tions 1, 2a and 3a are given in Table II. In the last column values of $\mathfrak{D} = \mathfrak{D}_{\text{obs}} + (\mathfrak{D} - \mathfrak{D}_0)_{\text{calc.}}$ are recorded. The mean value of $\mathfrak{D}'$ is equal to the limiting value $\mathfrak{D}_0$ and all the values are within ±0.2% of this mean. This confirmation of the adequacy of the theory at concentrations up to 0.01 molar is in accord with similar agreement found for lithium, sodium, potassium and rubidium chlorides.

TABLE II

CALCULATED AND OBSERVED DIFFUSION COEFFICIENTS OF CESIUM CHLORIDE AT 25

c	$\mathfrak{D} \times 10^5$ (obs.)	$\mathfrak{D} \times 10^5$ (calcd.)	$\mathfrak{D}' \times 10^5$
0.0000	...	(2.046)	(2.046)
.00122	2.007	2.010	2.043
.00131	2.012	2.009	2.049
.00134	2.011	2.008	2.049
.00179	2.002	2.002	2.046
.00266	1.990	1.994	2.042
.00275	1.988	1.993	2.041
.00314	1.994	1.991	2.049
.00368	1.990	1.987	2.049
.00849	1.965	1.963	2.048
.01287	1.946	1.950	2.042
		Mean	2.046

In Fig. 1, the observed and calculated diffusion coefficients of potassium, rubidium and cesium chlorides have been plotted against the square root of the concentration. The straight lines represent the limiting equation 4a and the solid lines the values derived from the theory. It is to be noted that the diffusion coefficient of rubidium chloride is about 0.5% higher than that of cesium chloride. This result is in complete accord with the recent values of the limiting conductances obtained by Dr. Walter E. Voisenet, Jr., in this Laboratory.

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NEW HAVEN, CONN.

[CONTRIBUTION FROM THE UNIVERSITY OF ARKANSAS]

Basic Salts of Lead Nitrate Formed in Aqueous Media[1]

BY J. L. PAULEY AND M. K. TESTERMAN

RECEIVED FEBRUARY 6, 1954

Conductometric and potentiometric titrations, analyses and solubility determinations were carried out on the system created by the addition of 1 *N* NaOH to 0.1 *N* $Pb(NO_3)_2$. Precipitates with compositions which correspond to the empirical formula $Pb(NO_3)_2 \cdot Pb(OH)_2$ and $Pb(NO_3)_2 \cdot 5Pb(OH)_2$ were formed. No $Pb(OH)_2$ was found even appreciably past the equivalence point. The results are in opposition to other published data.

Introduction

The addition of a solution of sodium hydroxide to a solution of lead nitrate might be expected to form a precipitate of lead hydroxide followed by dissolution of the precipitate with the formation of sodium plumbite. It has been found that the above system is not as simple as it was believed to be and discrepancies arise which have an important bearing upon the titration of systems containing the Pb^{++}, NO_3^- and OH^- ions as well as the preparation of lead salts in an aqueous medium in the presence of nitrate ions.

An examination of the literature reveals that numerous compounds of Pb, NO_3 and OH groups are proposed.[2-4] The formulas of many of the proposed compounds were deduced by indirect means and considerable confusion exists on certain points. Also, many of the proposed compounds were formed under very special conditions. Britton studied the precipitation of lead salts by hydroxyl ions but made assumptions as to the composition of the precipitates formed. For the compounds formed in aqueous media, Berton's work[3] is of greatest interest. He stated that the titration of $Pb(NO_3)_2$ with NaOH produced compounds with compositions in agreement with the following empirical formulas

$$3Pb(NO_3)_2 \cdot Pb(OH)_2$$
$$Pb(NO_3)_2 \cdot Pb(OH)_2$$
$$Pb(NO_3)_2 \cdot 3Pb(OH)_2$$

The system resulting from the addition of 1 *N* NaOH to an aqueous solution of 0.1 *N* $Pb(NO_3)_2$ was studied conductometrically, potentiometrically and analytically by the authors in an attempt to verify Berton's data.

Experimental

The conductance of the above system was measured as a function of the addition of carbonate-free sodium hydroxide to the lead nitrate at 25°. Sufficient time elapsed between the additions of sodium hydroxide and the conductance measurement to ensure equilibrium. The results of this investigation are presented in Fig. 1, in which the conductivity has been corrected for the dilution effect produced by the addition of the NaOH solution.

The graph shows a gradual decrease in conductivity until the region of the $^5/_6$ fraction of the equivalence point is reached, where a very sharp minimum is encountered. This minimum suggests the formation of a compound whose composition corresponds to the $^5/_6$ fraction of the equivalence point. Further, a white precipitate forms upon the addition of the first drop of NaOH solution and remains throughout the course of the titration. This fact, coupled with the gradually decreasing conductivity of the solution during the initial additions of sodium hydroxide, suggests the precipitation of some other compound, whose solubility is greater than that of the $^5/_6$ compound.

These results are in disagreement with the data published by Berton[3] in that he reports three breaks in the conductance *vs.* ml. of NaOH curve which occur at the $^1/_4$, $^1/_2$ and $^3/_4$ fractions of the equivalence point.

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(1) Presented before the Southwest-Southeast Regional Meeting of the American Chemical Society, New Orleans, La., 1953.

(2) V. J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. 7, Longmans and Co., New York, N. Y., 867ff.

(3) A. Berton, *Compt. rend.*, **220**, 693 (1945).

(4) H. T. S. Britton and F. H. Meek, *J. Chem. Soc.*, 183 (1932).

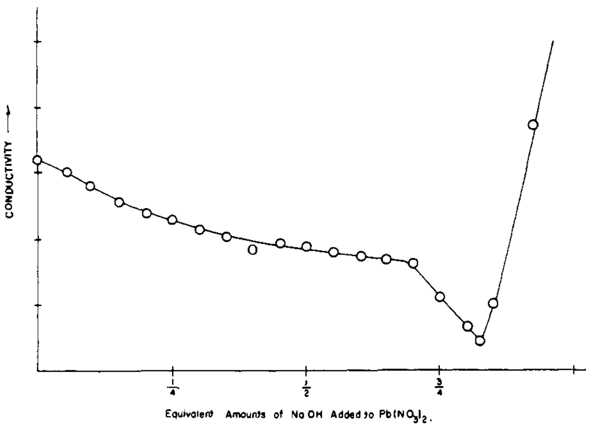

Fig. 1.—Conductometric titration of 0.1 N $Pb(NO_3)_2$ with 1 N NaOH, corrected conductivity expressed in arbitrary units.

The sodium hydroxide-lead nitrate titration was investigated potentiometrically at 25° by using a Model H Beckman *p*H meter as an indicator (*cf.* Fig. 2). Carbonate-free sodium hydroxide was used in the titration. A slight step was obtained in the *p*H *vs.* equivalents of NaOH curve at the $^1/_2$ equivalence point, and a large step was observed at the $^5/_6$ equivalence point. A region in which equilibrium is slowly attained occurs between these two steps and this condition apparently is due to the transformation of the precipitate from one composition to another. The graph may be anywhere within the area enclosed by the dotted and solid lines, depending upon the rate of addition of the NaOH to the $Pb(NO_3)_2$ solution. This is indicative of a solid-to-solution-to-solid reaction in this region.

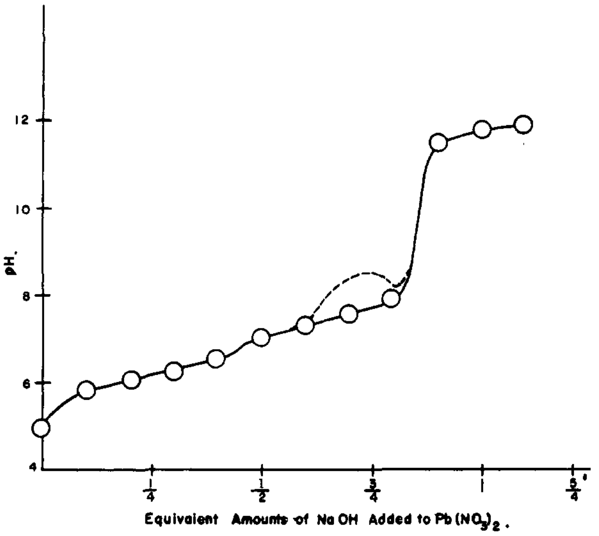

Fig. 2.—Potentiometric titration of 0.1 N $Pb(NO_3)_2$ with 1 N NaOH. Area between dotted and solid lines represents a non-equilibrium condition.

The precipitates formed in the above titration were analyzed for Pb^{++}, NO_3^- and OH^- ion content. Samples of $Pb(NO_3)_2$ were titrated with NaOH to various fractions of the equivalence point and the resulting precipitate was filtered, dried at 110°, and analyzed.

Analysis of the lead ion utilized a modification of the dithizone method.[5] The nitrate ion analysis was carried out by a nitrometer.[6] Of all the methods of nitrate analysis investigated, the nitrometer was the only one which gave reproducible, correct results. The phenoldisulfonic acid and Kjeldahl methods caused the loss of oxides of nitrogen. Various methods employing the reduction of the nitrate group by the ferrous ion yielded inconsistent results.

The hydroxyl ion was determined by potentiometric titration with nitric acid.

In addition, the water solubilities of the precipitates produced at various fractions of the equivalence point were determined at 30 ± 0.01°. An appreciable excess of sample was mixed with approximately 3 ml. of water and maintained with stirring at constant temperature for 24 hours. The solution was filtered through the very fine fritted glass filter and the undissolved sample was dried but not analyzed. The solubility was calculated from the amount of undissolved sample after it was corrected for the amount of solution retained in it.

The results of the analyses and solubility determination are given in Table I.

TABLE I

ANALYSIS AND SOLUBILITY OF PRECIPITATES FORMED WHEN VARIOUS EQUIVALENT AMOUNTS OF 1 N NaOH ARE ADDED TO 0.1 N $Pb(NO_3)_2$

Fraction of equiv. point	Pb, %	NO_3, %	OH, %	Solubility at 30°, g./100 g. of H_2O
1/4	72.6	21.7	6.2	1.42
1/3	72.3	21.5	5.9	1.43
1/2	72.0	21.5	6.1	1.40
2/3	78.3	13.5	9.6	1.03
3/4	79.2	8.4	10.7	0.25
5/6	79.7	8.2	11.2	0.25
1	80.2	7.8	11.9	0.25

The titration of 0.1 N lead acetate with 1 N sodium hydroxide was also studied potentiometrically. A small step was observed at $^1/_2$ equivalence point and a large step at the equivalence point. The precipitate associated with the $^1/_2$ equivalence point was so soluble that it contributed only a haze to the solution and thus was not analyzed. It would be expected to have the empirical formula $Pb(C_2H_3O_2)_2 \cdot Pb(OH)_2$. The equivalence point precipitate should be $Pb(OH)_2$ or one of the several $Pb(OH)_2 \cdot PbO$ complexes. No precise measurements were made upon it since its composition varied with treatment. However, the lead acetate system gave results in agreement with data previously reported.[7]

Results

When the analytical data of Table I are compared with the calculated percentage compositions of the basic lead salts presented in Table II, it is seen that the same precipitate predominates up

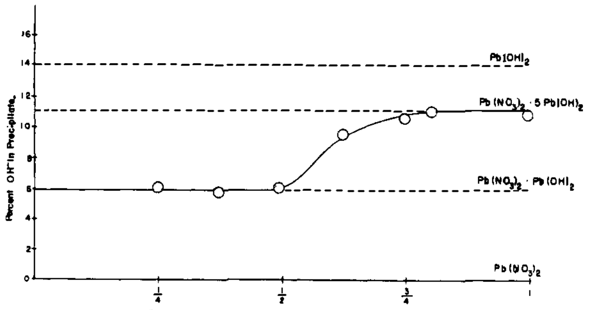

Fig. 3.—Variation in the composition of the precipitate formed by the titration of 0.1 N $Pb(NO_3)_2$ with 1 N NaOH expressed in terms of OH-analysis.

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[5] E. B. Sandell, "Colorimetric Metal Analysis," Vol. 3, Interscience Publishers, Inc., New York, N. Y., 1944, pp. 283-287.

[6] W. W. Scott, "Standard Methods of Chemical Analysis," D. Van Nostrand Co., Inc., New York, N. Y., 5th Edition, pp. 641, ff.

[7] R. Abegg and F. R. Auerbach, "Abeggs Handbuch der anorganischen Chemie," 2nd Ed., Vol. 3, Verlag von S. Hirzel, Leipzig, 1909, p. 736.

TABLE II

CALCULATED PERCENTAGE COMPOSITION OF BASIC LEAD SALTS

Formula	Pb, %	NO₃, %	OH, %
$Pb(NO_3)_2 \cdot Pb(OH)_2$	72.4	21.7	5.9
$Pb(NO_3)_2 \cdot 5Pb(OH)_2$	80.9	8.1	11.1
$Pb(OH)_2$	85.9	0	14.1

through the $^1/_2$ equivalence point and that it corresponds to the empirical formula $Pb(NO_3)_2 \cdot Pb(OH)_2$ (Fig. 3). The analysis of the precipitates at the $^3/_4$, $^5/_6$ and 1 fractions of the equivalence point corresponds to the formula $Pb(NO_3)_2 \cdot 5Pb(OH)_2$. The precipitate at the $^2/_3$ equivalence point appears to be a mixture of the two precipitates noted above. The results of the analysis and solubility are in agreement with the data obtained by the conductometric and potentiometric titrations. The results do not confirm Berton's work.

Up to *p*H of 12, which is past the equivalence point there was no evidence that any appreciable amount of $Pb(OH)_2$, PbO, or the $PbO \cdot Pb(OH)_2$ complexes was formed. The *p*H ranges of existence of the two precipitates formed were

$Pb(NO_3)_2 \cdot Pb(OH)_2$	5.0–7.0
$Pb(NO_3)_2 \cdot 5Pb(OH)_2$	7.0->12

The authors are indebted to W. J. Broach and J. M. Komarmy for the lead and nitrate analyses.

FAYETTEVILLE, ARKANSAS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

Complex Cyanide–Simple Cyanide Exchange Systems[1]

BY ALAN G. MACDIARMID[2] AND NORRIS F. HALL

RECEIVED AUGUST 6, 1953

The method of calculation of exchange data is discussed. The rate of exchange of free cyanide (labeled either with C^{14} or N^{15}) with the following complex cyanides is found to increase with decrease of *p*H: $K_4Fe(CN)_6$, $K_3Co(CN)_6$, $Na_3Fe(CN)_5(H_2O)$. The exchange reaction is found to be light-accelerated with the following complex cyanides: $K_4Fe(CN)_6$, $K_3Co(CN)_6$, $K_3Cr(CN)_6$, $Na_2Fe(CN)_5NO$, $Na_3Fe(CN)_5(H_2O)$. A relationship is found to exist between the rate of exchange of complex cyanides and the properties of their aqueous solutions on exposure to light, and to the lability of the cyanide ligand in ordinary chemical reactions. Exchange is found to be zero order with respect to the free cyanide concentration in the case of $K_4Fe(CN)_6$, $K_3Co(CN)_6$ and $K_3Cr(CN)_6$. All these effects are consistent with an exchange process proceeding by an aquation mechanism. A fairly satisfactory correlation of the rate of exchange with the electronic configuration of complex cyanides is observed.

Introduction

One of the main aims in isotopic exchange work is to attempt to correlate the essentially kinetic data obtained experimentally with the thermodynamic stability and electronic structure of the bond or bonds involved in the exchange process. Since complex metal cyanides all contain a common ligand, investigation of this class of compound should be profitable.

Previous work in the field of complex cyanide exchange reactions may be divided into three categories—those involving exchange of the central metal atom with metal ion,[3-6] those involving electron transfer between complex cyanides differing only in the oxidation state of the central metal atom[4,7,8] and those of Adamson, *et al.*, involving exchange of the cyanide ligand with cyanide ion or HCN.[8-10] A fourth category, which has not yet been investigated, would be the direct exchange of the cyanide ligands between ions of the same or different complexes.

Although slow exchange is reported in all the systems in the first category, it should be stressed that exchange between the pairs of ions in all these cases (except the $Fe(CN)_6^{-3}$–Fe^{+3} system) may actually be extremely rapid, since in all but one case, precipitates are formed on mixing solutions of the exchanging species. The value of the results is somewhat limited, and all that can be safely stated is that exchange is slow compared to the rate of precipitation of the compound formed, *i.e.*, $t_{1/2} >$ approx. 10^{-2} second.

The present investigation was carried out to expand the work of Adamson and co-workers in an endeavor to clarify the mechanism of the exchange in complex cyanide–simple cyanide systems, and to attempt to explain, qualitatively at least, the relationship between the observed rate of exchange and the *p*H, free cyanide concentration, and degree of illumination of the exchanging system.

Part I. Exchange Involving C^{14} Tagged Cyanide

Experimental

Preparation and Purity of the Complex Salts

Potassium hexacyanoferrate(II) trihydrate, potassium hexacyanoferrate(III), potassium hexacyanocobaltate(III), potassium octacyanomolybdate(IV) dihydrate, potassium hexacyanochromate(III) and potassium hexacyanomanganate(III) were prepared and analyzed as described in a previous publication.[11]

Sodium Aquopentacyanoferrate(II) Monohydrate.—This was prepared from sodium nitropentacyanoferrate(III)[12]

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[1] Based on portions of a thesis submitted by Alan G. MacDiarmid to the Graduate School of the University of Wisconsin, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] Sidney Sussex College, Cambridge, England.

[3] J. F. Flagg, THIS JOURNAL, **63**, 557 (1941).

[4] R. C. Thompson, *ibid.*, **70**, 1045 (1948).

[5] H. E. Menker and C. S. Garner, *ibid.*, **71**, 371 (1949).

[6] F. A. Long, *ibid.*, **73**, 537 (1951).

[7] J. W. Cobble and A. W. Adamson, *ibid.*, **72**, 2276 (1950).

[8] A. W. Adamson, *ibid.*, **73**, 5710 (1951).

[9] A. W. Adamson, J. P. Welker and M. Volpe, *ibid.*, **72**, 4030 (1950).

[10] A. W. Adamson, J. P. Welker and W. B. Wright, *ibid.*, **73**, 4786 (1951.)

[11] A. G. MacDiarmid and N. F. Hall, *ibid.*, **75**, 5204 (1953).

[12] K. A. Hofmann, *Ann.*, **312**, 1 (1900).