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ATTEMPTS TO FRACTIONATE MIXED ISOTOPES OF LEAD, AND THE ATOMIC WEIGHT OF THIS METAL

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The investigations of others[1] having yielded conflicting results concerning the possibility of separating mixed isotopes of lead, this further research (begun[2] in 1918) was undertaken with the hope of obtaining definitive evidence.

That the separation or "resolution" of isotopes presents a difficult problem is well known. Apparently the chief and perhaps the sole differences between isotopes in their chemical and physical behavior exist in properties dependent upon mass and weight. The theoretically possible methods of separation include counter-current diffusion, thermal diffusion, centrifugal diffusion, irreversible evaporation or condensation, and perhaps any chemical reactions in which differences of mass and therefore of inertia or gravitation might be effective.

Many of the more recent investigations of others have been published since the present work began. Nevertheless their results, at least as regards the isotopes of lead, have not been sufficiently definitive to make further research needless. Lead presents a more difficult problem than

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[1] (A) On lead and its isotopes, see (a) Soddy, *Nature*, **94**, 615 (1915); "Annual Reports on the Progress of Chemistry for 1916," Gurney and Jackson, London, **13**, 247 (1917). (b) Richards and Wadsworth, THIS JOURNAL, **38**, 221 (1916). (c) Richards and N. F. Hall, THIS JOURNAL, **42**, 1555 (1920). (d) Atkinson, *Nature*, **112**, 282 (1923); **113**, 495 (1924). (e) Brennen, *Ann. chim.*, [10] **4**, 149 (1925); *Compt. rend.*, **180**, 282 (1925). (f) Joly and Poole, *Phil. Mag.*, [6] **39**, 372 (1920). (g) Pfeiffer and Truskier, *Ber.*, **37**, 1125 (1904). (h) Hofmann and Wölfl, *Ber.*, **40**, 2425 (1907). (i) Ebert, *Ion*, **2**, 277 (1910). (j) Staehling, *Compt. rend.*, **157**, 1430 (1913). (k) Dillon, Clarke and Hinchy, *Sci. Proc. Roy. Dublin Soc.*, **17**, 53 (1922).

(B) On the theory and separation of isotopes, see (l) Strutt, The Rt. Hon. John William, 3d Lord Rayleigh, *Phil. Mag.*, [5] **42**, 493 (1896). (m) Hertz, *Wied. Ann.*, **17**, 177 (1882). (n) Langmuir, *Phys. Rev.*, [2] **2**, 329 (1913). (o) Knudsen, *Ann. Physik*, [4] **47**, 697 (1915). (p) Mulliken and Harkins, THIS JOURNAL, **44**, 37 (1922). (q) Chapman, *Phil. Mag.*, [6] **38**, 182 (1919). (r) Lindemann and Aston, *Phil. Mag.*, [6] **37**, 523 (1919); Aston, *ibid.*, [6] **39**, 449 (1920). (s) Harkins, *Science*, **51**, 289 (1920); Harkins and Hayes, THIS JOURNAL, **43**, 1803 (1921). Harkins and Jenkins, *ibid.*, **48**, 58 (1926). Harkins and Madorsky, *ibid.*, **45**, 591 (1923); and others. (t) Brönsted and Hevesy, *Nature*, **106**, 144 (1920); **107**, 619 (1921); **109**, 780 (1922); *Z. physik. Chem.*, **99**, 189 (1921). (u) Egerton, *Nature*, **110**, 773 (1922); Egerton and Lee, *Proc. Roy. Soc.*, **103A**, 499 (1923). (v) Hönigschmid and Steinheil, *Ber.*, **56B**, 1831 (1923).

(C) For an excellent, but brief review of the subject of separation of isotopes, see Soddy, "Annual Reports on the Progress of Chemistry for 1920," Gurney and Jackson, London, **17**, 225 (1921). Aston, *ibid.*, **19**, 276 (1922); **21**, 245 (1924).

[2] Richards and Schumb, THIS JOURNAL, **40**, 1409 (1918).

most of the other substances concerned, because of its high atomic weight, the slight difference in the atomic mass in the two most important isotopes, the non-volatility of most of its compounds, and the difficulty of determining with accuracy such separation as might be effected.

On account of the great molecular weights concerned, and therefore the slight percentage difference of mass between similar compounds of isotopes, any method depending on mere diffusion (even of lead tetramethyl) seemed hardly worth attempting.

Among the processes involving vapor phase, that of irreversible evaporation seemed the most likely to yield satisfactory results. The chemical method, having been claimed by some to effect considerable separation, also needed further investigation. Therefore these two methods form the subject of the present research. It was not hoped that anything beyond a barely perceptible difference would be found between fractions prepared by either method. Nevertheless, both demanded further trial.[3]

As will be seen, the pessimistic expectation was verified: the outcome was negative. Even such a result, however, is not without value. In addition, the investigation yielded an exact determination of the atomic weight of ordinary lead, which we find to be 207.217.

Irreversible Evaporation

According to this method, the substance to be evaporated is heated in a high vacuum, in which the mean free path of the evaporating molecules is longer than the space between the heated substance and the condensing surface. Thus the molecules, as they evaporate, fly at once to the condensing surface and remain there without the possibility of returning to the hot surface from which they have been emitted. Irving Langmuir suggested to us the desirability of using this method, which apparently has not yet been applied by others to metallic lead.

Ordinary lead, if it consists of two or more isotopes, should furnish excellent material for the test; but its isotopic composition was (and still is) uncertain. Nevertheless, its atomic weight (207.2) seems to indicate that this element is not "simple," since elements of high atomic number (beyond 21) which are known to be simple have without exception atomic weights *less* instead of *more* than whole numbers.[4] This conclusion is based upon Aston's work,[5] although he has not yet been able certainly to resolve ordinary lead by his actinographic mass spectra.[6] Evidence

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[3] The separation of the several fractions and the experiments concerning density were carried out by H. S. King; the purification of the products and the atomic weight determinations were effected by L. P. Hall, du Pont Fellow at Harvard University, 1923-24.

[4] See, for example, Richards and L. P. Hall, THIS JOURNAL, **48,** 704 (1926).

[5] Aston, numerous papers in *Phil. Mag.* and *Nature,* 1919-1920; and "Isotopes," E. Arnold and Co., London, **1925.**

[6] Aston, *Phil. Mag.,* [6] **49,** 1191 (1925).

as to its complexity is, however, furnished by the observations of Grebe and Konen who, in examining twenty lines in the band spectra of ordinary lead and of uranium lead, found that the lines from the former were less sharp than those from the latter.[7] Russell,[8] among others, has predicted that ordinary lead is a mixture, with mass numbers from 204–210.

In default of certainty, however, there remained two problems to be treated: first, is ordinary lead iostopic? and second, is either method proposed capable of separating isotopes in a specimen positively known to contain at least two? Accordingly, two series of trials were made, one series starting with ordinary pure lead, and the other with a mixture of this substance with much uranium-lead.

Experimental Details

The evaporation was conducted within a large, stout Pyrex bulb by means of electrically generated heat. The metal was placed in an inverted porcelain crucible-cover fitting into the top of a quartz frame, upon which was wound a heating coil of Nichrome ribbon—the whole being supported by a tungsten-steel rod attached to the accurately ground glass stopper of the bulb, whose wide neck was clamped in a horizontal position. The stopper (which was lubricated with a mixture of soft paraffin and melted rubber) bore also, through appropriate sealed joints, the stout wires conducting electricity to the heating unit. A sealed-in glass tube led to a Langmuir mercury-vapor pump backed by a Gaede and a Nelson pump. To prevent back-diffusion of mercury vapor into the bulb a trap immersed in carbon dioxide snow and alcohol was introduced between the stopper and the mercury pump. Before assembling the apparatus the bulb was thoroughly heated to drive off adsorbed moisture and air.

In each evaporation dealing with ordinary lead, about 22 g. of the pure metal was placed on the crucible cover. The bulb was then evacuated, and heated above to drive off any further adsorbed material, until no glow was caused by an induction spark. After the immersion of the bulb in a tank containing cold water, the lead was melted; and after about 30 minutes of further evacuation to remove traces of evolved gas, the fused metal was raised in temperature until it began to evaporate very slowly. Condensation occurred in a well-defined spot on the upper inside surface of the bulb; evidently there was but little diffusion of lead vapor. Heating for about an hour yielded a layer of lead opaque to the red glow of the heating coils below, whereupon the heating current was broken. Upon cooling and opening the apparatus, the condensed lead was dissolved by dil. nitric acid.

Knudsen[10] has found that a thin scum of impurity greatly retards evap-

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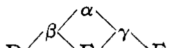
[7] Grebe and Konen, *Physik. Z.*, **22**, 546 (1921).

[8] Russell, *Nature*, **112**, 619 (1923).

oration. Hence the surface of the melted lead was kept bright by a very small quantity of potassium cyanide. This flux was first melted on the porcelain, wetting its surface. The trace of flux appeared not to spread over the metallic surface (which remained brilliantly clean), but rather clung to the porcelain. At the low temperature employed the potassium cyanide did not affect the high vacuum appreciably.

Thirteen hundred and sixty g. of pure, ordinary lead (A) was subjected to this treatment, of which a total of 31 g. (C) volatilized in 61 separate distillations, leaving 1.3 kg. of residue (B). In every case the temperature was kept below red heat.

Only 80 g. of lead of radioactive origin was available (atomic weight 206.4, from Australian carnotite).[1c] Hence the method was modified with this specimen. Twenty-g. samples were successively heated at about the same moderate temperature until about half of each had evaporated—an extremely laborious process. Each fraction was again separated into two fractions in like manner. The process may be represented by the following diagram.



The comparison of the products B, C, D, E and F is discussed later.

Fractionation by the Grignard Reaction

There is good reason for believing that the Pfeiffer-Truskier reaction,[9] $2PbCl_2 + 4RMgBr = Pb + PbR_4 + 2MgCl_2 + 2MgBr_2$, occurs in two stages. If the reaction between phenylmagnesium bromide and plumbous chloride is restrained by lowering the temperature, the deep red diphenyl lead is formed. This red color often appears in the early stages of the reaction even when the temperature is not reduced, showing that PbR_2 may be an intermediate product; thus: $2RMgBr + PbCl_2 = PbR_2 + MgCl_2 + MgBr_2$. Judging from its experimentally observed molecular weight (from 378 to 416) this substance PbR_2 may be somewhat associated. If so, there must exist in the solution an equilibrium, as follows: $2PbR_2 \rightleftharpoons R_2PbPbR_2$, and the associated molecule may be the intermediate in the production of PbR_4, thus: $R_2PbPbR_2 \rightleftharpoons Pb + PbR_4$. If the two lead atoms were identical, one would be as likely to take the metallic form as the other. If the two lead atoms were isotopic, one having a greater mass than the other, there might be a slight difference in this respect. Though this effect of mass would be extremely small, it might be perceptible. Because of the conflicting results of previous investigations and because of the above theoretical considerations, the Grignard method of fractionation seemed to deserve further investigation.

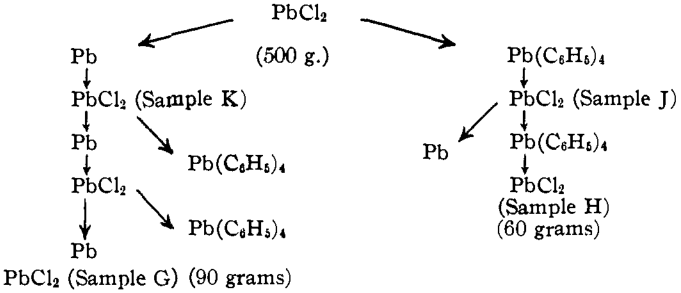
[9] In *Chem. Rev.*, **2**, 43 (1925), Calingaert presents a convenient summary of this topic.

The reagent used in the present work was that employed in the experiments of Hofmann and Wölfl, of Ebert, and of Staehling, namely, phenylmagnesium bromide.[1h,i,j] The methyl or the ethyl derivative would have been preferable experimentally, but seemed to involve unwarranted physiological danger. The Grignard reagent was prepared as follows: 565 g. of dry bromobenzene was added gradually to 87.4 g. of fine magnesium turnings in 1435 g. of dry ether and refluxed on a warm water-bath with the usual precautions to insure absence of moisture. A crystal of iodine was added to start the reaction, which was carried as nearly as possible to completion.

Pure lead chloride, after recrystallization from distilled water acidified with hydrochloric acid, was dried, fused in a current of dry hydrogen chloride and ground to a very fine powder. Two portions of 250 g. each of this product were added gradually to two equal portions of the Grignard reagent, refluxing was continued for several days, with frequent shaking, and the major part of the ether was then distilled. The residue was barely moistened with water and extracted with benzene, in which tetraphenyl lead is soluble. After the benzene had been removed from the extract by evaporation, the crude tetraphenyl lead was dissolved in carbon tetrachloride; subsequently the solution was heated and saturated with chlorine gas, when the solvent was distilled from the resulting lead chloride. The residue was heated with concd. sulfuric acid (with the addition of nitric acid, a few drops at a time, during the heating) until residual carbon compounds had been oxidized. The resulting lead sulfate was converted into lead carbonate by several treatments with boiling sodium carbonate solution. Lead nitrate was formed from this carbonate and its solution filtered; the metal was then reprecipitated as carbonate and again converted into chloride. The product, after being dried and fused in a current of dry hydrogen chloride, was very finely powdered (Sample J).

The residue from the benzene extraction (which contained metallic lead together with a quantity of the original unchanged lead chloride) was wholly dissolved in hot, concd. nitric acid and heated to "dryness" with concd. sulfuric acid; the resulting lead sulfate was treated as that described in the previous paragraph had been,—the final product being again dry, finely-ground lead chloride (Sample K).

For further fractionations several modifications in the procedure were adopted. It was found that carbon compounds could be removed more easily from the lead sulfate by means of potassium dichromate than by nitric acid, during the heating with sulfuric acid. Several experiments were performed with the object of making the Grignard reaction more complete, especially by raising the temperature of reaction. The substitution of *iso*-amyl ether for ethyl ether was not effective, but benzene gave more satisfactory results. After the ethyl ether had been distilled from the Grignard reagent, dry benzene was substituted for the latter before adding the lead chloride, and the reaction was effected over a steam-bath. The extraction of the resulting tetraphenyl lead was made less difficult by the addition of dil. hydrochloric acid after the excess of the Grignard reagent had been decomposed with water. This dissolved the sludge of magnesium hydroxide which otherwise coated the tetraphenyl lead, hindering its extraction. A diagram of the successive stages of fractionation follows.



Analysis of the Several Fractions

The following preparations were thus available for analysis: A, the original pure ordinary lead; B, residue from volatilization of ordinary lead; C, volatilized ordinary lead; D, extreme residue from volatilization of mixture containing lead of radioactive origin; E, middle fraction (twice volatilized) of this mixture; F, most volatile fraction (twice volatilized) of this mixture; G, extreme lead fraction from ordinary lead chloride treated by Grignard reagent (thrice fractionated); H, extreme lead-tetraphenyl fraction from ordinary lead chloride treated by Grignard reagent (twice fractionated).

For detecting a possible difference in isotopic proportions between these specimens, several methods of quantitative estimation were considered. Ordinary methods for the determination of density of solids are not sufficiently exact. Accordingly, two different types of comparative methods, dependent on density, were investigated in the hope of finding one with the necessary degree of accuracy for the determination of very slight differences in density.

First, the densities of saturated solutions of the lead salt to be tested were compared by means of floating equilibrium.[10] Since the more concentrated a solution, the more significant are such density determinations, lead perchlorate was used, because of its great solubility.[11] However, it is extremely difficult, if not impossible, to prepare this salt in a perfectly pure state, because of decomposition on dehydration. Other lead salts

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[10] Richards and Harris, THIS JOURNAL, **38**, 1000 (1916).

[11] Sérullas, *Ann. chim. phys.*, **46**, 306 (1831).

either resemble the perchlorate in this respect, or else are too slightly soluble to be used for the purpose in hand. Hence this method was abandoned.

Next, a method was devised for the comparative determination of the densities of different specimens of solids by supporting like weights on two precisely similar completely immersed floats, by the method of floating equilibrium. This method worked very well; the difficulty now became that of preparing different samples of any given specimen of metal so that they should have precisely the same density. The specific gravities of solids are notoriously ill defined.

While possibly the difficulty might have been overcome by continued research, this method also was abandoned in favor of the determination of a property already well tested, namely, atomic weight. It was hoped that by uniformity in execution of processes already well-known, accidental errors could be largely eliminated; thus the averages of several series of results could be compared with confidence even if there were a constant error, and thus very small differences might be detected.

Because descriptions of the methods used in the determination of the atomic weight of lead have frequently been published,[12] most of the details may be omitted here. Many precautions were taken to insure accurate results; in particular, every specimen involved in any given comparison was treated as nearly as possible in the same manner. New apparatus was constructed for the preparation of pure dry hydrogen chloride, dry nitrogen and dry air, all used in the treatment of lead chloride. These gases were rendered dust-free by passage through a fine porous cup.[13]

All reagents were purified according to the usual methods. Redistilled nitric acid and water were always tested nephelometrically and proved free from chloride. Fused silica or platinum vessels were employed for solutions. Pure silver was prepared[14] by repeated crystallizations of the nitrate, reduction by ammonium formate, electrolysis, fusion in a hydrogen atmosphere on a boat of pure lime, and desiccation in a vacuum at 400°.

Each sample, the metal or its chloride, resulting from the treatment of ordinary lead was purified by conversion to nitrate with recrystallization, precipitation as sulfate, conversion to carbonate by the action of purified

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[12] (a) Baxter and Wilson, THIS JOURNAL, **30**, 187 (1908). (b) Baxter and Thorvaldson, *ibid.*, **37**, 1020 (1915). (c) Baxter and Grover, *ibid.*, **37**, 1027 (1915). (d) Richards and Lembert, *ibid.*, **36**, 1329 (1914). (e) Richards and Wadsworth, *ibid.*, **38**, 2613 (1916). (f) Richards and N. F. Hall, *ibid.*, **39**, 536 (1917). (g) Richards and Sameshima, *ibid.*, **42**, 928 (1920). (h) Richards and Putzeys, *ibid.*, **45**, 2954 (1923). (i) Hönigschmid and Horovitz, *Monatsh.*, **36**, 355 (1915).

[13] Richards, Köthner and Tiede, THIS JOURNAL, **31**, 13 (1909). Richards and Cox, *ibid.*, **36**, 821 (1914).

[14] Richards and Wells, THIS JOURNAL, **27**, 473 (1905). Baxter and Grover, *ibid.*, **37**, 1056 (1915).

sodium carbonate followed by many washings, solution of the carbonate in nitric acid with five recrystallizations, and precipitation as chloride, followed by three recrystallizations. Centrifugal drainage was used throughout.

With each sample obtained from the irreversible evaporation of the mixture containing lead of radioactive origin, the purification was somewhat modified, although all were treated similarly. On account of the small amount of these specimens only three recrystallizations of nitrate were performed in each case, after the solution of the carbonate in nitric acid. Here, however, additional purification of the lead was introduced by precipitating it from the third crystals of nitrate as chloride, converting it again to nitrate (which was once recrystallized), and finally once more precipitating as chloride (which was thrice recrystallized). Such a succession of metatheses has been found to be a very efficient means of eliminating impurities.[12h] The final step of purification for every sample was the distillation of the dried lead chloride in a quartz apparatus.[15]

In some cases (Analyses 6, 13, 17, 18, 21, 22) the lead chloride thus obtained was weighed out directly, since it was found not to be hydroscopic. In two others (Analyses 3 and 4), it was fused again in an atmosphere of hydrogen chloride gas, while contained in a silica boat enclosed in the familiar bottling apparatus,[16] and cooled in that gas. In all the other cases, the salt was fused in an atmosphere of hydrogen chloride (likewise in the bottling apparatus), but while the salt was still molten, this gas was almost wholly displaced by nitrogen. Both these gases were always swept away by pure dry air after cooling, before the substance was enclosed in the weighing tube. These differences of procedure were arranged so as not to interfere logically with the comparison of the different samples of lead. As will be seen, the samples all gave practically the same result, but even if they had not done so, any difference between the different kinds of lead would not have been concealed.

The ratio of the several specimens of pure lead chloride thus obtained to metallic silver was determined by weighing nearly equivalent portions of these two substances, dissolving them respectively in hot water (with a trace of nitric acid) and in moderately concentrated nitric acid (later diluting greatly) and then, after cooling and completely mixing the two (0.03 *N*) solutions in a large glass-stoppered flask, by determining the end-point nephelometrically in the usual fashion. All this work was done in a deep red light.

The concomitant precipitation (adsorption or occlusion) of lead salts by silver chloride is well known. In connection with this disturbing circumstance, a special study was made of the time required to free as much as possible of this imprisoned impurity from the silver chloride. For

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[15] Ref. 12 i, p. 370.

[16] Richards and Parker, *Proc. Am. Acad. Arts Sci.*, **32,** 53 (1896).

ordinary purposes the end-point is reached in a few hours with moderate shaking; for most determinations of atomic weights a few weeks and occasional shaking may suffice; but for work of the precision now desired several months may be necessary. Usually, no change in the end-point occurred after a month, but in a few cases a change as large as one or two tenths of a milligram occurred after three or four months. Every solution (scrupulously protected from actinic light) was required to give a constant end-point for a month before its final condition was estimated. A long time seems to be needed for the diffusion of the occluded matter through the very small pores of the cheesy precipitate; too much shaking may even retard the process by prematurely consolidating the precipitate. In spite of the prolonged treatment above mentioned, the spectroscopic examination of the precipitated silver chloride showed that it still contained a small quantity of lead.[17] Judging from the relative intensities of the lines in the spectra, this amount was less than 0.001%. Continued washing of the precipitate made no difference, since similar samples, washed, respectively, 10 times, 15 times and 30 times by decantation, all showed indistinguishably similar spectra. While perhaps affecting somewhat the absolute value of the atomic weight of any such case, this occluded lead salt could hardly have affected the comparison of the different specimens of lead, because the quantity of the impurity in the precipitate must have been nearly the same in every case. The correction (if any) to be applied to the final value of the atomic weight is undetermined because there appears to be no means of knowing whether the lead is present as chloride or nitrate. If in the latter condition, the occlusion would, of course, make no difference in the atomic weight.

Four preliminary trials (1, 2, 3 and 4) showed that the methods were satisfactory and had been sufficiently mastered. They yielded, to be sure, results slightly lower than the later analyses; in previous investigations also the early analyses were usually too low. Such preliminary investigations are not worthy to be included in the final estimate of an atomic weight.

All weighings were reduced to the vacuum standard, 0.058 mg. being added for each gram of lead chloride and 0.031 being subtracted for each gram of silver. Silver and chlorine were assumed to have respectively the atomic weights 107.880 and 35.458. The data and results follow.

The experiments summarized below make possible, as has been said, several conclusions with regard to variations of treatment as well as concerning the main points at issue. Thus a comparison of the average result (207.212) of Analyses 1 and 2 (from which hydrogen chloride had been eliminated while the salt was still fused) with the result (207.208) of Analyses 3 and 4 (in which the salt was solidified while still in contact with the acid gas) may indicate that the latter contained a trace of residual hydro-

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[17] We are indebted to Professor G. P. Baxter for this examination.

TABLE I

PRELIMINARY ANALYSES

Analysis	Wt. of $PbCl_2$ in a vacuum	Wt. of Ag in a vacuum	At. wt. of lead
1	5.80433	4.50278	207.210
2	5.88331	4.56400	207.214
			Av. 207.212
3	6.15400	4.77405	207.210
4	6.63841	5.14990	207.207
			Av. 207.208
			Av. 1–4 207.210

TABLE II

ATOMIC WEIGHT OF RESIDUE FROM VOLATILIZATION OF ORDINARY LEAD. SAMPLE B

5	6.34617	4.92305	207.214
7	5.94908	4.61505	207.212
8	6.06445	4.70447	207.216
9	5.43000	4.21211	207.229
			Av. 207.218
6	5.35480	4.15388	207.222
13	5.62478	4.36351	207.209
			Av. 207.216
			Total av. 207.217

TABLE III

ATOMIC WEIGHT OF VOLATILIZED FRACTION OF ORDINARY LEAD. SAMPLE C

10	5.60375	4.34708	207.217
11	5.53665	4.29505	207.215
12	5.62345	4.36242	207.213
14	4.34037	3.36694	207.223
			Av. 207.217

TABLE IV

ATOMIC WEIGHT OF FRACTIONS OF MIXTURES CONTAINING URANIUM LEAD OBTAINED BY IRREVERSIBLE EVAPORATION

Sample D	23	4.68864	3.64742	206.436
	24	5.40318	4.20337	206.431
				Av. 206.434
Sample E	25	3.75115	2.91811	206.438
	26	4.16937	3.24344	206.439
				Av. 206.438
Sample F	27	4.85385	3.77601	206.431
	28	4.70148	3.65750	206.430
				Av. 206.431
				Av. of 23–28 206.434

TABLE V

ATOMIC WEIGHT OF LEAD FROM GRIGNARD PROCESS: EXTREME LEAD FRACTION

SAMPLE G

Analysis	Wt. of $PbCl_2$ in a vacuum	Wt. of Ag in a vacuum	At. wt. of lead
15	5.98464	4.64259	207.215
16	4.60637	3.57327	207.224
			Av. 207.219
17	7.55415	5.86020	207.212
18	4.57721	3.55077	207.215
			Av. 207.214
			Av. 15–18 207.217

TABLE VI

ATOMIC WEIGHT OF LEAD FROM GRIGNARD PROCESS: EXTREME TETRAPHENYL FRACTION

SAMPLE H

19	4.39785	3.41161	207.217
20	6.61651	5.13269	207.218
			Av. 207.218
21	4.35602	3.37909	207.222
22	3.85162	2.98786	207.218
			Av. 207.220
			Av. of 19–22 207.219

gen chloride, although these experiments were only preliminary. Accordingly with all subsequent preparations the method of Analyses 1 and 2 was adopted.[18]

Further evidence of the normal condition of the lead chloride employed is to be found in the practical identity of the average of Analyses 5, 7, 8 and 9, which is 207.218, with that of 6 and 13, which is 207.216; and also of the average of 15, 16, 19 and 20, which is 207.2185 with that of 17, 18, 21 and 22 which is 207.217. In each of these comparisons the first average concerns lead chloride from which the hydrogen chloride had been displaced by nitrogen when in the state of fusion, while the second average concerns lead chloride taken directly from the quartz tube after sublimation without a subsequent fusion.

Turning now to the main points at issue: the comparison of the isotopic nature of the several specimens of lead is perhaps best made in tabular form.

Evidently neither ordinary lead, nor the mixture known to contain uranium lead gave any effect of separation by irreversible evaporation greater than the experimental error.

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[18] Baxter and Grover on comparing lead chloride, thus fused, and crystallized lead chloride found that the latter was slightly the more basic of the two (probably due to hydrolysis) (Ref. 12 c). Tests of the neutrality of other more manageable salts fused in hydrogen chloride have revealed no important acidity or basicity. See, for example, Richards and Hönigschmid, THIS JOURNAL, **32,** 1577 (1910); **33,** 32 (1911).

TABLE VII

THE EFFECT OF IRREVERSIBLE EVAPORATION: ORDINARY LEAD (TABLES II AND III)

Atomic weight, residue from volatilization	207.217
volatilized fraction	207.217
MIXTURE OF URANIUM LEAD AND ORDINARY LEAD (TABLE IV)	
Atomic weight, residue from the volatilization	206.434
mean fraction	206.438
volatile fraction	206.431

Calculation either by the theory of Rayleigh or that of Harkins[19] predicts a change in atomic weight for the volatilized fraction of ordinary lead of 0.002 unit, and for the extreme fractions of lead of radioactive origin of 0.004, provided that the processes were carried out with full efficiency. Hence, the present investigation confirms the theory, in so far as both show the separation by irreversible evaporation to be extremely slight.

TABLE VIII

EFFECT OF GRIGNARD PROCESS

Atomic weight of extreme lead fraction (Table V)	207.217
from extreme tetraphenyl fraction (Table VI)	207.219

Here again no appreciable separation is apparent. Of course this outcome does not show that by much more extended treatment it might not be possible to effect perceptible separation. Our outcome agrees, however, with the conclusions of Lindemann and Aston that, while possible, it is nevertheless unlikely that a separation of isotopes can occur by chemical treatment.[20]

Francis Galton and other statisticians have advocated the adoption of the median value instead of the average as representing the true outcome of a number of results in which an occasional value shows much discrepancy.[21] There is something to be said for this contention; but in the present case the use of medians does not alter the conclusions drawn above.

The Atomic Weight of Ordinary Lead

Because the results for the several samples do not differ by an amount greater than the reasonable experimental error, they may all, except those of Table IV, be averaged together in order to give the atomic weight of ordinary lead. This is all the more permissible because even if there were a difference between the fractions, the average would be expected to give

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[19] Ref. 1 l and Ref. 1 p, pp. 44 and 45.

[20] Ref. 1 r, p. 526. See also Lindemann, *Phil. Mag.*, [6] **38**, 173 (1919). Levin, *Physik. Z.*, **7**, 692 (1906). McCoy and Ross, THIS JOURNAL, **29**, 1709 (1907). Boltwood, *Am. J. Sci.*, **24**, 99 (1907); **25**, 269 (1908). Szilard, *Le Radium*, **5**, 1 (1908). Herchfinkel, *ibid.*, **7**, 198 (1910). Ref. 1 j. Paneth and von Hevesy, *Sitzb. Akad. Wiss. Wien.*, **122** (IIA), 993 (1913); *Monatsh.*, **34**, 1393 (1913). Ref. 12 f. Ref. 1 e.

[21] Galton, "Memories of My Life," Methuen, London, **1908**, p. 281.

nearly the value pertaining to the original substance. The total average of the 18 individual analyses in Tables II, III, V and VI, is 207.217, with a "probable error" of less then 0.001. The median value is 207.2165—which is essentially identical. Table I is not included in these averages since it contains merely preliminary determinations, but this inclusion would have made but little difference.

The value is 0.005 unit higher than the value 207.212 obtained by Baxter and Grover from the 30 determinations of the same ratio and 0.013 lower than that recommended by Hönigschmid and Steinheil. The following table records these and other significant recent determinations of the atomic weight of lead (not including those which have been obtained by various experimenters merely for practice). The last three investigations employed distilled lead chloride.

TABLE IX

ATOMIC WEIGHT OF LEAD (Ag = 107.88)

Investigator	Source	At. wt.
Baxter and Grover[12c]	$PbCl_2$	207.212
Baxter and Grover[12c]	$PbBr_2$	207.19
Baxter and Parsons[22]	$PbCl_2$	207.21
Hönigschmid and Steinheil[1v]	$PbCl_2$	207.23
Richards, King and Hall	$PbCl_2$	207.217
	Av.	207.21

We take pleasure in acknowledging our indebtedness to the Carnegie Institution of Washington and to an anonymous benefactor of this Laboratory for substantial assistance; and likewise our indebtedness to the Staff of the Harvard College Observatory and to Professor Gregory P. Baxter for placing special facilities at our disposal when the Wolcott Gibbs Memorial Laboratory was closed during the summers of 1921 and 1922.

Summary

Two methods were used in an attempt to separate ordinary lead into its supposed isotopes, namely, the process of irreversible volatilization and the Grignard process. The former of these methods was applied also to a known mixture of uranium lead with ordinary lead. An investigation of methods of analysis dependent upon density showed that such methods are not at present sufficiently accurate to prove any possible separation. Therefore, the determination of the atomic weight of lead was refined, with especial study and equalization of possible disturbing influences; and this method was used for comparing the eight specimens resulting from the fractionations. The outcome showed that the separation attained was not in any case greater than the possible error of experimentation, which was very small.

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[22] Baxter and Parsons, *Carnegie Inst. Wash. Year Book*, **15**, 344 (1916).

Since all of the ordinary lead chloride concerned had been very carefully purified and sublimed in quartz, the 18 individual determinations yielded a significant result for the atomic weight of ordinary lead, namely, 207.217.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF TEXAS]

THE HEAT OF SOLUTION OF SULFUR DIOXIDE[1]

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Object of the Investigation

The object of this investigation was the direct determination of the total heat of solution of sulfur dioxide in water at various concentrations of sulfurous acid produced. From the data obtained the heat of solution of sulfurous acid solution can be calculated for the concentration range investigated. The data on the total heat of solution, as found recorded in the literature, are not concordant and only one direct determination of the heat of dilution was found recorded. Since, in an investigation in progress in this Laboratory, accurate data of the heat of solution were essential, it was decided to measure directly the heat values.

The Existing Data

The data on the total heat of solution are mostly older data and are not concordant. The values of $-\Delta H$, the total heat of solution per mole of sulfur dioxide dissolved range from 9130 to 6680 calories for concentrations of sulfurous acid produced, expressed by the ratio "moles of H_2O/mole of SO_2" from 6630 to 93. No regularity between $-\Delta H$ and concentration of sulfurous acid solution produced nor agreement between the different investigators[2] is observable.

The Experimental Procedure

The heat of solution of sulfur dioxide was measured directly by passing the gas into distilled water, measuring the temperature rise, and determining the concentration of the sulfurous acid produced.

The details of the calorimeter and accessories are given in Fig. 1.

The calorimeter consisted of a highly evacuated, silvered Dewar flask fitted with a closely fitting, hard rubber cover. Through this cover are fitted, except in case of very

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[1] Constructed from a thesis submitted by Angie G. Stiles in partial fulfilment of the requirement for the degree of Master of Arts at the University of Texas.

[2] The investigators who have made direct determinations are Thomsen ["Thermochemische Untersuchungen," J. A. Barth, Leipzig, **1882**, Vol. II, pp. 249 and 250] and Berthelot [*Ann. chim. phys.*, [VI] **1**, 74 (1884)]. Bichowsky [THIS JOURNAL, **44**, 130 (1922)] has used a datum by Thomsen and one by Mathias [*Compt. rend.*, **106**, 1148 (1888)] as well as some vapor-pressure data on sulfurous acid solutions by Linder [*Monatsh.*, **33**, 654 (1912)].