DOUBLE AND COMPLEX SALTS:

A STUDY OF SYSTEMS OF THE TYPE:

LEAD NITRATE - OTHER NITRATE - WATER.

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Thesis for Degree of Doctor of Philosophy.

By

Barbara Munro Henderson, B.Sc.

Chemistry Department,
University of Edinburgh.

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C O N T E N T S.

I N T R O D U C T I O N

In a series of papers on compound formation between organic substances, Kendall[1] and his collaborators investigated many binary systems and found, by examination of depression of the freezing point curves, a general rule that the formation and stability of addition compounds "increase with the differences of the character (i.e., the positive or negative nature of the constituent groups) of its components."

For example in systems of the type ester-acid $RCOOR' - HX$[2] compound formation increased as the acidic radical X became more negative or as the radicals R and R' were made more basic. In systems of the type aldehyde-acid $RCHO - HX$[3] and acid-acid $HX - HY$ (where the weaker acid acted as a base) the diversity rule was also found to hold.

The investigation was then extended to binary inorganic systems, and an examination of the types sulphuric acid-metal sulphate,[4] formic acid-metal formate[5] and the more general systems $MX_x - M'X_y$[6] (i.e. salts

with a common ion) showed the rule to hold also in these cases. In systems of the last class (MX_x - $M'X_y$) however, although the diversity factor was found to be the driving force in compound formation, many other factors had to be considered in accounting for the results obtained. These were valence of cation, unsaturation, position of the cation of the reference salt in electrode potential series, temperature, internal pressure differences between the two components, molecular and atomic volumes, atomic number and association.

In general, difficulty is found in examining binary systems of this type owing to the high freezing points of most inorganic salts, and the decomposition occurring at these temperatures. When a third component, namely water, is added, the difficulty is avoided, and Kendall, Davidson and Adler[7] predicted that the solubility of the salt AgCl would increase more and more, on addition of a second salt MCl, above the normal value, as M became more electropositive. This was confirmed by the data of Forbes[8], and Kendall and Sloan[9]. The latter pair of investigators also studied the solubility of lead chloride in aqueous solutions of other chlorides, and found that here again the stability of an addition compound is dependent upon the differences in electrode potential between the two positive radicals of its components. Thus in the case of the systems

$AgCl - MCl_x - H_2O$ the order of solubility (i.e. a measure of compound formation see p.36) as M was varied was $H < Ca < Sr < Ba < K$ or NH_4 which is exactly the order of their electrode potential diversity from silver.

The present investigation was undertaken in order to ascertain if this rule holds generally in ternary systems of the type $MX_x - M'X_y - H_2O$, where the salt MX_x is fairly soluble, and to examine to what extent other factors govern compound formation.

Systems $Pb(NO_3)_2 - M(NO_3)_x - H_2O$ were chosen for three reasons. Firstly, several systems of this type have already been investigated;[10,11,12] secondly, because lead lies about the middle of the electrode potential series and therefore the metal M may be varied widely in order to test the diversity factor; lastly, since the nitrates are all soluble, the choice of the second metal M is not restricted. The latter was so chosen, in the investigated systems, as to vary the different factors as much as possible.

Previous Work done on Systems $Pb(NO_3)_2 - M(NO_3) - H_2O$.

$Pb(NO_3)_2 - NaNO_3 - H_2O$. Glasstone and Saunders[10] studied the ternary system $Pb(NO_3)_2 - NaNO_3 - H_2O$ completely at 25°C and 50°C, and also partially at 0°C and 100°C. They found that at all temperatures the solubility of lead nitrate was lowered by the addition

of sodium nitrate, and as the temperature was decreased the effect diminished. They suggested that at still lower temperatures, in presence of fairly large quantities of sodium nitrate, the solubility of lead nitrate might be increased. Thus the tendency for compound formation to take place increases with fall in temperature.

$Pb(NO_3)_2 - KNO_3 - H_2O$. A. A. Noyes and Le Blanc[13] found that the solubility of lead nitrate in an aqueous solution of potassium nitrate was greater than its solubility in pure water, and attributed this to compound formation. Glasstone and Saunders[10] studied the system $Pb(NO_3)_2 - KNO_3 - H_2O$ completely at 25°C and 50°C and partially at 0°C and 100°C. The isotherms show in all cases that the solubility of lead nitrate is increased on addition of potassium nitrate although no compound was isolated. Further they show that as the temperature is raised, the increase in solubility becomes less, and the curves begin to resemble those of the system $Pb(NO_3)_2 - NaNO_3 - H_2O$. Ehret[14] studied the system completely at 0°C and although the increase in solubility of lead nitrate was even more marked at that temperature no compound was isolated.

Glasstone and Riggs[15], by the study of the quaternary system $KNO_3 - Pb(NO_3)_2 - Ba(NO_3)_2 - H_2O$, indicate the existence of the compound $2KNO_3, Pb(NO_3)_2$ in a mixed crystal with $2KNO_3, Ba(NO_3)_2$.

$Pb(NO_3)_2$ -NH_4NO_3 - H_2O. This system was studied at 0°C, 10°C and 20°C by Malquori[11] Examination of the isotherms shows although there is a small decrease in the solubility at 20°C and 10°C of lead nitrate by the addition of ammonium nitrate when calculated as weight per cent of saturated solution, there is an increase at 0°C. No isolable compound was obtained however.

$Pb(NO_3)_2$ - $LiNO_3$ - H_2O and $Pb(NO_3)_2$ - $CsNO_3$ - H_2O. Malquori[12] also determined the isotherms at 25°C of the two systems $Pb(NO_3)_2$ - $LiNO_3$ - H_2O and $Pb(NO_3)_2$ - $CsNO_3$ - H_2O. These show that while the solubility of lead nitrate falls off on addition of lithium nitrate it is increased by caesium nitrate. This indicates compound formation with caesium nitrate, although here again no compound was isolated.

$Pb(NO_3)_2$ -$Ba(NO_3)_2$ - H_2O and $Pb(NO_3)_2$ - $Sr(NO_3)_2$ - H_2O. Fock[16] and Glasstone and Riggs[15] showed that lead nitrate and barium nitrate form mixed crystals at 25°C and 50°C, and according to von Hauer, Ambronn and Le Blanc, and Fock,[17] lead and strontium nitrates also form isomorphous mixed crystals.

The author has continued this series of systems by studying the isotherms of the following:
$Pb(NO_3)_2$ - $Ca(NO_3)_2$ - H_2O , $Pb(NO_3)_2$ - $Mg(NO_3)_2$ - H_2O , $Pb(NO_3)_2$ - $AgNO_3$ - H_2O and $Pb(NO_3)_2$ - $Al(NO_3)_3$ - H_2O at 25°C.

Calcium nitrate and magnesium nitrate were chosen as second salts in order to complete the series of systems of lead nitrate - alkaline earth nitrate - water, two of which had already been investigated. Silver nitrate was used for two reasons, firstly because silver is a pseudo-alkali metal and could be compared with those systems with alkali nitrates already studied by Glasstone and Saunders and by Malquori, and secondly, because silver has a negative electrode potential. (Its position in the electrode potential series is on the opposite side of lead as compared with the other metals which have been used as the second metallic radical in the systems already discussed.) The system $Pb(NO_3)_2$ - $Al(NO_3)_3$ - H_2O was finally investigated as aluminium has a high valency and a very small ionic radius.

APPARATUS AND CHEMICALS.

Preparation of Materials.

$Pb(NO_3)_2$ Aytoun Scott's 'pure crystalline' lead nitrate was recrystallised from distilled water and dried at 100°C. Qualitative tests showed the absence of silver, iron, zinc, alkaline earth metals, potassium and chloride as impurities.

$Ca(NO_3)_2,4H_2O$ was prepared by Morgan's method[18] from Merck's 'pure crystalline' calcium nitrate. The salt was melted in its own water of crystallisation, a small quantity of water added to dissolve impurities, and recrystallised. As the crystals appeared they were ladelled on to a Buchner filter. After two recrystallisations the salt was found to be pure and free from strontium, barium, iron, zinc, copper, chloride and sulphate as impurities.

$Mg(NO_3)_2,6H_2O$. This was obtained from Griffin and Tatlock's 'pure crystalline' magnesium nitrate by the same method as that used for $Ca(NO_3)_2,4H_2O$. After two recrystallisations qualitative tests showed the

absence of iron, zinc, the alkaline earth metals, and chloride. A third recrystallisation was necessary to get rid of traces of sulphate impurity.

$AgNO_3$. B.D.H. 'Analytical Reagent' silver nitrate was used without further purification as qualitative tests gave no indication of the following impurities: copper, iron, lead or sulphate. Its solubility at 25°C was found to be exactly the same value as that found by Kazantzev (see experimental results).

$Al(NO_3)_3,9H_2O$. Qualitative tests done on Kahlbaum's 'alkali and sulphur-free' aluminium nitrate showed that no iron, alkali, chloride or sulphate impurities were present. The salt was used without further purification.

Apparatus.

An electrically heated thermostat at 25°C was used throughout. The temperature was controlled to within ± .01°C and was read by means of a Beckmann thermometer, which was frequently checked against a standard 'Deutche Reichsanstalt' thermometer. During the rotation of the mixtures containing silver nitrate, it was essential that they should be unaffected by light as far as possible. The thermostat cover provided adequate protection against day-light, and the heating lamps were completely encased in tin foil and painted over with black heat-proof lacquer to exclude light

from these.

The mixtures were shaken in Jena glass bottles, the glass stoppers of which were paraffined down and squares of rubber sheeting tied tightly over them, so that the solutions could not be contaminated with impurities from the water in the bath. They were then rotated in the thermostat , the bottles being clamped to a horizontal stirrer which was driven by a small electric motor. The driving belt which ran under the water was made of flax line joined by means of a long splice.

The flasks, pipettes and burettes used were calibrated accurately at room temperature, while the pipette and specific gravity bottle used in measuring samples of solution were calibrated at 25°C.

The balance used throughout gave results accurate to .0001 - .0002 grams for weights up to 50 grams. The weights were calibrated against each other and were found to agree.

EXPERIMENTAL PROCEDURE.

The solubilities of the single salts were determined by analysis of the solution formed after shaking excess of the salt with distilled water for six to seven days.* Successive portions of the second salt were then added, shaken for three to four days,* and samples of the solutions and wet solids analysed.

At first quantities of the solution in the system $Pb(NO_3)_2$ - $Ca(NO_3)_2$ - H_2O were measured out by means of a 25 cc. pipette which was kept when not in use in a long glass tube immersed in the thermostat. A small piece of filter paper was tied over the end in order to exclude solid particles from entering the pipette. The sample was then weighed in a small stoppered flask. As the solutions became more viscous it was found that the pipette did not deliver its true volume of solution, so a different method of extracting samples of solution was adopted and has been used in every system.

Portions of the solution were transferred to a specific gravity bottle by a 'wash-bottle' arrangement, as in the accompanying diagram.

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* Constancy of the results of analyses, after extension of time, showed that equilibrium had been attained during this period in each system.

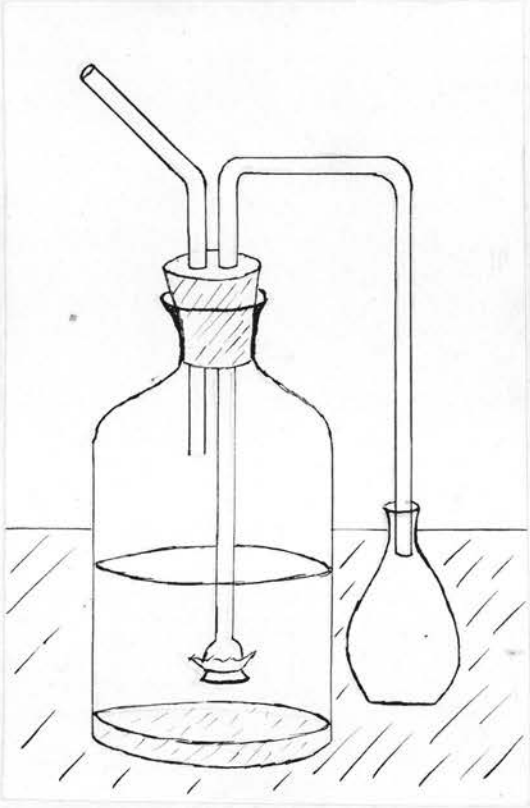


DIAGRAM I

A double thickness of muslin covered the thistle funnel, blown on the end of the glass tubing, which entered the solution. A portion of the solution was run through the glass tubing and rejected, before filling the specific gravity bottle, in order that crystallisation would not occur in the tubing by cooling.

The specific gravity bottle was placed for about an hour previously in a stoppered glass jar (weighed down with lead shot) which was kept in the thermostat, in order to attain the temperature of 25°C. It was held in the thermostat during the transference of the

solution, and, one minute after filling, the stopper was gently inserted, the outside carefully dried and allowed to cool before weighing.

At the same time about 10 grams of the 'wet solid' were transferred to a stoppered weighing bottle by means of a nickel spatula. This was allowed to cool and then weighed.

These samples were then diluted either to 250 cc. or to 500 cc. in a standard flask and suitable aliquots (10 cc. or 25 cc.) were analysed. The methods of analysis are dealt with separately under each system.

The results are plotted on triangular graph paper as weights per cent, and the solid phase in equilibrium with the solution is determined by means of Schreinemaker's residue method.[19]

The specific gravities of the solutions were determined so that the results could be expressed in terms of normality if necessary.

EXPERIMENTAL RESULTS.

The System $Pb(NO_3)_2$ - $Ca(NO_3)_2$ - H_2O at 25° C.

Method of analysis. The samples of the solutions and of the wet solids were diluted to 250 cc. and 10 cc. aliquots were analysed.

These aliquots were slightly diluted, 5 cc. of dilute acetic acid were added and the lead determined as chromate.[20, 21.] The lead chromate was collected in a Jena sintered glass crucible (no. $^{I}_{4}{}^{G}$), and dried to constant weight in an air oven at 120° C.

The filtrate was diluted to 150 cc., 3.5 cc. of dilute ammonia solution were added and the calcium precipitated as oxalate. It was then determined volumetrically with .1 N (or in cases where a large quantity of calcium was present, .25 N) potassium permanganate solution in the manner described by Cumming and Kay[22] and by Scott.[23]

The potassium permanganate solution, which had been filtered three times through asbestos, was standardised with Iceland spar which was dissolved in nitric acid, and then precipitated as the oxalate and dissolved in

acid in exactly the same manner, as was done with the solutions above. In this way no blank experiments were required. This method of standardisation was found to be in excellent agreement with that done against sodium oxalate.

From these determinations the weight percentages of lead nitrate and calcium nitrate were calculated and the percentage of water was found by difference.

The above method of separation was tested on mixtures made from known weights of pure metallic lead and Iceland spar. The error was found to be within one part in a thousand with both substances on weights of about .1 gram.

Results. Glasstone and Saunders[10] give the solubility of lead nitrate at 25°C as 37.17 grams per 100 grams of solution and that given by Malquori[12] at this temperature was37.07 per cent. International Critical Tables[24] give the value to be 1.80 M per 1000 grams of water i.e. 37.35 per cent. This last result is in excellent agreement with the result obtained here (37.34 per cent).

The solubility of calcium nitrate is given by Cameron and Robinson[25] as 139.30 grams per 100 grams of water (58.21 per cent), by Bassett and Taylor[26] as 57.98 per cent and by Ehret[27] as 58.35 per cent. The value given in International Critical Tables[28] is 8.41 M per 1000 grams of water. The result

obtained by the author (57.92 per cent) is in very close agreement with that of Bassett and Taylor.

The isotherm shows that the solubility of lead nitrate falls off on addition of calcium nitrate, the slope becoming less as the quantity of calcium nitrate is increased. The solubility of lead nitrate decreases to 1.14 per cent by weight at the invariant point. The addition of lead nitrate on the other hand, decreases the solubility of calcium nitrate only to a very small extent, the value at the invariant point being 57.01 per cent.

Beginning at the right hand end of the isotherm, the solutions are in contact with $Pb(NO_3)_2$ as the solid phase. The solid in equilibrium with the solutions at the left hand end of the curve is $Ca(NO_3)_2,4H_2O$ (α variety).

No isolable addition compound is formed, and the course of the curve indicates that little (if any) exists in solution.

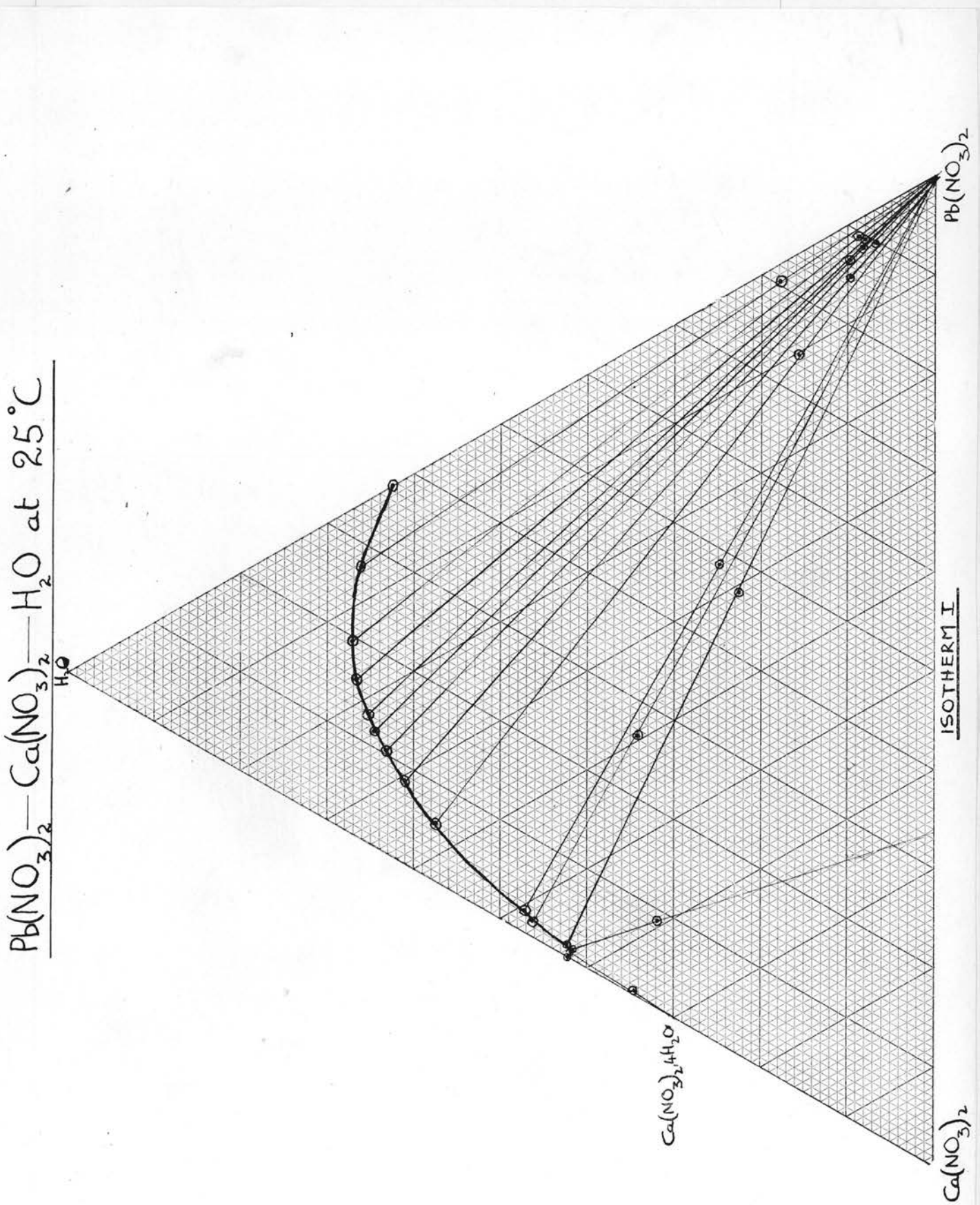

Pb(NO3)2—Ca(NO3)2—H2O at 25°C
H2O
Pb(NO3)2
Ca(NO3)2.4H2O
Ca(NO3)2
ISOTHERM I

TABLE I

The System $Pb(NO_3)_2$ - $Ca(NO_3)_2$ - H_2O at 25°C

SOLUTION

percentage by weight

No.	$Pb(NO_3)_2$	$Ca(NO_3)_2$	H_2O	$D_{25°C}$
1)	37.34	0.00	62.66	1.446
2)	27.35	6.49	66.16	1.370
3)	19.73	13.03	67.24	1.337
4)	15.95	17.61	66.44	1.333
5)	13.05	21.88	65.07	1.341
6)	11.69	23.96	64.33	1.348
7)	10.40	26.42	63.18	1.357
8)	8.31	30.82	60.87	1.376
9)	5.94	36.95	57.11	1.412
10)	2.09	50.71	47.20	1.524
11)	1.82	52.08	46.10	1.541
12)	1.17	56.58	42.25	1.586
13)	1.14	57.01	41.85	1.586
14)	1.13	57.06	41.89	1.586
15)	0.00	57.92	42.08	1.575

TABLE I

The System $Pb(NO_3)_2$ - $Ca(NO_3)_2$ - H_2O at 25°C.

WET SOLID

percentage by weight

No.	$Pb(NO_3)_2$	$Ca(NO_3)_2$	H_2O	Solid phase
1)	–	–	–	$Pb(NO_3)_2$
2)	80.53	1.73	17.74	"
3)	89.62	1.84	8.54	"
4)	89.69	2.37	7.94	"
5)	88.66	3.14	8.20	"
6)	86.64	3.85	9.53	"
7)	88.88	3.38	7.74	"
8)	84.97	5.26	9.77	"
9)	74.13	10.28	15.59	"
10)	48.37	26.95	24.68	"
11)	26.32	39.66	34.02	"
12)	46.78	30.65	22.57	"
13)	8.92	59.06	32.02	$Pb(NO_3)_2$ + $Ca(NO_3)_2,4H_2O$
14)	0.47	65.01	34.52	$Ca(NO_3)_2,4H_2O$
15)	–	–	–	"

The System $Pb(NO_3)_2$ - $AgNO_3$ - H_2O at 25°C.

Method of analysis. The percentages of lead nitrate and silver nitrate were obtained by determining the silver as chloride and the lead as chromate. The percentage of water was found by difference.

The weighed samples of the solutions and the wet solids were diluted to 250cc., and 10 cc. aliquots were taken for analysis. The silver was determined in the presence of lead by the method indicated by Scott.[29] The aliquots were diluted to 500 cc. and the solution heated to boiling. A 0.1 per cent solution of hydrochloric acid was added through a dropping tube till all the silver was precipitated, and the beaker was placed on the steam bath, and stirred frequently, till the silver chloride was completely coagulated. A few drops of the hydrochloric acid were added to ensure complete precipitation. After cooling, the silver chloride was filtered through a Jena sintered glass crucible (No. $^{I}_{3}{}^{G}$), washed with water containing a little dilute nitric acid and finally washed with distilled water. It was then dried to constant weight in an air oven at 130°C. Dark brown paper was wrapped round the beakers used in the precipitation of silver chloride, and the crucibles containing it were cooled in a desiccator which had been painted black in order to exclude light.

The filtrate was evaporated to 100 cc., 5 grams of sodium acetate were added and the lead determined as chromate in the same manner as in the previous system.

The separation was tested quantitatively with solutions made from known weights of A.R. silver nitrate and A.R. lead acetate. Results agreeing to one part in a thousand were obtained for silver nitrate on a weight of 25 grams and to two parts in a thousand for lead acetate on a weight of about 7 grams.

Results. International Critical Tables[30] give the solubility of silver nitrate as 14.00 M in 1000 grams of water (± 2 per cent), that is, 70.41 per cent. Siedell[31] gives the value found by Kazantzev to be 71.8 per cent. The author's result (71.81 per cent) is in complete agreement with this.

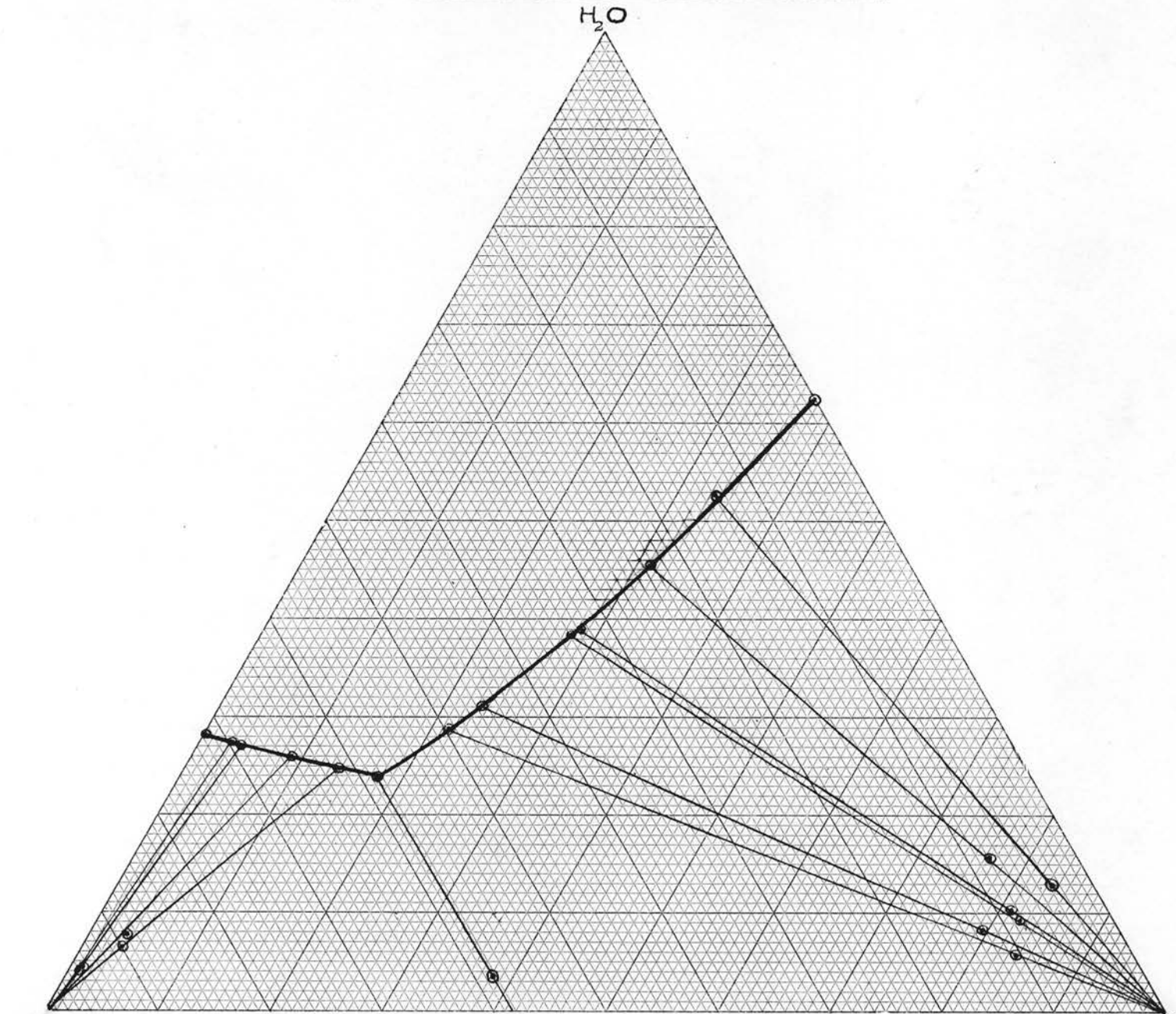
Examination of the isotherm for this system shows that silver nitrate and lead nitrate mutually reduce each other's solubility, when they are expressed as weight percentages. Silver nitrate, however, depresses the solubility of lead nitrate to a smaller degree than would be expected from the addition of a substance containing a univalent common ion.

The composition of the eutectic solution is silver nitrate 52.28 per cent, lead nitrate 17.68 per cent and water 24.04 per cent.

This indicates the existence of a compound in solution, but one which is not sufficiently stable to be

isolated. This will be dealt with more fully in a later section under 'discussion of results.'

$Pb(NO_3)_2$—$AgNO_3$—H_2O at 25°C.



ISOTHERM II

TABLE II.

The System $Pb(NO_3)_2$ - $AgNO_3$ - H_2O at 25° C.

SOLUTION

percentage by weight.

No.	$Pb(NO_3)_2$	$AgNO_3$	H_2O	$D_{25°C}$
1)	37.34	0.00	62.66	1.446
2)	33.55	13.93	52.52	1.628
3)	31.09	23.16	45.75	1.777
4)	28.15	32.83	39.02	1.952
5)	27.79	33.83	38.38	1.975
6)	27.72	33.98	38.30	1.976
7)	23.26	45.62	31.12	2.210
8)	21.45	49.84	28.71	2.259
9)	17.68	58.28	24.04	2.487
10)	13.96	61.32	24.72	2.445
11)	8.99	65.00	26.01	2.389
12)	3.89	69.08	27.03	2.336
13)	2.87	69.76	27.37	2.325
14)	0.00	71.80	28.20	2.297

TABLE II.

The System $Pb(NO_3)_2$ - $AgNO_3$ - H_2O at 25°C.

WET SOLID

percentage by weight

No.	$Pb(NO_3)_2$	$AgNO_3$	H_2O	Solid phase
1)	-	-	-	$Pb(NO_3)_2$
2)	83.51	3.81	12.68	"
3)	76.25	7.89	15.86	"
4)	81.04	8.94	10.02	"
5)	83.37	8.20	8.43	"
6)	82.39	8.54	9.07	"
7)	79.45	12.37	8.18	"
8)	83.97	10.40	5.63	"
9)	38.01	58.17	3.82	$Pb(NO_3)_2$ + $AgNO_3$
10)	3.29	89.93	6.78	$AgNO_3$
11)	3.52	88.90	7.58	"
12)	1.10	94.28	4.62	"
13)	1.01	94.89	4.10	"
14)	-	-	-	"

The System $Pb(NO_3)_2$ - $Mg(NO_3)_2$ - H_2O at 25°C.

Method of analysis. The weighed samples of the solutions were diluted to 500 cc. and those of the 'wet solids' to 250 cc. Aliquots (10 cc.) were analysed except in cases where there were very small quantities of magnesium nitrate present, when 25 cc. aliquots were taken for analysis.

The lead was determined by the chromate method as before, and the magnesium as pyrophosphate in the filtrate. The latter was evaporated to 100 cc. and the magnesium precipitated as magnesium ammonium phosphate by the method of B. Schmidt,[32] and filtered through a Jena sintered glass crucible (No. I_4^G) after standing for twenty-four hours. The precipitate was washed with a 2 per cent ammonia solution and dried in an air oven at 120°C for half-an-hour. The glass crucible was then placed inside a larger nickel crucible and ignited gradually. The temperature was increased slowly until it was finally heated with a full bunsen flame. Before cooling in a desiccator for twenty-five minutes, the crucible was placed in an oven at 120°C for five minutes in order to prevent the glass cracking.

Mixtures were made up from known weights of pure metallic lead (British Chemical Standards) and pure metallic magnesium dissolved in dilute nitric acid, and analysed. The results obtained showed errors of

0 to .1 milligrams on .06 grams of lead and the error on .018 grams of magnesium was .2 milligrams.

Results. The solubility of magnesium nitrate was found to be 42.03 grams per 100 grams of saturated solution. This value was also obtained by Hill and Moskowitz.[33] Jackman and Browne[34] in 1922 found it to be 43.25 per cent.

The isotherm shows only two branches. Firstly, solutions in contact with $Pb(NO_3)_2$ as the solid phase, and secondly, solutions in contact with crystals of $Mg(NO_3)_2,6H_2O$. This curve is very similar to that obtained in the system $Pb(NO_3)_2$ - $Ca(NO_3)_2$ - H_2O. It shows no isolable addition compound and if any be formed in solution it must only be to a very small degree.

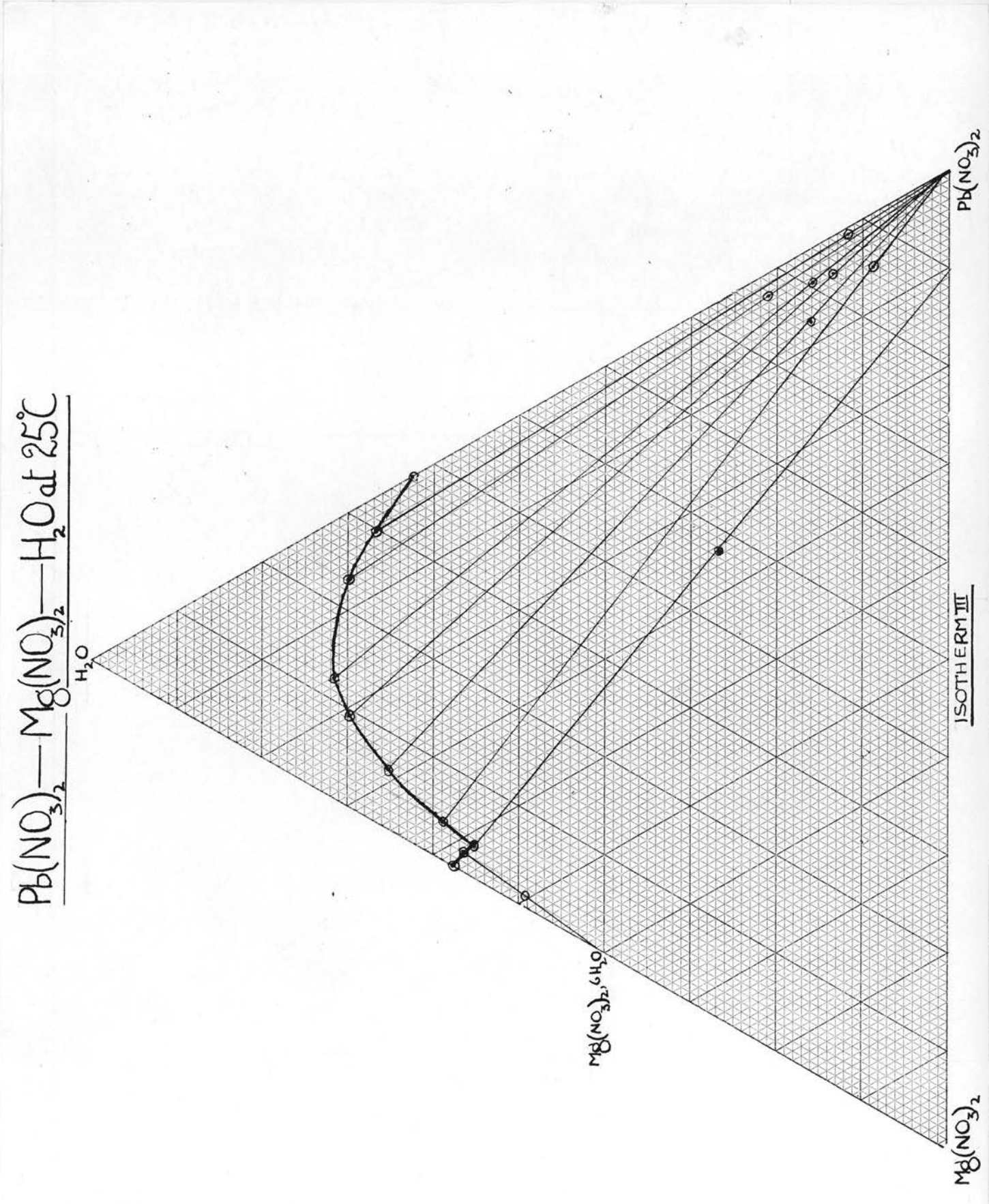

Pb(NO3)2—Mg(NO3)2—H2O at 25°C
H2O
Mg(NO3)2, 2H2O
Pb(NO3)2
Mg(NO3)2
ISOTHERM III

TABLE III.

The System $Pb(NO_3)_2$ - $Mg(NO_3)_2$ - H_2O at 25° C.

SOLUTION

percentage by weight

No.	$Pb(NO_3)_2$	$Mg(NO_3)_2$	H_2O	$D_{25°C}$
1)	37.34	0.00	62.66	1.446
2)	29.73	3.48	66.79	1.365
3)	23.11	6.99	69.90	1.310
4)	12.19	16.09	71.72	1.264
5)	9.19	20.85	69.96	1.274
6)	6.01	28.65	65.34	1.319
7)	3.91	37.03	59.06	1.385
8)	3.17	41.66	55.15	1.419
9)	2.09	41.15	56.76	1.408
10)	0.00	42.03	57.97	1.389

TABLE III.

The System $Pb(NO_3)_2$ - $Mg(NO_3)_2$ - H_2O at 25°C.

WET SOLID

percentage by weight

No.	$Pb(NO_3)_2$	$Mg(NO_3)_2$	H_2O	Solid phase
1)	-	-	-	$Pb(NO_3)_2$
2)	87.69	0.56	11.75	"
3)	76.66	2.26	21.08	"
4)	80.52	3.71	15.77	"
5)	82.69	3.91	13.40	"
6)	76.26	7.49	16.25	"
7)	85.84	5.34	8.82	"
8)	47.65	25.49	26.86	$Pb(NO_3)_2$ + $Mg(NO_3)_2,6H_2O$
9)	1.11	49.79	49.10	$Mg(NO_3)_2,6H_2O$
10)	-	-	-	"

The System $Pb(NO_3)_2$ - $Al(NO_3)_3$ - H_2O at 25° C.

Method of analysis. The weighed samples of the solutions and 'wet solids' were diluted to 250cc., and 10 cc. aliquots were analysed.

The lead was determined as lead chromate in essentially the same manner as in the previous systems. In this case however, a .1 N solution of sodium chromate (as sodium salts are less easily adsorbed than potassium salts by aluminium hydroxide) was added, drop by drop, from a burette to the boiling solution acidified with acetic acid, till no more lead chromate was precipitated. In this way only a very small excess of sodium chromate was present after complete precipitation. The lead chromate was filtered and washed as before.

The aluminium was determined as alumina. The filtrate was evaporated to 100 cc. and the aluminium precipitated as aluminium hydroxide by Blum's method.[35] Two precipitations were found necessary, and the precipitates were washed with a hot 2 per cent solution of ammonium chloride and also with a cold 2 per cent ammonium bicarbonate solution,[36] in order to eliminate traces of chromic acid formed during precipitation of aluminium hydroxide.

As slight suction was required in some of the aluminium hydroxide filtrations, a perforated platinum cone was used to strengthen the filter paper.

The percentages of lead nitrate and of aluminium nitrate were obtained by calculation from the results of the analyses, and the percentage of water was found by difference.

The method of analysis described above was tested on solutions made up from pure metallic lead (British Chemical Standards) and pure metallic aluminium (British Aluminium Company). The results for lead were found to agree exactly with the weights used, and those for aluminium were also found satisfactory, provided that sufficient care was taken to keep the excess of sodium chromate small during the precipitation of lead chromate, and to wash the precipitate of aluminium hydroxide thoroughly with ammonium bicarbonate solution.

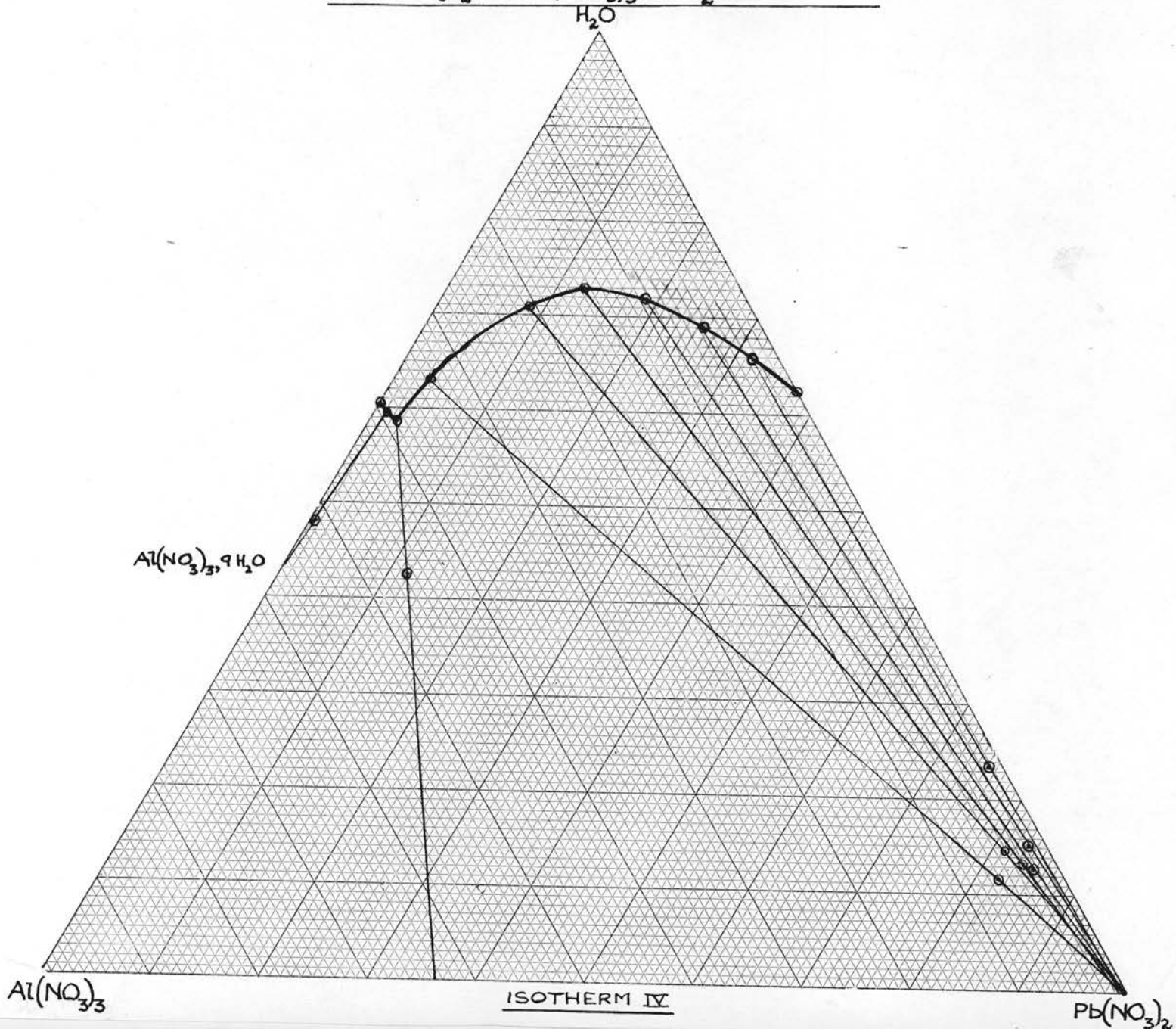
Results. Inamura's result for the solubility of aluminium nitrate at 25° C is given by Seidell[37] and International Critical Tables[38] to be 39.0 grams per 100 grams of saturated solution. The author obtains a higher value than this, namely 39.4 grams per 100 grams saturated solution.

Examination of the isotherm shows that the solubility of lead nitrate is depressed greatly by the addition of aluminium nitrate, while that of the latter is reduced only to a small extent by the addition of lead nitrate. It has only two branches, the solutions being in equilibrium with $Al(NO_3)_3,9H_2O$ crystals

at one end and with $Pb(NO_3)_2$ at the other end of the curve.

The composition of the solution at the invariant point is $Pb(NO_3)_2$, 2.39 per cent; $Al(NO_3)_3$, 38.86 per cent; H_2O, 58.75 per cent. There is no formation of an isolable addition compound.

$Pb(NO_3)_2$—$Al(NO_3)_3$—H_2O at 25°C.



ISOTHERM IV

TABLE IV

The System $Pb(NO_3)_2$ - $Al(NO_3)_3$ - H_2O at 25° C.

SOLUTION

percentage by weight

No.	$Pb(NO_3)_2$	$Al(NO_3)_3$	H_2O	$D_{25°C}$
1)	37.34	0.00	62.66	1.446
2)	31.72	2.31	65.97	1.388
3)	25.43	5.75	68.82	1.330
4)	18.57	9.36	72.07	1.283
5)	12.54	14.70	77.76	1.261
6)	8.43	20.75	70.82	1.268
7)	3.29	33.55	63.16	1.370
8)	2.39	38.86	58.75	1.413
9)	1.04	39.23	59.73	1.400
10)	0.00	39.40	60.60	1.390

TABLE IV

The System $Pb(NO_3)_2$ - $Al(NO_3)_3$ - H_2O at 25° C.

WET SOLID

percentage by weight

No.	$Pb(NO_3)_2$	$Al(NO_3)_3$	H_2O	Solid phase
1)	-	-	-	$Pb(NO_3)_2$
2)	75.18	1.19	23.63	"
3)	83.01	1.73	15.26	"
4)	84.80	2.47	12.73	"
5)	81.05	4.01	14.94	"
6)	83.58	3.13	13.29	"
7)	80.21	6.02	13.77	"
8)	11.96	45.59	42.45	$Pb(NO_3)_2$ + $Al(NO_3)_3$,$9H_2O$
9)	0.39	51.42	48.19	$Al(NO_3)_3$,$9H_2O$
10)	-	-	-	"

DISCUSSION OF RESULTS.

Although the law of the constancy of the ionic solubility product is only approximate in solutions of moderately soluble salts, it must hold at least qualitatively in solutions saturated with lead nitrate. The equilibrium is expressed as follows:

$$\left[Pb^{++}\right]\left[NO_3^{-}\right]^2 = K \text{ (a constant)}$$

Now in every system studied here, the added salt contains a common ion, namely the nitrate ion. It follows from the constancy of the ionic solubility product that if the concentration of the nitrate ion be increased, that of the lead ion must fall off in order to maintain equilibrium. The solubility of lead nitrate should consequently decrease on addition of a salt containing a nitrate ion.

If an increase in the solubility be observed, this must be due to some of the effective lead ions being removed as part of a molecular or ionic complex. The increase in solubility of a salt, on addition of a second salt containing a univalent common ion, can therefore be regarded as a measure of the degree of compound formation in the solution.

In a previous section under 'Experimental Results', it was stated that there were no isolable addition compounds formed between lead nitrate and calcium, magnesium, aluminium or silver nitrates.

In order to see to what extent different factors, namely the diversity in electrode potential between lead and the other metal, ionic radii, and valency, govern compound formation, the results of the above systems, along with those done by Glasstone and Saunders, and Malquori, have been put in the form of a diagram (diagram 2). Gram-equivalents of lead nitrate per 100 grams of water have been plotted against gram-equivalents of $M(NO_3)_x$ per 100 grams of water. Malquori compared the results of the systems $Pb(NO_3)_2$ - KNO_3 - H_2O, $Pb(NO_3)_2$ $NaNO_3$ - H_2O, $Pb(NO_3)_2$ - $CsNO_3$ - H_2O, $Pb(NO_3)_2$ - $LiNO_3$ - H_2O and $Pb(NO_3)_2$ - NH_4NO_3 - H_2O, by simply plotting the weight per cent of lead nitrate against weight per cent of alkali nitrate in the solution. Although it does not seem justifiable to compare weights of the nitrates of different metals with each other, because of their different atomic weights, it is found that the curves fall in the same order as in the method adopted here.

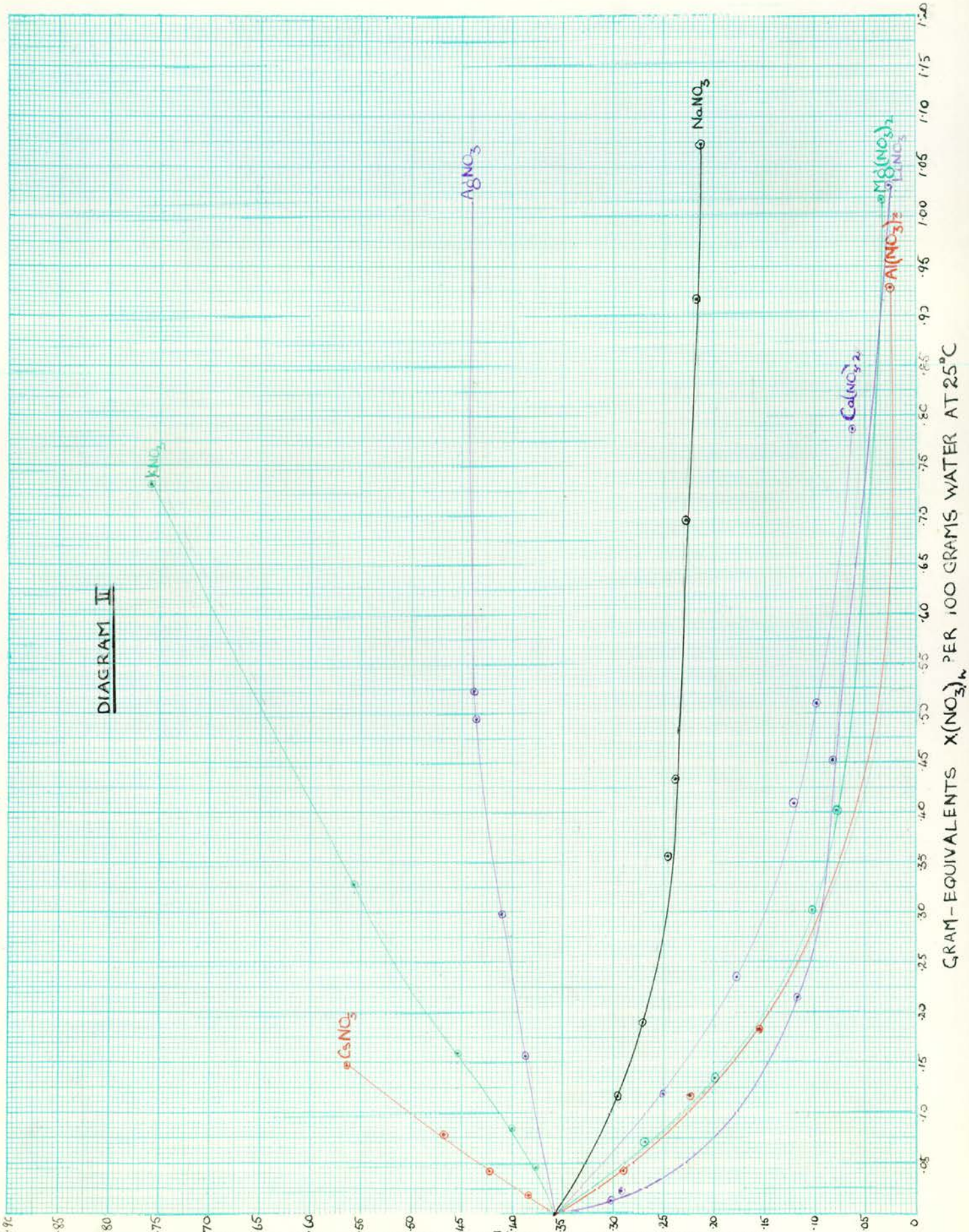


DIAGRAM II
GRAM-EQUIVALENTS $Pb(NO_3)_2$ PER 100 GRAMS WATER AT 25°C
GRAM-EQUIVALENTS $X(NO_3)_n$ PER 100 GRAMS WATER AT 25°C
$CsNO_3$
KNO_3
$AgNO_3$
$NaNO_3$
$Ca(NO_3)_2$
$Al(NO_3)_3$
$Mg(NO_3)_2$
$LiNO_3$

TABLE V.

Temperature 25° C

Gram-molecules per 100 grams water		Gram-equivalents per 100 grams water	
$Pb(NO_3)_2$	$NaNO_3$	$Pb(NO_3)_2$	$NaNO_3$
0.179	0.00	0.358	0.00
0.148	0.112	0.296	0.112
0.135	0.190	0.270	0.190
0.123	0.356	0.246	0.356
0.119	0.434	0.238	0.434
0.113	0.695	0.226	0.695
0.109	0.918	0.218	0.918
0.106	1.073	0.212	1.073
$Pb(NO_3)_2$	KNO_3	$Pb(NO_3)_2$	KNO_3
0.179	0.00	0.358	0.00
0.188	0.0455	0.376	0.0455
0.200	0.0848	0.400	0.0848
0.227	0.159	0.454	0.159
0.278	0.328	0.556	0.328
0.379	0.731	0.758	0.731

TABLE V

Temperature 25° C

Gram-molecules per 100 grams water		Gram-equivalents per 100 grams water	
$Pb(NO_3)_2$	$LiNO_3$	$Pb(NO_3)_2$	$LiNO_3$
0.178	0.00	0.356	0.00
0.151	0.0129	0.302	0.0129
0.146	0.0211	0.292	0.0211
0.0636	0.214	0.127	0.214
0.0409	0.452	0.0818	0.452
0.0141	1.031	0.0282	1.031
$Pb(NO_3)_2$	$CsNO_3$	$Pb(NO_3)_2$	$CsNO_3$
0.178	0.00	0.356	0.00
0.194	0.0185	0.384	0.0185
0.211	0.0411	0.422	0.0411
0.234	0.0790	0.468	0.0790
0.282	0.146	0.564	0.146
$Pb(NO_3)_2$	$AgNO_3$	$Pb(NO_3)_2$	$AgNO_3$
0.180	0.00	0.360	0.00
0.193	0.156	0.386	0.156
0.205	0.298	0.410	0.298
0.218	0.495	0.436	0.495
0.219	0.522	0.438	0.522
0.222	1.427	0.444	1.427

TABLE V

Temperature 25° C.

Gram-molecules per 100 grams water		Gram-equivalents per 100 grams water	
$Pb(NO_3)_2$	$Ca(NO_3)_2$	$Pb(NO_3)_2$	$Ca(NO_3)_2$
0.180	0.00	0.360	0.00
0.125	0.0598	0.250	0.119
0.0886	0.118	0.177	0.236
0.0605	0.205	0.121	0.410
0.0497	0.255	0.0994	0.510
0.0314	0.394	0.0628	0.788
$Pb(NO_3)_2$	$Mg(NO_3)_2$	$Pb(NO_3)_2$	$Mg(NO_3)_2$
0.180	0.00	0.360	0.00
0.134	0.0351	0.268	0.0702
0.0998	0.0674	0.199	0.134
0.0513	0.151	0.103	0.302
0.0397	0.201	0.0794	0.402
0.0174	0.509	0.0348	1.018
$Pb(NO_3)_2$	$Al(NO_3)_3$	$Pb(NO_3)_2$	$Al(NO_3)_3$
0.180	0.00	0.360	0.00
0.145	0.0164	0.290	0.0492
0.112	0.0392	0.224	0.118
0.0778	0.0609	0.155	0.183
0.0123	0.310	0.0246	0.930

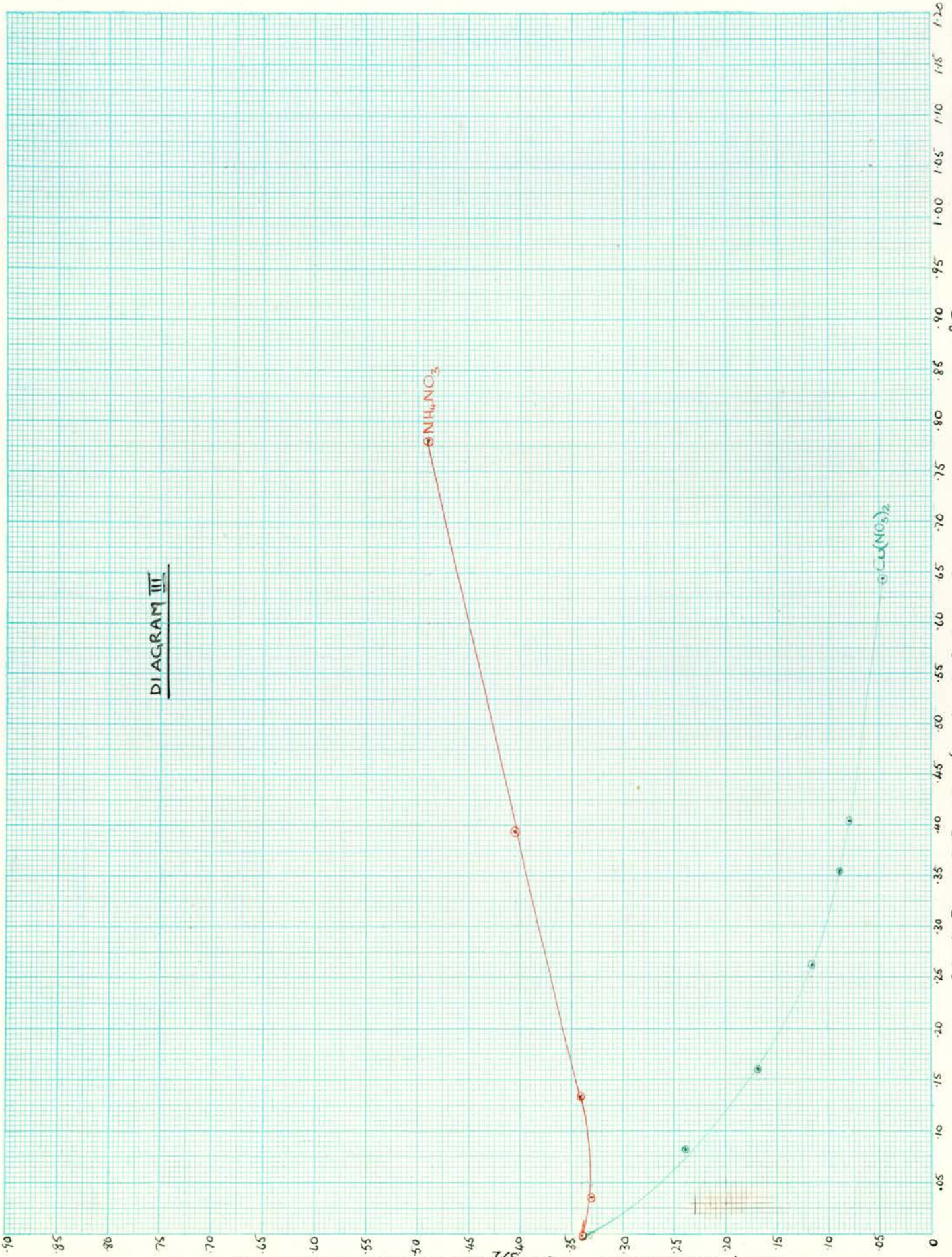


DIAGRAM III
NH_4NO_3
$Ca(NO_3)_2$
GRAM-EQUIVALENTS $Pb(NO_3)_2$ PER 100 GRAMS WATER AT 20°C
GRAM-EQUIVALENTS $X(NO_3)_n$ PER 100 GRAMS WATER AT 20°C

TABLE VI

Temperature 20° C.

Gram-molecules per 100 grams water		Gram-equivalents per 100 grams water	
$Pb(NO_3)_2$	NH_4NO_3	$Pb(NO_3)_2$	NH_4NO_3
0.170	–	0.340	–
0.165	0.0359	0.330	0.0359
0.170	0.136	0.340	0.136
0.202	0.394	0.404	0.394
0.245	0.781	0.490	0.781
0.341	1.688	0.682	1.688
$Pb(NO_3)_2$	$Cu(NO_3)_2$	$Pb(NO_3)_2$	$Cu(NO_3)_2$
0.166	–	0.332	–
0.119	0.0411	0.238	0.0822
0.0840	0.0802	0.168	0.1604
0.0575	0.131	0.115	0.262
0.0444	0.177	0.0888	0.354
0.0395	0.202	0.0790	0.404
0.0247	0.322	0.0454	0.644

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Diagram 2 shows the solubility of lead nitrate at 25°C, in presence of other nitrates, and at low concentrations of the added salts, to be in the order Cs > K > Ag > Na > Ca > Mg or Al > Li. The results are compared at low concentrations because under these conditions, disturbing factors must be at a minimum.

By this method of representing solubilities, we see that the solubility of lead nitrate, when expressed as gram-equivalents or gram-molecules per 100 grams of water, is raised by the addition of silver nitrate. Compound formation must take place between lead nitrate and silver nitrate in solution.

Sturenberg[40] stated in 1870 that, when a boiling concentrated solution of lead and silver nitrates was cooled in vacuo, he obtained crystals of a salt $Pb(NO_3)_2,2AgNO_3$. It is very probable, however, that what he obtained was a mixture of the two salts in approximately the proportions of one molecule of lead nitrate with two molecules of silver nitrate. The results of Malquori[11] and Fedotéeff[39] are shown in diagram 3. Addition of ammonium nitrate causes first a decrease and then an increase, and cupric nitrate a decrease, in the solubility of lead nitrate at 20°C. This shows that in aqueous solution there is compound formation between lead nitrate and ammonium nitrate at this temperature, but little, if any, between cupric nitrate and lead nitrate.

Diversity factor. The following table gives the electrode potentials of the metals which we are considering: that is the potential difference between the metal and a normal aqueous solution of its ions, referred to the normal hydrogen electrode as zero.

TABLE VI.

Li , Li^+	= + 2.96	volts.[41]
K , K^+	= + 2.92	"
Na , Na^+	= + 2.71	"
Pb , Pb^{++}	= + 0.12	"
Cu , Cu^{++}	= - 0.35	"
Ag , Ag^+	= - 0.80	"
Sr , Sr^{++}	= + 2.92	volts.[42]
Ba , Ba^{++}	= + 2.90	"
Ca , Ca^{++}	= + 2.87	"
Mg , Mg^{++}	= + 2.40	"
Al , Al^{+++}	= + 1.69	"

The order of the metals in the electrode potential series is therefore
Cs, Li, K and NH_4, Sr, Ba, Ca, Na, Mg, Al, Pb, Cu, Ag.
Although no value for the electrode potential of caesium is given, its position in the series is probably above that of lithium, because it is the most active of the alkali metals. Abegg[43] places ammonium close to

potassium in the series, although here again the electrode potential of ammonium cannot be determined.

The diversity factor is undoubtedly here, as in numerous examples of binary systems and in the ternary systems AgCl - MCl_x - H_2O and $PbCl_2$ - MCl_x -H_2O, a significant factor governing compound formation. It is only the nitrates of those metals which are very highly positive, e.g. caesium and potassium, or very highly negative, e.g. silver, which cause increases in the solubility of lead nitrate, indicating compound formation in solution.

However from diagram 2 the increase in solubility of lead nitrate at 25°C was found to be in the order Cs > K > Ag > Na > Ca > Mg or Al > Li. When this series is compared with that of the electrode potentials, it is obvious that there must be other factors acting, namely ionic size and valency. For example lithium nitrate decreases the solubility of lead nitrate instead of increasing it markedly as would be expected from its highly positive electrode potential. This clearly must be due to the ionic size factor, as lithium has the same valency and approximately the same electrode potential as potassium, but has a very small ionic radius.

Another discrepency is in the order of calcium and sodium in this series, when compared with the electrode potential series. As seen from diagram 2, calcium nitrate decreases the solubility of lead nitrate to a

much greater extent than does sodium nitrate, whereas sodium stands nearer to lead in the electrode potential series. The valency factor would appear to account for this as the ionic sizes of calcium and sodium are practically equal.

We may now proceed to discuss these factors in turn in greater detail.

Ionic size. In order to study this factor separately, we may take a series of metals whose electrode potentials are approximately equal, and whose valencies are the same. The alkali metals furnish such a series as each has an electrode potential of about + 2.9 volts (sodium has a slightly lower value + 2.7 volts) and a valency of one.

Pauling[44] gives the ionic radii of the metals with which we are concerned to be as follows:

TABLE VII

Li^+	0.60 Å	Mg^{++}	0.65 Å	Al^{+++}	0.50 Å
Na^+	0.95 "	Ca^{++}	0.99 "		
Ag^+	1.26 "	Sr^{++}	1.13 "		
K^+	1.33 "	Ba^{++}	1.35 "		
Cs^+	1.69 "	Pb^{++}	1.21 "		

From diagram 2 the order of solubility of lead nitrate in presence of the alkali nitrates is seen to be $Cs > K > Na > Li$. This is exactly in the order of their ionic radii. Glasstone and Saunders[10] and Malquori[12] explained this as being caused by the different

degrees in hydration of the alkali metal ions.

Sidgwick[45] regards hydration as the combination of water molecules by a co-ordination link to another atom. In the case of the hydration of a cation, this is accomplished by the oxygen of the water acting as a donor thus: $X^+ \longrightarrow \left[X \longleftarrow O\begin{matrix}H\\H\end{matrix}\right]^+$, and so forming a co-ordinate link. Now according to Fajans' theory the tendency of an ion to form a covalent link (that is, here the co-ordination link between oxygen and the cation) will increase (1) as the charge on the cation increases (2) as the size of the cation diminishes.

In the case of the alkali metals the charges on the cations are the same, so hydration should be in the following order: Li > Na > K > Cs as this is the order of their ionic radii, increasing from lithium to caesium.

Hydration of the cation of the alkali nitrate must have a two-fold influence on the solubility of lead nitrate. In the first place it removes some effective solvent, in the form of water molecules from the lead nitrate and therefore causes a decrease in its solubility. Secondly, the greater the hydration of the cation the less easily will it be able to form a covalent link with the ions or molecules of lead nitrate, as there is a limit to the number of covalent bonds that an ion can possess.

From these considerations it may be said that the larger the cation of the added nitrate, the greater is the tendency to compound formation in lead nitrate solutions -

other things being equal.

This explains why lithium nitrate shows no compound formation with lead nitrate although lithium is highly positive. The lithium ion is very small (0.60 Å) and, therefore, will be highly hydrated in solution.

The alkaline earth metals (calcium, strontium and barium) form another series which we may examine, as each has an electrode potential of approximately + 2.9 volts. Magnesium may also be compared with these metals although its electrode potential is slightly lower (+ 2.4 volts) than those of the others. They all have also the same valency of two.

Mixed crystals are formed in the two systems $Pb(NO_3)_2$ - $Sr(NO_3)_2$ - H_2O and $Pb(NO_3)_2$ - $Ba(NO_3)_2$ - H_2O, but this was not found to be the case in the systems $Pb(NO_3)_2$ - $Ca(NO_3)_2$ - H_2O, and $Pb(NO_3)_2$ - $Mg(NO_3)_2$ - H_2O.

According to measurements made by Vegard,[46] lead nitrate, barium nitrate, strontium nitrate and calcium nitrate form an isomorphous group, and show almost complete identity of crystalline form. Some isomorphous substances have the property of forming mixed crystals with another substance in the same group, but this is not possessed by all members in an isomorphous group. For example, although sodium chloride and potassium chloride have the same crystalline form, they do not form mixed crystals.

Kolthoff[47] points out that if the absolute size of the 'building stones' - i.e. if the sizes of the ions are

the same - in two isomorphous substances, then mixed crystal formation will take place. He states "it seems that mixed crystal formation is still possible if the radii of the ions do not differ by more than 15 per cent." This explains why sodium and potassium chlorides do not form mixed crystals (Na^+ = 0.95 Å: K^+ = 1.33 Å), as the difference in their ionic radii is greater than 15 per cent.

The condition is however fulfilled by the lead and strontium ions (1.21 Å and 1.13 Å respectively), and by the lead and barium ions (Ba^{++} = 1.35 Å). The difference between the sizes of the lead and the calcium ions (Ca^{++} = 0.99 Å) exceeds 15 per cent and so we should not expect that mixed crystals would be formed in the system $Pb(NO_3)_2$ - $Ca(NO_3)_2$ - H_2O. This agrees with the experimental evidence.

The difference in the effect of magnesium and calcium nitrates on the solubility of lead nitrate must be due mainly to the difference in hydration of the magnesium and calcium ions. The magnesium ion being the smaller (Mg^{++} = 0.65 Å : Ca^{++} = 0.99 Å) must be more highly hydrated than the calcium ion and consequently depresses the solubility to a greater extent.

Valency. Although sodium and calcium stand very near to one another in the electrode potential series, and sodium nearer to lead than is calcium, yet the addition of calcium nitrate causes a much greater

depression in the solubility of lead nitrate than does sodium nitrate.

The electrode potentials of sodium and calcium are very close, and their ionic radii approximately equal, but the charge on the nucleus of the calcium ion is twice that on the sodium ion nucleus. According to Fajans' distortion theory and Sidgwick's hydration theory, the hydration of the cation will increase as the charge on it becomes greater. Hence the calcium ion must be hydrated to a greater extent than the sodium ion, and as their electrode potentials are very close it would be expected that calcium nitrate would cause a greater depression than would sodium nitrate in the solubility of lead nitrate.

It follows that, if other factors be the same, there is a greater tendency to compound formation between lead nitrate and other nitrates in aqueous solution, the smaller the valency of the cation of the second nitrate.

We should predict in the system $Pb(NO_3)_2$ - $Al(NO_3)_3$ - H_2O that as the aluminium ion has a very small radius (0.50 Å), and its charge high (valency of three), that no compound formation would take place, and that the solubility of lead nitrate would be greatly depressed. An examination of isotherm 4 and diagram 2 shows that the experimental results agree with this expectation.

The results obtained by Malquori on adding ammonium nitrate are also those that would be anticipated. The ammonium ion must be large, and we should not

expect it to be highly hydrated, as the nitrogen must be covalently saturated. Its position in the electrode potential series is put close to that of potassium, and it has a valency of one. These factors all agree with the compound formation that is indicated by the isotherms of the system $Pb(NO_3)_2$ - NH_4NO_3 - H_2O [11] and by diagram 3. The cupric ion on the other hand has a valency of two, and is rather close to lead in the electrode potential series. From these two factors we should not expect compound formation to take place.

The factors dealt with however are not independent of each other. The size of an ion must depend to a great extent on the nuclear charge, that is on its valency. The higher the charge the greater will be the pull on the planetary electrons and therefore the greater the tendency for the ion to have a small radius.

The relation between ionic size and electrode potential can be seen when the ionising and electrode potentials of the alkali metals are compared. From their ionising potentials we see that the ease with which an electron is removed from the metal ($M\ (gas) = M^+(gas) + E^-(gas)$) is in the order $Li < Na < K < Rb < Cs$. The electrode potential is a measure of the ease with which the metals form ions and electrons in aqueous solution. This must involve also the hydration of the ion M^+. The lithium ion being the smallest attracts the water molecules most strongly.

This sets free a large amount of energy and the lithium reacts with water to give a high electrode potential in aqueous solution, instead of a low value as we should expect from its ionising potential.

S U M M A R Y.

The isotherms of the following ternary systems have been determined at 25°C :

(1) $Pb(NO_3)_2$ - $Ca(NO_3)_2$ - H_2O.

(2) $Pb(NO_3)_2$ - $AgNO_3$ - H_2O.

(3) $Pb(NO_3)_2$ - $Mg(NO_3)_2$ - H_2O.

(4) $Pb(NO_3)_2$ - $Al(NO_3)_3$ - H_2O.

There is little, if any, compound formation between lead nitrate, and calcium, magnesium and aluminium nitrates, but there is evidence of compound formation in solution in the case of the system $Pb(NO_3)_2$ - $AgNO_3$ - H_2O.

The following factors have been found to affect compound formation in solutions of lead nitrate when another salt containing a nitrate ion is added.

(a) Electrode potential. As a general rule the greater the difference in electrode potential between lead and the other metal the greater is the tendency to compound formation in solution.

(b) Ionic size. The larger the size of the cation of the added salt, the greater will be its tendency to compound formation, as hydration increases with diminution in the size of the ions.

(c) Valency. The greater the valency of the cation of the added salt the less the tendency to compound formation.

In conclusion, the writer wishes to express her thanks to Professor James Kendall for his valuable advice and encouragement during the course of this study, and to Dr W. F. Ehret for his guidance at the beginning of the research.

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