

In conclusion, the writer wishes to express his appreciation of the valuable assistance of Mr. S. P. Sweetser, who carried out the experimental part of this investigation.

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[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY OF HARVARD UNIVERSITY.]

THE REFRACTIVE INDEX AND SOLUBILITIES OF THE NITRATES OF LEAD ISOTOPES.

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Many investigations during the last few years have shown that among all the properties of the isotopes of lead which have been investigated only those which concern mass and radioactivity differ in different specimens.¹

Most of these investigations (although not all of them) have concerned the metallic form of the isotopes, but it is worth while also to investigate very fully the salts. Among other properties, the comparative refractive indices of like salts of different isotopes seemed to be worth studying, for obvious reasons. The comparison of solubilities also seemed worthy of more accurate determination than has yet been accorded it.² Accordingly, both of these subjects have been studied in the present investigation; and the results are recorded herewith.

I. The Refractive Indices of the Nitrates of Lead Isotopes.

The method of total reflection employing a crystal refractometer of the Abbé type, improved and manufactured by Zeiss, was used for the determination, since this is an accurate method and requires only a small, smooth, plane surface of the crystal. The microscopic method of immersion in liquid of equal refractive index is troublesome and less accurate, while the method of minimum deviation requires a crystal of some size possessing an accurately measured transparent crystal angle between perfectly plane surfaces.

The nitrate was chosen for the present purpose, since it is isotropic

¹ See, for example, "Reports on Radioactivity," by F. Soddy, in the *Annual Reports of the Progress of Chemistry*, published by the Chemical Society (London); also five papers in THIS JOURNAL, Richards and Lambert, **36**, 1229 (1914); Richards and Wadsworth, **38**, 221, 1658 and 2613 (1916); Richards and Hall, **39**, 531 (1917). Comment by Soddy, THIS JOURNAL, **39**, 1614 (1917). The exceedingly small differences in spectra found by Harkins and Aronberg (*Proc. Nat. Acad. Sci.*, **3**, 710 (1917)) may perhaps be referred to differences in mass.

² Fajans and Fischler, *Z. anorg. allgem. Chem.*, **95**, 284 (1916); Fajans and Lambert, *Ibid.*, **95**, 297 (1916). They determined the solubilities of ordinary and radioactive lead nitrates, and found no difference greater than the wide range, 0.75%, of their experimental error.

and crystallizes readily. The usual crystal habit is a combination of the cube and octahedron, the cubic faces being often prominently developed. Small crystals may be perfectly clear, but larger ones are almost invariably somewhat opaque in parts. Little difficulty is encountered in preparing crystals with bright natural surfaces 10 sq. mm. in area. If, as is sometimes the case, the surfaces are a trifle rough, careful polishing on fine silk fabric yields an artificial plane surface of a fairly high degree of luster.

The two samples of nitrate were prepared: one from salt made from "test lead" free from silver and tin, which was dissolved in very pure nitric acid and the product recrystallized several times from faintly acid solution; and the other from pure Australian uranio-lead nitrate remaining from earlier investigations in this laboratory.¹

Warm concentrated solutions of these salts were surrounded by non-conducting material and allowed to cool slowly to room temperature in a covered large porcelain dish, which stood undisturbed for days, until the crystals had grown to the required size. The usual precautions were taken with regard to crusts and scattered crystals. Picked crystals were chosen for measurement.

The choice of the fluid which served as the medium of contact between the crystal and the flat upper surface of the glass hemisphere of the refractometer offered difficulty at first, since it must have a refractive index at least as high as that of the solid to be measured. Few liquids possess a refractive index as high as 1.78, and some of these, reacting with lead salts, were not applicable. Considerable time was wasted in preparing phenyl sulfide, $(C_6H_5)_2S$, which was given in a recently published text-book as having an index 1.95; but when obtained in a state of purity, boiling at 292.5° , it possessed the index of refraction 1.635 (agreeing with the determination, 1.63, of Marpmann²). After this disappointment it was found that a saturated solution of sulfur in methylene iodide (CH_2I_2) would answer the purpose, since it does not appreciably attack lead nitrate and has a refractive index of about 1.79. Roll sulfur was warmed in commercial colorless methylene iodide; on cooling, the mixture was filtered through hardened filter paper to remove excess of sulfur. A clear, light yellow and comparatively stable solution was thus obtained, having as an index of refraction with sodium light the value 1.7908 at room temperature. It was kept in the dark.

The refractometer belongs to the Mineralogical Museum of Harvard University, and was very kindly placed at our disposal by Professor J. E. Wolff. We are greatly indebted to him, also, for having saved us

¹ Richards and Hall, *THIS JOURNAL*, **39**, 531 (1917).

² Marpmann, *Z. anal. Chem.*, **1892**, 476.

much time in making the preliminary adjustments and in giving us the benefit of his experience.

Upon the flat upper surface of the glass hemisphere of the refractometer was placed a small drop of the fluid just described, and the crystal to be measured was gently pressed into this drop so as to be in intimate contact with the glass surface. The mirror and telescope of the instrument were now so arranged that the boundary between light and dark was brought into the center of the field of view, and final adjustment was made with the micrometer screw. The crystal was now rotated gradually in the horizontal plane, and afterwards slightly displaced from its original position, a new set of readings being secured after each shift, to verify the results and exclude any error from incorrect placement.

That assurance should be made doubly sure the refractometer was tested by means of a polished glass prism for which $n_D = 1.7512$ —a value not very far from that of lead nitrate. In this case the value could be found accurately also by the method of minimum deviation; the comparison of the value thus found with that given by the Abbé refractometer was wholly satisfactory, since the angle observed in the refractometer $67^\circ 48' 17''$ (the mean of 7 readings) agreed within the limit of error with the value $67^\circ 48' 29''$, corresponding to the known refractive index. This test proved that the graduation of the scale of the refractometer was correct in the vicinity of the readings given by the crystals themselves.

The results of our 51 determinations on ten different samples of ordinary lead nitrate ranged from $70^\circ 26'$ to $70^\circ 19'$ with a mean of $70^\circ 23'$ (probable error 0.2'), corresponding to a refractive index $n_D = 1.7815$; and the results of 25 determinations on 5 different samples of uranio-lead nitrate ranged from $70^\circ 25'$ to $70^\circ 19'$ with a mean of $70^\circ 22'$ (probable error 0.3'), corresponding to a refractive index $n_D = 1.7814$. No systematic difference could be detected, in either series, between natural faces of crystals and carefully polished surfaces. The temperature was not far from 20° in every case.

Thus it appears that the difference in refractive indices of the two specimens does not exceed the error of experimentation, which is small enough to give significance to the outcome.

II. The Solubilities of the Nitrates of Lead Isotopes.

In the work already mentioned Fajans and Fischler and Fajans and Lembert showed that the difference in the molecular solubility of the nitrate of two different isotopes of lead (namely, common lead and uranio-lead) was not beyond their limit of experimental error, but, unfortunately, this limit of experimental error was of the order of possible variations to be expected in the concentrations. The work, therefore, seemed to be worth repeating with greater accuracy, and the following discussion

describes experiments which show beyond question that the solubilities by weight show just that degree of difference which one would expect from the atomic weights—in other words, that the molecular solubilities are really identical to within one-tenth of one per cent.

The method used was similar to that described in a recent paper by one of us in collaboration with Victor Yngve.¹ The several samples of lead nitrate in large excess were rotated with distilled water in large, closed test tubes immersed in a thermostat, until equilibrium had been attained. Weighed portions of the solutions were then removed and evaporated with sulfuric acid in small, clean, weighed "Pyrex" beakers, the lead sulfate being weighed, after gradually heating to a high temperature (350°)² until constant in weight.

The chief difficulty was the extremely slow saturation of the solution with lead nitrate. Whereas sodium sulfate had been found in the investigation just mentioned to require only about 15 minutes for saturation at 25°, lead nitrate required at least 24 hours. Earlier determinations, approaching the equilibrium from opposite sides, indicated this fact clearly, since equality was not attained until that time had elapsed. It is, of course, essential that throughout this time, especially toward the end, the temperature should be kept very constant. A fluctuating bath will not give a constant result, even if the temperature is perfectly constant throughout the last two or three hours. Rotation was slow, and the crystals sufficiently coarse so that when the rotation was stopped, the solid particles settled rapidly to the bottom of the tube, leaving a clear, supernatant liquid. The temperature, 25.02°, was verified by a standard thermometer. Since much depends upon the details, these are recorded in full below.

The test tube, thoroughly cleaned, was filled with the distilled water to within a few centimeters of the top and an appropriate excess of solid was added. The rubber stopper, provided with a short length of wide glass tubing, which passed through its center, and having been previously boiled with dilute sodium hydroxide and then with distilled water, was forced into place. The outer end of the projecting glass tube was closed by means of a short rubber tube and glass plug, the whole stopper and tube, as well as the lip of the test tube, being dried and coated with paraffin to render it water-tight and keep it clean. This arrangement made possible the withdrawal of the solution from the tube, by means of a pipet, without necessitating the removal of the stopper—an operation entailing

¹ THIS JOURNAL, 40, 164 (1918).

² Mostowich, *C. A.*, 11, 931 (1917); *J. Russ. Met. Soc.*, 1915, I, 303. Mostowich shows that lead sulfate begins to decompose at 800°, while some authorities set the temperature of initial decomposition still lower. Our experience shows that incautious heating, especially by a Bunsen burner, may lead to decomposition and error.

the possibility of error through the liability of entrance of water into the tube from outside, as well as danger of evaporation.

The filled tube, affixed by strong rubber bands to the rotating device, was now set in motion, end-over-end, in the thermostat bath, the power being derived, through a suitable system of belts and pulleys, from the thermostat motor. After at least 24 hours, the rotation was stopped, and the tube raised to the surface of the thermostat bath, the plugged vent alone being permitted to emerge from the water. The exterior of this plug was dried by wiping, and the rubber tube with the glass plug cut off with shears just above the upper end of the vent.

A filtering device, consisting of a short length of glass tubing drawn down at one end, containing a small loose plug of "absorbent cotton," was attached by a piece of rubber tubing to the lower end of a thoroughly clean and dry 50-cc. pipet, which was now inserted through the vent into the solution, and a sample of the latter withdrawn. When not in use, the pipet was kept in a long, glass tube, sealed at one end, and immersed in the thermostat, so that the temperature of the pipet might not be very different from that of the solution. The filtering cotton was so small in amount as to have exercised no important adsorptive effect. If any, this effect would have been identical in the two series.

The filtering tube having been removed, the sample of solution was run into 3 weighing bottles, previously cleaned, dried and weighed. The stoppers of the weighing bottles were inserted immediately, and the weights of bottle plus solution determined as rapidly as possible. Care was taken in filling the weighing bottles not to allow the ground joint of the stopper to become wet. The stopper thus remained perfectly dry and clean and did not require subsequent rinsing.

The weighed solutions were then quantitatively transferred to small, clean, weighed Pyrex beakers, holding about 50 cc. The beakers were found to stand the subsequent heating (to 350°) very well, and the weight of a given beaker did not diminish in successive analyses by more than a few tenths of a milligram. Lead sulfate does not adhere to the glass nor attack it to any appreciable degree. A quartz dish, and a platinum dish, were also used in several determinations, but the glass beakers were found to be equally satisfactory.

To the lead nitrate solutions, pure dilute sulfuric acid was now added in excess of the amount required to precipitate completely the lead sulfate. The water and nitric acid were expelled as far as possible on the steam bath, the last portions being driven off with care, because of the danger of spattering. The residual liquid, consisting of the excess of sulfuric acid, was now expelled by cautious heating in a carefully constructed and electrically heated air bath, the temperature of which was very gradually raised to about 350°. The bath was maintained at this

temperature until fumes of sulfur trioxide could no longer be seen; and then for about an hour longer. It was found by trial that this procedure sufficed to bring the lead sulfate to constant weight without decomposition.

The two samples of isotopic lead employed were those already described earlier in this paper.

The data (the weights having been corrected to the vacuum standard)¹ are as follows:

TABLE I.—SOLUBILITY DATA.

Wt. soln.	Wt. PbSO ₄ .	g. Pb(NO ₃) ₂ per 100 g. soln.	
		Common Lead.	At. wt. 207.20.
20.4632	6.9930	37.325	
35.3191	12.0748	37.340	
21.0670	7.2053	37.355	
36.0289	12.3208	37.350	Mean, 37.342
		Uranio Lead.	At. wt. 206.41.
23.9090	8.1554	37.263	
16.6518	5.6809	37.270	
18.0814	6.1666	37.258	
20.8373	7.1116	37.284	
17.6898	6.0364	37.278	
17.2890	5.8992	37.275	
20.6875	7.0630	37.297	
14.6074	4.9870	37.296	
15.5598	5.3119	37.295	Mean, 37.280

The solubility values, expressed also in other terms than those indicated in Table I, are given below.

TABLE II.—SOLUBILITY VALUES.

	Common lead.	Uranio lead.	Diff. (g.).	Diff. %.
g. Pb(NO ₃) ₂ per 100 g. solution.....	37.342	37.280	0.062	..
g. Pb(NO ₃) ₂ per 100 g. water.....	59.597	59.439	0.158	0.26
g. Pb per 100 g. water.....	37.281	37.130	0.151	0.41
Molal solubility per 1000 g. water..	1.7993	1.7991

The percentage difference in molecular weight of the two forms of lead nitrate is equal to 0.24%, whereas the observed difference in solubilities in equal weights of water was 0.26%.

Similarly, the percentage difference in atomic weight of the two kinds of lead is equal to 0.38%, whereas the observed difference in lead contents corresponding to like weights of water was 0.41%.

Thus the difference in solubility by weight is seen to be due (within the possible error of experiment) solely to the different atomic weights of the two specimens of lead. Another way of emphasizing the same fact is to

¹In Table I, the density of precipitated PbSO₄ is taken as 6.2 (from Schröder, *Pogg. Ann. Ergb.*, 6, 622 (1874); the density of saturated solutions of Pb(NO₃)₂ at 25° as 1.44 (from Fajans and Lambert, *Loc. cit.*); the density of brass as 8.5.

compare the last two differences in grams in the third column of figures above. Evidently the divergence is due primarily to the lead and not to the nitrate ion contained in the solution. Yet another way, of course, is to compare the molal solubilities of lead nitrate per 1000 g. of water, which are, respectively, 1.7993 for common lead nitrate and 1.7991 for uranio lead nitrate.

The outcome of this work, then, by finding no appreciable difference in either the refractive index or molal solubility of samples of lead nitrate containing isotopes of widely different atomic weights, confirms earlier work upon other properties of these interesting substances, and affords further support for the hypothesis due to Russell, Fleck, Soddy and Fajans. Evidently weight (or mass) is the prime distinguishing feature of the two kinds of lead here studied, as it was in other cases.

If this is found universally to be the case, weight (or mass) must, of course, be chosen as the basis for any method of separating the isotopes when they have been mixed. In view of these considerations, clearly the only reasonable hope of separating the isotopes of lead lies in the method of fractional diffusion, as has been already suggested by many other experimenters on this subject. Mr. Harold S. King, of this University, has made very promising preliminary experiments preparatory to such an undertaking, and expects to continue them (in collaboration with one of the present authors) when his time, now devoted to war work, is freed at the conclusion of the world conflict.

We are glad to acknowledge our indebtedness to the Carnegie Institution of Washington for financial assistance in this research.

Summary.

This paper recounts measurements of the refractive indices and molal solubilities of two samples of ordinary lead nitrate and uranio lead nitrate. No differences between the two samples within the limit of error of measurement were found, as regards either property. The indices of refraction of the crystalline nitrate (for the sodium lines) were found to be, respectively, 1.7815 and 1.7814, and the molal solubilities, respectively, 1.7993 and 1.7991 per thousand grams of water.

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NOTES.

A Still for the Continuous Preparation in Quantity of Water of High Purity.—Two 5-liter pyrex glass bulbs are set at an angle of about 60°. The first of these is equipped with a pressure tube, raw distilled water supply and delivery tubes, the second, with inlet tube and exit column. The latter is a tube 2 × 20 cm. The upper end of the exit column is blown in such a way as to form a trap device, which reduces the possibility of impurities being carried over into the condenser. The column finally