with that of metallic sodium.   If we may judge from the experiments below 1100°, which give somewhat more consistent values for $P^2_{Na}/P_{Na_2C_2}$, it appears that the value of this constant decreases or, in other words, the stability of sodium carbide increases, with increasing temperature, as would be predicted from the endothermic character of sodium carbide.

Acknowledgment

The authors take pleasure in acknowledging their indebtedness to Dr. J. M. Braham for helpful criticisms and suggestions during the progress of this investigation.

Summary

1. A method is described for the preparation of sodium cyanide of high purity.

2. A method has been developed for the study of the thermal dissociation of sodium cyanide and the results are shown for the dissociation in an atmosphere of helium at 600°, 1000° and 1050° and in an atmosphere of nitrogen at 1050°, 1100°, 1200°, 1220° and 1255°.

3. Sodium carbide is shown to result from the dissociation as well as sodium, carbon and nitrogen.

4. The vapor above sodium cyanide is shown to consist largely of decomposition products.   Thus, at 1050°, the partial pressures in millimeters of mercury in a helium atmosphere are approximately as follows: sodium 117; sodium carbide 21.0; nitrogen 108; sodium cyanide 21.

5. At all temperatures employed, sodium carbide is largely dissociated to sodium and carbon.

WASHINGTON, D. C.

THE ATOMIC WEIGHT OF URANIUM LEAD AND THE AGE OF AN ESPECIALLY ANCIENT URANINITE

BY THEODORE W. RICHARDS AND LAWRENCE P. HALL

Measurement of geological time by radioactive disintegration appears at present to be the most trustworthy method for determining the age of minerals.   In particular the lead-uranium ratio, as first suggested by Boltwood,[1] yields relative ages for geological strata which agree in general with those obtained from the helium-uranium ratio, and which can be reconciled, in part at least, with estimated ages depending upon purely geological observations.[2]

[1] Boltwood, *Am. J. Sci.*, **23**, 77 (1907).

[2] (a) Barrell, *Bull. Geol. Soc. Am.*, **28**, 745 (1917).   (b) Chamberlin, *Proc. Am Phil. Soc.*, **61**, 247 (1922).

Calculations of the age of the earth by the method of radioactive dis-
integration are based upon several assumptions: that the rate of disinte-
gration of uranium has been constant during very long periods of time
(an assumption based upon experimental evidence under conditions of
temperature and pressure within our present control); that the mineral
was free from lead at its genesis (ordinary minerals in igneous rocks con-
tain a negligible amount of lead); that the lead found in a uranium mineral
consists entirely of lead of radioactive origin, without extraneous addition or
loss during its production. In connection with the last two assumptions
there are two criteria: the constancy of the lead-uranium ratio for un-
altered primary specimens of the same geological age, and the value of
the atomic weight of the lead in the specimen.

This paper deals with the latter criterion, in particular with the atomic
weight of lead from a sample of uraninite yielding an unusually large lead-
uranium ratio. We are directly indebted for this sample of lead to Pro-
fessor Alfred C. Lane, of Tufts College, Chairman of the Committee
of the National Research Council on the Measurement of Geological
Time by Atomic Disintegration, and also to Mr. Frank L. Hess, a member
of this Committee, who was instrumental in collecting this specimen.
Part of a letter from Mr. Hess gives a description of the mineral and the
geological history of the dike from which it comes:

"The Ingersoll No. 3 dike, from which the specimen of uraninite came, is located
about two and a half miles west of Keystone, South Dakota, and is a lenticular pegma-
tite mass containing big, individual, anhedral crystals and large, monomineralic masses.
The history of the dike is very complicated. Like others of the region it was probably
originally injected into the Algonkian schists as a comparatively fine-grained igneous
mass. The injection was followed by a flow of solutions extending over a very long
period. The solutions, probably gaseous, carried many of the less common elements,
including tin, zirconium, lithium, boron, fluorine, tantalum, columbium and uranium.
As the fluid flowed through the dike the original minerals were replaced by other min-
erals which gradually formed masses of various size, according to the quantity held in
solution by the fluid. Uranium was carried in very minute quantity, so that the masses
of uraninite found are very small. There was never any fusion of the dike after the
uraninite and other minerals of the generation to which it belonged were formed.

"No uraninite of comparably great age is fresh. It is probably inherent in the dis-
integration of the uranium, the setting free of the oxygen with which it was combined
as UO_2, and the oxidation of other molecules to UO_3, that the uraninite is brecciated and
re-cemented. However, the lead which is present either in the altered mineral or in the
original mineral is necessarily of the same kind, of the same origin, and from the same
mass. The scheme of analysis followed by Mr. Davis, in which the mineral was treated
by hydrochloric acid, removed the altered part of the mineral and left only the least
changed uraninite. There could be no accretion of other uranium-lead from other
masses of uraninite, because they are too few and too widely separated.

"No lead minerals, using the word in its ordinary sense, are found in the pegmatites
of the Ingersoll claims, and from the geology it is very sure that there is no accretion of
ordinary lead. Your atomic weight determination proves the geologic findings.

"If any change in the quantity of lead has taken place it has probably been a re-

moval of lead by circulating water, so that, provided the constants of atomic age have been correctly determined, the age as given is probably less, rather than more than, the true age."

Analyses by Dr. C. W. Davis[3] present the following values for the important constituents:

UO$_3$ 28.58%	PbO 16.42%	He 0.08%
UO$_2$ 48.87%	ThO$_2$ 2.15%	

The lead-uranium ratio 0.228[4] (corrected for the presence of thorium %Pb/(%U + 0.357%Th) = 0.225) indicates the oldest Pre-Cambrian mineral yet found, provided that all the lead had its source in the uraninite.

Hence the atomic weight of this lead becomes a matter of capital significance.

Recovery of the gas and lead content of the specimen concerned was effected by Dr. Davis at the United States Bureau of Mines, Reno, Nevada. His account of the procedure follows.

"The sample consisted of a single lump of about 160 g. Mr. Hess, who furnished the material, says that this specimen 'is an actual part of the specimen on which Mr. Davis made his analysis and has special interest in that it is the largest piece of uraninite known to have been found in the Black Hills.' About 10 g. was broken from the lump and saved for reference. The remaining lump was crushed, a few of the larger lumps of gangue minerals removed, and the rest of the material pulverized in an agate mortar. At the suggestion of Mr. Hess the gas evolved in decomposing the sample with sulfuric acid was collected and sent to Mr. Kennedy of the United States Bureau of Mines, Washington, D. C., for analysis. Nitric acid was then added to complete decomposition and the whole was evaporated until sulfur trioxide fumes were evolved, then diluted, filtered and washed. The residue was extracted repeatedly with ammonium acetate, filtered and washed. The acetate solution was diluted and lead precipitated with hydrogen sulfide, filtered and washed. The lead sulfide was decomposed with dilute nitric acid and filtered. The residue was treated with concentrated nitric acid, fumed with sulfuric acid, diluted, and the lead sulfate treated as before, the process being repeated until all the lead was present in solution as the nitrate. The lead was crystallized once as the nitrate, twice as the chloride from hydrochloric acid solution, and once as the chloride from distilled water. The crystals were then dried and sealed in a glass container. Even the lead nitrate crystals were colorless so that the final chloride crystals should be fairly pure."

As the first step in our procedure, the lead chloride was converted to lead nitrate by repeated treatment with pure nitric acid. Throughout the purification quartz vessels and thorough centrifugal drainage were used. Three crystallizations were performed with the nitrate. Lead chloride was precipitated from a hot, dilute solution of the purest nitrate by the addition of pure hydrochloric acid. The chloride was thrice recrystallized in the usual way before being dried. Finally the chloride was distilled in

[3] Davis (private communication, about to be published).

[4] The helium-uranium ratio does not correspond to this. Probably there has been a large loss of gas, particularly as the helium ratio does not correspond to that obtained from minerals known to be much younger.

an atmosphere of hydrogen chloride in a quartz apparatus, yielding a clear, colorless product.[5]

The lead chloride (fused in the Richards and Parker bottling apparatus) was weighed on a sensitive balance in the usual way with carefully standardized weights. After the chloride had been dissolved in purest water, a solution of carefully weighed pure silver was added to it and the end-point was determined nephelometrically. The full details will soon be published in a paper on a similar topic.

TABLE I

ATOMIC WEIGHT OF LEAD FROM SOUTH DAKOTA URANINITE

	Ag = 107.880		Cl = 35.458
Analysis	Wt. of PbCl$_2$ in a vacuum	Wt. of Ag in a vacuum	Atomic weight
1	4.37550	3.40841	206.063
2	4.83808	3.76860	206.074
3	4.88040	3.80155	206.075
4	5.31437	4.13960	206.074
			206.071

From the atomic weight 206.07 there can be no doubt that the lead is almost entirely derived from uranium. Comparable values are those of 206.08 and 206.05 obtained from selected samples of cleveite[6] and uraninite.[7] Professor Lane has calculated ·that the 2.15% of thorium present in the Black Hills uraninite would correspond to an increase in atomic weight of 0.05 unit. From this consideration it appears highly probable that the atomic weight of pure uranium lead is lower than 206.02.

Possibly the true atomic weight of uranium-lead may be even less than 206—the value which is usually assumed for purposes of calculation. The existence of an isotope with lower atomic weight is not impossible, although not indicated by present theory. The parent of this radioactive series, uranium, is probably complex, and there is no certainty that all of its isotopes yield the same kind of lead. But even if they do, the fact that uranium yields radium with atomic weight 225.96 points toward an atomic weight for uranium-lead yet more discrepant with the whole number rule. If loss of energy causes loss of mass, the atomic weight of the lead derived from radium ought to be even more deviant than that of radium itself.

In confirmation: the elements of high atomic weight which have been shown by Aston to be non-isotopic all give, by exact quantitative analysis, atomic weights slightly below the corresponding integral values.[8] Provided that there are no undiscovered isotopes for these elements the

[5] Hönigschmid and Horovitz, *Monatsh.*, **36**, 370 (1915).

[6] Richards and Wadsworth, THIS JOURNAL, **38**, 2613 (1916).

[7] Hönigschmid and Birckenbach, *Ber.*, **56B**, 1837 (1923).

[8] Compare Baxter and Dorcas, THIS JOURNAL, **46**, 366 (1924).

inference is obvious.   If Pb_{206} is simple, it should behave in like fashion and may have an atomic weight as low as 205.9.

It is indeed unreasonable to suppose that all the possible "packing" effect happens during the formation of the oxygen atom—a notion which is tacitly assumed if the sixteenth part of the atomic weight of oxygen is taken as the "whole number" unit.   Indeed, if the packing effect is a reality, exact whole numbers would be out of the question in a majority of cases.

From the evidence now at hand the age of the uraninite from the Black Hills must be very great, and because of the nature of pegmatites, that of the strata in which it was found even greater.   If there has been no concentration of lead, an age of about 1,500,000,000 years must be assigned as a minimum, using the present value of 4.66×10^{-18}/sec. of λ_{UI}. The greatest previous estimate of this kind (based on comparably accurate data) was for Canadian rocks, and was of the order of 1,200,000,000 years.[9]

Summary

A specimen of uranium lead from the Black Hills, South Dakota, was found to have an atomic weight of 206.07.   Correction for known thorium content on the assumption of accepted inferences concerning thorium would reduce this value to 206.02.   Since the lead in question is so nearly pure uranium lead, the high lead-uranium ratio, 0.23, indicates an age of at least 1,500,000,000 years.   This extends yet further the earlier estimates of the age of the earth's crust.

CAMBRIDGE, MASSACHUSETTS

NOTES

The Use of Subscript and Superscript Exponents in Chemistry.[1]— Subscripts and superscripts are used in logic, in algebra and in higher mathematics in a manner consistent enough to permit the generalization that subscripts are used to *designate* the various members of a series or group of related symbols; while superscripts denote the same operation that would be represented by the *repetition* of the symbol to which the (superscript) exponent belongs, as many times as the exponent indicates. It would conduce to clearness of thought and ease of expression to preserve this distinction in the notations of arithmetic and of chemistry.

[9] Ellsworth, *Am. J. Sci.*, [5] 9, 143 (1925).

[1] An abridgment of a paper presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society at Washington, April, 1924.