We found that when the vapors pass through a furnace and condense on a liquid nitrogen cooled finger, only white phosphorus condenses when the furnace is below 600°. Above this temperature the condensed material is colored and when the furnace temperature is about 1000°, or higher, a dark brown deposit is obtained. The material is insoluble in propane and ethylene at their boiling points and in carbon bisulfide at $-103°$. A qualitative test with a powerful magnet indicated that the material is not paramagnetic. Brown phosphorus is stable indefinitely at liquid nitrogen temperatures, but on heating, changes irreversibly to a mixture of red and white phosphorus. This change occurs at a measurable rate in the range -100 to $-50°$ but almost instantly at room temperature or higher. We analyzed the mixture by subliming off the volatile white phosphorus onto another cold finger and weighing each separately. Analysis of samples obtained by heating brown phosphorus to $-80°$, room temperature and 100° all gave the same result (within $\pm 5\%$), namely, 20% red phosphorus and 80% white phosphorus. The non-volatile red phosphorus remaining on the finger after evaporation of the white phosphorus varied somewhat in color according to the method of preparation, a heavy coating of brown phosphorus heated to room temperature or higher giving an almost black material. We determined that the density of this almost black material was 2.05 to 2.06 by a flotation method using aqueous barium iodide of varying densities. The density at room temperature of white phosphorus is 1.83, of red phosphorus 2.04 to 2.34 (depending on the method of preparation)[10] and of the high pressure black phosphorus, 2.69. Since our black material did not conduct electricity and had a density in the range of red phosphorus, we have assumed that the polymerization of P_2 may yield substances somewhat different in color depending on the molecular weight but are all essentially "red" phosphorus.

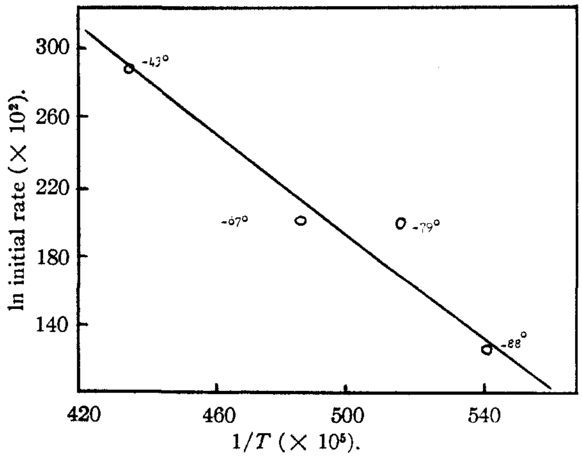

Fig. 1.

Brown phosphorus may also be prepared by heating ordinary red phosphorus in an evacuated jacket at 350–360° or higher and condensing the vapor on a liquid nitrogen cooled finger. The material prepared in this way seems to be identical in all respects with that prepared in the manner described for white phosphorus. We have also found that white phosphorus at $-190°$ exposed to the light from a quartz mercury lamp, gradually changes to the brown form.

We tried a number of different methods for measuring the rate of change of brown phosphorus at various temperatures and finally adopted a method of distilling a thin layer of P_2 onto a liquid nitrogen cooled finger. The P_2 was produced by heating ordinary red phosphorus in a small side arm to 350° for a fixed length of time so that a layer of constant thickness would be obtained. The whole apparatus was then surrounded by a vacuum vessel containing a window and the liquid nitrogen cooled finger was rotated so that the deposit of brown phosphorus was opposite the window. Light from a tiny electric bulb in the cold finger passed through the brown phosphorus and onto a photocell attached to a galvanometer. We measured the rate of change in arbitrary units of galvanometer deflections at four temperatures obtained by filling the vacuum vessel and cold finger with ethane (b.p. $-88°$), hydrogen bromide (b.p. $-67°$), chlorotrifluoromethane (b.p. $-79°$) and propane (b.p. $-43°$). From the graphs we estimated the initial rate of change in terms of galvanometer deflection per minute and plotted the initial rate against $1/T$. The result is shown in Fig. 1 and gives an activation energy of about 3 kcal. for the change.

DEPARTMENT OF CHEMISTRY
THE CATHOLIC UNIVERSITY OF AMERICA
WASHINGTON 17, D. C.

A Preparation of Carrier-free Sb^{125} from Neutron Irradiated Stannous Chloride[1]

BY JOSEPH D. ROBINSON AND MILTON KAHN

RECEIVED NOVEMBER 29, 1952

Only one method for the preparation of carrier-free[2] antimony has been reported.[3] This method involves the deuteron bombardment of tin followed by one precipitation and two distillations to effect the separation of the antimony. Since facilities for deuteron bombardment are often not available and the separation procedure reported requires considerable time, a search for a simpler method which would require only thermal neutron irradiation of the target was undertaken.

This communication reports a procedure for the separation of 2.7-year Sb^{125} from solutions of irradiated stannous chloride employing deposition of the antimony from halide acid solution on metallic copper without the use of external electro-

---

[10] See E. Cohen and J. Olie, *Z. physik. Chem.*, **71**, 1 (1910); P. Jolibois, *Compt. rend.*, **151**, 383 (1910).

[1] This communication is based on work done under the auspices of the Los Alamos Scientific Laboratory and the Atomic Energy Commission and submitted in partial fullfilment of the requirements for the degree of Master of Science in the Graduate School of the University of New Mexico, August, 1952, by Joseph D. Robinson.

[2] The term carrier-free as used by the authors denotes that no isotopic carrier has been knowingly mixed with the nuclide under discussion.

[3] R. Maxwell, H. Haymond, W. Garrison and J. Hamilton, *J. Chem. Phys.*, **17**, 1340 (1949).

motive force, the Reinsch reaction, which has been subsequently studied by Evans.[4]

Experimental

Chemicals and Glassware.—The anhydrous stannous chloride used as a target was obtained from the Metal and Thermit Corporation and was found to be spectrographically free from antimony.[5] The stannic chloride pentahydrate also used as a target was Mallinckrodt analytical reagent grade and was found to be spectrographically free from antimony.[6] Standard antimony trichloride was prepared by dissolving the Baker and Adamson reagent grade salt in 6 *f* hydrochloric acid, and titrating with 0.01 *N* potassium bromate, using sodium indigo sulfonate as an indicator. A correction was made for the indicator blank. Compressed gases were employed from tanks as supplied. All of the other chemicals employed were of analytical reagent grade. None of the glassware used in experiments with solutions containing carrier-free antimony had a history of previous use with solutions containing macro amounts of antimony. Glassware was cleaned with an Alconox[7] solution followed by chromic acid cleaning solution. A separate stock of cleaning solution (free from carrier antimony) was used for glassware coming in contact with carrier-free antimony solutions.

Radioactivity and Counting.—Samples of target material were weighed into quartz vessels and irradiated in a thermal column of a Los Alamos reactor. The irradiated samples were dissolved in the desired solvent and stored in glass-stoppered flasks.

To determine the total Sb^{125} activity in a solution of an irradiated tin chloride, a measured volume of standard antimony trichloride carrier was added to an aliquot of the active solution and the antimony precipitated as the trisulfide from a solution 2 *f* in hydrochloric acid and 1 *f* in hydrofluoric acid containing the tin in the tetravalent state. The precipitation was repeated three times, the antimony counted and the over-all yield determined by titration with potassium bromate. As a verification of the sulfide procedure, a separation of antimony by the distillation method of Scherrer[8] was performed on a duplicate sample and the results were in agreement.

Liquid samples of Sb^{125} were prepared for counting by dilution to a standard height in calibrated 18 × 150 mm. Pyrex tubes. The γ-ray associated with the decay of Sb^{125} was detected with a sodium iodide scintillation counter. The Te^{125m} which grows from Sb^{125} [9] was not detected in the above counting arrangement. Thus, when tellurium carrier was added to a solution of irradiated stannous chloride in 6 *f* hydrochloric acid which was six months old and the tellurium separated by the procedure of Novey,[10] no activity was found associated with the tellurium, and an antimony fraction separated by the sulfide procedure exhibited no growth in a period of two months following irradiation of the stannous chloride.

Procedure.—The metallic copper employed in the deposition of Sb^{125} consisted of spirals of #18 B&S gage wire formed on a quarter inch mandrel. The wires were so prepared that the first bend of the spiral portion occurred at the point such that the spiral had an apparent surface area of 5 sq. cm. When immersed in a solution up to the first bend, the stated area of copper was in contact with the solution. The straight ends of the wires were sealed into 6 × 1.25 mm. capillary tubing, about 15 cm. long, using jewelers' wax. In operation the spirals served both as reactants and stirrers. The copper was prepared for an experiment by washing the formed spiral for three 10-minute periods with carbon tetrachloride, drying and inserting in a glass capillary using forceps to manipulate the wire, and, just prior to use, immersing for three 10-minute periods in concentrated hydrochloric acid. Before inserting in a test solution the copper was dried with absorbent tissue. The copper was rotated in the test solution at about 100 r.p.m. The rate of rotation did not affect the rate of deposition of Sb^{125} over the range 1–150 r.p.m.

The test solutions were 0.21 *f* in tin, either 3 *f* or 6 *f* in hydrochloric acid, and contained 1000 to 1500 counts/minute of Sb^{125} in a total volume of 4 ml. The reaction tubes containing the test solutions were thermostated throughout the period of deposition and for at least 30 minutes prior to insertion of the copper. A separate spiral was immersed in a separate test solution for each experiment.

Upon removal from a test solution the copper was rinsed by three brief immersions in 3 *f* hydrochloric acid and placed in a counting tube. Three ml. of 6 *f* nitric acid was added and the dissolution of copper and antimony allowed to proceed for two minutes. The copper was rinsed with water, the washings added to the counting tube and the activity determined. Antimony, tin and indium carriers were added to the Sb^{125} activity and the antimony separated from the other carriers *via* sulfide precipitation. The constancy of the specific activity of the separated antimony served as a check on the radiochemical purity of the Sb^{125} activity.

The separation of Sb^{125} from copper was effected by adding 1 *f* sodium hydroxide to the nitric acid solution of the metals, with constant stirring, until the desired *p*H or sodium hydroxide formality was attained in the supernatant liquid. The antimony was retained in the supernatant liquid.

Results

The fraction of the total Sb^{125} deposited as a function of time from solutions of irradiated stannous chloride was determined at three temperatures. A typical deposition curve is shown in Fig. 1.

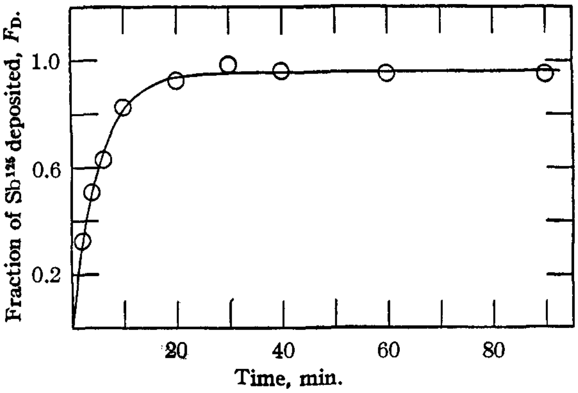

Fig. 1.—Rate of deposition of Sb^{125} at 31° from 6 *f* hydrochloric acid solutions of irradiated stannous chloride. The circles represent experimentally determined values of F_D. The curve was calculated from equation (1) using values of $k_1 = 0.185$ and $k_2 = 0.0074$.

The deposition was found to be consistent with the equation

$$F_D = \left[\frac{k_1}{k_1 + k_2}\right][1 - e^{-(k_1+k_2)t}] \qquad (1)$$

where k_1 and k_2 are constants whose values were determined empirically from curves fitted to the experimental data and F_D is the fraction of Sb^{125} deposited on the copper in time, t. Equation (1) was obtained by assuming that the rate of deposition on copper is proportional (k_1) to the amount of antimony in solution and the rate of dissolution is proportional (k_2) to the amount of antimony on the copper. The deposition of polonium on a gold cathode was found to obey an analogous equation.[11] In Table I are recorded values of k_1

---

(4) B. S. Evans, *Analyst*, **47**, 1 (1922).

(5) (a) W. B. Coleman and Co., Philadelphia, Pennsylvania, performed the spectrographic analyses. (b) The limit of detection was 0.004%.

(6) See ref. 5.

(7) Manufactured by Alconox Inc., Jersey City, N. J.

(8) J. A. Scherrer, *J. Research Natl. Bur. Standards*, **21**, 95 (1938).

(9) G. Friedlander, M. Goldhaber and G. Scharff-Goldhaber, *Phys. Rev.*, **74**, 981 (1948).

(10) C. D. Coryell and N. Sugarman, "Radiochemical Studies: The Fission Products," McGraw-Hill Book Co., Inc., New York, N. Y., 1951, pp. 1611–1612.

(11) F. Joliot, *J. chim. phys.*, **27**, 119 (1930).

and k_2 for various experimental conditions. The logarithms of the rate constants bear a linear relation to the reciprocal of the absolute temperature. The fraction deposited, F_D, was found to have the same value in a solution 3 *f* in both sodium chloride and hydrochloric acid as it had in a solution 6 *f* in hydrochloric acid under otherwise identical experimental conditions.

When solutions of irradiated stannous chloride in 3 *f* hydrochloric acid were oxidized with chlorine, F_D was 0.01 at 30 minutes at 25°. When the oxidized solution was reduced with sulfur dioxide at room temperature, F_D was 0.18 at 30 minutes, and when the reduction was continued at 95°, F_D was 0.08 at 30 minutes.

TABLE I

EMPIRICALLY DERIVED VALUES OF THE RATE CONSTANTS

Temp., °C.	Hydrochloric acid, *f*	k_1, min.$^{-1}$	k_2, min.$^{-1}$
20.25 ± 0.05	3	0.102	0.0145
	6	.102	.0040
25.15 ± 0.05	3	.135	.0169
	6	.135	.0056
30.95 ± 0.05	3	.185	.0204
	6	.185	.0074

Solutions of irradiated stannic chloride in 6 *f* hydrochloric acid were found to change in such a manner that the amount of antimony removable by copper in two-minute immersions was reduced by a factor of two for each three days of age of the solution. Because of the aging of the irradiated stannic chloride solutions reproducible deposition curves were not obtained. Aging of solutions of irradiated stannous chloride in 6 *f* hydrochloric acid did not occur until after three months.

In the separation of antimony from copper in nitric acid solution by the addition of sodium hydroxide, the amount of antimony retained in solution was found to increase with increasing *p*H from 33% at a *p*H of 10, to 74% when the supernatant liquid was 0.1 *f* in sodium hydroxide. Thus, the maximum over-all yield of Sb^{125} attainable from neutron irradiated stannous chloride under the experimental conditions investigated is 71%.

Acknowledgment.—The coöperation of Dr. Roderick W. Spence, Mr. James Sattizahn and Mr. Gordon Knobeloch of the Los Alamos Scientific Laboratory in the performance of the neutron irradiations is gratefully acknowledged.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF NEW MEXICO
ALBUQUERQUE, NEW MEXICO

Thermodynamic Functions of 2,2,3-Trimethylbutane

BY DONALD W. SCOTT AND GUY WADDINGTON

RECEIVED DECEMBER 29, 1952

The thermodynamic functions of four methyl-substituted butanes, 2-methylbutane,[1] 2,2-dimethylbutane,[2] 2,3-dimethylbutane[1] and 2,2,3,3-tetramethylbutane,[3] have previously been calculated from spectroscopic and molecular-structure data by the methods of statistical mechanics. This note reports a similar calculation of the thermodynamic functions of 2,2,3-trimethylbutane, the remaining member of the group of compounds.

Calorimetric values of the vapor heat capacity and entropy of 2,2,3-trimethylbutane were available for the evaluation of certain necessary parameters. The values of the vapor heat capacity had been reported in a previous publication from this Laboratory.[4] The values of the entropy were computed as shown in Table I from data from several different sources.

TABLE I

MOLAL ENTROPY OF 2,2,3-TRIMETHYLBUTANE, CAL. DEG.$^{-1}$

T, °K.	298.16	313.84	353.96
Entropy of liquid[a]	69.88	72.54	79.12
Vaporization, $\Delta H_{vap.}/T$[b]	25.68	23.77	19.54
Gas imperfection[c]	0.06	0.08	0.16
Compression, $R \ln (p/760)$[d]	−3.98	−2.70	0.00
Entropy (±0.30) of ideal gas at 1 atm.	91.64	93.69	98.82

[a] Unpublished results from this Laboratory. [b] Heat of vaporization at 298.16°K., N. S. Osborne and D. C. Ginnings, *J. Research Natl. Bur. Standards*, **39**, 453 (1947); at the other two temperatures, ref. 4. [c] Calculated from the equation for the second virial coefficient, $B = (PV - RT)/P = -643 - 22.98 \exp (1200/T)$ cc. mole^{-1}, based on data of ref. 4. [d] Vapor pressure equation from American Petroleum Institute Research Project 44 at Carnegie Institute of Technology, Selected Values of Properties of Hydrocarbons, Table No. 2k, dated Dec. 31, 1948.

The thermodynamic functions were calculated by means of the usual rigid rotator, harmonic oscillator, independent internal rotator approximation. The moments and reduced moments of inertia were computed by the methods of Kilpatrick and Pitzer.[5] All bond angles were assumed to be tetrahedral and the bond distances were taken to have their normal values (C–C, 1.54 Å., C–H, 1.09 Å.) with one exception. The exception is the central C–C bond distance, which is expected to be longer than normal on account of steric repulsion between the isopropyl and tertiary butyl groups. The estimated value that was used for this distance, 1.56 Å., is midway between the normal value and that in 2,2,3,3-tetramethylbutane, 1.58 Å.[6] The product of the three principal moments of inertia was calculated to be 4.638×10^{-113} g.^{3} cm.^{6} The diagonal elements of the reduced internal rotational kinetic energy matrix were 68.50×10^{-40} for the skeletal rotation, 5.239×10^{-40} for one methyl rotation, and 5.221×10^{-40} g. cm.^{2} for the other four methyl rotations. The off-diagonal elements were small enough that these diagonal elements could be used as the reduced moments of inertia. An average value of 5.225×10^{-40} g. cm.^{2} was used for all five methyl rotations.

(1) D. W. Scott, J. P. McCullough, K. D. Williamson and Guy Waddington, THIS JOURNAL, **73**, 1707 (1951).

(2) J. E. Kilpatrick and K. S. Pitzer, *ibid.*, **68**, 1066 (1946).

(3) D. W. Scott, D. R. Douslin, M. E. Gross, G. D. Oliver and H. M. Huffman, *ibid.*, **74**, 883 (1952).

(4) G. Waddington, S. S. Todd and H. M. Huffman, *ibid.*, **69**, 22 (1947).

(5) J. E. Kilpatrick and K. S. Pitzer, *J. Chem. Phys.*, **17**, 1064 (1949).

(6) S. H. Bauer and J. Y. Beach, THIS JOURNAL, **64**, 1142 (1942).