

TABLE I. Data used in the calculations.

T°K	$p_4^0$ mm	$p_3^0$ mm	$B_4$ cc	$B_3$ cc
2.4	62.59	291	-136	-98
2.3	50.19	254	-143	-102
2.2	39.55	213	-150	-106
2.1	30.85	181	-158	-111
2.0	23.38	150	-168	-116
1.9	17.25	125	-178	-121

TABLE II. Partial vapor pressures of He<sup>3</sup>, He<sup>4</sup> solutions.

T°K	Real gas			Ideal gas		
	$p_4$	$p_3$	Z/X	$p_4$	$p_3$	Z/X
2.4	62.08	2.51	3.89	61.96	2.91	4.49
2.3	49.78	2.20	4.23	49.69	2.54	4.86
2.2	39.22	1.87	4.55	39.15	2.13	5.16
2.1	30.61	1.86	5.73	30.55	2.11	6.46
2.0	23.22	2.02	8.08	23.16	2.27	8.93
1.9	17.15	2.22	11.46	17.09	2.48	12.67

for a given composition of the liquid phase (He<sup>3</sup> mole fraction  $X$ ) the mole fraction of the He<sup>4</sup> in the normal state adjusts itself to such a value ( $\bar{y}_e$ ) that the free energy of the whole system is a minimum. The latter assumption seems the more reasonable to the writer and will be used here.

Gorter and De Boer<sup>3</sup> give equations for the partial pressures of He<sup>3</sup> and He<sup>4</sup> in equilibrium with a liquid solution. In this treatment they have used the vapor pressure of pure He<sup>4</sup> as a measure of the free energy of the liquid but have not included a correction for the gas imperfection of the vapor. This correction makes a considerable difference and must be included for consistency since the Keesom 1937 He<sup>4</sup> vapor pressure scale<sup>4</sup> below the lambda-point is consistent with the observed sixth-power variation of heat capacity with temperature and with the Sackur-Tetrode equation for the free energy of a monatomic gas including De Boer's<sup>5</sup> values for the second virial coefficient of He<sup>4</sup>. This point is clearly shown by a plot of  $\mu_{4e}^0(p_4^0, T)$ , calculated statistically, both with and without the gas imperfection correction ( $\mu_{real} - \mu_{ideal}, M_B = p_4^0 B_4$ ), against  $T^7$ . Both plots are essentially straight lines but the latter has a slope corresponding to  $S_\lambda = 0.55R$  while the former gives  $S_\lambda = 0.80R$ , the experimental value.

The second virial coefficient of a gaseous solution of He<sup>3</sup> and He<sup>4</sup> should be given by

$$B = N_3^2 B_3 + 2N_3 N_4 B_{34} + N_4^2 B_4,$$

where  $N_3$  and  $N_4$  are mole fractions,  $B_3$  and  $B_4$  the second virial coefficients of pure He<sup>3</sup> and He<sup>4</sup>, and  $B_{34}$  the cross second virial coefficient.  $B_{34}$  should be calculated in the same way that De Boer and Michels<sup>5</sup> calculated  $B_4$  but with the B.E. or F.D. term omitted, with all  $l$ -values allowed, and with the He<sup>3</sup>, He<sup>4</sup> reduced mass. It should be intermediate between  $B_3$  and  $B_4$ .

Lewis and Randall<sup>6</sup> propose that the ratio of the fugacity to the partial pressure of a component of a gaseous solution be taken to be the same as for that component pure, at the same temperature and total pressure. This is equivalent to assuming  $B_{34} = \frac{1}{2}(B_3 + B_4)$ . Lacking any direct knowledge of  $B_{34}$ , we will use that assumption here.

The chemical potentials of He<sup>3</sup> and He<sup>4</sup>, vapor and liquid, can be shown to be in the form

$$\mu_{3e} = \mu_{3e}^0(T, P) + RT \ln Z, \quad (1)$$

$$\mu_3 = \mu_3^0(T) + RT \ln X_e, \quad (2)$$

$$\mu_{4e} = \mu_{4e}^0(T, P) + RT \ln(1-Z), \quad (3)$$

$$\mu_4 = \mu_4^0(T, y) + yRT \ln(1-X_e), \quad (4)$$

where <sup>0</sup> means pure component,  $Z = p_3/P$ ,  $P$  is the total vapor pressure,  $X_e = X/[X + y(1-X)]$ , and  $y$  is the fraction of He<sup>3</sup> in the normal state. The chemical potential of pure liquid He<sup>4</sup> (below the lambda-point) can be taken in the form<sup>1</sup>

$$\mu_4^0(T, y) = E_0 - yTS_\lambda + (\sigma/\sigma + 1)T_\lambda S_\lambda y^{(\sigma+1)/\sigma}. \quad (5)$$

We take  $\sigma=6$  and ignore the small effect of pressure on the entropy and free energy of the liquid. With this expression for  $\mu_4^0$  we have the equation for the equilibrium  $\bar{y}_e$  at a He<sup>3</sup> concentration  $X$ :

$$\ln(1-X_e) + (S_\lambda/R)(\bar{y}_e^{1/6} y_e^{-1/6} - 1) = 0, \quad (6)$$

where  $X_e = X/[X + \bar{y}_e(1-X)]$  and  $y_e = (T/T_\lambda)^6$ .

Equations can now be written showing the equality of chemical potentials between liquid and vapor phases for He<sup>4</sup>:

$$W + RT \ln p_4 + B_4 P = E_0 - \bar{y}_e TS_\lambda + (6/7)T_\lambda S_\lambda \bar{y}_e^{7/6} + \bar{y}_e RT \ln(1-X_e) \quad (7)$$

$$W + RT \ln p_4^0 + B_4 p_4^0 = E_0 - (1/7)y_e TS_\lambda \quad (8)$$

$$W = RT[7.282 - 3/2 \ln M_4 - 5/2 \ln T]. \quad (9)$$

We have then for He<sup>4</sup> (and the corresponding equation for He<sup>3</sup>):

$$RT \ln p_4 / p_4^0 + B_4(P - p_4^0) = \bar{y}_e RT \ln(1-X_e) + (6/7)T_\lambda S_\lambda \bar{y}_e^{7/6} - \bar{y}_e TS_\lambda + (1/7)y_e TS_\lambda \quad (10)$$

$$RT \ln p_3 / p_3^0 + B_3(P - p_3^0) = RT \ln X_e. \quad (11)$$

These equations hold for  $T \leq T_{\lambda z}$ . For  $T > T_{\lambda z}$  the last three terms of Eq. (10) are dropped. For the case  $X=0.01$  ( $T_{\lambda z}=2.159^\circ\text{K}$ ) we have obtained numerical solutions at several temperatures. The data used are shown in Table I and the results in Table II.

The values of  $p_4^0$  are from Keesom,<sup>4</sup>  $p_3^0$  from Sydorjak, Grilly, and Hammel,<sup>7</sup>  $B_4$  and  $B_3$  from de Boer<sup>5,8</sup> as read from a smooth graph of  $B_4 T^{3/2}$  and  $B_3 T^{3/2}$  against  $T$ .

The Gorter-Taconis-de Boer theory shows very definitely a sharp rise in the relative concentration of He<sup>3</sup> in the vapor as compared with the liquid as the temperature is decreased below the lambda-point of the solution. The effect of gas imperfection is to decrease  $p_3$  and  $Z/X$  by a considerable amount and to slightly increase  $p_4$ . An interesting minimum in  $p_3$  occurs at about  $T_{\lambda z} = 2.159^\circ\text{K}$ .

<sup>1</sup> C. J. Gorter, *Physica* **15**, 523 (1949).

<sup>2</sup> J. De Boer, *Phys. Rev.* **72**, 852 (1949).

<sup>3</sup> C. J. Gorter and J. de Boer, *Phys. Rev.* **77**, 569 (1950).

<sup>4</sup> W. H. Keesom, *Helium* (Elsevier Publishing Company, Inc., New York, 1942), p. 196.

<sup>5</sup> J. De Boer and A. Michels, *Physica* **6**, 409 (1939).

<sup>6</sup> G. N. Lewis and M. Randall, *Thermodynamics* (McGraw-Hill Book Company, Inc., New York, 1923), p. 226.

<sup>7</sup> Sydorjak, Grilly, and Hammel, *Phys. Rev.* **75**, 303 (1949).

<sup>8</sup> Van Kranendork, Compaan, and de Boer, *Phys. Rev.* **76**, 1728 (1949).

## The Isotopes of Americium\*

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**I** NTERMITTENT investigation of the isotopes of americium during the past two years has resulted in the production of three new americium activities and has also yielded some additional information about previously<sup>1</sup> reported activities. Since the work on americium is still in progress, this letter will give only a brief report of the new results obtained and a detailed description of the experiments will be deferred until a later date.

Am<sup>238?</sup>.—Bombardment of Pu<sup>239</sup> with 50-Mev deuterons in the 184-in. cyclotron results in the production of a new americium activity of ca. 1.2 hours half-life in addition to the previously reported 12- and 50-hour activities.<sup>1</sup> Differential counting with beryllium and lead absorbers indicates that the decay is accompanied by the emission of conversion electrons and x-rays. The same activity is produced in good yield with 17-Mev deuterons in the 60-in. cyclotron, thus its mass number is probably greater than 237, since there is good evidence<sup>2,3</sup> that even with the heavy elements the yield of the ( $d, 4n$ ) reaction is very small at 17 Mev. In view of its half-life, radiation characteristics, and method of formation, this activity is probably an orbital electron capturing isotope and is best assigned to Am<sup>238</sup>.

Am<sup>239</sup>.—The 12-hour orbital electron capturing Am<sup>239</sup> has been previously reported to decay by alpha-particle emission of unknown energy to the extent of *ca.* 0.1 percent.<sup>1</sup> A re-determination of the alpha-branching ratio yielded the better value *ca.* 0.01 percent. The energy of the alpha-particle has been determined by means of a multichannel pulse analyzer to be  $5.77 \pm 0.05$  Mev.

Am<sup>240</sup>.—The 50-hour electron capturing americium activity was tentatively assigned<sup>1</sup> to Am<sup>240</sup>. This assignment has been confirmed. The 50-hour activity is produced in good yield from the bombardment of Pu<sup>239</sup> with 10-Mev deuterons and is not observed in the bombardment of Pu<sup>239</sup> with 9-Mev protons (60-in. cyclotron) in which Am<sup>239</sup> is produced in good yield. Since the yield of the (*d*, 3*n*) reaction is low at 10 Mev and since (*p*, *n*) should be the principal reaction producing americium with 9-Mev protons, the 50-hour activity is best assigned to Am<sup>240</sup>. No alpha-particles associated with the 50-hour americium have been observed. This is consistent with its assignment to Am<sup>240</sup> since the systematics of alpha-radioactivity<sup>4</sup> predict for this odd-odd nucleus a partial half-life for alpha-decay of some 10<sup>3</sup> years.

Am<sup>241</sup>.—The production of this isotope in milligram amounts by the neutron irradiation of plutonium<sup>5</sup> makes it possible to study the higher mass isotopes of americium produced by (*n*,  $\gamma$ ) reactions and the results of such experiments are reported in the following paragraphs. Recent specific activity measurements by Cunningham, Thompson, and Lohr<sup>6</sup> give a somewhat shorter half-life for Am<sup>241</sup> than that previously reported.<sup>7</sup> The new half-life is 475 years.

Am<sup>242</sup>.—In addition to the 16-hour Am<sup>242m</sup>, a long-lived Am<sup>242</sup> produced by the (*n*,  $\gamma$ ) reaction on Am<sup>241</sup> has been reported;<sup>1</sup> alpha-decay of this isotope was demonstrated by separating the Np<sup>238</sup> daughter and 0.5-Mev beta-particles in the americium fraction were also ascribed to Am<sup>242</sup>. The fact that the observed beta-particles do belong to Am<sup>242</sup> has now been demonstrated by observing the growth of Cm<sup>242</sup> (half-life 162 days) in the purified pile neutron-bombarded americium in an amount corresponding to the number of beta-particles observed. Mass spectrographic analysis of this americium shows Am<sup>242</sup> to be present to the extent of *ca.* 0.5 percent. This analysis together with the results from the above Cm<sup>242</sup> growth experiment and the yield from a Np<sup>238</sup> extraction allow both the alpha- and beta-decay half-lives of Am<sup>242</sup> to be estimated. The partial half-life obtained for beta-particle emission is roughly 10<sup>2</sup> years and that for alpha-particle emission is *ca.* 10<sup>4</sup> years. O'Kelley, Crane, Barton, and Perlman,<sup>8</sup> using the beta-ray spectrometer in this laboratory, have determined the beta-particle energies of Am<sup>242</sup> and Am<sup>242m</sup> to be  $0.575 \pm 0.010$  and  $0.630 \pm 0.005$  Mev, respectively. The (*n*,  $\gamma$ ) cross section for the formation of Am<sup>242</sup> is very roughly 10<sup>-22</sup> cm<sup>2</sup> but this may be off by a factor of several due to the many uncertainties involved, especially the neutron flux.

Am<sup>243</sup>.—Neptunium separations from the americium fraction of an irradiation of Am<sup>241</sup> with pile neutrons show the presence of equilibrium amounts of both Np<sup>238</sup> and Np<sup>239</sup>. The presence of Np<sup>239</sup> proves the existence of the new isotope Am<sup>243</sup> which is produced by two successive neutron capture processes in Am<sup>241</sup> and decays by alpha-particle emission to Np<sup>239</sup>. Mass spectrographic analysis of the americium of this bombardment showed Am<sup>243</sup> present to the extent of *ca.* 0.5 percent. This together with the yield of Np<sup>239</sup> determined in the chemical extraction experiments gives a partial half-life for alpha-particle emission for Am<sup>243</sup> of roughly 10<sup>4</sup> years. Alpha-particle pulse analysis of americium from another irradiation (containing approximately ten percent Am<sup>243</sup>) showed the alpha-particle energy to be  $5.21 \pm 0.03$  Mev. This energy and half-life indicate that alpha-emission in this odd-even nucleus is not prohibited,<sup>4</sup> but like the case of the analogous nucleus Am<sup>241</sup>, the measured alpha-particle energy may not represent the ground state transition. If one takes 5.89 Mev for the alpha-particle energy<sup>9</sup> of the ground state transition of Cm<sup>243</sup> and closes a decay cycle using the measured alpha-particle energy of Am<sup>243</sup> and 0.68 Mev for the beta-decay disintegration energy<sup>10</sup> of Np<sup>239</sup>, one finds that Cm<sup>243</sup> could be unstable with

respect to electron capture by *ca.* 0.01 Mev. However, due to the uncertainties in the above energies (especially Np<sup>239</sup>) it is entirely possible that Am<sup>243</sup> is not beta-stable; the alpha-particle energy of Cm<sup>243</sup> is also very uncertain and it is not known whether it corresponds to the ground state transition. In order to test this point curium was separated from an aged sample containing Am<sup>243</sup> and no detectable Cm<sup>243</sup> was found; this experiment places a lower limit of about 10<sup>3</sup> years on the partial half-life of Am<sup>243</sup> for negative beta-emission. The cross section for the reaction Am<sup>242</sup>(*n*,  $\gamma$ )Am<sup>243</sup> seems to be large, of the order of some  $4 \times 10^{-21}$  cm<sup>2</sup>, a value which is subject to large error because of the uncertainty in the neutron flux.

Am<sup>244</sup>.—Irradiation of americium containing approximately ten percent of the isotope Am<sup>243</sup> with thermal neutrons in the uranium-heavy water pile at the Argonne Laboratory produced a new americium activity of *ca.* 25-min. half-life at a yield corresponding to a cross section of roughly  $\frac{1}{2} \times 10^{-22}$  cm<sup>2</sup>. This activity is probably caused by the beta-emitting isotope Am<sup>244</sup>, formed by an (*n*,  $\gamma$ ) reaction.

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<sup>2</sup> James, Florin, Hopkins, and Ghiorso, National Nuclear Energy Series, Plutonium Project Record, Vol. 14B, *The Transuranium Elements: Research Papers*, Paper No. 22.8 (McGraw-Hill Book Company, Inc., New York, 1949).

<sup>3</sup> Magnusson, Thompson, and Seaborg, Phys. Rev. **78**, 363 (1950).

<sup>4</sup> Perlman, Ghiorso, and Seaborg, Phys. Rev. **77**, 26 (1950).

<sup>5</sup> Ghiorso, James, Morgan, and Seaborg, Phys. Rev. **78**, 472 (1950).

<sup>6</sup> Cunningham, Thompson, and Lohr, unpublished work (1949).

<sup>7</sup> B. B. Cunningham, National Nuclear Energy Series, Plutonium Project Record, Vol. 14B, *The Transuranium Elements: Research Papers*, Paper No. 19.2 (McGraw-Hill Book Company, Inc., New York, 1949).

<sup>8</sup> O'Kelley, Crane, Barton, and Perlman, unpublished work (1950).

<sup>9</sup> Thompson, Ghiorso, and Seaborg (to be published).

<sup>10</sup> G. T. Seaborg and I. Perlman, Rev. Mod. Phys. **20**, 585 (1948).

## The Low Terms of Ti II

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THE Ti II spectrum has as its lowest levels a pair of terms of the same multiplicity and name, 860 cm<sup>-1</sup> apart. These terms are *a*<sup>4</sup>*F* and *b*<sup>4</sup>*F*, one of which arises from the configuration 3*d*<sup>2</sup>4*s* and the other from 3*d*<sup>3</sup>. As they are very close together it is difficult to be sure which is which. Russell<sup>1</sup> concluded from the intensities of the combinations that *a*<sup>4</sup>*F* arose from 3*d*<sup>2</sup>4*s*, and *b*<sup>4</sup>*F* from 3*d*<sup>3</sup>. From theoretical calculations of the low even terms the writer<sup>2</sup> proposed that the assignments should be interchanged. In a later paper<sup>3</sup> Russell concluded from considerations of the series limits of the higher even terms of Ti I that his original assignments were correct.

We thought it desirable to find a further criterion which would indicate the correct assignments independently of the position of the two terms. Using the formulas for the spin-orbit interaction integrals,<sup>4</sup> we calculated  $\zeta_d$  from the intervals of the terms arising from 3*d*<sup>2</sup>4*s* and 3*d*<sup>3</sup>. We excluded the terms 3*d*<sup>3</sup>*a*<sup>2</sup>*P* and 3*d*<sup>3</sup>*a*<sup>1</sup>*P* as these terms are closed together and consequently the departure from (*LS*) coupling is considerable. Table I gives the calculated values of  $\zeta_d$ . Excluding the  $\zeta_d$  values of the two <sup>4</sup>*F* terms, it is seen that the mean value of  $\zeta_d$  for 3*d*<sup>2</sup>4*s* is 113 and that for 3*d*<sup>3</sup> is 91. By comparing these values with the values of  $\zeta_d$  calculated