18. A theory as to the factors conditioning variations of cohesion is given.
19. The ordinary theory, that the atoms in solids do not occupy all of the space is supported.

Several problems related to the periodic system are now under investigation in this laboratory. One of these is the endeavor to prove whether or not the exceptional atomic weight of chlorine is due to its existence in two isotopic forms. This is a very important problem in its bearing on the theory of complex atoms, whatever may be the facts. Work is also being done upon the melting point of lead derived from radium. A third problem is the attempt to prove whether ordinary lead is or is not a mixture of isotopes.

The writers wish to thank Mr. W. A. Roberts for aid in the construction of the model of the periodic system.

The next paper in this series will be on "The Evolution of the Elements and the Stability of Complex Atoms."

[Contribution from the Wolcott Gibbs Memorial Laboratory of Harvard University.]

THE DENSITY OF LEAD FROM RADIOACTIVE MINERALS.

By Theodore W. Richards and Charles Wadsworth, 3rd.

Received December 4, 1915.

The startling differences observed by several investigators[1] in the atomic weight of lead from radioactive sources obviously suggest that other properties also may vary in different specimens; and the comparison of these may be of service in tracing the true causes of the differences in atomic weight. The phenomena are of interest whether or not one accepts the plausible hypothesis of Soddy and Fajans concerning the "isotopes." In a new field of this sort, of course, as great a variety of facts as possible is peculiarly important.

The present paper details one of a number of lines of research in this direction which are in progress in this laboratory, with the idea of finding out more about the substance admixed with ordinary lead in radioactive minerals—a substance so like ordinary lead that the usual modes of purification do not separate it, and that it produces no change in the ultraviolet spectrum.

The first among the properties to be studied was density.[2] The densi-

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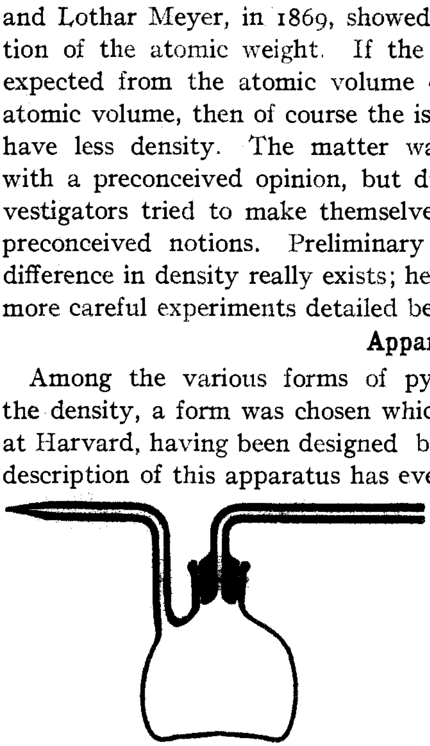
[1] Richards and Lembert, This Journal, 36, 819 (1914); Honigschmid and St. Horovitz, *Compt. rend.*, 158, 1798 (1914); M. Curie, *Compt. rend.*, 158, 1676 (1914); Soddy and Hyman, *J. Chem. Soc.*, 105, 1402 (1914); also especially, Hönigschmid, *Sitzb. k. Akad. Wiss. Wien.*, 123, IIa (Dec. 1914).

[2] The density of lead from thorianite has already been studied by Soddy, and discussed by Lindemann, respectively, *Nature*, 94, 615 and 95, 7 (1915). Professor F. W. Clarke has kindly called our attention to the desirability of studying also several other properties.

ties of the elements have assumed peculiar interest ever since Mendeléeff and Lothar Meyer, in 1869, showed this property to be a periodic function of the atomic weight. If the various isotopes have, as would be expected from the atomic volume curve, nearly if not quite the same atomic volume, then of course the isotope with less atomic weight should have less density. The matter was, therefore, inevitably approached with a preconceived opinion, but during the experimental work the investigators tried to make themselves as independent as possible of any preconceived notions. Preliminary experiments gave evidence that a difference in density really exists; hence the matter seemed worthy of the more careful experiments detailed below.

Apparatus.

Among the various forms of pycnometer available for determining the density, a form was chosen which for many years has been in use at Harvard, having been designed by one of us in 1898. No adequate description of this apparatus has ever been given, however, hence a brief account of it is now in place. It consists in principle simply of an Ostwald-Sprengel pycnometer modified for use with solids by the introduction of a glass stopper, as indicated in the diagram, and has the ease of adjustment familiar to those who have used the Ostwald form. Several details concerning it should be mentioned. In the first place, the stopper should not be too nearly cylindrical. In a stopper 8 mm. high the upper diameter should be 8 mm. and the lower 7. With this angle the stopper attains on successive settings almost precisely the same point, but is not so conical as to fall out easily. When the joint is very thoroughly ground, it is sufficiently watertight for long periods even without a lubricant, but certainty of closure is increased by spreading about 0.5 mg. of a lubricant (such as a mixture of hard and soft paraffin and melted rubber) upon the ground joint. This precaution was adopted in the present research.



For the best results, the pycnometer should of course be but little larger than the bulk of the substance to be studied; and the internal diameter of its tubes should not exceed 1 mm. Both of these specifications have been recently unheeded by a German firm which has advertised it.

To determine its volume the instrument was filled either with hot water, or else in an evacuated apparatus with cold previously boiled water. The two methods gave identical results. It was then left for a long time in an accurately adjusted thermostat kept at 19.94°.

Before weighing, the pycnometer was always wiped with a clean, lint-free cloth and was weighed in a balance case containing no drying agent.

Twenty minutes in the balance case sufficed amply for the attainment of constant weight, which did not change on standing twenty minutes more.

The following readings of the weight of water contained in the pycnometer—two settings and weighings for each of three adjustments of the stopper—show how accurately the instrument serves its purpose:

TABLE I.—WEIGHTS OF WATER REDUCED TO VACUUM STANDARD.
TEMPERATURE 19.94°.

5.7264	5.7264	5.7264
5.7264	5.7263	5.7264

Five of these six weighings were identical and the other differed only by 0.1 mg.

The pycnometer was used with the lead in the same way as with water alone. After drying in an air-bath a thin coating of the lubricant was smeared upon the ground glass stopper. A carefully weighed quantity of lead, prepared in a manner to be described later, was introduced after weighing the pycnometer with its lubricant; and in the first series of experiments (called "1st method" in the table below) the vessel was filled through the pointed jet with pure hot water, which, if previously boiled, was found to be without action on the lead. The pycnometer was then placed in the water of a clean thermostat carefully regulated to within one-hundredth of a degree and allowed to come to thermal equilibrium. After the setting of the meniscus, the pycnometer was removed, and carefully dried and reweighed—just as it had been when containing water alone. In the experiments designated "2nd method" in the table below, the filling was conducted with cold boiled water in a vacuum according to the method used by Kahlbaum and others.[1] This is by far the more trustworthy method with a porous substance, but it will be seen that in the present simple case the two methods gave essentially identical results.

Preparation of Materials.

The best method of purifying lead salts is by crystallization of the nitrate.[2] A large quantity of lead from radioactive sources (obtained through the kindness of Mr. S. Radcliff and Mr. E. R. Bubb, of the Radium Hill Co. of Australia) was dissolved in nitric acid and the nitrate was recrystallized five times by dissolving the crystals in hot water and adding a large excess of nitric acid. In this way the crystals separated from a large volume of mother liquor and the purification was very rapid. The pure nitrate was then divided into several portions, of which one was immediately afterward electrolyzed in quartz vessels from hot solution, using electrodes of platinum wire. This procedure gives a very beautiful crystalline deposit, which is easier to wash and for this reason purer than

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[1] *Z. anorg. Chem.*, **29**, 237 (1901).

[2] Baxter and Grover, THIS JOURNAL, **37**, 5 (1915).

the somewhat spongy deposits obtained from cold solution. The subsequent treatment of these crystals will be described later. (Sample C.)

Another portion of the pure lead nitrate was precipitated as chloride by pure hot hydrochloric acid obtained by distilling pure acid of constant boiling point. The precipitate was thoroughly washed and recrystallized as chloride four times. This chloride was then electrolyzed, using a fine-grained porous cup to surround the anode, in hot, slightly acid solution; and the crystals of lead thus obtained were thoroughly washed and treated like the preceding. (Sample D.)

Finally, samples of ordinary lead chloride, which had been carefully purified by Dr. J. W. Shipley, were treated in the same way. This lead chloride had been twice recrystallized after precipitation from a solution of the acetate which had itself been several times recrystallized. The electrolytic crystals of pure ordinary lead were thoroughly washed and treated like the radioactive metal. Two such preparations were made and designated A and B.

Each of these samples of clean lead crystals was finally fused in a mould of pure sugar charcoal made for the purpose. This mould or boat had been made from a paste of powdered sugar charcoal, sugar and water, packed into an "alundum" boat, moulded into the desired shape, heated cautiously in an air bath, and when dry thoroughly ignited before the lead was placed upon it. Upon the hard, smooth surface of this charcoal boat each bar of lead was melted, the boat having been placed in a hard glass tube, in a current of pure, dry hydrogen. This, in turn, was made from the electrolysis of sodium hydroxide containing some baryta, passed over red hot copper, and finally dried by potassium hydroxide previously fused with a little permanganate. The resulting bars of lead were beautifully bright and clean. After cooling, each was removed, carefully freed from adhering carbon, cut into small pieces and hammered on a polished anvil with a clean steel hammer. Finally these hammered bars were scrubbed with clean sea-sand, dried and polished with a clean cloth and placed in a desiccator over fused potash. Each of the three samples was subjected to precisely the same treatment, so that no difference in density could arise from any difference in the preparation of the metal.

With each of these varieties at least four determinations of the density were made, using different amounts of material, so as to be sure that no systematic error existed in the method. The data are given below in full, the weighings both in air and corrected to vacuum being recorded. It will be remembered that the weight of water contained by this pycnometer was 5.7264 g. in vacuum, the average amount in air being 5.7203. The temperature was in every case 19.94°.

Table II.—Density of Common Lead. Temperature 19.94°.

Method.	Sample.	Obs. weight of lead.	Weight of lead in vac. (W).	Obs. wt. water not displaced.	Corresp. volume.	Volume of Pyc.	Volume V of water (displaced).	Density W/V.
1st	A......	11.3274	11.3270	4.7236	4.7369	5.7364	0.9995	11.333
	A......	5.7889	5.7887	5.2111	5.2258	5.7364	0.5106	11.337
	A......	5.5202	5.5200	5.2348	5.2496	5.7364	0.4868	11.339
2nd	A......	7.3297	7.3294	5.0758	5.0901	5.7364	0.6463	11.341
	B......	15.9150	15.9144	4.3205	4.3327	5.7364	1.4037	11.337
							Av.,	11.337

Table III.—Density of Radioactive Lead. Temperature 19.94°.

Purified by 5 recrystallizations of nitrate.

1st	C......	13.5713	13.5708	4.5217	4.5345	5.7364	1.2019	11.291
	C......	8.2967	8.2964	4.9874	5.0014	5.7364	0.7350	11.288
2nd	C......	13.4788	13.4783	4.5294	4.5422	5.7364	1.1943	11.286
	C......	7.5013	7.5010	5.0576	5.0719	5.7364	0.6645	11.288
							Av.,	11.288

Further purified by 5 recrystallizations as chloride.

1st	D......	12.9527	12.9522	4.5764	4.5893	5.7364	1.1471	11.291
	D......	7.9345	7.9342	5.0196	5.0338	5.7364	0.7026	11.292
2nd	D......	11.5183	11.5179	4.7026	4.7159	5.7364	1.0205	11.287
	D......	6.6672	6.6670	5.1312	5.1457	5.7364	0.5907	11.287
							Av.,	11.289

Hence the results are as follows:

Density of ordinary lead	11.337
Density of radioactive lead from nitrate	11.288
Density of radioactive lead from chloride	11.289

Evidently the density of the lead from radioactive sources is 0.049 that is to say, 0.43% lower than that of ordinary lead—a very striking difference, in the sense which was expected.

Before considering these results further, the results of others on the density of ordinary lead may receive a moment's consideration. As usual, these are highly conflicting, for the determination of the density of solids has been highly uncertain; good results are rare. Earlier values for the density of lead have varied from 11.19 to 11.37.[1] The most accurate of these seems to have been that of Kahlbaum, Roth and Siedler, who, however, used only distillation as a means of purifying their metal. Their values were 11.341 and 11.347 for unpressed and pressed lead, respectively.[2] As they themselves showed that the common metallic impurities in lead were easily volatile under the conditions which they employed, and, therefore, might have contaminated their distillate, their result, although good, cannot be deemed certainly accurate. The qualitative experiment in

[1] See, for example, Kahlbaum and others; *Z. anorg. Chem.*, **29**, 278 (1901).

[2] *Z. anorg. Chem.*, **29**, 280 (1901).

which they distilled a ten-pfennig piece is hardly convincing as evidence of precision.[1] Of course these criticisms do not apply to their interesting conclusions about the effect of pressure, except insofar as possible impurities might affect the crystalline habit of the solid metal, and perhaps cause small vacant spaces in the structure.

The difference between the result of Kahlbaum and his collaborators, 11.341, and our result, 11.337, for ordinary lead, is only 0.004 or 0.04%. As density determinations go, this is a good agreement. The only impurities likely to have been in our sample are hydrogen and carbon, which might possibly cause a deviation of this magnitude, although we have no definite evidence that either of these elements is soluble in melted lead to an appreciable extent. Another possible cause of difference lies in a conceivable allotropy in the metal.[2]

Whatever may be the cause of this slight difference, it does not affect the arguments to be drawn from our comparative results, for each of our samples of metal was treated precisely in the same way. Hence each sample of lead must have been equally saturated with carbon and hydrogen, if any dissolved, and each must have been of the same modification. It will be noted that the greatest deviation from the mean is 0.004 in the case of the common lead and only 0.003 in the case of each sample of radioactive lead. The difference, on the other hand, between ordinary lead and the mean of the two samples of radioactive lead is, as has been said, 0.049, over twelve times the greatest deviation from the mean and over twelve times the difference between our pure lead and that of Kahlbaum and his collaborators. There can be no question, therefore, that these results show a real difference between the two kinds of lead, which must be referred to the admixture causing the low atomic weight of radioactive lead.

Furthermore, it should be noted that the five additional recrystallizations of the second radioactive sample (D) as chloride produced no essential change in the purity of the lead, as indicated by its density. Hence it is clear that more drastic means than recrystallization must be taken to separate the modifications.

It is interesting to compare these results with those of Soddy, who found in lead from thorite slightly higher density than that of ordinary lead[3]—just the opposite to the phenomenon described in this paper. Soddy earlier found in lead from thorite (presumably a similar sample) also an atomic weight higher than that or ordinary lead, whereas the atomic weight of our Australian radioactive lead has been found, in experiments not yet published, to be much lower than that of ordinary lead, namely 206.3 instead of 207.2. Hence Soddy's results are not inconsistent

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[1] *Loc. cit.*, p. 195.

[2] Cohen and Inouye, *Chem. Weekblad*, 1910, p. 1.

[3] *Loc. cit.*

with ours. They seem rather to indicate that a different admixture was present in his material.

Returning to our results, it is interesting to note that the atomic volume of the Australian radioactive lead is very nearly the same as that of ordinary lead, because 206.3/11.288 = 18.276, whereas for ordinary lead 207.2/11.337 = 18.277. The difference between these values for the atomic volume is so small as to be no greater than the probable limit of error of the experiment. Hence it is clear that the atomic volume of radioactive lead is essentially equal to that of ordinary lead.

Of course, no one knows as yet what proportion of impurity exists in this radioactive sample, which doubtless contains some ordinary lead. If the true atomic weight of the pure isotope is really 206, this sample must have consisted chiefly of the isotope, and the atomic volume of the pure isotope must be very nearly 18.3. On the other hand, it is possible that the theory is incomplete and that the lowering of atomic weight and density is due to the admixture of a much smaller amount of a substance with much lower atomic weight. In that case the atomic volume of the admixture is, of course, less certain, but it probably is near 18.

It is a pleasure to express our indebtedness to the Carnegie Institution of Washington for generous pecuniary support in this investigation.

Summary.

The density of ordinary lead (having an atomic weight of 207.2) and of lead from Australian radioactive sources (having an atomic weight of 206.3) was carefully determined in a convenient pycnometer which is described in detail for the first time, although long in use. The density of ordinary lead reduced to the vacuum standard was found to be 11.337, and that of radioactive lead 11.288. Continued fractionation produced no change in this low density, and it could not have been due to any irregularity in preparing the metal since the samples were all prepared in the same way. This difference in density is especially interesting, because it almost exactly parallels the difference in atomic weight. Thus the atomic volume of radioactive lead is found to be almost exactly equal to that of ordinary lead, the figures being each very nearly 18.28.

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A THEORY OF CHEMICAL REACTION AND REACTIVITY. FURTHER NOTE.[1]

BY E. C. C. BALY.

Received December 26, 1915.

In the addenda to his original criticism, Dr. Dehn has carried the matter no further. I will therefore only add very few words.

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[1] This reply was received too late to be published in the January number of THIS JOURNAL as was originally intended.—EDITOR.