

TABLE III

DENSITIES OF ADSORBED ACETONE				
G. acetone adsorbed	Eq. press., cm.	PV of He units:cm.-ml.	$\Delta V$	Density ads. layer
0.391	0.10	521.7	0.425	0.920
.878	.25	751.4	1.144	.767
1.466	.36	632.3	2.035	.721
1.878	(.34)	549.2	2.700	.690
3.060	1.54	613.2	4.403	.694
3.791	11.48	592.9	5.100	.743
3.919	20.83	376.2	5.290	.741
1.171	0.27			
2.38	.63			
2.78	1.02			
Density of normal liquid, 30°			0.779	
Vapor pressure, 30°			28.27 cm.	
Volume of free space in bulb			23.077 ml.	
Weight of charcoal sample			10.23 g.	

The authors are indebted to the National Research Council for the Grant-in-Aid with which a Gaertner cathetometer was purchased.

### Summary

1. The average densities of adsorbed carbon tetrachloride and acetone on a steam-carbon dioxide activated coconut charcoal were determined at 30°.

2. The average densities show a sharp decline after which a rise occurs.

3. About 15 to 20% of the surface is covered with condensed vapor held by active center forces. The remainder of the surface seems to be covered by a different process.

WEST LAFAYETTE, IND. RECEIVED DECEMBER 12, 1938

[CONTRIBUTION OF THE RESEARCH LABORATORY OF INORGANIC CHEMISTRY, No. 68, AND OF THE GEORGE EASTMAN LABORATORY OF PHYSICS, OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

## The Determination of the Vapor Pressure of Thorium Acetylacetonate by Radioactivity Measurements

BY RALPH C. YOUNG, CLARK GOODMAN AND JULIUS KOVITZ

Minute quantities of the radioactive elements can be measured accurately from the ionization produced by their radiations. Because of these electrical effects, properties of compounds of such elements can be determined which are outside the sensitivity of ordinary methods of measurement. In these particular investigations, consideration is given to those elements occurring in the thorium and uranium series which emit alpha particles. The subjects under immediate study are those of

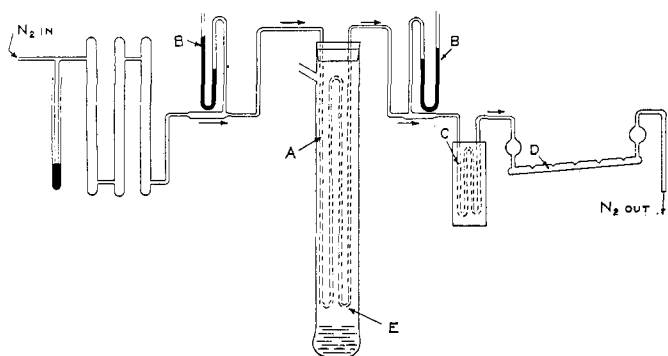


Fig. 1.—Apparatus for saturating nitrogen gas with thorium acetylacetonate.

vapor pressure and solubility, and the first report to be presented is that of the vapor pressure of thorium acetylacetonate at 100°.

Radioactively inert nitrogen was passed through tubes (Fig. 1) of calcium chloride, potassium hydroxide, and phosphorus pentoxide into a 5 mm. X 600 cm. saturator tube A containing finely powdered thorium acetylacetonate. The saturator was constructed to fit into an insulated glass jacket, E. The temperature was maintained between 99.6 and 100.4° by steam. Mercury manometers, B, were joined to each side of the saturator. It was found by experiment that equilibrium conditions could be attained readily if the nitrogen flow was maintained at a slow rate (see Table I). The length of the column and the fineness of subdivision of the compound were contributory factors. The nitrogen from the saturator was passed through tube C, which was cooled in ice, and then into an absorber D, containing acidified alcohol (3% hydrogen chloride). The volume of the nitrogen was measured by displacement of water.

After two to four liters of the gas had passed through the apparatus, the tubes beyond the saturator were washed out with acidified alcohol, the total volume of which, including that of the absorber, amounted to about 150 cc. After standing for at least thirty days, a small portion, usually 10 cc. of this solution, was evaporated on a clean platinum foil 5 cm. X 5 cm. The alpha activity of this basic thorium chloride deposit was then measured by means of an alpha counter similar to that described by Finney and Evans.<sup>1</sup> From these data the saturation concentration of thorium acetylacetonate in nitrogen at 100° can be calculated.

(1) Finney and Evans, *Phys. Rev.*, **48**, 509 (1935).

TABLE I

EXPERIMENTAL DATA FOR THE DETERMINATION OF THE VAPOR PRESSURE OF THORIUM ACETYLACETONATE				
Run number.....	I	II	III	IV
Duration of N <sub>2</sub> flow, hours.....	145	168	120	290
Nitrogen passed over the thorium acetylacetonate	{ Vol. cc..... 3775 temp. °K..... 301.5	2173	2448	2976
		298.0	301.5	301.5
Average barometer pressure, mm.....	756.4	758.7	761.5	761.8
Av. diff. of manometer readings (B), mm.....	134.6	73.0	129.0	54.0
Av. total press. in saturator tube, mm.....	891.0	831.7	890.5	815.8
Thorium in N <sub>2</sub> detd. by $\alpha$ count, in 10 <sup>-6</sup> g.....	8.8 $\pm$ 0.8	7.8 $\pm$ 0.6	4.5 $\pm$ 0.3	8.6 $\pm$ 0.6
V. p. of Th acetylacetonate at 100° in 10 <sup>-4</sup> mm.....	2.3 $\pm$ .2	3.2 $\pm$ .2	4.0 $\pm$ .3	3.4 $\pm$ .2
Av. v. p., 3.2 $\pm$ .3				

The conversion of the observed alpha count from the solution deposit into equivalent concentration of thorium acetylacetonate was made by calibrating the apparatus with deposits from an acidified alcohol solution containing the equivalent of  $1.43 \times 10^{-6}$  g. of thorium acetylacetonate per cc. Deposits from 4-cc. portions of this solution gave average counting rates of  $42 \pm 3$  alphas per hour above a background count of  $22 \pm 1.5$  per hour, which corresponds to  $7.3 \pm 0.7$  alphas per hour per  $10^{-6}$  g. of thorium acetylacetonate. These calibrations were made ten months after purification by sublimation of the thorium compound. During this time the activity of radiothorium, and hence also of its decay products, had fallen to 75% of the equilibrium amounts<sup>2,3</sup> (see Kovarik and Adams, Fig. 5). In order to have a common basis of comparison, all measurements were corrected back to the time of preparation of the thorium acetylacetonate. The calibration factor on this basis is  $9.0 \pm 0.9$  alphas per hour per  $10^{-6}$  g. of thorium acetylacetonate. This value was used in calculating the quantities of sublimate given in Table I. The vapor pressures were obtained by use of the perfect gas equation; the average for the four runs being  $3.2 \times 10^{-4}$  mm. (with an estimated probable error of 10%).

In all of the measurements a rapid flow of radioactively inert nitrogen was maintained in the ionization chamber. This procedure largely eliminates the activity of thoron and its immediate decay product thorium A, both of which are alpha emitters. Assuming complete removal of these elements, a theoretical estimate of the calibration factor can be made. Based on the decay constant,  $1.58 \times 10^{-18}$  sec.<sup>-1</sup>, of Kovarik and Adams,<sup>2</sup>

(2) Kovarik and Adams, *Phys. Rev.*, **54**, 413 (1938).

(3) The thorium nitrate, from which the thorium acetylacetonate, Th(C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)<sub>4</sub>, was prepared, contained very nearly equilibrium amounts of the thorium decay products as was shown by emanation measurements.

thorium alone emits  $1.48 \times 10^7$  alphas per hour per gram. On this basis, the four alpha emitters, thorium, radiothorium, thorium X and thorium C present in the deposit give a calibration factor of 10.9 alphas per hour per  $10^{-6}$  g. of thorium acetylacetonate (36.6% Th). This value is somewhat higher than that found experimentally and suggests that the geometry of the ionization chamber does not permit exactly half of the alphas to be counted as has been assumed in this theoretical estimate. Since nearly all thorium bearing minerals contain some uranium, a third isotope of thorium, namely, ionium, may also contribute to the alpha activity. Radon measurements, using Evans'<sup>4</sup> double ionization chamber apparatus, indicated that the thorium acetylacetonate contained  $1.8 \pm 0.2 \times 10^{-12}$  g. of radium per gram eleven months after sublimation of the compound. This value corresponds to an ionium content of  $6.0 \pm 0.7 \times 10^{-8}$  g. per gram of thorium or only  $3.5 \pm 0.4 \times 10^{-3}$  g. of uranium per gram of thorium in the original mineral from which our supply of thorium was prepared. Thus the ionium contributes less than 0.4% of the total observed activity and can be completely neglected in this consideration.

The preparation and purification of thorium acetylacetonate differed in some respects from those by Biltz. Twenty-five grams of acetylacetonate was added to 50 g. of water and a solution of 6 normal ammonium hydroxide was added to the mixture from a buret drop by drop with stirring until solution was complete. This solution was mixed with one containing 25 g. of thorium nitrate in 200 cc. of water. To this mixture, a solution of 6 normal ammonium hydroxide was added drop by drop until it became alkaline to litmus. The precipitated thorium acetylacetonate was filtered, washed, and air-dried. It was

(4) Evans, *Rev. Sci. Instruments*, **6**, 100 (1935).

(5) Biltz, *Ann.*, **331**, 353 (1904).

then sublimed in a vacuum of 0.1 mm. at 160°. A white crystalline sublimate was recovered, m. p. 170.8–171°. The yield was over 90% of the theoretical.

The authors wish to express their appreciation to Dr. N. B. Keevil for his assistance in thoron measurements and to Professor Robley D. Evans for his constructive suggestions and the use of his apparatus for the radium measurements.

This investigation has been aided by a grant from the Cyrus M. Warren Fund of the American Academy of Arts and Sciences.

### Summary

By the use of radioactivity measurements, the vapor pressure of thorium acetylacetonate has been obtained at 100° as  $3.2 \pm 0.3 \times 10^{-4}$  mm. The gas-saturation method was employed, nitrogen being used, and from the latter the thorium compound was extracted and converted into thorium chloride by alcohol acidified with hydrochloric acid. A basic thorium chloride deposit was made on a platinum foil, and by means of an alpha count of this deposit, the molar quantity of sublimed thorium acetylacetonate was obtained.

CAMBRIDGE, MASS.

RECEIVED JANUARY 11, 1939

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

## The Density of Pure Deuterium Oxide

BY HERRICK L. JOHNSTON

Tronstad and Brun<sup>1</sup> recently reported a value of  $d_{25}^{25}$  1.10750  $\pm$  0.00001 for the specific gravity of pure D<sub>2</sub>O at 25° and Swift<sup>2</sup> refers to a private communication from one of Tronstad's associates which revises this to  $d_{25}^{25}$  1.10764. Either of these figures is considerably below the value generally accepted at present, namely,  $d_{25}^{25}$  1.10790  $\pm$  0.00005, determined by Taylor and Selwood.<sup>3</sup>

Observations made several months ago in our own Laboratory confirm the conclusions of Tronstad and co-workers that the Princeton value for the density is considerably too high and agree quantitatively with Tronstad's revised value communicated to Swift.<sup>2</sup> At the same time they indicate definitely that Tronstad's published value of 1.10750 is somewhat low. We obtain the value  $d_{25}^{25}$  1.10763, which we regard as reliable to better than  $\pm$ 0.00005. We desire to report, here, our observations.

Our observations were made on two occasions incident to the preparation of some quantities of extremely pure D<sub>2</sub>O. In both instances we electrolyzed relatively large volumes of deuterium-rich water made alkaline with potassium hydroxide. The cells were equipped with Armco iron electrodes and were known to possess a separation factor,  $\alpha$ , toward the hydrogen isotopes, of a little more than 8. This factor had been determined repeatedly in the same and in similar cells during two years of service in the preparation of extensive quantities of heavy water.

This factor had proved constant with time and showed no significant variation either with current density or with deuterium concentration. The latter had been established with determinations in the concentration range 0.5 of 1% to about 60%.

In both electrolyses, which we will distinguish as Electrolysis A and Electrolysis B, the electrolytic gases were freed of moisture by passage through a trap cooled with a dry ice-ether mixture; passed through a small explosion trap of clean dry sand; recombined at a jet in an atmosphere of dry oxygen supplied from a commercial cylinder at a rate just sufficient to maintain oxygen in excess; and condensed out of contact with air. Successive fractions of the condensate were distilled, with a few crystals of pure dry potassium permanganate added to the still, and their specific gravity determined, at 27°, with an 11-cc. pycnometer of special design. Weighings were accurate to 0.1 mg., or better, and were significant to this figure. Buoyancy corrections were applied. This yielded specific gravities with a precision of  $\pm$ 0.00001. The residues in the cells, after electrolysis was carried as far as desired, were likewise distilled from the potassium hydroxide electrolyte to which a few crystals of dry potassium permanganate were added and, after a second distillation without addition of any reagent, were determined in the pycnometer. Precautions were taken, in all steps, to avoid contamination with atmospheric moisture.

In Electrolysis A we started with 350 cc. of 75% D<sub>2</sub>O and electrolyzed to a residual volume of 100 cc. before samples of combustion water were separately collected. A preliminary calculation indicated that the concentration of this 100 cc. in the cell should be about 99.5% D at this stage. Then a single fraction of 60 cc. was electrolyzed off and separately collected and the 40-cc. residue recovered without further electrolysis. In Electrolysis B the initial charge was 100 cc. of 95% D<sub>2</sub>O. One 40-cc. and two 20-cc. fractions of the combustion water were separately collected and the 20-cc. residue recovered. Volumes of

(1) L. Tronstad and J. Brun, *Trans. Faraday Soc.*, **34**, 766 (1938); cf. also, Tronstad, Nordhagen and Brun, *Nature*, **136**, 515 (1935).

(2) E. Swift, *THIS JOURNAL*, **61**, 198 (1939).

(3) H. S. Taylor and P. W. Selwood, *ibid.*, **56**, 998 (1934); **57**, 642 (1935).