tion no further experiments of this type will now be carried out by us. Kinetic experiments are now in progress and it is hoped to evaluate the rate constants k, k_A and k_B for several pairs of alkoxides and corresponding ketones.

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RECEIVED APRIL 25, 1950

Analysis of Ore Residues for Ionium and Protactinium[1]

BY L. I. KATZIN, Q. VAN WINKLE AND J. SEDLET

With the availability of large amounts of pitchblende ore residues, due to the processing of uranium for atomic power developments, it has been possible to consider the recovery of long-lived members of the uranium and actinium radioactive decay series in appreciable amount. These materials are of use as radiation sources, and sources of other isotopes, in addition to their intrinsic interest. This report deals with analysis of some residue fractions which have not previously been considered as sources for protactinium (Pa^{231}) and ionium (Th^{230}), but which may prove to be convenient sources of these materials.

The isotope Pa^{231} occurs in nature approximately to the extent that radium (Ra^{226}) occurs, which is about 0.15 part per million in pitchblende ore containing about 60% by weight of U_3O_8. The sum total of this material which has been extracted and purified, according to literature reports, is probably not significantly more than 2 g., considerably less than the amount of radium recovered.

After initial manipulations, pitchblende ores are usually treated with sulfuric acid and sodium nitrate, giving an acidic solution of uranyl salts (and other salts) with an insoluble residue in which is found the radium. Some polonium, ionium and protactinium dissolve with the uranium. A fraction at least of the protactinium presumably remains with the insoluble gangue, from the fact that protactinium has been obtained from such material. Thus, von Grosse[2] and Graue and Käding[3,4] used the ultimate residues following removal of the radium as their sources of protactinium.

The acid solution of uranyl nitrate is treated with excess sodium carbonate to precipitate some of the non-uranium materials appearing in solution, the uranium remaining in solution as the carbonate complex. It is to be expected that the protactinium dissolved in the first step should precipitate with the other hydroxides and carbonates at this point. The behavior of ionium is less definite, since thorium forms a soluble carbonate complex under the proper conditions. It seems likely that there might be at least a partial precipitation at this point. The analytical data bear out this presumption.

The carbonate solution of uranium is then treated with NaOH to precipitate uranium, the uranium dissolved in acid and reprecipitated with ammonia. It is to be expected that any protactinium and ionium present in the carbonate solution would follow the uranium through these steps. The ammonium diuranate is next calcined to U_3O_8, the oxide dissolved in nitric acid, and the concentrated nitrate solution extracted with ether. The ether solution of uranyl nitrate is washed repeatedly with portions of water until no further UX$_1$ activity (Th^{234}) can be detected. After steps for recovery of additional uranium from the washes and original solution, the residual solutes are combined and saved, together with any insoluble residue from treatment of the oxide with nitric acid. It is to be expected that this residue, therefore, may be a rich source of ionium, if an appreciable portion survives the carbonate precipitation.

In the classical isolations of protactinium,[2,3,4,5] the starting material was the ultimate residue remaining after extraction of radium, following preliminary removal of uranium. These residues were obtained from the Joachimsthal mine in Czechoslovakia. From the fact that these were residues from extensive chemical treatments, it might be expected that the isolation of protactinium from them might be beset by difficulties in addition to those inherent in the chemical nature of the protactinium. Therefore it was considered highly worthwhile to investigate a less refractory source. The carbonate precipitates from the uranium process were a logical point of attack, since they represented the probable site of any protactinium that might have dissolved in the original acid treatment, while at the same time the material had already been in solution and should be amenable to redissolution with simple acid treatment. The ionium content of this fraction similarly would be more available than that in the original ore or the radium residues. Another possible source of ionium is the residue of the ether extraction procedure, as already stated.

The analyses of these fractions, to be reported in this paper, show that the carbonate fraction is indeed a relatively rich and readily worked source of both protactinium and ionium, and that the ether extraction residues contain ionium essentially free of protactinium or polonium. Their ionium content is something over 6 parts per million. The data further show that more than half of the protactinium and ionium may

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(1) Work done in 1944 under auspices of the Manhattan Engineer District at the "Metallurgical Laboratory," University of Chicago, predecessor of the Argonne Laboratory.

(2) A. von Grosse, *Ber.*, **61B**, 233 (1928).

(3) G. Graue and H. Käding, *Naturwissenschaften*, **22**, 286 (1934).

(4) G. Graue and H. Käding, *Angew. Chem.*, **47**, 650 (1934).

(5) A. von Grosse and M. Agruss, THIS JOURNAL, **56**, 2200 (1934); *Ind. Eng. Chem.*, **27**, 422 (1935).

TABLE I

RADIOACTIVE ANALYSES OF URANIUM PROCESS RESIDUES

Sample origin	Fraction	Total alpha (c./m./g. at 50%)	Analyses Protactinium % of act.	Protactinium p. p. m.	Ionium % of act.	Ionium p. p. m.	Polonium % of act.	Polonium microcurie/g.
1. Carbonate ppt. from 65% pitchblende (African), no. 3-1	HNO_3 soln.	4.5×10^5	<0.3	<0.03	78	16	20	0.08
	Silicious residue	3.5×10^4	40	0.27	<20	<0.3	25	0.008
2. As above, but another shipment, no. 3-2	HNO_3 soln.	2.2×10^4	<1	<0.04	...	.....	....	.....
	Silicious residue	2.4×10^4	75	0.35	<5	<0.05	20	0.004
3. As above, but from another processor, no. 7	HNO_3 soln.	4.4×10^5	....	....	⩽94	⩽19	4-6	0.02
	Gelatinous residue	7×10^4	25	0.38	10	0.3	>50	>0.03
4. Sulfate residue, 65% African pitchblende, no. 1	Soln. HCl after NaOH	6.0×10^5	⩽3.6	⩽0.4	90	24	0-5	0-0.03
	Soln. HCl after Na_2CO_3	2×10^6	<0.2	<0.08	5-10	5-9	0-5	0-0.1
5. Residue of ether extraction of uranium, no. 8	HNO_3-HF soluble	1.4×10^5	<0.05	<0.01	~100	6	....	.....
	Insoluble fluoride				Not analyzed			

be dissolved in the initial acid treatment of the ore, and appear in the carbonate fraction.

Experimental

Several analytical procedures have been reported in the literature for determination of protactinium in ores, which make use of coprecipitation. One procedure, first employed by Hahn and Meitner, and developed further by Wildish,[6] makes use of tantalic oxide as a carrier for protactinium. Another procedure developed by several workers has involved coprecipitation with titanium, especially by hydrolysis of the hydroxide from salts such as the sulfate. Von Grosse[2] has pointed out the inadequacy of tantalum carrier and has suggested instead of the use of zirconium phosphate. Through dissolution of this precipitate in hydrofluoric acid, precipitations of carriers for contaminating radioactivities can be made to give radiochemical purification of the protactinium. A manganese dioxide carrier also has been used.[7] In some circumstances zirconium iodate may be a useful carrier precipitate.[8]

The principal long-lived alpha activities present in the fractions examined (excluding the uranium isotopes) are radium, polonium, ionium and protactinium. The polonium, short-lived in comparison to the others, is still of appreciable half-life (140 days) and is supported by its long-lived parent lead isotope RaD (22 years). Radiochemical analytical procedures must therefore be capable of distinguishing these four isotopes where they occur together, and never less than the last three.

The procedures finally adopted depend primarily on the following behavior of trace concentrations of the activities in question: (1) barium sulfate will carry radium quantitatively but not protactinium; thorium isotopes are partially carried; (2) zirconium phosphate will carry protactinium (and thorium) well under the proper conditions, and will not carry radium; (3) manganese dioxide formed *in situ* from manganous ion and permanganate will carry polonium quantitatively both in the presence and absence of fluoride; (4) manganese dioxide will carry protactinium except in the presence of fluoride; (5) when Th^{232} is added to a detectable concentration, manganese dioxide carries no significant amount of ionium activity; (6) when thorium is precipitated with hydrofluoric acid (thereby precipitating the isotopic ionium) neither protactinium nor polonium is carried appreciably; (7) a silver wire will collect polonium from a halogen acid solution. Three types of residues have been analyzed so far. These consist of the carbonate fraction discussed earlier (three samples), the ultimate sulfate residue mentioned (one sample) and the residue of ether extraction (one sample).

Carbonate Residues.—These consisted of two samples from one process, and a third sample from a process operated by a different producer. Treatment with concentrated nitric acid yielded a gelatinous residuum composed mainly of silica; the readily soluble portion and the residue were analyzed separately.

Following separation by centrifugation, the gel was treated with HF and perchloric acid, the perchloric acid eventually fumed off, and the remaining solid matter fused with alkali carbonate. The carbonate melt was leached with hot potassium hydroxide solution (0.05 M) to remove any tantalum present, and the leaches discarded. The remaining solid was dissolved by fusing it with $KHSO_4$ and dissolving in normal hydrochloric acid. After the addition of some Pa^{233} to act as tracer for the protactinium, radiochemical analysis was carried out.

Sulfate Residues.—The solid material was fused with sodium hydroxide and the melt leached with dilute hydrochloric acid, dissolving about 18% of the solids. This solution was analyzed separately. The remaining solids were fused with carbonate and the melt leached with water which was discarded. The solid carbonates then dissolved completely in dilute hydrochloric acid. Following addition of Pa^{233} tracer, the two solutions were analyzed separately.

Ether Residues.—A uniform sample was dried, then fused with carbonate. A water leach of the melt was discarded. The residue was treated with hydrofluoric and nitric acid several times, evaporating to dryness. Following a final evaporation, the material was dissolved in nitric acid, leaving a white granular residue insoluble in nitric or hydrofluoric acid (probably alkaline earth fluoride). The acid solution was analyzed further. Unfortunately the fluoride residue, which may have been composed in part of thorium fluorides, was discarded. Another analysis, carried out subsequently by Mr. C. C. Bard, gave complete solution. The value from this analysis is found in Table I.

Analytical Results.—A summary of the analytical findings for the residue samples investigated is found in Table I. The exact values of the analyses are not significant, and should be considered only as an indication of relative orders of magnitude. This is necessitated in part by analytical uncertainties, and in part by the inhomogeneity of the material itself. The variability from the latter standpoint is necessarily quite large. Decay of polonium is another source of variability. Material balances are not complete, as can be seen; this is in part due to analytical failure, but in part due to radioactivities other than those being reported (short-lived activities and, in the case of sample 5, radium and its daughters).

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(6) J. E. Wildish, THIS JOURNAL, **52**, 168 (1930).

(7) A. von Grosse and M. Agruss, *ibid.*, **57**, 438 (1935).

(8) G. T. Seaborg, J. W. Gofman and R. W. Stoughton, *Plutonium Project Record*, Vol. **17B**, paper No. 1.1

The carbonate fractions are seen to contain on the order of 0.3–0.35 part per million of protactinium, which is mainly bound with the acid-insoluble silicious portion of this fraction. The ionium, present to some 15–20 parts per million, is found in the readily soluble portion of the fraction. Information furnished about the carbonate fraction is that it is 215 parts by weight for 580 parts by weight of the crude ore—*i. e.*, 37%. For pitchblende which is 65% by weight U_3O_8, this indicates that on the order of two-thirds the original protactinium content of the ore was dissolved in the sulfuric–nitric acid treatment, and precipitated by the carbonate treatment, with more than three-fourths of the ionium content following the same path. The apparent high level of ionium in the sulfate residues is in part at least a reflection of the fact that much of the soluble portion of the ore has been removed, giving a bulk concentration. For example, removal of the uranium alone gives a concentration of about threefold. It is interesting to note that the radioactivity surviving to the ether residues is practically entirely ionium (together with a certain amount of uranium). It is difficult to assign a concentration factor for this material, but it must be rather large due to the previous treatments.

On the basis of the results obtained, a number of milligrams of protactinium and approximately one-half gram of ionium (with three times as much Th^{232}) have been obtained in pure state, from a carbonate fraction.[9,10,11] The yields obtained for the protactinium correspond to 50–60% of the material indicated by preliminary analysis. No attempt was made to obtain complete recovery of ionium.

(9) K. Kraus and Q. Van Winkle, "PPR," Vol. **17B**, No. 6.2.

(10) R. Larson, L. I. Katzin and E. Hausman, *ibid.*, Vol. **17B**, No. 6.3.

(11) R. C. Thompson, Q. Van Winkle and J. G. Malm, *ibid.*, Vol. **17B**, No. 6.4.

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RECEIVED MAY 1, 1950

The Melting Point of Lead Bromide

BY L. M. KNOWLES

The literature references to lead bromide may be divided into two general groups which report the melting point at approximately 370°[1] and 495°,[2] respectively. Recent investigations in this Laboratory, which are summarized below, reveal that the cause of this discrepancy was the failure of many investigators to procure pure lead bromide. We have determined the melting point of lead bromide to be 370.0 ± 0.2° for various rates of heating and cooling; in contact with platinum, quartz, Vycor, Pyrex and magnesium oxide crucibles; and under atmospheres of air and nitrogen, and *in vacuo*. Each sample, tested chemically and spectroscopically both before and after each thermal run, contained at least 99.7% lead bromide. Temperature measurements with iron–constantan and platinum–platinum 10% rhodium thermocouples, gave a consistent melting point of 370.0 ± 0.2°. In no case was a value near 495° obtained.

The literature references to lead bromide are wholly inadequate in reporting methods of preparation or analyses. Consequently, it is impossible to determine the true composition of the material reported to melt near 495°. However, recent unpublished data from our laboratory on the lead bromide–lead oxide system show a persistent transformation temperature at 497° for compositions of 35–55 mole % lead oxide. It is this oxybromide transition temperature which the authors reporting the higher value probably measured.

The accepted correlation of the heat capacities and heat of fusion of lead bromide is the work of Kelley.[3] Unfortunately Kelley's calculations are based on the physical properties of a lead bromide sample reported to melt at 488°. Consequently, the accepted specific heat equations and other thermodynamic data apply to the basic salt rather than to pure lead bromide.

[1] Ramsay and Eumorfopoulos, *Phil. Mag.*, **41**, 360 (1896); Herrmann, *Z. anorg. allgem. Chem.*, **71**, 287 (1911); C. Sandonnini, *Gazz. chim. ital.*, **41**, II, 145 (1911); Lorenz and Fox, *Z. physik. Chem.*, **63**, 109 (1908); Tubandt and Eggert, *Z. anorg. Chem.*, **110**, 219 (1920); Mönkemeyer, *Neues Jahrb. Mineral. Geol.*, **22**, (B. B.) 1 (1906); Calingaert, Lamb and Meyer, THIS JOURNAL, **71**, 3709 (1949).

[2] Czepinski, *Z. anorg. allgem. Chem.*, **19**, 208 (1899); Goodwin and Kalmus, *Phys. Rev.*, **28**, 1 (1909); Helfstein, *Z. anorg. Chem.*, **23**, 255 (1900); Weber, *ibid.*, **21**, 305 (1899); Ehrhardt, *Ann. Physik*, **24**, 215 (1885); Camelley, *J. Chem. Soc.*, **33**, 278 (1878).

[3] Kelley, *U. S. Bureau of Mines Bull.*, **371**, 31 (1934); **383**, 61 (1935); **476**, 95 (1949); Quill, "The Chemistry and Metallurgy of Miscellaneous Materials, Thermodynamics," McGraw-Hill Book Co., Inc., New York, N. Y., 1950; Natl. Bur. Standards, Selected Values of Chemical Thermodynamic Properties, Table I: 27-3, Sept. 30, 1948; Table II: 27-2, Sept. 30, 1948.

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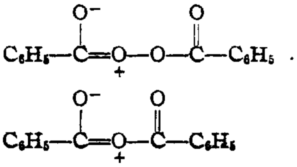
RECEIVED MAY 29, 1950

The Interaction of Diacyl Peroxides with Diazomethane

BY JOHN E. LEFFLER[1]

Diacyl peroxides might be expected to react with diazomethane either by analogy with acid anhydrides[2] or by analogy with sources of free radicals like hexaphenylethane.[3] However, no reaction was found between benzoyl peroxide and diazomethane in ether solution, the peroxide being recovered unchanged. This result may be due to a lesser degree of positive charge on the carbonyl group of the peroxide. The resonance form shown below would be of lower energy in the peroxide than in the acid anhydride, since in the anhydride the positive charge would be adjacent to the positive end of a carbonyl group.



$$C_6H_5-\overset{\overset{O^-}{|}}{C}=\underset{+}{O}-O-\overset{\overset{O}{\|}}{C}-C_6H_5 \quad .$$

$$C_6H_5-\overset{\overset{O^-}{|}}{C}=\underset{+}{O}-\overset{\overset{O}{\|}}{C}-C_6H_5$$

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[1] Department of Chemistry, Florida State University, Tallahassee, Florida.

[2] Bradley and Robinson, THIS JOURNAL, **52**, 1558 (1930).

[3] Schlenk, *Ann.*, **394**, 183 (1912).