

ture at a definite temperature, depending upon the sample, which in some respects resembles the melting of crystals. It is also interesting to observe that although the densities and transition temperatures of these two samples are different, the slopes of the curves are identical.

Recently Jenckel and Ueberreiter<sup>4</sup> published a long paper describing the change in specific volume of polystyrene with temperature which confirms the general phenomena described above, and in addition they conclude that the transition temperature is depressed not only by a low average molecular weight of the polymer, but also by the presence of impurities in the resin such as monomeric styrene, paraffin, or polystyrene of very low molecular weight. Their data indicate an upper limit for transition temperature of slightly above 100° regardless of molecular weight, although their data for transition temperature and molecular weight do not fall upon a smooth curve. Neither do their values for density bear any regular relationship to average molecular weight or to transition temperature, although some such relationship might be expected. And, finally, their values for coefficient of expansion, as indi-

cated by the slopes of the specific volume-temperature curves, show no regular relationship to molecular weight. This lack of regularity may indicate either that their measurements are in error by quantities greater than the differences found, or that the measured properties are influenced greatly by factors which have but little influence upon the viscosities of solutions of the polymers.

This bi-linear thermal expansion of polystyrene, the sharp transition temperature, and the closely accompanying sharp "high elasticity temperature" all point to the conclusion that polystyrene is a body of fairly definite composition and structure. It would be interesting to examine other linear polymers in the light of these observations, and to investigate the effect of cross-linking on the transition temperature.

### Summary

This paper includes the density, thermal expansion, vapor pressure, and refractive index of styrene, and the density and thermal expansion of polystyrene. A discussion of these latter properties is given in relation to other properties of the polymer.

(4) Jenckel and Ueberreiter, *Z. physik. Chem.*, **182A**, 361 (1938).

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[JOINT CONTRIBUTION FROM THE RESEARCH LABORATORY OF INORGANIC CHEMISTRY,\* No. 75, AND THE GEORGE EASTMAN LABORATORY OF PHYSICS,† MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

## The Radioactive Determination of Protactinium in Siliceous Terrestrial and Meteoritic Material

BY WALTER C. SCHUMB,\* ROBLEY D. EVANS† AND JANE L. HASTINGS\*

In order to test more completely the validity of the general rule that the abundance ratio of the isotopes of any element is a constant, independent of the source or of the mode of combination of the element, it is of interest and importance to determine such abundance ratios in meteorites, which represent the only available specimens of extra-terrestrial matter. Atomic weight or isotopic abundance ratios have been determined for carbon, oxygen, silicon, chlorine, iron, cobalt and nickel, by various workers<sup>1</sup>; and in the case of all

the elements studied the isotopic abundance ratios are not measurably different in meteoritic and in terrestrial matter.

In the case of radioactive elements, such as uranium, these abundance ratios assume additional interest, in that by means of them a knowledge may be obtained of the difference in age between these atoms in the meteorite specimen and in terrestrial substances containing the same element. This subject was discussed in some detail by Evans,<sup>2</sup> who on the working assumption that the "isotopic ratio of any element is a constant of nature, and is independent of its place of origin in the galactic system," derived the following expression for the differential age in years of

(1) Baxter and Thorvaldson, *THIS JOURNAL*, **33**, 337 (1911); Baxter and Hoover, *ibid.*, **34**, 1657 (1912); Baxter and Parsons, *ibid.*, **43**, 507 (1921); Baxter and Hilton, *ibid.*, **45**, 694, (1923); Baxter and Dorcas, *ibid.*, **46**, 357 (1924); Jaeger and Dykstra, *Koninkl. Akad. Wetenschappen. Amsterdam*, **27**, 393 (1924); Harkins and Stone, *THIS JOURNAL*, **48**, 938, 3233 (1926); Baxter and Ishimaru, *ibid.*, **51**, 1729 (1929); Manian, Urey and Bleakney, *ibid.*, **56**, 2601 (1934); Jenkins and King, *Publ. Astr. Soc. Pac.*, **48**, 323 (1936); Nier and Gulbransen, *THIS JOURNAL*, **61**, 697 (1939).

(2) Evans, *Pop. Astronomy*, **46**, 159-170 (1938).

uranium atoms in a meteorite and in the earth:<sup>3</sup>

$$t_m - t_e = 2.8 \times 10^8 \log (R_e/R_m) \quad (1)$$

where  $t_m$  and  $t_e$  are the respective ages in the meteorite and in the earth,  $R_e$  is the  ${}^{92}\text{U}^{235}$ : ${}^{92}\text{U}^{238}$  activity ratio observed in the earth today, and  $R_m$  is the same ratio measured in the meteorite.

The present paper reports the results obtained in a portion of a program for the determination of isotopic abundance ratios in meteorites being carried on jointly in these laboratories, in particular, the determination of the isotopic ratio of  ${}^{92}\text{U}^{235}$  (or AcU) to  ${}^{92}\text{U}^{238}$  (or UI) in a specimen of the Pultusk<sup>4</sup> meteorite, which, because of its reported<sup>2</sup> high heliocentric velocity (56 km. per sec.) has been considered as representing not only extra-terrestrial but possibly extra-solar material.<sup>5</sup> The sample used in this work was very kindly furnished to Professor Evans by Dr. C. C. Gregg and Mr. H. W. Nichols of the Field Museum of Natural History, Chicago. Nier<sup>6</sup> has recently checked the constancy of the isotopic abundance ratio of  $\text{U}^{235}/\text{U}^{238}$  in terrestrial material by means of mass spectroscopic determinations on Pb<sup>207</sup> and Pb<sup>208</sup> for twenty-one uranium minerals and on  $\text{U}^{238}$  and  $\text{U}^{235}$  for three minerals.

In all but very young rocks radioactive equilibrium has been established in the three radioactive series, that is, the rate of disintegration is equal to the rate of formation of all members of each series derived from the three parent elements,  ${}^{92}\text{U}^{238}$ ,  ${}^{92}\text{U}^{235}$  and  ${}^{90}\text{Th}^{232}$ . Therefore, by determining the amount of any one member of a series present, the quantity of any other may be calculated. Thus the determination of the protactinium content of a specimen permits the calculation of the amount of the parent element AcU, and the determination of the radon content of the sample makes possible the calculation of the amount of the parent element UI present, and from these two values the abundance ratio  $\text{U}^{235}/\text{U}^{238}$  may be obtained.

(3) The numerical factor 2.8 has been changed from 1.46, given in the reference cited, to 2.8 as the result of more recent work on the actinium series branching ratio by A. O. Nier, *Phys. Rev.*, **55**, 150 (1939).

(4) A shower of fragments of a stony meteorite fell in Pultusk, Poland, on Jan. 30, 1868.

(5) Professor C. C. Wylie of the State University of Iowa has kindly communicated to us the results of his recent recalculation of the Pultusk trajectory observations, originally reported by Galle in 1868, following interviews with those who observed the meteorite fall. Professor Wylie's extensive experience in such interviews leads him to reduce the reported height of appearance of the meteorite. This has the effect of reducing the computed velocity so that the Pultusk meteorite would be of solar-system origin rather than extra-solar. Professor Wylie has just summarized his work in *Science*, **9**, 264 (1939).

(6) Nier, *Phys. Rev.*, **55**, 150, 153 (1939).

A method has been worked out by v. Grosse<sup>7</sup> and others for the isolation of protactinium from other radioactive elements. The present method is a modification of that of v. Grosse in that provision had to be made for the elimination of large amounts of silica and some 5% of free metal along with metal sulfides. The chemical analysis of two specimens of the Pultusk meteorite, as given in Farrington's<sup>8</sup> compilation, are presented in Table I.

TABLE I  
PREVIOUS ANALYSES OF PULTUSK METEORITE

	G. von Rath, 1869	R. Rammelsberg, 1870
Specimen no.	82	101
SiO <sub>2</sub>	41.54	35.85
Al <sub>2</sub> O <sub>3</sub>	1.17	1.96
FeO	14.04	12.12
CaO	0.28	1.56
Na <sub>2</sub> O	1.34	0.95
K <sub>2</sub> O	...	0.39
Fe	11.51	15.55
Ni	0.65	2.21
MgO	26.73	24.95

## Experimental

**Preliminary Work.**—The preliminary work for testing the method was carried out on granite of known radium content. All solid reagents to be used were tested separately and a record made of their alpha activity. The efficiency of the method for the removal of radioelements other than protactinium and their isotopes was checked by adding known amounts of solutions of the salts of uranium, thorium, and polonium, respectively, and repeating all operations. These experiments proved that three separations (as described in Table II and the section on analytical procedure) removed 94% of the added uranium, 100% of the thorium and 95% of the polonium. Finally, a small sample of pure protactinium, deposited in zirconium pyrophosphate, and kindly furnished us for the purpose by Dr. v. Grosse, was converted into a highly dilute solution. The alpha activity of a portion of this solution was measured, and a known amount of it was carried through the chemical procedure. The activity of the recovered protactinium was determined, whereby it was demonstrated that  $90 \pm 6\%$  of the protactinium could be recovered. In view of the many steps required in the analytical procedure employed, this recovery is considered to be satisfactory.

**Sampling.**—Due to the probability of surface leaching and contamination, only the inner portions of specimens of granite were used. These were ground, first in a steel mortar and finally in agate, both mortars being "rinsed" by grinding inactive sodium carbonate in them before use. After thorough mixing, a third of the finely ground material was reserved in a stoppered bottle for the radon de-

(7) A. v. Grosse, *Phys. Rev.*, **42**, 565 (1932); Francis and Datchang, *Phil. Mag.*, **20**, 823 (1935).

(8) O. C. Farrington, *Field Museum of Natural History, Geological Series*, **3**, 195-229 (1911).

terminations and the remainder used for the separation of protactinium. In the case of the Pultusk meteorite sample, all of the outer black layer, or "skin," was carefully removed and samples of the inner portions were prepared as in the case of the granite.

**Analytical Procedure.**—A 50-g. sample of the siliceous material was treated with 100 cc. of aqua regia and heated on the steam-bath for a half hour. After cooling, the diluted acid solution was filtered and the residue dried and ignited in platinum. The filtrate was evaporated and the residue dehydrated. The residue was taken up with concd. hydrochloric acid, followed by water, and the silica filtered and combined with the original residue. The dehydration process was then repeated. The combined residues were treated several times with 47% hydrofluoric acid to which a few drops of concd. sulfuric acid had been added, and evaporated to fumes after each treatment. Three times the calculated amount of hydrofluoric acid was used to ensure complete removal of silica, assuming the latter to be 50% of the original sample. The residue then was heated to dull red heat and after cooling was treated with hot, concd. hydrochloric acid followed by hot water. There remained very little residue and this was filtered off and washed with hot water, dried, ignited and reserved for future work, if necessary.

The filtrate was combined with that from the final dehydration and the solution was evaporated to 200 cc. To the cooled solution zirconyl chloride solution was added equivalent to 100 mg. of  $ZrO_2$ . An excess of 6 *N* phosphoric acid was added and the solution stirred for several minutes. The precipitate of zirconium phosphate was allowed to stand for at least two hours before filtering. The precipitate was washed with 5% hydrochloric acid, dried, ignited, and weighed. The filtrate was reserved.

To the zirconium pyrophosphate, which contained the protactinium, 20 cc. of 2% hydrofluoric acid was added and the vessel heated until solution was complete. After cooling, solutions of the nitrates of barium, lead, lanthanum, and bismuth, equivalent to 4 mg. of each element, were added. The insoluble sulfates and fluorides of these elements co-precipitate those of radioactive elements other than protactinium, as indicated in Table II.

TABLE II

RADIOACTIVE SEPARATIONS FROM SOLN. OF  $ZrP_2O_7 + Pa$   
IN 2% HF

Reagent	Radioactive elements and isotopes removed
$Ba(NO_3)_2$	Ra, $MsTh_1$ , AcX, ThX
$Pb(NO_3)_2$	RaB, ThB, AcB, RaD, ThD, AcD, RaG
$Bi(NO_3)_3$	Po, RaC, ThC, AcC, RaE
$La(NO_3)_3$	Ac, $MsTh_2$

After standing for one hour, the precipitates were filtered, using hard rubber funnels. The residues were discarded. This operation was carried out three times to assure satisfactory elimination of radioactive contaminants, because blanks on which only two separations had been made occasionally showed residual counts. The third filtrate was evaporated to dryness, the residue ignited at red heat for ten minutes, and after cooling each residue so obtained was placed in a separate desiccator to avoid possible contamination.

A portion of the residue was transferred to an agate mortar and finely ground under alcohol. A suspension of the ground material was made in ethyl alcohol and poured upon a weighed silver disk, which had been sealed to a brass evaporating cylinder by means of rubber cement. The alcohol was evaporated in a heated cabinet in an atmosphere of well-aged and hence radioactively inert nitrogen. When the sample was dry, the cylinder and rubber cement were quantitatively removed from the disk and the disk plus the sample was weighed.

**Measurement of Activity.**—The weighed disk, containing the protactinium with zirconium pyrophosphate deposit, was placed in the recording alpha counter. An ionization chamber of the parallel plate condenser type was used, the design and operation of which has been discussed fully by Finney and Evans.<sup>9</sup> The ions formed by the alpha rays are collected, the current amplified, and the resulting galvanometer deflections recorded photographically upon sensitized bromide paper contained in a Telechron-driven drum camera which makes one revolution every two hours. Twenty consecutive hours of observation were generally employed in order to minimize the probable error. These could be recorded on a single sheet of  $5 \times 37.5$  in. paper, by using a laterally moving light source.

The inner parts of the ionization chamber are made of spun copper and are easily removable for cleaning. Some contamination is, of course, inevitable, due to radioactive material in the walls of the ionization chamber, so that even without a radioactive sample in the chamber the record obtained will show some countable  $\alpha$ -rays. Careful cleaning and the use of inactive silver for the metal disks minimizes this "background."

A blank on all reagents was carried along in parallel with the samples, and this served as a check on the completeness of removal of radioactive contaminants and on the overall manipulative procedures.

**Calculated Results and Conclusions.**—A sample of granite from Ontario, designated as "K. D. Fine," known to be low in radioactive material, was selected for a representative terrestrial material. The protactinium content was calculated from the observed alpha count per sq. cm. of source by means of the following two equations, discussed in the paper of Finney and Evans.<sup>9</sup>

$$n_a' = \frac{N\mu\tau}{4} \left[ \frac{2(R - \rho) - \tau}{(R - \rho)} \right] \quad (2)$$

in which

$n_a'$  = alpha counts observed per cm.<sup>2</sup> of source  
 $N$  = alpha rays per cm.<sup>2</sup> emitted in the source  
 $R$  = 3.61 air-cm. = mean range in air at 15° and 760 mm. for alpha particles from Pa  
 $\rho$  = 0.5 air-cm. (assumed maximum range of short range  $\alpha$ -rays not detected)  
 $\mu$  =  $15.6 \times 10^{-4}/d$  = ratio of range of  $\alpha$  rays in the solid to the range in air  
 $\mu\tau$  = thickness of source in cm.  
 $\tau$  = mass/(area  $\times$  density  $\times \mu$ ) = source thickness in air-cm.

$$N = \frac{6.02 \times 10^{23} Q \lambda d}{W} \quad (3)$$

(9) Finney and Evans, *Phys. Rev.*, **48**, 503 (1935).

TABLE III  
 PROTACTINIUM CONTENT OF MINERALS

Sample no.	Original rock sample, g.	ZrP <sub>2</sub> O <sub>7</sub> + Total	Pa, mg. Tested	Observed count		For sample	Pa in 10 <sup>-12</sup> , g./g. rock
				Over background	Over blank		
Granite							
Blank	...	210	41.5	1.7 ± 1.1	.....	.....	.....
No. 1	15.04	199	28.5	0.8 ± 1.3	0.0 ± 1.7	0.0 ± 12	0.00 ± 0.23
			42.1	10.0 ± 1.2	8.3 ± 1.6	39 ± 8	.76 ± .16
No. 2	15.18	231	52.4	5.6 ± 1.0	3.9 ± 1.5	17 ± 7	.32 ± .13
			47.7	7.4 ± 0.9	5.7 ± 1.4	28 ± 7	.52 ± .13
Mean						24.1 ± 4.6	0.46 ± 0.09
Pultusk Meteorite							
Blank	...	111	42.7	0.0 ± 0.8	.....	0.0	0.0
Rock	51	110	27.3	0.8 ± 0.6	.....	3.2 ± 2.4	.018 ± 0.013
			34.2	2.7 ± 0.8	.....	8.7 ± 2.6	.049 ± .013
Mean						6.0 ± 1.7	0.035 ± 0.011

where

$W$  = 231 = at. wt. of Pa  
 $\lambda$  =  $2.5 \times 10^{-9}$  hr.<sup>-1</sup> = decay constant of Pa  
 $Q$  = concentration of Pa in g. per g. of source  
 $d$  = density of ZrP<sub>2</sub>O<sub>7</sub>.

The probable error for each background run and determination of alpha rays due to protactinium was calculated in the usual way:

$$P. E. = 0.67 \left[ \frac{\sum (x - \bar{x})^2}{n(n-1)} \right]^{1/2}$$

where  $\bar{x}$  is the average of  $n$  individual observations of  $x$ .

Table III summarizes the results obtained with the granite and Pultusk meteorite.

In equation (1) above the quotient of the activity ratios  $R_e/R_m$  is equal to the quotient of the mass ratios, since the radioactive decay constants and the atomic weights involved cancel out in the quotient.

The mean values of the radium content of these two specimens, as determined by Mr. Clark Goodman of the Physics Department, are  $0.28 \pm 0.02 \times 10^{-12}$  g. Ra per g. for the granite and  $0.023 \pm 0.005 \times 10^{-12}$  for the Pultusk meteorite. The corresponding observed weight ratios, Pa/Ra for the granite, and similarly for the meteorite, become  $1.64 \pm 0.5$  and  $1.52 \pm 0.5$ , respectively. From these results the conclusion may be drawn that, if the probable errors are considered, there is no appreciable difference in the age of terrestrial uranium atoms and those in this specimen of the Pultusk meteorite.

The observed Pa/Ra ratio, and consequently the  $U^{235}/U^{238}$  ratio, is about twice the value observed by Nier<sup>6</sup> in terrestrial uranium minerals.

Our probable error is based on the observed fluctuations in the  $\alpha$ -ray counting rates, and does not include the contributions of any unknown systematic errors. Our observed Pa/Ra ratio,  $1.64 \pm 0.5$ , is higher than Nier's value by 1.5 times our probable error. According to the theory of errors, there is a 30% chance that the true value differs from the observed by more than 1.5 times the probable error. Therefore, the two values are compatible with each other. The differential age estimated from these observations depends (Equation 1) only on the logarithm of the ratio of the observations on meteoritic and terrestrial material, and is therefore much more accurate than the observations themselves.

From the chemical standpoint a more definite conclusion may be arrived at: the method employed for the separation and estimation of protactinium has proved satisfactory for as little as  $10^{-18}$  g. of protactinium per g. of siliceous material, and with larger samples this limit probably could be set much lower.

This investigation was materially assisted by a grant from the Cyrus M. Warren Fund of the American Academy of Arts and Sciences, which is hereby gratefully acknowledged.

### Summary

The protactinium contents of a granite and of a specimen of a meteorite (Pultusk), both high in silica, have been determined by the co-precipitation of the protactinium with zirconium phosphate, followed by purification of the ignited pyrophosphate, employing a modification of the method of v. Grosse. The alpha activity of the protactinium thus isolated was measured on a re-

cording alpha-counter and the concentration of protactinium in the two specimens of terrestrial and of meteoritic material calculated.

From these data and the corresponding radium concentrations of the same specimens determined independently, the weight ratios Pa/Ra have been derived for the two materials. From these results the conclusion has been reached that within the

limits of error the age of the uranium atoms in this specimen of the Pultusk meteorite is the same as for terrestrial uranium.

The method is capable of estimating as little as  $10^{-13}$  g. of Pa per g. of siliceous material, and the limit may probably be lower than this if larger samples are taken.

CAMBRIDGE, MASS.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]  
No. 432]

## Rates of the Thermal Reduction of Dichromic Acid by Quinine, Hydroquinine, and Cinchonine in Dilute Sulfuric Acid at 0 to 60°

BY LAWRENCE J. HEIDT

Quinine and ten similar alkaloids reduce dichromic acid when ultraviolet light is absorbed by the alkaloid.<sup>1</sup> This reaction was studied in dilute sulfuric acid at 0 to 30°. The variations in the photochemical efficiencies with structural changes in the alkaloids suggested that the hexavalent chromium was reduced mostly by the secondary hydroxyl group.<sup>1d</sup> The kinetics of the photochemical reaction were also studied and interpreted.<sup>1c</sup> This paper presents a study of the kinetics of the thermal reaction in the same environment.

**Materials.**—The source and purification of the reagents were the same as in the photochemical work. Acid solutions were standardized by comparison with sample 84 of U. S. Bureau of Standards potassium acid phthalate.

Stock solutions of ferrous ammonium sulfate were made from clear green crystals of Analytical Reagent material and were stored in the dark. They were standardized against dichromate solutions each week they were used and the proper factors at other times interpolated.

**Apparatus and Procedure.**—One of the two reaction cells is sketched<sup>2</sup> in Fig. 1a. The stirrer was the Pyrex plunger, D. In the cell not sketched, the part of D containing the disks was replaced with a Pyrex ribbon twisted like a screw. The fall of each plunger was cushioned by a Pyrex button fused onto the end that struck the bottom of the cell. An iron nail, B, was sealed into the top of each plunger whereby it was lifted at intervals by an electromagnet and fell when a "flasher" interrupted the current in the magnet. The cell outlet, C, used in the preliminary work, was replaced by a glass joint whose cap contained the male part made of solid glass. An umbrella fused

to this cap fit loosely around the joint and extended as far down as the female part illustrated in the sketch. The volume of each cell was 100 cc. Their other characteristics have been published,<sup>3</sup> although these cells and the accompanying apparatus were used first in this research.



Fig. 1a.

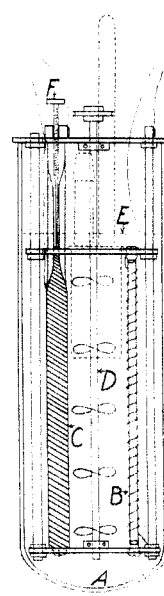


Fig. 1b.

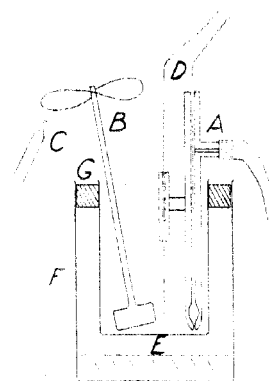


Fig. 1c.

The arrangement of the apparatus in the thermostat is sketched in Fig. 1b. The thermoregulator was a relay operated by a vacuum tube whose grid was in series with the contact, F, made in the glass capillary. This capillary was sealed to a welded steel tube filled with mercury. The quick response of the mercury in the steel tube to changes in the temperature of the bath enabled all adjustments for a new temperature setting to be completed within an hour. The bath then remained within 0.01° for ten hours and within 0.03° for several days. The container was the silvered dewar flask, A. The level of the thermo-

(1) (a) Luther and Forbes, *THIS JOURNAL*, **31**, 770 (1909); (b) Forbes, Heidt and Boissonas, *ibid.*, **54**, 960 (1932); (c) Forbes, Heidt and Brackett, *ibid.*, **55**, 588 (1933); (d) Forbes and Heidt, *ibid.*, **55**, 2407 (1933); (e) Heidt and Forbes, *ibid.*, **55**, 2701 (1933); and (f) Forbes, *Cold Spring Harbor Symposia Quant. Biol.*, **2**, 1 (1935).

(2) Mr. Arnold J. Levine made the drawings in Fig. 1, with financial aid from the National Youth Administration.

(3) Heidt and Purves, *THIS JOURNAL*, **60**, 1206 (1938).