NOTES

The Vapor Pressure of Americium Metal

By Stephen C. Carniglia and B. B. Cunningham

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The vapor pressure of americium has been measured over the temperature range 1103 to 1453°K., by the same method and with the same equipment described elsewhere for PuF_3 and AmF_3.[1,2] Measurements were made independently on two samples of metal in which extreme care was exercised in the preparation, cleaning and loading of the samples, in an effort to prevent the formation of an impervious oxide "skin" which is known to cover molten americium metal upon exposure to trace amounts of oxygen. Fairly self-consistent data were obtained in the two runs, using about a milligram of metal in each case. However, it was not possible to make critical examinations of the contents of the effusion vessels after firing. Owing to the fact that some degree of contamination was inescapable, and to the somewhat unpredictable behavior of small samples of liquid americium with respect to tantalum effusion vessels, the experiments were felt to be insufficiently controlled to regard the results as final. The measurements are presented as preliminary values—the first which have been obtained on pure metallic americium—with the expectation that they will be re-examined at a later date. All data used in our calculations were obtained at temperatures above the melting point of the metal, and therefore refer to vaporization from the liquid state.

The two runs resulted in two linear curves of $\log_{10} p_{(\mathrm{mm})}$ *vs.* $10^4/T$, separated vertically by about 10% of the vapor pressure and differing in slope by about 1%. Average scattering of the points about each curve was ± 7% of the vapor pressure.

The equation for the best straight line is: $\log p = 7.563 - 13{,}162/T$. If a ΔC_p of vaporization from the liquid of -2 cal. mole^{-1} deg.$^{-1}$ is assumed, the best fit is obtained by: $\log p = 11.092 - 13{,}700/T - \log T$. The free energy of vaporization equation is: $\Delta F = 62{,}690 - 50.76\ T - 2.303(-2)T \log T$. Other calculated thermodynamic quantities are: $\Delta H_{1273} = 60.2$ kcal. mole^{-1}; $T_B = 2880$°K.; $\Delta H_{2880} = 57$ kcal. mole^{-1}; $\Delta S_{2880} = 20$ cal. mole^{-1} deg.$^{-1}$. No attempt is made to state the error in each quantity, owing to the nature of the uncertainty in the measurement. The value 20 for ΔS_{2880} is distinctly low, by comparison not only with Trouton's rule but also with similar constants for other metals of comparable volatility. Relatively small errors in our data would suffice to create such a discrepancy upon extrapolation to the boiling point.

An earlier estimate of the vapor pressure of americium by Erway and Simpson,[3] giving considerably higher pressures, was obtained from observations of the volatilization of americium from a dilute solution in plutonium. It was assumed that the two metals form an ideal solution. Since americium[4] and plutonium[5] differ substantially in their metallic properties, this assumption is open to some question.

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(1) S. C. Carniglia and B. B. Cunningham, This Journal, **77**, 1451 (1955).

(2) S. C. Carniglia and B. B. Cunningham, *Rev. Sci. Instr.*, in press.

(3) N. D. Erway and O. C. Simpson, *J. Chem. Phys.*, **18**, 1451 (1950).

(4) Edgar F. Westrum, Jr., and LeRoy Eyring, This Journal, **73**, 3396 (1951).

(5) W. B. H. Lord, *Nature*, **173**, 534 (1954).

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Some New Intermetallic Compounds with the "β-Wolfram" Structure

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A recent paper by Hägg and Schönberg[1] has shown that "β-wolfram" is actually wolfram oxide W_3O, with the W and O atoms randomly distributed among the two- and sixfold positions of the A15 type[2] structure. Many intermetallic compounds with the A15 structure are now known. In all of these the atoms are ordered. Several have been found to be superconducting above 1.2°K.[3] V_3Si[4] has a superconducting transition temperature between 16.9 and 17.1°K., which is one of the highest known. The compounds to be described in this paper were discovered in the search for superconductors with high transition temperatures. One of these, Nb_3Sn, has the highest transition temperature, 18.05 ± 0.1°K., known to date.[5]

The new compounds with the β-W structure are Nb_3Sn, Nb_3Os, Nb_3Ir, Nb_3Pt, Ta_3Sn and V_3Sn. The superconducting transition temperatures of the niobium compounds are[6] 18.0, <1.0, 1.7 and 9.2°K., respectively. The transition temperature of Ta_3Sn[5] is 6°K. and of V_3Sn, 7°K.

Experimental

The preparation of the tin compounds was described earlier.[5] The others were prepared by mixing the metals in proper proportion and causing them to react using an arc furnace in helium atmosphere. X-Ray powder photographs were taken using Cu K radiation and Straumanis type Norelco camera with 114.6 mm. diameter. Intensities of the lines were estimated visually. The Norelco diffractometer was used to determine X-ray intensities of the Nb_3Ir and Ta_3Sn samples mainly for corroboration. The new specimen spinner which rotates a circular disc sample in the

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(1) G. Hägg and N. Schönberg, *Acta Cryst.*, **I**, 251 (1954).

(2) *Strukturbericht*, **2**, 6 (1937).

(3) G. F. Hardy and J. K. Hulm, *Phys. Rev.*, **93**, 1004 (1954).

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(5) B. T. Matthias, T. H. Geballe, S. Geller and E. Corenzwit, *ibid.*, **95**, 1435 (1954).

(6) B. T. Matthias, *ibid.*, Jan. 1, 1955.

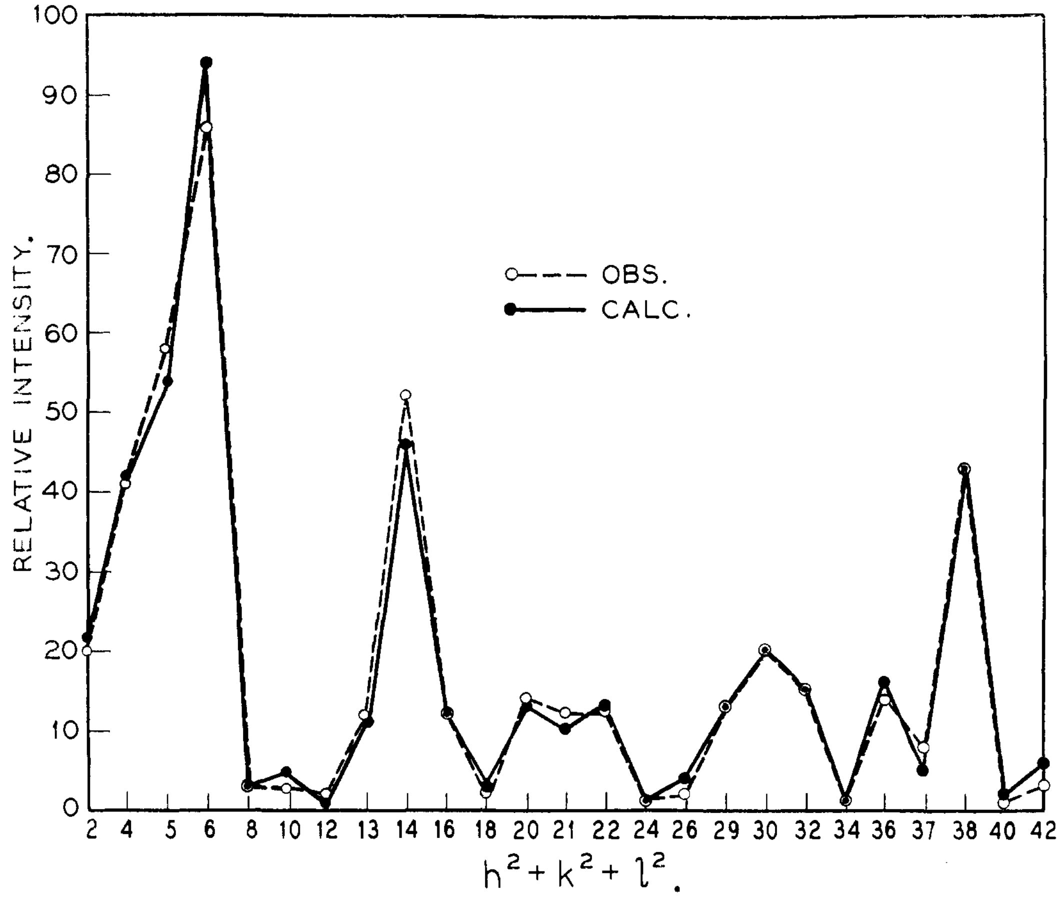

Fig. 1.—Comparison of calculated with observed X-ray intensities of Nb_3Ir.

plane of the circle was used. The data were recorded on charts and relative integrated intensities measured with a Keuffel and Esser compensating polar planimeter.

Structure Determination.—The Nb_3Ir and Nb_3-Pt photographs show these compounds to be pure. All lines were indexed on a cubic cell. The Nb_3Sn photograph had two extra very faint lines which were the two strongest niobium lines. The Nb_3Os photograph had three extra very faint lines one of which could not be accounted for by niobium or osmium. The Ta_3Sn appeared to contain both excess tantalum and tin and the V_3Sn contained both excess vanadium and tin.

In all cases, reflections of the type (*hhl*) were observed only if $l = 2n$. Thus the possible space groups are $O_h(3)$-Pm3n and $T_d(4)$-P$\bar{4}$3n. The twofold and sixfold special positions of these space groups are identical, and therefore the higher symmetry is chosen. In addition to the above extinctions, also absent were the reflections (410), (430), (531), (540), (621). These special extinctions lead to the choice of positions 6(c) or 6(d) for the atoms in sixfold positions. The sets 6(c) and 6(d) lead to the same structure, 6(c): $\pm(^1/_4\ ^1/_2\ 0;$ Ↄ) being the set chosen. The atoms in the twofold positions occupy positions 2(a): (000, $^1/_2\ ^1/_2\ ^1/_2$).

Relative intensities were computed using the relation

$$I = p\ |F_{hkl}|^2\ \frac{1 + \cos^2 2\theta}{\sin^2\theta\ \cos\theta} \times 10^{-5}$$

where p is the multiplicity and F_{hkl}, the structure amplitude.

The comparison of calculated with observed intensities indicated that the structures are correct. The results of the quantitative measurements on Nb_3Ir are shown in Fig. 1.

In all of the above structures the atoms are ordered. However, Ta_3Sn offered a special problem. When the first Ta_3Sn photograph was taken, the (110) line was completely absent. This was disturbing because on the basis of an ordered structure this line should have appeared. Four months later the original material was used to make a sample for a diffractometer record. The (110) line appeared on this record, though still not of adequate intensity for the completely ordered structure. Another powder photograph was taken and this time the (110) line did appear. It is possible that the first exposure was too short. The other possibility is that the original material was completely disordered and undergoes a very slow transition to the ordered structure. The comparison of calculated with observed intensities for both the completely disordered and completely ordered cases (see Table I) indicates that the Ta_3Sn investigated is neither one nor the other but is probably partially disordered.

The lattice constants, calculated X-ray densities and interatomic distances of the compounds designated A_3B are given in Table II. Each B atom is

TABLE I

COMPARISON OF CALCULATED WITH OBSERVED INTENSITIES OF Ta_3Sn

hkl	Obs.	Calcd. disord.	Calcd. ord.
110	3	0	10
200	58	60	50
210	184	175	210
211	128	134	110
220	0	0	2
310	0	0	2
222	22	15	25
320	49	38	46
321	68	67	55
400	32	27	35
411, 330	0	0	2
420	24	20	16
421	44	36	43
332	14	17	20
422	0	0	1
510, 431	0	0	2
520, 432	45	42	50
521	22	27	22
440	24	28	28
530, 433	0	0	1
600, 442	16	20	16
610	15	16	19
611, 532	38	51	40
620	0	0	1
541	0	0	2
622	22	30	50
630, 542	106	111	135

coördinated to twelve A atoms at the distance B-A. Each A atom is coördinated to 2 A atoms at distance $(A\text{-}A)_1$, 8 A atoms at distance $(A\text{-}A)_2$ and 4 B atoms at distance B-A.

TABLE II

STRUCTURAL DATA

Compound	a_0, Å.	ρ X-ray, g./cc.	Interatomic distances, Å.		
			B-A	$(A\text{-}A)_1$	$(A\text{-}A)_2$
Nb_3Os	5.121 (±0.002)	11.59	2.862	2.561	3.316
Nb_3Ir	5.131 (±0.001)	11.52	2.869	2.566	3.143
Nb_3Pt	5.153 (±0.003)	11.50	2.880	2.577	3.155
Nb_3Sn	5.289 (±0.002)	8.92	2.956	2.645	3.238
Ta_3Sn	5.276 (±0.001)	8.81	2.949	2.638	3.231
V_3Sn	4.94 (±0.01)	5.39	2.76	2.47	3.02

Reactions of 75 atomic % Ta with 25 atomic % Ir, Pt, and Os were tried. The compounds formed are isomorphous but do not have the A15 type structure. These compounds will be investigated further.

It appears that vanadium will dissolve at least 25 weight per cent. of platinum. The lines on the powder photograph of this alloy were broad and therefore no change in lattice constant of the vanadium could be detected.

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Some Kinetic Studies of the Tin(II) Reduction of Uranium(VI)[1] in Hydrochloric Acid Media

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Stannous chloride is one of the few common reducing agents which will readily reduce uranium(VI) to uranium(IV) in acid solutions. Furthermore, the potentials are such that no uranium(III) is formed. However, it is found that the rate and degree of reduction are markedly dependent on the conditions and appear to be strongly influenced by the concentrations of the reactants, the temperature and the acidity. A kinetic study of this reaction was accordingly carried out in our laboratory to determine the effect of these variables.

Experimental

The solutions studied were made up from weighed amounts of reagent grade stannous chloride ($SnCl_2 \cdot 2H_2O$), standardized hydrochloric acid and an analyzed stock solution of uranyl chloride which was prepared by dissolving uranium trioxide (UO_3) in hydrochloric acid. Solutions of uranium(VI) and tin(II), which upon mixing would give the desired initial composition, were prepared separately and brought to the reaction temperature in a water-bath maintained to ±0.1° of the desired temperature. Volume changes accompanying mixing were ignored.

The reaction was followed spectrophotometrically. Small aliquots of solution were removed periodically from the stoppered, thermostated reaction vessel. These were chilled with ice to inhibit the reaction and the absorption curves determined on a Model 12M Cary recording spectrophotometer. A complete scan required only about four minutes and the extent of the reaction during this time is believed to have been negligible in most cases. The uranium(IV) absorption peaks at about 555 and 655 mμ, where U(VI) is completely transparent, and the (VI) absorption at 410 mμ, where there is very little overlap, were used to compute the extent of reaction. The excellent agreement obtained between the amount of U(IV) formed and the U(VI) left indicated that no detectable concentrations of the other states (particularly V) were formed. Since the molar extinction coefficients and the exact location of the absorption maxima varied somewhat with the acidity, it was necessary to determine standard absorption curves for pure U(IV) and pure U(VI) for each hydrochloric acid concentration employed. In addition, a curve for U(IV) was also determined for most of the experiments after the reaction had gone to completion.

Discussion of Results

Order of the Reaction.—The rate of the reduction was shown to be first order in U(VI) by means of a series of experiments in which the stannous chloride was present in large excess (10- or 20-fold) and hence essentially constant. The Sn(II) dependence was established by means of a series of experiments in which the initial stannous chloride concentration was varied tenfold, from 0.1 to 1 *M*, as shown in Table I. A plot of the reciprocal of the half time of uranium reduction *versus* the logarithm of the average Sn(II) concentration had a slope of unity. In addition, the rate data were well correlated by means of a second order equation, *i.e.*, first order in U(VI) and first order in Sn(II), as shown by the tabulated rate constants. The second-order rate constants for experiments at the same temperature and acidity generally agreed to within ±15%, which is considered satisfactory in

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