very insoluble compound. The thulous ion, for which there is only a little experimental evidence,[3] should be the most unstable of these four principal bivalent rare earth ions.

Conclusion

The oxidation potential of the Yb^{+++}–Yb^{++} electrode is $E_0 = 0.578$ v., sign on the solution. This is considerably greater than that for Eu^{+++}–Eu^{++}, $E_0 = 0.43$ v., but the Yb^{++} ion is the most stable representative of its type in the yttrium group. It is again predicted that the corresponding value for Sm^{+++}–Sm^{++} will be still larger and that for Tm^{+++}–Tm^{++} will be the largest of the four couples.

LAFAYETTE, INDIANA RECEIVED SEPTEMBER 25, 1940

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

Amperometric Titrations. VI. The Titration of Sulfate and Some Other Anions with Lead and the Reverse Titrations

BY I. M. KOLTHOFF AND YU-DJAI PAN[1]

In a previous paper[2] the amperometric titration of lead with dichromate or chromate, using the dropping mercury electrode as indicator electrode, has been described. In the present paper results obtained in the amperometric titration of sulfate with lead nitrate are presented, using the same indicator electrode as in previous work. In addition, titrations of oxalate, ferrocyanide and iodate with lead nitrate and the reverse titrations of lead with the different anions have been investigated. The present study does not exhaust the possible application of lead nitrate as a reagent in the amperometric titration of anions. Undoubtedly, several other anions which yield slightly soluble lead salts and which have not been considered in the present work can be titrated amperometrically under the proper conditions. In a subsequent paper we will deal with the titration of molybdate with lead.

Experimental.—The materials were C. P. products which had been recrystallized several times from water and dried at proper temperatures. The dried products were analyzed by standard procedures. The amperometric titrations were carried out at room temperature in the absence of oxygen. Details are given in the previous paper.[2]

Sulfate.—Some thirteen years ago Heyrovsky[3] mentioned that it should be possible to titrate sulfate with lead amperometrically (polarographically). Several years later, his student, Majer,[4] described some of these (polarometric) titrations. In order to suppress the solubility of lead sulfate, Spalenka[5] recommended carrying out the titration in a medium containing 33% ethanol. These authors did not use a simple graphical method in locating the end-point.[2] Majer's graphical method is fairly involved and requires the knowledge of the solubility of lead sulfate in the titration medium. Since this solubility varies greatly with the ionic strength of the medium, the solubility of the precipitate under the working conditions is rarely known exactly, and his procedure is of limited practical application. In our method[2] of locating the end-point a knowledge of the solubility of the precipitate is not required, and it is not necessary, as in Majer's method, to make many measurements close to the end-point.

The following study shows that the amperometric titration of sulfate, even in very dilute solutions, yields satisfactory results, and that conditions can be found under which indifferent salts do not interfere if their concentration is not too great. In Fig. 1 the results of titrations of 50 ml. of 0.01 M potassium sulfate with 0.1 M lead nitrate are given. In order to suppress maxima one drop of 0.1% methyl red solution was added to the liquid in the cell. The air from the cell was removed, as usual, with nitrogen. After each addition of reagent nitrogen was passed through for one minute, unless otherwise stated, and the current was measured. The titrations were carried out at a potential of the dropping electrode of -1.2 v., at which potential lead yields a diffusion current. All the values of the current have

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(1) From the experimental part of a thesis presented by Y. D. Pan to the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the Doctor's degree (1940).

(2) I. M. Kolthoff and Y.-D. Pan, THIS JOURNAL, **61**, 3402 (1939).

(3) J. Heyrovsky, *Bull. soc. chim.*, **41**, 1224 (1927); Heyrovsky and S. Berezicky, *Collection Czechoslov. Chem. Commun.*, **1**, 42 (1929).

(4) V. Majer, *Z. Elektrochem.*, **42**, 120, 123 (1936).

(5) M. Spalenka, *Collection Czechoslov. Chem. Commun.*, **11**, 146 (1939).

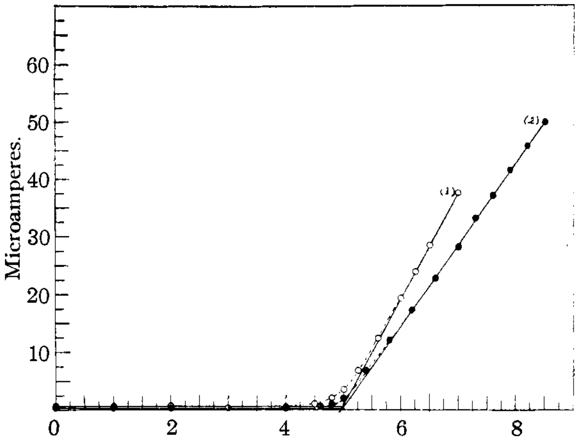

Fig. 1.—(1) Titration of 50 ml. of 0.01 *M* K_2SO_4 with 0.1 *M* $Pb(NO_3)_2$, at $E_c = -1.2$ v. (2) Titration of 50 ml. of 0.01 *M* K_2SO_4 plus 0.01 *M* HCl in 20% ethanol with 0.1 *M* $Pb(NO_3)_2$.

been corrected for the volume increase. From titration set 1 in Fig. 1 it is seen that the solubility of lead sulfate is quite marked at the end-point. However, at distances more than about 20% removed from the end-point the solubility becomes negligibly small as a result of the common ion effect. If points are taken far enough away from the end-point, two straight lines are found which intersect at the end-point. Measurements in the neighborhood of the end-point are of no analytical interest. The above titration of 0.01 *M* sulfate with lead nitrate gave results which were accurate and precise within 0.2%. In these titrations it is not necessary to add an indifferent electrolyte, as enough of the latter is present beyond the end-point to suppress the migration current of lead. The presence of indifferent salts causes an increase of the solubility of lead sulfate, and also enhances supersaturation. Since indifferent salts are usually present in the titration of sulfate, it is recommended to carry out the titration of about 0.01 *M* sulfate solutions in a medium of 20% ethanol. From set 2 in Fig. 1 it is seen that the solubility of lead sulfate in the alcoholic medium is markedly less than in the aqueous medium, even though in set 2 the solution was 0.01 *M* in hydrochloric acid. In the presence of 20% ethanol the results were found 0.5 ± 0.2% high as a result of coprecipitation of lead nitrate with lead sulfate. In the experiments reported below, in which the effect of salts was studied in the titration of 0.01 *M* sulfate solutions, the determinations were carried out in a medium of 20% ethanol. In the presence of 0.1 *M* potassium nitrate the end-point was found to coincide with the equivalence point. However, when the potassium nitrate concentration was increased to 0.5 *M* the end-point was found after addition of 2.5 ml. instead of 5 ml. of reagent. On the other hand, at the same concentration of sodium nitrate the end-point was found at the right location. The striking difference between potassium and sodium nitrate is shown in Fig. 2, and is explained by the fact that in the presence of much potassium salt a double salt is formed of the composition $PbSO_4 \cdot K_2SO_4$.[6] From the analytical view-point it should be added that the end-point found in the presence of much potassium salt fluctuated in an irregular way between 2.5 and 3 ml. of reagent (Fig. 2). This probably is due to the instability of the double salt beyond the end-point.

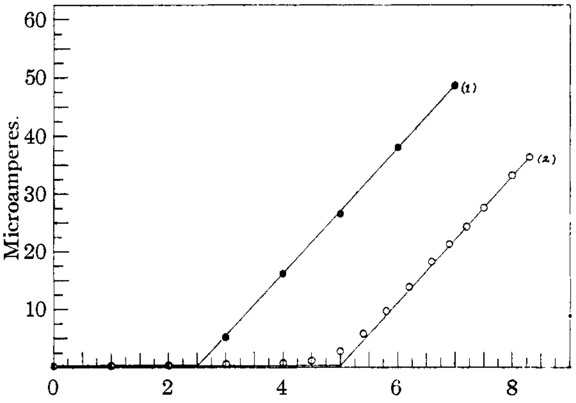

Fig. 2.—Titration of 50 ml. of 20% alcoholic solution of 0.01 *M* K_2SO_4; (1) in 0.5 *M* KNO_3; (2) in 0.5 *M* $NaNO_3$ with 0.1 *M* $Pb(NO_3)_2$ at $E_c = -1.2$ v.

Alkali chlorides do not interfere in the titration of 0.01 *M* sulfate in 20% alcohol when the concentration is equal to or smaller than 0.1 *M*. With larger concentrations of chloride, difficulties were encountered due to the large increase of the solubility of lead sulfate and precipitation of lead chloride with a slight excess of reagent. The effects are shown in Fig. 3. Calcium chloride in large concentrations interfered due to precipitation of calcium sulfate in a medium of 20% ethanol. However, it was possible to titrate a 0.01 *M* sulfate solution which was 0.01 *M* in calcium chloride with an accuracy of ±0.3%. If much calcium is present in the solution it should

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(6) Comp. J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. VII, 812 (1927); M. Randall and D. L. Shaw, THIS JOURNAL, **57**, 427 (1935); I. M. Kolthoff and W. von Fischer, *ibid.*, **61**, 191 (1939).

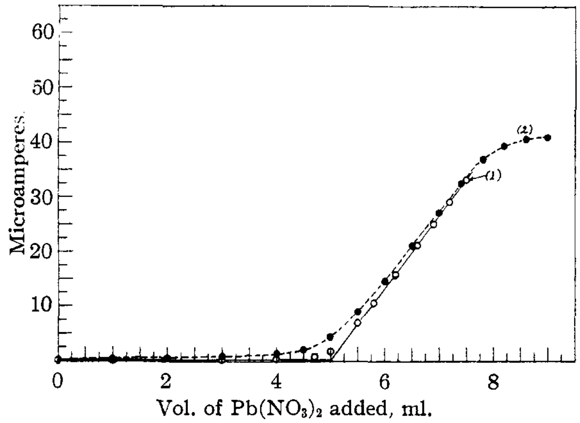

Fig. 3.—Titration of 50 ml. of 20% alcoholic solution of 0.01 *M* K_2SO_4; (1) in 0.1 *N* NaCl; (2) in 0.25 *N* NaCl with 0.1 *M* $Pb(NO_3)_2$ at $E_e = -1.2$ v.

be removed by precipitation with sodium carbonate. The filtrate is made acid with nitric acid using methyl orange, tropeolin 00, or thymol blue as the indicator, and the titration is performed after addition of ethanol. Even an excess of 0.01 *M* acid does not affect the results (see Fig. 1).

Solutions which were 0.001 *M* in sulfate were titrated with 0.01 *M* lead nitrate in a medium of 30% ethanol with an accuracy of ± 0.3%. Solid lead sulfate had to be added to the solutions as an aid in overcoming supersaturation during the titration. When the sulfate solution was 0.01 *M* in potassium nitrate the results were 1% high, and in 0.05 *M* nitrate 2% high (see Fig. 4). This is attributed to coprecipitation of lead nitrate with lead sulfate. On the other hand, when the potassium nitrate concentration was raised to 0.1 *M* the results were very low due to precipitation of the double salt. A summary of analytical data listed in Table I shows that the amperometric titration of dilute sulfate solutions with lead nitrate yields good results under various conditions.

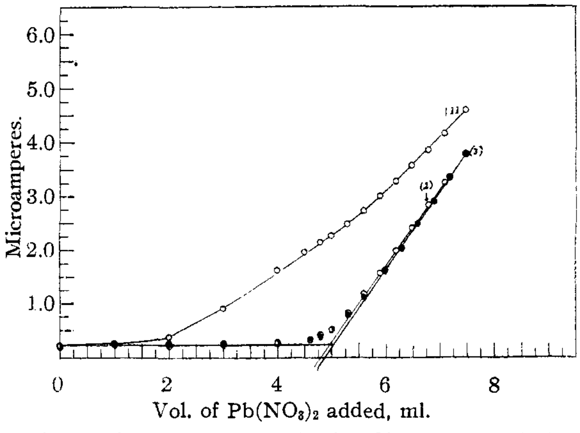

Fig. 4.—Titration of 50 ml. of 30% alcoholic solution of 0.001 *M* K_2SO_4, saturated with $PbSO_4$; (1) in 0.1 *M* KNO_3; (2) in 0.002 *M* KNO_3; (3) in 0.01 *M* KNO_3 with 0.01 *M* $Pb(NO_3)_2$, at $E_e = -1.2$ v.

Table I

Amperometric Titration of Potassium Sulfate with Lead Nitrate at a Potential of the Dropping Electrode of −1.2 v. (S. C. E.)

Concn. of K_2SO_4, *M*	Medium	Kind and concn. (*M*) of indifferent electrolyte	Concn. of $Pb(NO_3)_2$, *M*	Error in %
0.01	Water	.....	0.1	0.0 to +0.2
.01	20% ethanol	.....	.1	+ .3 to +.8
.01	20% ethanol	0.1 KNO_3	.1	.0 to −.3
.01	20% ethanol	.5 $NaNO_3$	.1	± .2
.01	20% ethanol	.1 NaCl	.1	+ .2
.01	20% ethanol	.01 $CaCl_2$	.1	− .2
.01	20% ethanol	.01 HCl	.1	.0 to + .2
.005	20% ethanol	.....	.05	.0 to + .2
.001	30% ethanol[a]	.....	.01	− .2
.001	30% ethanol[a]	.002 KNO_3	.01	− .2
.001	30% ethanol[a]	.01 KNO_3	.01	+1.0
.001	30% ethanol[a]	.05 KNO_3	.01	+2
.001	40% ethanol[a]	.05 KNO_3	.01	+2.5
.001	30% ethanol[a]	.1 KNO_3	.01	..[b]
.001	30% ethanol[a]	.01 HCl	.01	..[c]

[a] Solid lead sulfate added to alcoholic solution before titration. [b] Irregular results due to double salt formation. [c] Solubility too great.

Titration of Lead with Sulfate.—Several experiments were carried out in which 0.01 *M* lead solutions in a medium of 20% ethanol were titrated at a potential of −1.2 v. with 0.1 *M* solutions of alkali sulfates. In order to eliminate the migration current of lead, potassium or sodium nitrate was added to the solution in a concentration of 0.1 *M* before the titration was started. The results were 0.5 to 1% low due to coprecipitation of lead nitrate. Since coprecipitation phenomena were not found in the titration of lead with potassium dichromate,[2] and the solubility of lead chromate is much smaller than that of lead sulfate, it is preferred to titrate lead with dichromate instead of with sulfate.

Oxalate with Lead.—Solutions which were 0.01 *M* in alkali oxalate were titrated with 0.1 *M* lead nitrate at a potential of the dropping electrode of −1.2 to −1.4 v. A drop of 0.1% methyl red solution was added to suppress lead maxima. The titrations which were carried out in the absence of oxygen yielded results which were accurate to within 0.2%. Even 0.001 *M* solutions of oxalate could be titrated with an accuracy of better than +0.5%. No alcohol had to be added to suppress the solubility.

Lead with Oxalate.—In the reverse titration the solution was made 0.1 *M* in potassium nitrate in the determination of 0.01 M lead solutions, and 0.01 M in alkali nitrate in the titration of 0.001 M lead solutions, to suppress the migration current of lead. Other conditions were the same as in the titration of oxalate with lead. The titration of 0.01 M lead was found accurate to within 0.2% and that of 0.001 M lead to within 0.5%.

Ferrocyanide with Lead.—Solutions which were about 0.005 M in potassium ferrocyanide were titrated under the conditions described above with 0.1 M lead nitrate solutions. The end-point corresponded to a composition of the precipitate of $Pb_2Fe(CN)_6$.

Lead with Potassium Iodate.—Since iodate yields a reduction wave with a diffusion current which is about three times as great as that of an equimolecular lead solution, the amperometric titration of lead with iodate has been investigated in detail. The potentials at which iodate yields reduction waves depend upon the pH of the medium when the latter is smaller than 7. Dependent upon the pH it was possible to titrate lead with iodate at potentials at which lead yielded a diffusion current, and at which iodate either was not reduced or also yielded a diffusion current. Solutions which were 0.01 M in lead nitrate and 0.1 M in potassium nitrate were titrated with 0.2 M solutions of potassium iodate in neutral media and in the presence of acetic acid at various potentials. Under all conditions the end-point (point of intersection of precipitation and reagent lines) was found about 3% before the equivalence point. Upon further investigation it appeared that the deviations were due to the tenacious tendency of lead iodate to stay in supersaturated solution. Addition of solid lead iodate was not of sufficient aid to make the titration practicable. Titrations have been carried out in a medium of 30% ethanol to decrease the solubility of lead iodate and to overcome supersaturation. However, again the results were found to be low, as a result of coprecipitation of lead nitrate with lead iodate. A detailed account of all the experiments is given in the thesis of the junior author,[1] and is not reported here, especially since we found that the simple iodometric back titration of an excess of standard iodate solution added to the lead solution yielded accurate results.

Summary

1. Sulfate has been titrated amperometrically with lead nitrate in concentrations between 0.01 and 0.001 M in the presence of various indifferent electrolytes. Conditions have been described under which these titrations yield accurate results.

2. Results of the amperometric titrations of lead with sulfate, oxalate, and iodate, and titrations of oxalate and ferrocyanide with lead have been reported.

MINNEAPOLIS, MINNESOTA

RECEIVED SEPTEMBER 23, 1940

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Adsorption of Vapors at Solid Surfaces and the Change of Surface Electrical Potential[1]

BY ARTHUR A. FROST AND VICTOR R. HURKA

It is well known that adsorbed gases affect the thermionic work functions and photoelectric thresholds of metals. Therefore it would be expected that Volta potentials or surface potentials in general would also depend on the extent of adsorption. Measurement of changes in surface potential would be an indirect measurement of adsorption. Dean, Gatty and Rideal[2] have recently discussed various sources of potential at phase boundaries and have used the term *adsorption potential* to denote a potential difference arising from the formation of an adsorbed layer. It was with the purpose of studying such adsorption potentials at solid surfaces that the present work was begun. This paper is of the nature of a survey and deals with methods of measurement and a discussion of typical results.

Two experimental methods have been employed. The first method was direct but only semi-quantitative. The second method, involving a vibrating electrode, proved to be more satisfactory. A third possible method[3] depending upon ionization of vapor was not tried because it was felt probable that ionization of the vapor

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(1) A portion of this paper was presented at the Cincinnati meeting of the American Chemical Society, April, 1940.

(2) Dean, Gatty and Rideal, *Trans. Faraday Soc.*, **36**, 161 (1940).

(3) Such a method has been used for observing potential changes due to monomolecular films on water. See for example, Harkins and Fisher, *J. Chem. Phys.*, **1**, 852 (1933).