

atm. pressure, and from direct measurements of the compressions of these solutions, we have calculated the partial volumes of ammonium nitrate and of water in different solutions under pressure from atmospheric to 10 kilobars. The partial volumes of the salt do not exhibit the large increases with rising pressure that were observed in solutions of sodium chloride or potassium sulfate except in the case of the 15% solutions where a small increase is observed at low pressures. Indications are that above 5 kilobars the partial volume of the salt in solutions containing more than 15% of ammonium nitrate is independent of the concentration.

From these data, together with the values of the chemical potential of the salt and water in the solutions at room temperature and pressure, we have calculated exactly the solubility curve of ammonium nitrate and the freezing curve of ice_{VI} up to a pressure of 12 kb. and have constructed an equilibrium diagram for the system, $\text{NH}_4\text{NO}_3\text{-H}_2\text{O}$, under pressure. The solubility of ammonium nitrate decreases continuously as the pressure is raised, diminishing from 67.6% at atmospheric pressure to 43.6% at 5 kilobars, 29.7% at 10 kilobars, and 25.3% at 12.1 kilobars, the eutectic pressure. At three points, namely, the freezing pressure of a 15% solution, the pressure eutectic at 25°, and the concentration of the solution in equilibrium with NH_4NO_3 IV at 12,300 bars, we have checked the diagram by direct observations of equilibria and found very satisfactory agreement.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF DUKE UNIVERSITY]

THE SYSTEM LEAD ACETATE, ACETIC ACID, WATER¹

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In connection with the study of certain voltaic cells it was found desirable to have further information concerning the system lead acetate, acetic acid, water. Sandved² found that the solubility of lead acetate trihydrate in mixtures of acetic acid and water increases with the proportion of acetic acid. He found a transition point at which the percentage of lead acetate was 67.90. Beyond this transition point the solubility data were somewhat uncertain, but he considered that anhydrous lead acetate was the stable solid form. He pointed out, however, that his data do not prove the non-existence of acid lead acetates.

Davidson and McAllister³ studied the system lead acetate-acetic acid by the freezing point method. They obtained no evidence of solvates of lead

¹ Part of a thesis presented by Grady Tarbutton in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of Arts and Sciences of Duke University.

² Sandved, *J. Chem. Soc.*, 2971 (1927).

³ Davidson and McAllister, *THIS JOURNAL*, 52, 512 (1930).

acetate. The compound that crystallized on the lead acetate side of the eutectic point was the unsolvated compound. They reported difficulty in getting the lead acetate to crystallize from a supersaturated solution, and had no points between 49° and the eutectic, about 2° .

The authors have attempted to prepare the cell with an acetic acid— $\text{Pb(Hg)} \mid \text{Pb(C}_2\text{H}_3\text{O}_2)_2 \text{ Satd.} \mid \text{Pb(C}_2\text{H}_3\text{O}_2)_2 \text{ Satd., Hg}_2\text{(C}_2\text{H}_3\text{O}_2)_2 \mid \text{Hg}$ water mixture or pure acetic acid as the solvent, and with anhydrous lead acetate as the solid phase in equilibrium with the saturated solution. If the solid phase in this cell is unsolvated lead acetate, the electromotive force should be independent of the composition of the solution. Sandved's data indicated a range of compositions within which this might be expected to be true. It was found, however, that when the cells had attained equilibrium, the electromotive force varied with the composition of the solution throughout the entire range, indicating that the solid phase was solvated. A further investigation of the solubility of lead acetate in acetic acid—water mixtures was therefore undertaken.

It has been found that two others olvates of lead acetate beside the familiar trihydrate exist, $\text{Pb(C}_2\text{H}_3\text{O}_2)_2 \cdot 0.5\text{H}_2\text{O}$ and $\text{Pb(C}_2\text{H}_3\text{O}_2)_2 \cdot 0.5\text{HC}_2\text{H}_3\text{O}_2$. Anhydrous lead acetate in contact with a saturated solution is metastable.

Materials and Apparatus

Acetic Acid.—Chromic acid was added to c. p. glacial acetic acid in the proportion of 2 g. per 100 cc. and the acid distilled in an all-glass still. The first and last portions were rejected and about 80% collected.⁴ The melting point of the product varied from 15.0 to 15.6° for different preparations.

For the experiments in which an acetic acid preparation of very small water content was desired, the water was removed from the purified acid by distilling with acetic anhydride. The quantity of water present was calculated from the freezing point,⁵ and the required quantity of acetic anhydride added. Chromic acid was added as a catalyst, 2 g. per 100 cc., and the mixture refluxed for thirty minutes and then distilled, with protection from moisture.⁶ The freezing point of the product was 16.48° as compared with 16.6° for pure acetic acid according to De Visser.⁷

Lead Acetate.—Some of the lead acetate was prepared by recrystallizing c. p. material three times. Other preparations were made by adding lead carbonate or litharge in excess to glacial or 6 molar acetic acid. The solution was concentrated by evaporation and crystallized. The product was recrystallized twice from dilute acetic acid solution.

Anhydrous Lead Acetate.—Several methods for the dehydration of lead acetate were tried. The trihydrate was kept in a vacuum over concentrated sulfuric acid with some glacial acetic acid present for eighteen days. After fourteen days it seemed to lose no more weight, but it still contained considerable water. In an oven at 40° with a current of dry air passing over it, the trihydrate lost most of its water in four or

⁴ Orton and Bradfield, *J. Chem. Soc.*, **125**, 960 (1924).

⁵ Seidell, "Solubilities," D. Van Nostrand Company, New York, 2d ed., Vol. I, p. 5.

⁶ Orton and Bradfield, *J. Chem. Soc.*, 983 (1927).

⁷ De Visser, *Rec. trav. chim.*, **12**, 118 (1893).

five days. The most satisfactory method when completely anhydrous lead acetate was desired was first to dry the trihydrate in a porcelain dish placed 45 cm. above a hot-plate, then fuse the product, a small quantity at a time. The water present boiled off and the salt resolidified. It was then heated again to fusion and poured into the acetic acid in which it was to be dissolved. Attempts to fuse the trihydrate without the preliminary dehydration resulted in charring.

Apparatus.—An electrically controlled oil thermostat having a capacity of about 50 gallons was used for maintaining constant temperature. The temperature was measured either by a thermometer certified by the Bureau of Standards, reading to 0.01° , or by one certified by the Physikalisch-Technische Reichsanstalt and correct to $\pm 0.02^\circ$. The temperature did not fluctuate more than $\pm 0.02^\circ$.

A device for agitating samples in the bath was constructed of a circular brass plate 14 cm. in diameter mounted on a shaft and having eight holes near its outer edge. In these holes test-tubes, 1.6×15 cm., could be mounted securely by means of cork stoppers. The shaft was suspended in the thermostat from another shaft by means of belts passing over pulleys on the two shafts. The samples to be analyzed were sealed in test-tubes and mounted in the disk parallel to the shaft and the whole device was made to rotate slowly in the bath.

Volumetric apparatus and weights were calibrated.

Methods of Analysis

Determination of Acetic Acid in the Presence of Lead Acetate.—When acetic acid in a solution containing a lead salt is to be titrated with standard sodium hydroxide solution, the lead must be removed before titration. It was found that lead can be removed satisfactorily as the oxalate by slowly adding an excess of a neutral solution of potassium oxalate and allowing the mixture to stand for three hours before titrating. No difficulty was found in getting a sharp end-point with phenolphthalein as the indicator. Experiments showed that the interference of lead acetate could be entirely prevented by this method.

Determination of Lead Acetate.—To a weighed sample of the solution to be analyzed was added 10 cc. of concentrated sulfuric acid and 10 cc. of concentrated nitric acid. The solution was slowly evaporated, without boiling, until fumes of sulfur trioxide were noticeable. It was then diluted to 100 cc. and allowed to cool to room temperature, when an equal volume of alcohol was added. The lead sulfate was filtered off, using either a Munroe or porcelain Gooch crucible, washed with 50% alcohol, dried at 110° to constant weight and weighed.

Solubility Determinations.—To prepare a saturated solution, a quantity of lead acetate was first dissolved at an elevated temperature in a mixture of acetic acid and water. The proportions were adjusted on the basis of preliminary experiments so that on bringing the temperature to 25° and seeding, a considerable excess would crystallize out,⁸ but not so much that sampling the solution was difficult. Portions of the supersaturated solution were then sealed in test-tubes along with some seed

⁸ Sandved found difficulty in getting lead acetate to crystallize from solutions of high acetic acid content. In this investigation not much trouble was experienced in this respect. A highly supersaturated solution was allowed to stand at room temperature for about twenty-four hours, and a large quantity of crystals was obtained. These crystals were preserved and used to seed other solutions. Crystals are obtained easily on seeding with the proper crystal form.

crystals. The tubes were rotated in the thermostat at 25° until equilibrium was attained.

It was found that equilibrium was reached within eight days if the excess solid was allowed to separate from the supersaturated solution at room temperature before placing in the thermostat, or within fourteen days if allowed to crystallize in the thermostat. It was shown that the same final state was attained by both methods. The samples selected for these experiments were among the most viscous. In view of the above results, all other samples were allowed to crystallize at room temperature and remain in the thermostat for at least fourteen days before analyzing.

At the proper times the test-tubes containing the samples were removed from the rotating device and clamped in an upright position in the bath. After allowing the solution to drain from the sides of the tube, the top was

TABLE I
ANALYSIS OF SATURATED SOLUTION AND WET SOLID

Sample	Sample, g.	0.2731 N NaOH, cc.	PbSO ₄ , g.	HC ₂ H ₃ O ₂ , %	Pb(C ₂ H ₃ O ₂) ₂ , %
Satd. solution No. 13	1.4251	21.00	0.9079	24.15	68.31
		20.96	.9082	24.10	68.34
Wet solid No. 13	1.6982	21.25	1.1490	20.50	72.55
		21.25	1.1490	20.50	72.55

TABLE II
SOLUBILITY DETERMINATIONS AT 25°

Sample	Saturated solution			Wet solid			Solid phase
	HC ₂ H ₃ O ₂ , %	Pb(C ₂ H ₃ O ₂) ₂ , %	H ₂ O, %	HC ₂ H ₃ O ₂ , %	Pb(C ₂ H ₃ O ₂) ₂ , %	H ₂ O, %	
1	8.21	35.44	56.35	1.45	77.33	21.22	Pb(C ₂ H ₃ O ₂) ₂ ·3H ₂ O
2	19.14	39.13	41.73	3.33	78.29	18.38	Pb(C ₂ H ₃ O ₂) ₂ ·3H ₂ O
3	26.91	47.11	25.98	10.99	70.00	19.01	Pb(C ₂ H ₃ O ₂) ₂ ·3H ₂ O
4	26.55	57.38	16.07	13.28	71.19	15.53	Pb(C ₂ H ₃ O ₂) ₂ ·3H ₂ O
5	22.15	68.06	9.79	11.15	77.78	11.07	} Pb(C ₂ H ₃ O ₂) ₂ ·3H ₂ O + Pb(C ₂ H ₃ O ₂) ₂ ·0.5H ₂ O
6	22.40	67.75	9.85	15.20	76.93	7.87	
7	23.25	68.13	8.62	17.31	75.54	7.15	Pb(C ₂ H ₃ O ₂) ₂ ·0.5H ₂ O
8	23.07	68.15	8.78	17.53	75.30	7.17	Pb(C ₂ H ₃ O ₂) ₂ ·0.5H ₂ O
9	23.25	68.15	8.60	7.27	88.43	4.30	Pb(C ₂ H ₃ O ₂) ₂ ·0.5H ₂ O
10	23.28	68.06	8.66	16.26	76.65	7.09	Pb(C ₂ H ₃ O ₂) ₂ ·0.5H ₂ O
12	24.11	68.35	7.54	21.46	71.67	6.87	Pb(C ₂ H ₃ O ₂) ₂ ·0.5H ₂ O
13	24.13	68.33	7.54	20.50	72.55	6.95	Pb(C ₂ H ₃ O ₂) ₂ ·0.5H ₂ O
14	25.89	69.10	5.01	23.29	71.76	4.95	Pb(C ₂ H ₃ O ₂) ₂ ·0.5H ₂ O
15	25.59	70.12	4.29	23.34	72.57	4.09	Pb(C ₂ H ₃ O ₂) ₂ ·0.5H ₂ O
16	25.50	70.54	3.96	18.61	77.78	3.61	Pb(C ₂ H ₃ O ₂) ₂ ·0.5H ₂ O
17	25.49	70.81	3.70	15.75	81.20	3.05	Pb(C ₂ H ₃ O ₂) ₂ ·0.5H ₂ O
18	25.51	70.71	3.78	19.63	77.00	3.37	Pb(C ₂ H ₃ O ₂) ₂ ·0.5H ₂ O
19	25.20	71.54	3.26	19.27	77.59	3.14	Pb(C ₂ H ₃ O ₂) ₂ ·0.5H ₂ O
22	30.94	66.00	3.06	18.56	80.77	0.67	Pb(C ₂ H ₃ O ₂) ₂ ·0.5HC ₂ H ₃ O ₂
23	31.71	65.66	2.63	23.70	74.54	1.76	Pb(C ₂ H ₃ O ₂) ₂ ·0.5HC ₂ H ₃ O ₂
24	40.19	58.29	1.52	20.69	78.51	0.80	Pb(C ₂ H ₃ O ₂) ₂ ·0.5HC ₂ H ₃ O ₂
25	41.82	57.06	1.12	22.41	76.85	.74	Pb(C ₂ H ₃ O ₂) ₂ ·0.5HC ₂ H ₃ O ₂
26	44.56	54.95	0.49	Pb(C ₂ H ₃ O ₂) ₂ ·0.5HC ₂ H ₃ O ₂

opened and as much of the liquid as possible drawn through a filter device (which had been brought to the bath temperature) into a small weighed flask. The test-tube containing the remaining wet solid was weighed, and after dissolving out the solid and drying, the empty tube was weighed.

The samples of both saturated solution and wet solid were diluted to 500 cc., and 100-cc. portions were measured out for analysis. Determinations of acetic acid and lead were made in duplicate by the methods described above. Results of duplicate determinations did not differ by more than two parts in a thousand in any case. The details of a typical analysis are given in Table I, the mean values of the results of all the analyses are given in Table II and are represented graphically in Fig. 1 by the method of Roozeboom.⁹ The compositions of the solid phases were determined graphically from a large-scale plot.¹⁰

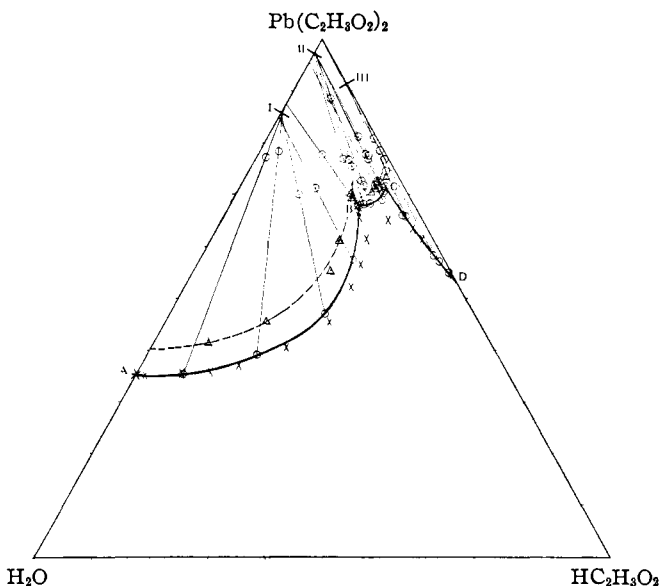


Fig. 1.—Composition of saturated solutions and solid phases. The results obtained at 30° are designated by triangles, those at 25° by circles and Sandved's results at 25° by crosses. The composition $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$ is designated by I, $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 0.5\text{H}_2\text{O}$ by II and $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 0.5\text{HC}_2\text{H}_3\text{O}_2$ by III.

Points I, II and III of Fig. 1 are the theoretical points for the compounds $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$, $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 0.5\text{H}_2\text{O}$ and $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 0.5\text{HC}_2\text{H}_3\text{O}_2$, respectively. Compounds II and III have not been reported before as far as the authors are aware.

⁹ Roozeboom, *Z. physik. Chem.* 15, 147 (1894).

¹⁰ Findlay, "The Phase Rule," Longmans, Green and Co., Ltd., London, 6th ed., 1927, p. 263.

Compound I, $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$, is well known and needs no discussion. It exists in stable equilibrium at 25° with solutions in which the ratio of acetic acid to water by weight is less than 2.3. The value for the solubility in pure water in Fig. 1 was taken from Jackson's¹¹ data.

Compound II, $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 0.5\text{H}_2\text{O}$, consists of thin needles, usually small when first formed but on standing in contact with a saturated solution they sometimes grow to about 12 mm. in length. This compound is capable of existing in stable equilibrium at 25° with saturated solutions in which the ratio of acetic acid to water is between 2.3 and 7.7. Solutions in equilibrium with Compound II are quite viscous, and it was difficult to separate a large proportion of the mother liquor from the solid phase. On this account the extrapolation from the composition of the wet solid to that of the dry solid was rather long.

To check the graphic extrapolation, the percentage of water was calculated from the analysis of each of Samples 7-19 by the algebraic extrapolation method described by Hill and Ricci.¹² Assuming that the compound contained no acetic acid, the average value for the percentage of water was 2.64, with an average deviation from the mean of ± 0.66 , as compared with the theoretical value of 2.69%. That Compound II was a solvated lead acetate was shown also by the variation of the electromotive force with the composition of the solution when voltaic cells were made with Compound II as the solid phase.

Compound III, $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 0.5\text{HC}_2\text{H}_3\text{O}_2$, can exist in stable equilibrium with solutions in which the ratio of acetic acid to water is larger than 7.7. The points representing the compositions of the saturated solutions and the solid phases lie so close to the side of the triangle that small errors in composition make a relatively large uncertainty in the convergence point.

In fact algebraic extrapolation showed that the solubility measurements were not sufficiently precise for the establishment of a formula. Therefore a direct analysis of the solid phase was made. The sample was dried in a vacuum desiccator over sodium hydroxide.¹³

Compound III is quite different in crystalline form from Compounds I and II; it crystallizes in plates. Its solubility decreases rapidly as the concentration of water approaches zero.

Several times when fused lead acetate was dissolved in acetic acid of small water content and the solution cooled, the crystals formed were thin needles and the mother liquor was extremely viscous. Only once in five times was Compound III obtained under these conditions. After that,

¹¹ Jackson, *THIS JOURNAL*, **36**, 50 (1914).

¹² Hill and Ricci, *ibid.*, **53**, 4306 (1931).

¹³ Calculated for $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 0.5\text{HC}_2\text{H}_3\text{O}_2$, lead acetate 91.58%; acetic acid 8.42%; found, lead acetate, 90.52, 90.53%; acetic acid, 8.92, 8.86%.

supersaturated solutions were seeded when Compound III was desired, and no trouble was experienced in getting it.

When a sample of the fine needle crystals in contact with a saturated solution was seeded with Compound III, the whole mass changed over to the plate form, showing that the latter form is the more stable. Anhydrous lead acetate did the same. It seems probable that the fine needle crystals are the anhydrous form and that it was this form that Davidson and McAllister obtained in their freezing point determinations. It was impossible to make a precise analysis of the solution saturated with the needle crystals because the very high viscosity interfered too much with filtration. The solution saturated with Compound III was much less viscous and gave no trouble.

A series of solubility determinations was made at 30.00° before all of the technique described above was perfected. The results are sufficiently precise, however, to give an idea of the effect of temperature on the solubility. The solutions were saturated by stirring mechanically for about fourteen days. It was found that at least ten days was required for constancy in acetic acid content to be attained. Samples were taken and analyzed as in the case of the solutions saturated at 25°. The results are given in Table III and by the broken line in Fig. 1.

TABLE III

COMPOSITION OF SATURATED SOLUTIONS OF LEAD ACETATE IN ACETIC ACID AT 30°

Sample	HC ₂ H ₃ O ₂ , %	Pb(C ₂ H ₃ O ₂) ₂ , %	H ₂ O, %	Sample	HC ₂ H ₃ O ₂ , %	Pb(C ₂ H ₃ O ₂) ₂ , %	H ₂ O, %
A	9.64	41.61	48.75	G	20.49	69.27	10.24
B	17.47	45.81	36.72	H	24.36	73.50	2.14
C	23.78	55.43	20.79	J	23.66	72.13	4.21
D	22.45	63.08	14.47	K	19.92	70.18	9.90
E	23.86	71.08	5.06	L	23.39	70.45	6.16
F	25.40	69.45	5.15				

The results given in Table III are subject to uncertainty in at least some cases. Some of the solutions were prepared with dried lead acetate. The anhydrous salt changed over to the stable form, but in at least one case the transition was incomplete. The values for solutions in equilibrium with the trihydrate are probably reliable since the trihydrate was used for saturating the solutions.

It was found to be quite difficult to prepare saturated solutions of lead acetate in fairly concentrated acetic acid at room temperature that would be saturated at 30° and yet not contain too much solid phase. The trouble arose because of the large increase of solubility with temperature.

Summary

The existence of the compounds $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 0.5\text{H}_2\text{O}$ and $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 0.5\text{HC}_2\text{H}_3\text{O}_2$ has been shown.

The former compound can exist in equilibrium with saturated solutions at 25° in which the ratio of acetic acid to water is between 2.3 and 7.7 by weight, and the latter can exist in equilibrium with saturated solutions in which the ratio is larger than 7.7.

Anhydrous lead acetate in contact with a saturated solution is metastable.

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

THE ACTIVATION OF MOLECULAR OXYGEN BY ELECTRON IMPACT

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Introduction.—In the case of hydrogen² it was found that electrons of 11.4 e. volts or greater energy can transfer hydrogen molecules to an excited state ($^1\Sigma_g^+ \longrightarrow ^3\Sigma_g^+$) and that such molecules can react with a copper oxide plate. Thus hydrogen molecules need not be ionized; excited states serve equally well as activated species. These studies were continued on oxygen and in the meantime Dalton³ reported that oxygen molecules, activated by 8-volt electrons, react with a carbon surface. Wansbrough-Jones⁴ studied the activation of oxygen, and detected no ozone below 25 e. volts nor below 0.8 mm. pressure. L. A. M. Henry⁵ found however formation of ozone at much lower pressures than did Wansbrough-Jones, reporting critical voltages of 9.0 and 21.2 e. volts. In our own investigations on oxygen which were begun before any of the papers cited above appeared, it was decided to study the formation of ozone and the chemical reaction between a mercury surface and oxygen activated by electron impact and other materials. Since our results differ to some extent from those in the literature, they are reported in this paper. We have extended also the mode of interpretation of such experiments and interpret them in terms of efficiencies of energy transfer and of reaction.

Experimental Procedure

Both static and flow methods were used. At first we followed the reaction by freezing out the product formed and determined its behavior with potassium iodide solution. Such experiments, however, were not very reproducible although we obtained

¹ This article is based upon a thesis presented to the Faculty of the Graduate School of the University of Minnesota by John L. Wilson in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

² Glockler, Baxter and Dalton, *THIS JOURNAL*, **49**, 58–65 (1927).

³ Dalton, *ibid.*, **51**, 2366–2374 (1929).

⁴ Wansbrough-Jones, *Proc. Roy. Soc. (London)*, **127A**, 530–539 (1930).

⁵ Henry, *Bull. soc. chim. Belg.*, **40**, 339–360 (1931).