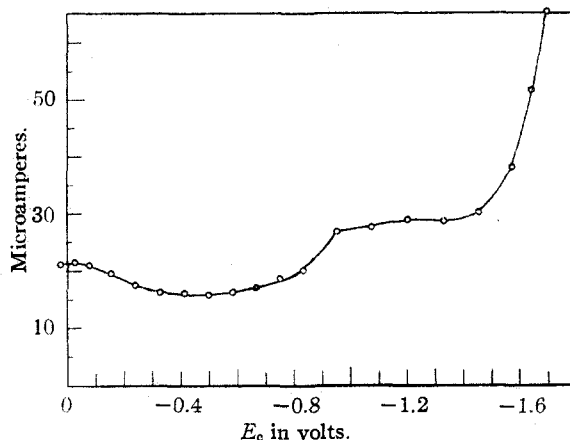


Fig. 6.—Current-voltage curve of 0.001 *M*  $\text{K}_2\text{Cr}_2\text{O}_7$  in an acetate buffer of *pH* 4.2.

simple from the practical point of view, the lead is not electro reduced and does not yield a diffusion current. The current remains practically zero until the equivalence point is reached and increases very rapidly (diffusion current of chromate) upon addition of an excess of reagent. An example of such a titration is given in Fig. 7, in which 0.01 *M* lead nitrate in the acetate buffer of *pH* of 4.2 was titrated with 0.05 *M* dichromate without the application of an external e. m. f. Similar results were obtained in more acid media. The performance of the lead titration without application of an external e. m. f. is of particular advantage in cases in which the solution contains constituents which are electro-reduced at potentials at which lead yields a diffusion current. Such a titration can be carried out simply by short circuiting the dropping electrode and the anode and

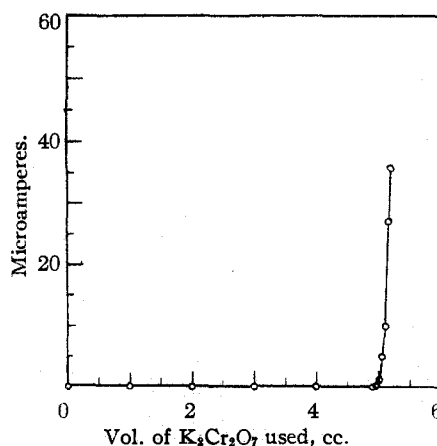


Fig. 7.—Titration of 50 cc. of 0.01 *M*  $\text{Pb}(\text{NO}_3)_2$  in acetate buffer of *pH* 4.2 with 0.05 *M*  $\text{K}_2\text{Cr}_2\text{O}_7$  at  $E_0 = 0$ .

measuring the current in one of the ways described before. It is also possible to use a microammeter for the measurement of the current. We have used a Weston microammeter with 150 scale divisions, each division corresponding to 0.2 microamp. The disadvantage of the instrument is the relatively large fluctuations of the needle during the formation of a drop of mercury, making the determination of the average value of the current relatively difficult.

In the above we have discussed the titration of 0.01 *M* lead solutions under varying conditions. The titration of 0.001 *M* solutions can also be carried out quickly and accurately. In Fig. 8 the data are listed which were obtained in the titration of 50 ml. of 0.001 *M* lead nitrate in 0.01 *M* potassium nitrate with 0.005 *M* dichromate at  $E_c = -1.0$  v.

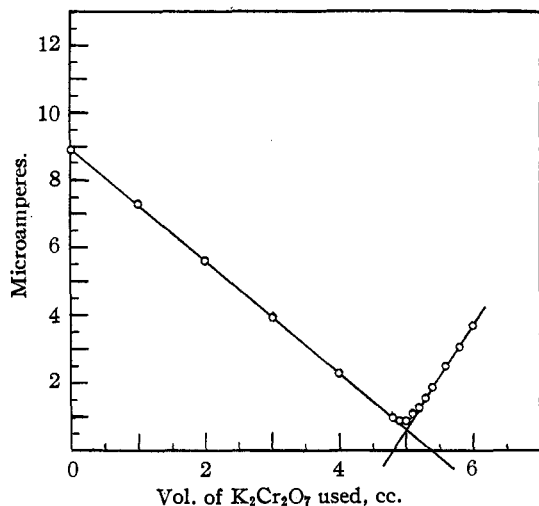


Fig. 8.—Titration of 50 cc. of 0.001 *M*  $\text{Pb}(\text{NO}_3)_2$  in 0.01 *N*  $\text{KNO}_3$  with 0.005 *M*  $\text{K}_2\text{Cr}_2\text{O}_7$  at  $E_0 = -1.2$  v.

In three titrations the amount of dichromate used at the point of intersection corresponded within 0.3% with the theoretical amount. When the titration was carried out with potassium chromate instead of dichromate solution the error was even greater than in the titration of more concentrated lead solutions with chromate. The point of intersection with 0.001 *M* lead solutions at  $E_c$  values of from  $-1$  to  $-1.4$  v. occurred 3–5% before the equivalence point (coprecipitation of basic salt). The error was eliminated or at least reduced to less than 0.5% by performing the titrations in an acetate buffer with a *pH* of about 4.0.

**Titration of Lead in the Presence of Barium.**—Although both lead and barium chromate are

slightly soluble, the latter differs from the former in that it is freely soluble in dilute acid. Several titrations with 0.05 *M* dichromate were carried out with 50 ml. of a mixture which was 0.01 *M* in lead, 0.01 *M* in barium and 0.01 *M* in perchloric acid. The point of intersection was found 0.1 to 0.3% before the lead equivalence point. The concentration of the barium even could be increased to 0.1 *M* without affecting the results. In three titrations with a mixture in which the ratio of lead to barium was 1 to 10 and the perchloric acid concentration was 0.01 *N*, the end-point was found within 0.3% of the theoretical value. No irregularities were noticed during the titration (see Fig. 9).

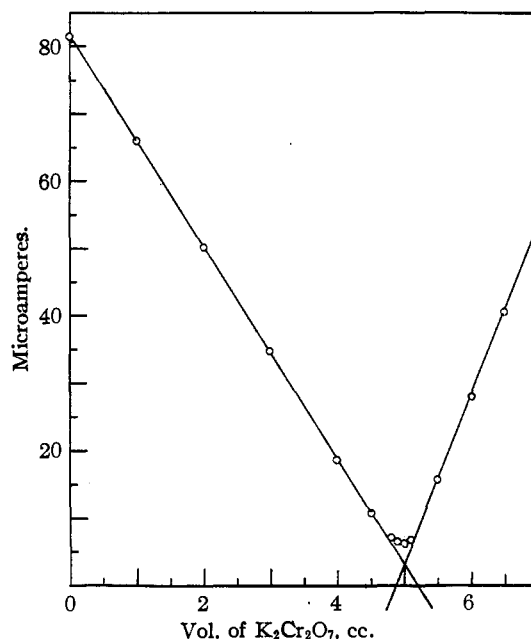


Fig. 9.—Titration of 50 cc. of 0.01 *M*  $\text{Pb}(\text{NO}_3)_2$  in 0.1 *M*  $\text{Ba}(\text{NO}_3)_2$  and 0.01 *N*  $\text{HClO}_4$  with 0.05 *M*  $\text{K}_2\text{Cr}_2\text{O}_7$ , at  $E_0 = -1.0$  v.

In acid medium the lead also can be titrated in the presence of barium without applying an external e. m. f. The titration curves were identical with that given in Fig. 7.

Since the lead chromate is much less soluble than barium chromate an attempt has been made to determine both lead and barium in one titration by fractional precipitation with potassium chromate at cathode potentials ( $-0.8$  to  $-1.4$  v.) at which the lead yields a diffusion current and the barium is not electro-reduced. If all of the lead would precipitate before the precipitation of barium the current would decrease to practically

zero at the point where all of the lead is precipitated, it would then remain very small until all of the barium is precipitated, and it would increase in the usual way with an excess of chromate. It is evident from Fig. 10 that a marked coprecipitation of barium chromate occurs during the precipitation of lead. In the titration of 50 ml. of a mixture which was 0.01 *M* in lead and 0.01 *M* in barium nitrate, with 0.2 *M* potassium chromate at  $E_c = -1.0$  v., the first end-point (precipitation of lead) was found about 20% after the equivalence point. The second end-point corresponding to quantitative precipitation of lead and barium was found at the correct location. In a subsequent paper the amperometric titration of barium will be discussed more in detail.

### Summary

1. The word "amperometric titration" is coined and the historical development of this type of titration is discussed.
2. Lead can be titrated accurately, precisely and rapidly by amperometric titration with dichromate or chromate, using the dropping mercury electrode as an indicator electrode. The titration can be carried out without applying an external e. m. f.
3. Even 0.001 *M* lead solutions can be titrated with a high degree of accuracy.

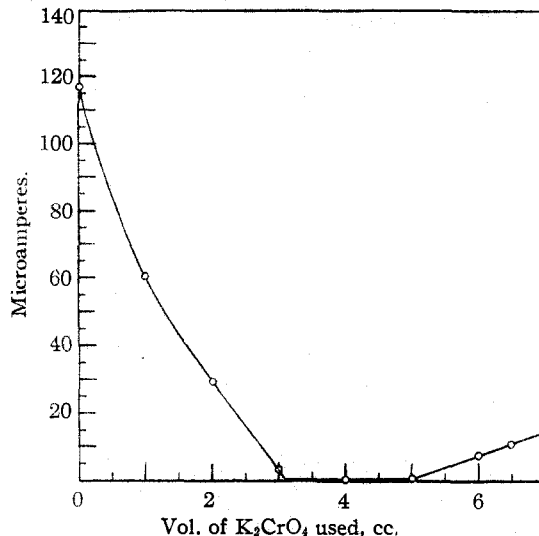


Fig. 10.—Titration of 50 cc. of 0.01 *M*  $Pb(NO_3)_2$  in 0.01 *M*  $Ba(NO_3)_2$  with 0.2 *M*  $K_2CrO_4$  at  $E_c = -1.0$  v.

4. Lead can be titrated amperometrically in the presence of large amounts of barium when the solution is slightly acid with perchloric acid. The fractional precipitation of lead and barium in neutral medium with potassium chromate does not yield good results due to coprecipitation of barium chromate with lead chromate.

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## Studies on Aging and Formation of Precipitates. XXX. The Determination of the Specific Surface of Silver Bromide by the Radioactive and Dye Methods

BY I. M. KOLTHOFF AND A. S. O'BRIEN<sup>1</sup>

In studies on aging of silver bromide it was of interest to determine the specific surface of various products. Dyes, such as orthochrom T,<sup>2</sup> methylene blue,<sup>3</sup> or pinacyanol<sup>4</sup> have been used for this purpose. In this Laboratory wool violet has proved to be of great value in the determination of the specific surface of various precipitates. For this reason, the adsorption of this dye on silver bromide was studied under varying conditions and compared with the adsorption of methylene blue. In order to know the density of occupation of the adsorbed dye on the saturated sur-

face it was necessary to have available the magnitude of the specific surface of the various products used. Particularly when dealing with freshly prepared, heterodisperse precipitates of silver bromide, consisting of extremely fine particles, it was hardly possible to determine the surface microscopically or ultra-microscopically, as the precipitates could not be peptized completely. For this reason, we have made a study of the radioactive method for the determination of the specific surface, the principles of which originate with Paneth<sup>5</sup> and have been successfully applied in this Laboratory. In the present study it was attempted to determine the kinetic equilibrium in

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