forces may well prove inadequate for extremely small ions. Unfortunately, such salts are not usually soluble, particularly in solvents of lower dielectric constant. The fact remains that in liquid ammonia, at any rate, a dissociation constant of approximately 10×10^{-4} is about the lower limit of this constant for ordinary electrolytes, which corresponds to an a-value of about 3×10^{-8}. It is only the acids and bases that exhibit extremely low K-values, and it may well be that quantum mechanical forces are here involved.

V. Summary

The electrical conductance of the following electrolytes has been measured in liquid ammonia: sodium phenyl amide, sodium diphenyl amide, sodium triphenylboron ammide, potassium diphenyl amide, and potassium triphenylboron ammide.

The dissociation constants have been evaluated. They range from 8.2×10^{-4} for sodium phenyl amide to 150×10^{-4} for sodium triphenylboron ammide. The dissociation constant increases with increasing size of the negative ion. The results are in agreement with the theory developed by Bjerrum and by Fuoss and Kraus, which attributes the process of ion association to Coulomb forces.

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[CONTRIBUTION FROM THE T. JEFFERSON COOLIDGE, JR., MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

The Atomic Weight of Lead from Katanga Pitchblende

BY GREGORY P. BAXTER AND CHESTER M. ALTER

The atomic weights of several samples of lead from uranium ores occurring in East Africa have already been determined. Hönigschmid and St. Horowitz[1] obtained their material from selected crystals of uraninite from Morogoro. Hönigschmid and Birckenbach[2] used material which had been extracted from the yellow and green secondary minerals associated with Katanga pitchblende. Richards and Putzeys[3] started with metal extracted from a mixture of primary and secondary minerals from Katanga. Perette[4] determined the densities of common lead and a specimen extracted from Katanga pitchblende.[3]

		Atomic weight
Hönigschmid and St. Horowitz	Morogoro	206.046
Hönigschmid and Birckenbach	Katanga	206.048
Richards and Putzeys	Katanga	206.20
Perette	Katanga	206.14

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(1) Hönigschmid and St. Horowitz, *Sitzber. Kais. Akad. Wiss. Wien.*, **123**, 19 (1914).

(2) Hönigschmid and Birckenbach, *Ber.*, **56**, 1837 (1923).

(3) Richards and Putzeys, THIS JOURNAL, **45**, 2954 (1923).

(4) Perette, *Compt. rend.*, **180**, 1589 (1925).

Of the two varieties of material, that from Katanga is more interesting for the present purpose since the Katanga pitchblende is nearly free from thorium, whereas the Morogoro uraninite contains several tenths of a per cent. of thorium.[5] Barring secondary alteration and contamination, the lead from Katanga pitchblende should represent nearly pure uranium lead.

Through Professor Alfred C. Lane, Chairman of the Committee of the National Research Council on the Measurement of Geologic Time, we were fortunate enough to secure a fine specimen of pitchblende from Katanga. The specimen weighed 550 g. and was apparently nearly free from secondary products. Microscopic examination by Professors Lindgren and Newhouse of Massachusetts Institute of Technology, who prepared a polished section, showed the black base to be intimately veined by a softer, yellow substance occupying 5 to 10% of the polished area. This has already been noted by Davis,[6] who found the yellow substance to be readily soluble in dilute hydrochloric acid, while the black pitchblende dissolves very slightly, if at all.

It is a matter of speculation whether the yellow material is the result of infiltration and deposition or is the product of alteration within the mineral. Since the Pb/U ratio is appreciably higher for the yellow than for the black material this is a matter of considerable importance in age estimation. Most analysts have cleaned the mineral with hydrochloric acid in preparation for analysis.[6,7] Since we have found the atomic weight of the lead in the yellow material to be even lower than that in the black, the advisability of this procedure is at any rate open to question.

At the outset we decided to attack the problem in such a way that the final result could be expressed with reference to the mineral as a whole or to the yellow and black components. About four-fifths of the original specimen was first broken into small pieces with a clean hammer and then was finely ground in a previously cleaned Quaker mill. This treatment was followed by further powdering with a hammer on a steel plate and finally the product was ground in small portions in an agate mortar until the largest particles were not over 0.1 mm. in greatest dimension, while by far the larger part consisted of particles not more than 0.01 mm. in greatest dimension. In this way nearly all the softer yellow material was mechanically separated from the black, a result to be expected from the structure of the mineral.

Four hundred and six grams of the powdered mineral were digested for twenty minutes on a steam-bath with 5% hydrochloric acid, the resulting yellow solution was decanted and the residue washed with hot water. The treatment with hydrochloric acid was then repeated. The second acid extract was much less highly colored than the first, and a third extract of a small portion was only very slightly yellow, so treatment was discontinued. After thorough washing and collecting, the black residue was dried and found to weigh 313.5 g., or 77.2% of the original.

Petrographic examination of the residue by Professor E. S. Larsen failed to indicate any of the yellow material. While the separation of the yellow thus seems to have been

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[5] Bull. Nat. Research Council, "Physics of the Earth, IV, The Age of the Earth," 1931, pp. 367, 369.

[6] Davis, *Am. J. Sci.*, [5] **11,** 201 (1926).

[7] Fenner, *ibid.*, [5] **16,** 382 (1928).

complete, the possibility remains that the acid extraction removed lead from the black residue.

At this point a rough analysis of the black residue for lead and uranium was carried out. From a sample weighing 1.0019 g. the weights of $PbSO_4$ and U_3O_8 obtained were 0.0983 g. and 0.8848 g., respectively, whence the corresponding percentages of lead and uranium are 6.7 and 74.9 and the Pb/U ratio 0.089.

The lead was then extracted from 200 g. of the black residue. The material was dissolved in 8*n* nitric acid and the solution was filtered. Evaporation with an excess of sulfuric acid followed. After extraction with dilute sulfuric acid the lead sulfate was dissolved in ammonium acetate, the solution was filtered, and the lead sulfate was again precipitated by evaporation with sulfuric acid. The weight of lead sulfate obtained, 19.64 g. or 6.7%, agrees with that to be expected from the analysis of the small sample. Further purification of the lead was effected according to the following outline: (1) conversion of sulfate to carbonate by metathesis with sodium carbonate, (2) solution of the carbonate in nitric acid, (3) five crystallizations of the nitrate from concentrated nitric acid in quartz vessels, (4) conversion of nitrate to chloride by evaporation with hydrochloric acid in quartz, (5) five crystallizations of the chloride in quartz, (6) two distillations of the chloride in a current of dry hydrogen chloride in a quartz tube. This material was used in Analyses 1 and 2. A second sample was obtained from the combined mother liquors of the nitrate and chloride crystallizations by five crystallizations as nitrate and five as chloride. This was used in Analysis 3.

The greater portion of the lead contained in the hydrochloric acid solution of the yellow material crystallized as chloride on cooling. This was once recrystallized, collected, dried and weighed (8.15 g.). The remainder was converted to sulfate by evaporation, dissolved in ammonium acetate, precipitated as chromate, washed, collected and dried (2.72 g.). Since the weight of yellow material was 92.5 g., the percentage of lead was 8.4. The solution from which the lead had been removed was diluted to 2000 ml. and in a rough determination of uranium in a 50-ml. portion, 1.594 g. of U_3O_8 was obtained. The percentage of uranium is therefore 58.5 and the Pb/U ratio 0.144, nearly twice that of the black material.

If the mineral is taken as a whole the percentages of lead and uranium are 7.1 and 71.2 and the Pb/U ratio is 0.100, about ten per cent. higher than the ratio for the insoluble part.

The lead chloride obtained from the hydrochloric acid extract was converted to nitrate by evaporation with nitric acid. The chromate was converted to carbonate by metathesis with sodium carbonate and this carbonate was dissolved in nitric acid. The two portions of nitrate were then combined and subjected to five crystallizations from nitric acid in quartz. Conversion to chloride was followed by five crystallizations as chloride, twice in quartz and three times in platinum. The chloride was finally twice distilled in a current of hydrogen chloride. This material was used in Analyses 4 and 5.

As soon as these analyses had been completed the resulting lead nitrate solution was freed from silver with hydrochloric acid and combined with the mother liquors of the original nitrate and chloride crystallizations. After conversion to chloride by evaporation with hydrochloric acid, the lead was precipitated as sulfide from dilute acid solution. The sulfide was filtered and dissolved in hydrochloric acid and then converted to nitrate. Further purification followed the outline given above. This material was used in Analyses 6 and 7.

For purposes of comparison, experiments were carried out with lead from Bedford cyrtolite and with common lead.[8] The cyrtolite lead was purified as described in the preceding paragraph. Common lead chloride,

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(8) Baxter and Alter, THIS JOURNAL, **55**, 1445 (1933); *Science*, **76**, 524 (1932).

from Coeur d'Alêne lead–silver ores was crystallized three times as nitrate and five times as chloride, and finally was twice distilled. This material was provided through the courtesy of Dr. J. P. Marble and Mr. A. D. Bliss. Mr. Bliss has already found the atomic weight of this lead to be 207.218.[9]

Acids and water were purified by distillation. Other reagents were proved to be lead-free before use. Centrifugal drainage of crystals followed by centrifugal rinsing in platinum baskets was always used in order to secure maximum efficiency of each crystallization. Pure silver was prepared by methods found by past experience to be adequate.[10]

The lead chloride was ordinarily prepared for weighing by fusion in a weighed quartz boat in a quartz bottling apparatus in an atmosphere of dry hydrogen chloride and was allowed to solidify only after nearly all the hydrogen chloride had been displaced by nitrogen. In Analysis 9, of common lead chloride, the fused salt was allowed to solidify in hydrogen chloride. In Analysis 10, of common lead chloride, the fusion atmosphere was nitrogen containing a few per cent. of hydrogen chloride and the salt solidified only after the greater part of the hydrogen chloride had been displaced by nitrogen. After the nitrogen had been displaced by air the boat was transferred to the weighing bottle and weighed.

Solution of the salt was effected in hot water containing a trace of nitric acid, in such volume that the final solution was from 0.02 to 0.1 normal. Precipitation followed with a weighed nearly equivalent amount of pure silver dissolved in an equal volume of dilute nitric acid. The silver solution was added to the chloride in all experiments except Analysis 5, where the reverse method was followed. Precipitations were carried out at room temperature.

The end-point of the comparison was found by the equal opalescence method, the final observations being made from six to twelve weeks after precipitation, although only small changes occurred after the first week or two. Ordinarily the solutions were not chilled before removing samples for the nephelometer tests. This was done, however, in Analyses 6 and 8 after the end-point had been adjusted.[11] In these cases nephelometric tests, after the portions removed had been brought to room temperature, yielded the same results as tests made without chilling.

In Analysis 10 after the end-point had been found, the supernatant solution was replaced by an equivalent solution of chloride-free lead nitrate and nitric acid.[12] This solution when tested was found to have equivalent chloride and silver concentrations and a repetition of the replacement yielded the same result. A saturated solution of silver chloride in such a

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(9) Baxter and Bliss, THIS JOURNAL, **52**, 4848 (1930).

(10) For an outline, see Baxter and Ishimaru, *ibid.*, **51**, 1729 (1929).

(11) See Richards and Willard, *ibid.*, **32**, 16 (1910).

(12) Johnson, *J. Phys. Chem.*, **35**, 2237, 2581 (1931).

solution behaves therefore normally with respect to the equal opalescence end-point.

Because the sensitiveness of the equal opalescence method has recently been subject to severe adverse criticism by Briscoe, Kikuchi and Peel[13] and by Johnson,[14] we have made experiments to test this sensitiveness in one of the experiments with common lead chloride.

In the following table the history of the tests made in this analysis is given in chronological sequence. The second column gives the ratio of the length of the exposed column of the nephelometer tube to which excess silver was added to that of the other tube. In the curve is plotted nephelometric ratio against excess silver per liter. Correction has been made for material removed in the tests. Since the curve evidently passes close to the intersection of the axes the assumption of the deficiency of 0.06 mg. of silver after the sixth test appears to be justifiable. It also appears that an addition of silver of 0.1 mg./liter near the end-point will alter the nephelometric ratio by about 10%, an amount considerably larger than the error in determining the ratio.

Pptd. Jan. 11, 1933	Time after precipitation, days	Nephelometric ratio		Ag added after test, mg.	Net excess Ag after addn., mg.	Volume after addn. of Ag, ml.	Excess Ag per liter after addn., mg.
		I	II				
Jan. 14	3	0.87		+0.15			
Jan. 20	9	.96		.00			
Jan. 24	13	.91	0.90	+ .15	−0.06[a]		−0.03
Jan. 28	17	.98		.00			
Feb. 3	23	1.00		.00			
Feb. 20	40	0.98		.00			
Mar. 18	66	.95		− .20	− .26	1950	− .13
Mar. 20	68	.81		+ .40	+ .14	1920	+ .07
Mar. 21	69	(.95)		.00		1890	
Mar. 23	71	(.97)	(1.06)	.00		1830	
Mar. 25	73	1.14	1.13	.00		1770	
Mar. 27	75	1.11	1.09	− .20	− .06	1710	− .04
Mar. 31	79	0.94	0.90	.00		1650	
Apr. 6	85	.93	.92	− .60	− .66	1590[b]	− .38
Apr. 17	96	.66	.70	.00		1730	
Apr. 20	99	.66		+1.20	+ .58	1700	+ .34
Apr. 22	101	1.20	1.18	.00		1640	
Apr. 26	105	1.21	1.12	− .60	− .09	1580	− .06
Apr. 28	107	0.90	0.98	.00		1520	
May 4	113	.94	.94	−1.20	−1.28	1460	− .88
May 9	118	.50	.50	+2.40	+1.18	1400	+0.84
May 15	124	1.67	1.68	0.00			
May 23	132	(1.33)	(1.30)	.00			
June 8	148	1.69	1.62	.00			

[a] Assumed. [b] 200 ml. of water added at this point.

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(13) Briscoe, Kikuchi and Peel, *Proc. Roy. Soc.* (London), **A133**, 440 (1931).

(14) Johnson, *J. Phys. Chem.*, **36**, 1942 (1932).

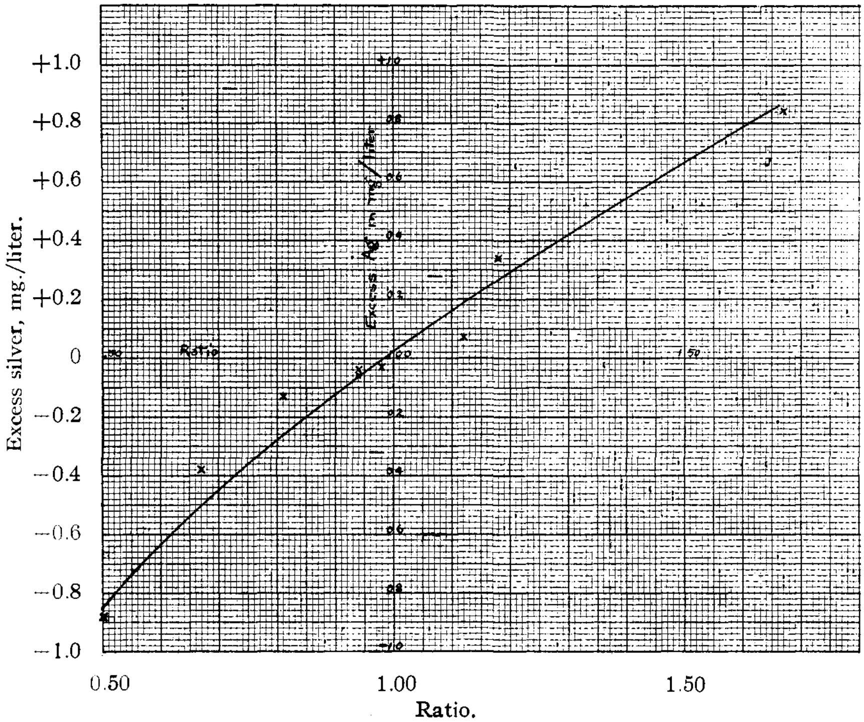

Fig. 1.

The small weighing bottle and boat were weighed by substitution with the use of a similar counterpoise. The system remained remarkably constant in weight, for the net change in weight in 8 analyses was only

TABLE I

THE ATOMIC WEIGHT OF LEAD

		Ag = 107.880				Cl = 35.457	
No. of analysis	Source of $PbCl_2$	$PbCl_2$ in vacuum, g.	Ag in vacuum, g.	Ag added, mg.	Corr. wt. of Ag in vacuum, g.	Ratio $PbCl_2$:2Ag	Atomic weight of Pb
1	Katanga	4.57229	3.56311	−0.50	3.56261	1.28341	205.995
2	Pitchblende	6.20083	4.83183	− .40	4.83143	1.28344	206.001
3		4.45460	3.47074	+ .20	3.47094	1.28340	205.992
						Average	205.996
4	Katanga	2.62575	2.04595	+0.20	2.04615	1.28326	205.962
5	Pitchblende extract	3.75342	2.92474	.00	2.92474	1.28333	205.977
6		3.28347	2.55847	+ .20	2.55867	1.28327	205.964
7		3.19222	2.48780	− .35	2.48745	1.28333	205.977
						Average	205.970
8	Bedford cyrtolite	0.59044	0.46025	−0.10	0.46015	1.28315	205.938
9	Common	2.56818	1.99194	+ .40	1.99234	1.28903	207.207
10		4.34481	3.37040	+ .10	3.37050	1.28907	207.216
						Average	207.212

+0.02 mg. Silver was weighed by substitution for weights. Vacuum corrections of +0.058 mg. and −0.031 mg. were applied for each gram of lead chloride and silver, respectively.

The results obtained with common lead are nearly identical with the value approved by the International Committee on Atomic Weights, 207.22. The agreement of these values indicates that little is to be feared from retention of hydrogen chloride from the fusion atmosphere by lead chloride.

The value obtained with lead from Bedford cyrtolite is essentially identical with that from two of the four earlier experiments and only 0.01 unit higher than a third. The average of all five experiments with this material is 205.93 and is probably nearer the truth than the former average 205.92.

The lead from the black Katanga pitchblende insoluble in dilute hydrochloric acid seems to have an atomic weight, 205.996, definitely higher than that contained in the yellow material soluble in dilute hydrochloric acid, 205.970. The average value for the combined yellow and black portions is 205.99. The significance of the difference is not apparent, especially if the two sorts of material are of equal age. If, as may be presumed, the yellow material is of more recent date than the black, the two obvious possibilities are (1) infiltration from the outside and deposition, (2) alteration of the original mineral owing to decay of uranium and production of lead. The former requires an external source of lead of atomic weight 205.97. In the absence of detailed information as to the occurrence of this particular specimen of Katanga pitchblende it is impossible to decide definitely between the two possibilities although it seems to us more probable that the yellow material is an alteration product in spite of the fact that this hypothesis does not explain the difference in atomic weights. This difference may be due to different rates of decay of different isotopes of uranium. On the basis of experimental values for uranium leads v. Grosse[15] has already suggested that U^{239} possesses a greater rate of decay than U^{238} and therefore that the lead from older uranium minerals should possess a higher atomic weight than that from younger. If the yellow material was formed from the black it might be supposed to contain lead of an average age greater than that contained in the black material. Since the atomic weight of the lead from the yellow material is the lower, this point of view is not in accord with v. Grosse's hypothesis.

There is also the possibility, as suggested to us by Professor Lane, that some leaching process in the past has contributed an unknown factor. The whole situation is evidently far from clear.

If this Katanga lead contains chiefly the isotopes Pb^{206} and Pb^{207} in the proportions found by Aston,[16] 14 to 1, the low value 205.90–205.92 results for the isotopic weight of Pb^{206}.

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(15) V. Grosse, *Phys. Rev.*, **42**, 565 (1932).

(16) Aston, *Nature*, **129**, 649 (1932).

The experimental results of the foregoing investigation have yielded the atomic weights of different varieties of lead as follows:

	Atomic weight
Common	207.21
Bedford cyrtolite	205.94
Katanga pitchblende	206.00
Katanga pitchblende extract	205.97

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Notes

The Specific Heat of Sorbed Matter

BY J. L. PORTER AND R. C. SWAIN[1]

The heat capacity of a substance varies considerably with the state. A study of the heat capacity of matter in the sorbed state should give some indication of the state of the sorbed molecules, whether they can move freely, vibrate, rotate, or show still more restricted motion, and also the strength or type of binding of the sorbed molecules to the solid. When the molecule is sorbed, certain degrees of freedom may be "frozen out" or suppressed.

The specific heat of bound water in crystalline hydrates is found to be about the same, in a number of hydrated salts, as that of ice, which is about half that of liquid water. The partial molal heat capacity of water in 25 mole per cent. hydrochloric acid solution is about two-thirds that of pure liquid water,[2] presumably because the permanent dipole of the water molecule is oriented and also attracted to the ion. Bridgman[3] found that at 0° and under an external pressure of 4000 kg./sq. cm. C_p of water is 0.92 calories and at 0° and 6000 kg./sq. cm. pressure C_v of water is 0.85 calories.

In connection with his studies on the sorption of water by charcoal, one of us (J. L. P.) prepared a system consisting of 6 g. of water sorbed in 18 g. of highly active sugar charcoal. Dr. S. B. Thomas then undertook measurements of the heat capacity of this system and, while the investigation encountered unforeseen difficulties, he was able to obtain a value of about 8.5 (±0.1) calories for this system in the neighborhood of 10°. If we then assume that the charcoal in this system has the same heat capacity per gram as graphite, we have left about 5.6 (±0.2) calories as the heat capacity of the 6 g. of sorbed water. Hence the water in this system seems to be essentially in the state of the ordinary liquid rather than in that of

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(1) National Research Fellow in Chemistry.

(2) By the graphical method of Lewis and Randall on the data in the "International Critical Tables," 1929, Vol. V, p. 85.

(3) P. W. Bridgman, *Proc. Am. Acad. Arts Sci.*, **48**, 359 (1912).