

177 T

The Influence of Some Dissolved Salts
Chiefly Nitrates, Upon the Precipitation
of Lead Chloride in Qualitative Analysis

Thesis for Master's Degree

By

Zella A. McWhorter

Masters of Science, 1915

The Influence of Some Dissolved Salts Chiefly
Nitrates, Upon the Precipitation of Lead Chloride
in Qualitative Analysis

Introduction

In following the various procedure of Qualitative Analysis the purpose of the operator is to separate, as completely as possible, the substances present and to identify each in its proper order. Experience has shown the value of working with solutions, whenever the substance to be examined can be dissolved, either in whole or in part, by the ordinary solvents. If more than one compound is present in aqueous solution, however, it very frequently becomes impossible for the analyst to do more than determine the various ions. Since ions are best removed from solution by adding other ions with which they will form relatively difficulty soluble compounds, the analyst adds to the solution, in a definite order, those reagents containing the ions which he chooses. Having arbitrarily added a certain kind of ion, under given conditions, the production of precipitate indicates that certain ions were in the solution. He then examines the precipitate to determine which of the possible ions are present.

The reagents which are added in order, to the solution are called " group reagents "and their value depends upon the low solubility of the compounds resulting from the

T378
M2572
1915

309274

union of the ions of a particular group with the arbitrarily shown ion of the reagent. Hydrochloric acid in solution is the reagent of the first group. Of the metallic chlorides, all are quite soluble except silver chloride, Mercurous Chloride and Lead Chloride. Silver chloride and mercurous chloride have such a low solubility that only a negligible amount of silver and mercurous ions remain in solution. Lead Chloride, however, has a variable solubility and therefore Lead ions may still remain in solution after the first group is precipitated. The solubility of Lead Chloride varies greatly with temperature. With a fixed temperature the precipitation of Lead Chloride is influenced by the presence of other ions in solution.

This paper is a report of a preliminary investigation to determine the effect of some soluble salts upon the precipitation of Lead Chloride in Qualitative Analysis.

Part 1 Theoretical

Arrhenius in 1887 (Z. phys. chem.1, 631-1887) first made the ⁵observation that those salts which in solution have abnormal osmotic pressures, and abnormal disturbing of boiling and freezing points, and which by calculation thus would have abnormally low molecular weights, were those which could conduct an electric current. These facts he explained by his ingenious theory of Ionization which he

expressed by the formula,

$$\frac{(\text{Cation}) (\text{Anion})}{\text{Molecules}} = K_{\text{Ionization}} \quad (1)$$

The cation and anion are raised to a power corresponding to the number of ions produced by the ionization of one molecule of the electrolyte.

Nernst working along the lines of development of this theory early observed (Z. phys. Chem. 4, 372, 1889) a very simple relation existing between the chemical equilibrium (Ionization K) and physical equilibrium. This relation was only proven to hold for sparingly soluble electrolytes.

When such an electrolyte, for example PbCl_2 , is put in contact with water it will dissolve. If an excess of PbCl_2 is added it dissolves to a certain limit, at a given temperature, or it becomes saturated. In other words a condition of physical equilibrium between the two phases of PbCl_2 present (Viz-the solid and dissolved) is set up.



Simultaneously a condition of equilibrium is set up between the dissolved salt and its ion.



As this is a reversible action the law chemical equilibrium or ionization theory finds application.

$$\frac{(\text{Pb}^{++})(\text{Cl}^-)^2}{(\text{PbCl}_2)} = K_{\text{Ionization}} \quad (4)$$

As the concentration of the solid salt may be considered constant at a given temperature, equation (2) may be made

$$\text{PbCl}_2 = K \quad (5)$$

This constant may be called the molecular solubility. This constant holds for a saturated solution of PbCl_2 at a given temperature. Since the concentration of unionized PbCl_2 in equation (4) may be considered constant, equation (4) may be changed to read

$$(\text{Pb}^{++})(\text{Cl}^-)^2 = K_{\text{Ionization}} \times K_{\text{Mol. Sol.}} \quad (6)$$

This term $K_{\text{Ion.}} \times K_{\text{molecular solubility}}$ is a constant and may be designated the ion. product constant.

$$K_{\text{Ionization}} \times K_{\text{Mol. Sol.}} = K_{\text{I.P.C.}} \quad (7)$$

From (6) and (7) we get

$$(\text{Pb}^{++})(\text{Cl}^-)^2 = K_{\text{I.P.C.}} \quad (8)$$

Further if we assume that foreign electrolytes in not too concentrated amounts, do not effect either $K_{\text{molecular solubility}}$ or $K_{\text{Ionization}}$ then the $K_{\text{I.P.C.}}$ would hold, not only for pure aqueous solutions, but also dilute solutions of foreign electrolytes.

From a consideration of equation (8) it is self-evident that if the concentration of either Pb^{++} or Cl^- be

increased the constant will be exceeded and precipitation of PbCl_2 will follow.

This is the explanation of the partial precipitation of Pb which occurs in the first group in ordinary qualitative analysis. In this procedure, while a certain amount of PbCl_2 is precipitated, some always remains dissolved and Pb^{++} is precipitated in the second group as PbS and later determined.

It was to determine the effect of the addition of other salts, chiefly nitrates, on the ion product constant of PbCl_2 that this work was undertaken. Theoretically when the NO_3^- is increased (Pb^{++}) is diminished in

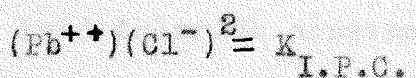
$$\frac{(\text{Pb}^{++})(\text{NO}_3^-)^2}{(\text{Pb}(\text{NO}_3)_2)} = K_{\text{Ionization}} \quad (9)$$

and consequently a higher amount of Cl^- is allowed in $(\text{Pb}^{++})(\text{Cl}^-)^2 = K_{\text{I.P.C.}}$ before precipitation commences. The total amount of PbCl_2 from a solution of $\text{Pb}(\text{NO}_3)_2$ should be inversely proportional to the second power of the NO_3^- concentration. In other words the more of another nitrate added the less PbCl_2 should be precipitated.

Part II Experimental

PbCl_2 is soluble in approximately 100 parts cold water and 25 parts hot water. From the latter, on cooling

PbCl_2 will separate out and will precipitate in the form of long needle-like crystals. PbCl_2 is more insoluble in dilute HCl than in water as would appear in equation



It would appear from a superficial examination of the above equation that the ideal conditions for the precipitation of PbCl_2 would be a high concentration of the Cl^- ion, but this holds true only up to a certain limit and concentrated HCl dissolves it very perceptibly, (Fresenius, New System of Qualitative Analysis 1897, page 167) due to the formation of a complex ion H_2PbCl_4 . Thus to secure the most complete precipitation of PbCl_2 possible, the addition of HCl should be stopped when lead ceases to precipitate.

The general method of procedure was as follows:

Twenty cubic centimeters of the stock solution of lead nitrate were put in beakers. To No. 1 eighty cc of the stock solution of a foreign nitrate were added. To No. 2 sixty cc of the same solution and 20cc of H_2O were added. To No. 3 forty cc of the nitrate solution and 40cc of H_2O were added. To No. 4 twenty cc of the nitrate solution and 60cc of H_2O were added. Thus in each case the beakers contained a total volume of one hundred cubic centimeters of solution. The temperature of each solution was maintained at twenty degrees.

A burette was then filled with the stock solution of hydrochloric acid. From this the hydrochloric acid solution was run in the four beakers until no further precipitation of lead chloride appeared, which showed that the conditions for maximum precipitation of $PbCl_2$ were fulfilled. A reading of the burette each time was taken and recorded as the number of cc of HCl used. This served as additional check on the accuracy of the work.

The precipitates were then transferred to fine filter papers. A filter paper of the same size as those used for the precipitates was then wet with the filtrate and reserved for use in weighing. The precipitates were placed in a drying oven and dried to constant weight.

The dry filter papers containing the precipitates were removed from the funnels and weighed, the filter paper which was previously wet with filtrate and dried, being used to counterbalance that containing the precipitate. Thus the error due to hygroscopic moisture was automatically removed and the necessity of rapid weighing obviated.

The weights were then recorded with the composition of their respective solutions and the amount of hydrochloric acid required to precipitate the lead chloride in each. Most of the work was done with $Pb(NO_3)_2$ and foreign

nitrates but in some cases $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ with other acetates were used:

The results were as follows:

Table No 1

	HCl	Wt. PbCl_2
20cc $\text{Pb}(\text{NO}_3)_2$	13.1cc	1.4619
80 $\text{Ca}(\text{NO}_3)_2$		
20 $\text{Pb}(\text{NO}_3)_2$		
60 $\text{Ca}(\text{NO}_3)_2$	13.8cc	1.278
20 H_2O		
20 $\text{Pb}(\text{NO}_3)_2$		
40 $\text{Ca}(\text{NO}_3)_2$	13.6cc	1.5461
40 H_2O		
20 $\text{Pb}(\text{NO}_3)_2$		
20 $\text{Ca}(\text{NO}_3)_2$	13.9cc	1.964
60 H_2O		

Table No 2

HCl	PbCl_2
8.2cc	0.7916
8.4cc	1.1616
9.1cc	1.4762
10.2cc	1.8493

Table No 3

	HCl	Wt PbCl ₂
20ccPb(NO ₃) ₂	10.1cc	1.0103
80 KNO ₃		

20 Pb(NO ₃) ₂		
60 KNO ₃	10.1	1.1534
20 H ₂ O		

20 Pb(NO ₃) ₂		
40 KNO ₃	10.4	1.4241
40 H ₂ O		

20 Pb(NO ₃) ₂		
20 KNO ₃	10.7	2.107
60 H ₂ O		

Table No 5

	HCl	Wt PbCl ₂
20 Pb(C ₂ H ₃ O ₂) ₂	10.1cc	1.10103
80 KNO ₃		

20 Pb(C ₂ H ₃ O ₂) ₂		
60 cc KNO ₃	11.0	1.6487
20 cc H ₂ O		

20 Pb(C ₂ H ₃ O ₂) ₂		
40 KNO ₃	10.6	1.3981
40 H ₂ O		

20 Pb(C ₂ H ₃ O ₂) ₂		
20 KNO ₃	10.7	1.8154
60 H ₂ O		

Table No 4

	HCl	Wt PbCl ₂
20 Pb(NO ₃) ₂	9.6cc	1.3549
80 CA(NO ₃) ₂		

20 Pb(NO ₃) ₂		
60 CA(NO ₃) ₂	9.9	1.0541
20 H ₂ O		

20 Pb(NO ₃) ₂		
40 CA(NO ₃) ₂	10.3	1.4192
40 H ₂ O		

20 Pb(NO ₃) ₂		
20 CA(NO ₃) ₂	11.5	1.8991
60 H ₂ O		

Table No 6

	HCl	Wt PbCl ₂
20 Pb(C ₂ H ₃ O ₂) ₂	10.1cc	1.1181
80 CA(NO ₃) ₂		

20 Pb(C ₂ H ₃ O ₂) ₂		
60 CA(NO ₃) ₂	10.2	1.2834
20 H ₂ O		

20 Pb(C ₂ H ₃ O ₂) ₂		
40 CA(NO ₃) ₂	10.4	1.4376
40 H ₂ O		

20 Pb(C ₂ H ₃ O ₂) ₂		
20 CA(NO ₃) ₂	10.7	1.691
60 H ₂ O		

Table No 7

	HCl	Wt PbCl ₂
20 Pb(C ₂ H ₃ O ₂) ₂	10.2cc	--1.6602
80 AL(NO ₃) ₃		

20 Pb(C ₂ H ₃ O ₂) ₂		
60 AL(NO ₃) ₃	10.0	--1.574
20 H ₂ O		

20 Pb(C ₂ H ₃ O ₂) ₂		
40 AL(NO ₃) ₃	10.4	--1.574
40 H ₂ O		

20 Pb(C ₂ H ₃ O ₂) ₂		
20 AL(NO ₃) ₃	10.6	--1.9263
60 H ₂ O		

Table No 8

	HCl	Wt PbCl ₂
20 Pb(C ₂ H ₃ O ₂) ₂	14.8	--1.2624
80 CD(NO ₃) ₂		

20 Pb(C ₂ H ₃ O ₂) ₂		
60 CD(NO ₃) ₂	14.1	--1.3794
20 H ₂ O		

20 Pb(C ₂ H ₃ O ₂) ₂		
40 CD(NO ₃) ₂	14.5	--1.6694
40 H ₂ O		

20 Pb(C ₂ H ₃ O ₂) ₂		
20 CD(NO ₃) ₂		
60 H ₂ O	13.9	--1.9658

Table No 9

	HCl	Wt PbCl ₂
20 Pb(NO ₃) ₂		
20 AGNO ₃	10.9	---1.9263
60 H ₂ O		

20 Pb(NO ₃) ₂		
10 AGNO ₃	11.4	---1.9859
70 H ₂ O		

20 Pb(NO ₃) ₂		
5 AGNO ₃	11.7	--1.9882
75 H ₂ O		

Table No 10

	HCl	Wt PbCl ₂
20 Pb(NO ₃) ₂		
10 HNO ₃	10.4	---2.055
70 H ₂ O		

20 Pb(NO ₃) ₂		
5 HNO ₃	10.4	--2.1908
75 H ₂ O		

Table No 11

	HCl	Wt PbCl ₂
20 Pb(C ₂ H ₃ O ₂) ₂	20.7cc	--1.5208
50 NH ₄ C ₂ H ₃ O ₂		
30 H ₂ O		
20 Pb(C ₂ H ₃ O ₂) ₂		
40 NH ₄ C ₂ H ₃ O ₂	20.2	--1.9960
40 H ₂ O		
20 Pb(C ₂ H ₃ O ₂) ₂		
30 NH ₄ C ₂ H ₃ O ₂	19.9	--2.086
50 H ₂ O		
20 Pb(C ₂ H ₃ O ₂) ₂		
20 NH ₄ C ₂ H ₃ O ₂	19.9	--1.9254
60 H ₂ O		

Table No 12

	HCl	Wt PbCl ₂
20 Pb(C ₂ H ₃ O ₂) ₂		
50 NaC ₂ H ₃ O ₂	21.8cc	--1.2139
30 H ₂ O		
20 Pb(C ₂ H ₃ O ₂) ₂		
40 NaC ₂ H ₃ O ₂	21.1	---1.7459
40 H ₂ O		
20 Pb(C ₂ H ₃ O ₂) ₂		
30 NaC ₂ H ₃ O ₂	20.6	---2.639
50 H ₂ O		
20 Pb(C ₂ H ₃ O ₂) ₂		
20 NaC ₂ H ₃ O ₂	20.5	---1.799
60 H ₂ O		

Table No 13

	HCl	Wt PbCl ₂
20 Pb(C ₂ H ₃ O ₂) ₂		
CA(C ₂ H ₃ O ₂) ₂	29.0	--1.8576
30 H ₂ O		
20 Pb(C ₂ H ₃ O ₂) ₂		
40 CA(C ₂ H ₃ O ₂) ₂	28.2	--1.947
40 H ₂ O		
20 Pb(C ₂ H ₃ O ₂) ₂		
30 CA(C ₂ H ₃ O ₂) ₂	27.1	--2.1636
50 H ₂ O		
20 Pb(C ₂ H ₃ O ₂) ₂		
20 CA(C ₂ H ₃ O ₂) ₂	26.8	--2.1566
60 H ₂ O		

Table No 14

	HCl	Wt PbCl ₂
20 Pb(NO ₃) ₂		
80 HNO ₃	11.3cc	--.9468
20 Pb(NO ₃) ₂		
60 HNO ₃	11.4	--1.000
20 H ₂ O		
20 Pb(NO ₃) ₂		
40 HNO ₃	11.6	---1.1264
40 H ₂ O		
20 Pb(NO ₃) ₂		
40 HNO ₃	11.7	--1.2582
60 H ₂ O		

The following experiments were made to determine at what point, during the addition of HCL, precipitation of $PbCl_2$ was the greatest:

Table No 15	HCl	Wt $PbCl_2$	Table No 16	HCl	Wt $PbCl_2$
20 $Pb(NO_3)_2$ 40 $Ca(NO_3)_2$ 40 H_2O	2cc	---.0006	20 $Pb(NO_3)_2$ 30 KNO_3 50 H_2O	2cc	----.0036
20 $Pb(NO_3)_2$ 40 $Ca(NO_3)_2$ 40 H_2O	4cc	---.2104	20 $Pb(NO_3)_2$ 30 KNO_3 50 H_2O	4cc	----.1974
20 $Pb(NO_3)_2$ 40 $Ca(NO_3)_2$ 40 H_2O	6cc	---.6140	20 $Pb(NO_3)_2$ 30 KNO_3 50 H_2O	6cc	----.5434
20 $Pb(NO_3)_2$ 40 $Ca(NO_3)_2$ 40 H_2O	8cc	---.9622	20 $Pb(NO_3)_2$ 30 KNO_3 50 H_2O	8cc	----1.0904

Table No 17	HCl	Wt $PbCl_2$	Table No 18	HCl	Wt $PbCl_2$
20 $Pb(NO_3)_2$ 60 $Al(NO_3)_3$ 20 H_2O	2cc	-- .0054	20 $Pb(NO_3)_2$ 40 NH_4NO_3 40 H_2O	2cc	-----.0000
20 $Pb(NO_3)_2$ 60 $Al(NO_3)_3$ 20 H_2O	4cc	----.0000	20 $Pb(NO_3)_2$ 40 NH_4NO_3 40 H_2O	4cc	-----.00000
20 $Pb(NO_3)_2$ 60 $Al(NO_3)_3$ 20 H_2O	6cc	---.229	20 $Pb(NO_3)_2$ 40 NH_4NO_3 40 H_2O	6cc	-----2 29
20 $Pb(NO_3)_2$ 60 $Al(NO_3)_3$ 20 H_2O	8cc	----1.0604	20 $Pb(NO_3)_2$ 40 NH_4NO_3 40 H_2O	8cc	----1.0604
			20 $Pb(NO_3)_2$ 40 NH_4NO_3 40 H_2O	10cc	----1.1942

Stock Solutions.

HCl	106.24grams	in	1000cc		
Pb(C ₂ H ₃ O ₂) ₂	81.38 grams	in	500 cc		
Pb(NO ₃) ₂	82.77	--	--	--	--
KNO ₃	20	--	--	200	--
CD(NO ₃) ₂	20	--	--	--	--
CA(NO ₃) ₂	20	--	--	--	--
NH ₄ NO ₃	20	--	--	--	--
CA(NO ₃) ₂	20	--	--	--	--
AL ₂ (NO ₃) ₆	20	--	--	--	--
AGNO ₃	20	--	--	--	--
CA(C ₂ H ₃ O ₂) ₂	20	--	--	--	--
NH ₄ (C ₂ H ₃ O ₂) ₂	20	--	--	--	--
125 cc HNO ₃	in 375 cc				
125 CH ₃ COOH	in 375 cc				

A study of the tables, 1 to 10, will clearly show that with Lead Nitrate in solution the amount of Lead chloride precipitated in each case is regularly diminished by an increasing quantity of another nitrate in solution when volume and temperature are constant.

It will be seen from tables 11-13 that with Lead Acetate in solution other acetates present decrease the amount of Lead Chloride precipitated in proportion to the quantity of added acetate. The quantity of Hydrochloric Acid required for precipitation in case of the acetates is more than twice that required for the nitrates.

We may, then, be justified in concluding from the experiment that the greater the concentration of NO_3^- or of $\text{C}_2\text{H}_3\text{O}_2^-$ the greater the quantity of Cl^- may be in solution according to equations (8) and (9). If in the course of a qualitative analysis lead is found abundantly in the second group and sparingly in the first the conclusion that considerable quantities of the nitrates and acetates are present would be justified.