

Thermodynamic Study of the Zirconium–Aluminum System

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The heats of formation of the zirconium–aluminum intermetallic compounds $ZrAl_3$, $ZrAl_2$, Zr_2Al_3 , $ZrAl$, Zr_5Al_4 , Zr_3Al_2 , Zr_5Al_3 , and the solid solution of aluminum in bcc zirconium have been studied using a Knudsen cell mass spectrometric technique. The high-temperature compound Zr_5Al_4 was identified in the residue of some of these experiments and this led to further heat treatment/X-ray diffraction experiments which indicated that Zr_4Al_3 , previously reported to form from the melt, decomposes in the solid state at temperature in excess of 1050°C. By measuring aluminum vapor pressures over the two-phase ranges of the system from $0 < X_{Al} < 0.75$ the enthalpy changes for the decomposition reactions were determined by second- and third-law methods, and these were used along with the measured vapor pressure of aluminum over the solid solution of aluminum in bcc zirconium to derive the enthalpies of formation of the intermetallic phases (in kcal/mole): $ZrAl_3$, -38.96 ; $ZrAl_2$, -32.86 ; Zr_2Al_3 , -56.12 ; $ZrAl$, -21.36 ; Zr_5Al_4 , -93.76 ; Zr_3Al_2 , -48.78 ; Zr_5Al_3 , -74.57 .

Introduction

Zirconium–aluminum alloys have found potential application in the nuclear energy field for use as fuel-element-cladding materials due to their low neutron capture cross sections. There are also numerous applications of zirconium–aluminum alloys as hydrogen getters in vacuum systems and microwave lasers. The zirconium–aluminum system is characterized by a number of intermetallic compounds which have been studied crystallographically by several investigators (1–9). The initial phase diagram work on the system was done by McPherson and Hansen (10) in 1960 by DTA and metallographic methods. The compounds they reported included $ZrAl_3$, $ZrAl_2$, Zr_2Al_3 , $ZrAl$, Zr_4Al_3 , Zr_3Al_2 , Zr_5Al_3 , Zr_2Al , and Zr_3Al . Some uncertainty about the ex-

istence and crystal structures of these phases has been reported. Edshammar (1) in 1962 failed to detect the phase $ZrAl$, and Pötschke and Schubert (9) reported the existence of a high-temperature compound Zr_5Al_4 , and claimed that Zr_4Al_3 decomposed above 1000°C in the solid state, a result which differs from the phase diagram of McPherson. The phase diagram (Fig. 1) of the system which appears in several handbooks (11–13) appears to be basically that of McPherson and Hansen, the modifications suggested by Pötschke and Schubert have not been adopted. The reported structures of the compounds are listed in Table I.

To date few thermodynamic data have been reported for this system. The only data that are available are the free energies of formation of three compounds: $ZrAl_2$,

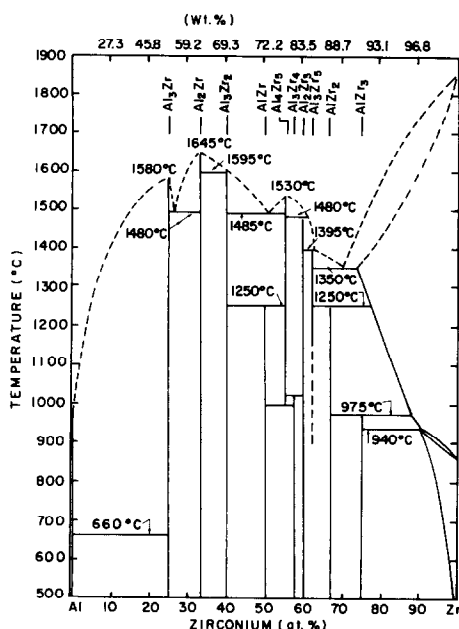


FIG. 1. The zirconium-aluminum phase diagram (Ref. (13)), as modified by Ref. (9).

Zr_2Al_3 , Zr_4Al_3 measured by solution calorimetry at one temperature only by Schneider *et al.* (14).

In this paper we report the results of high-temperature vaporization experiments undertaken to provide more basic data on this system.

Experimental

Zirconium-aluminum alloy samples were prepared by arc-melting appropriate amounts of elemental zirconium and aluminum (m3N and m3N8, respectively, Alfa Ventron) on a water-cooled copper plate in a helium atmosphere. A zirconium button was melted prior to the samples to help remove traces of oxygen from the helium atmosphere. The samples were turned over and remelted several times to help ensure homogeneity. Losses during the melting process could be held to around 1% with careful technique. Chemical analysis of the samples was not generally performed, so compositions mentioned herein should be considered nominal. The phases present in the arc-melted samples were determined by Guinier X-ray powder diffraction patterns (NBS Si internal standard) and lattice parameters calculated by least-squares fitting of the observed $\sin^2 \theta$ values. Samples were annealed approximately 24 hr at a residual pressure of 10^{-6} Torr or better before being placed into the Knudsen effusion apparatus.

The Knudsen effusion apparatus used in these experiments has been described previously (15). The sample is placed in a tungsten effusion cell with a knife-edge orifice

TABLE I
REPORTED STRUCTURES OF ZIRCONIUM ALUMINUM COMPOUNDS (FROM PEARSON)

		Lattice parameters, Å		
$ZrAl_3$	b.c. tetragonal	$a = 4.013$	$c = 17.320$	
$ZrAl_2$	Hexagonal ($MgZn_2$)	$a = 5.2824$	$c = 8.7482$	
Zr_2Al_3	Orthorhombic	$a = 9.601$	$b = 13.906$	$c = 5.574$
$ZrAl$	Orthorhombic (CrB)	$a = 3.353$	$b = 10.866$	$c = 4.266$
Zr_5Al_4 (H.T.)	Hexagonal (Ti_5Ga_4)	$a = 8.447$	$c = 5.810$	
Zr_4Al_3	Hexagonal	$a = 5.433$	$c = 5.390$	
Zr_3Al_2	Tetragonal	$a = 7.630$	$c = 6.998$	
Zr_5Al_3 (H.T.)	Tetragonal (W_5Si_3)	$a = 11.049$	$c = 5.396$	
Zr_2Al	Hexagonal (Ni_2In)	$a = 4.8939$	$c = 5.9283$	
Zr_3Al	Cubic (Cu_3Au)	$a = 4.372$		
$Zr_5Al_3O_x$	Hexagonal (Mn_5Si_3)	$a = 8.184$	$c = 5.702$	

on the bottom, is suspended from the arm of a Cahn recording microbalance, and is heated by radiation from a tungsten-mesh heating element. The temperature of the cell is measured by a tantalum-sheathed W-W 26% Re thermocouple whose tip is within a few millimeters of the cell, this thermocouple was calibrated in separate experiments against another thermocouple placed into a dummy cell and suspended into the furnace assembly. The material effusing from the Knudsen cell is directed toward a UTI quadrupole mass spectrometer. Using both the Cahn balance and the mass spectrometer it is possible to make simultaneous measurement of weight loss and ion intensity of 27 AMU. The absolute vapor pressure calculated from the rate of weight loss via the Knudsen equation

$$P = C/A * R * \sqrt{TM},$$

where A = orifice area (cm^2), T = temperature, R = rate of weight loss (mg/min), M = molecular weight, $C = 3.76 \times 10^{-7}$ = dimensional constants, P = pressure, could be used to calibrate the mass spectrometer since $P = k * I * T$, where I = measured ion current (amperes), and k = proportionality constant.

The mass spectrometer can then be used, because of its sensitivity, to provide many more measurements than would be possible with the balance alone. Mass spectrometer ion intensities were obtained by subtracting readings taken with a shutter blocking the effusing vapor from those obtained with the shutter open. The only vapor species detected in these experiments were Al (27 AMU) and Al_2O (70 AMU). The Al_2O signal was constantly present, but at a level approximately 1000 times lower than the aluminum signal.

The exact procedure used in the vaporization experiments varied somewhat with the composition of the solid sample being studied. Compositions up to about 82 wt% zirconium were examined by loading a

more aluminum-rich sample and measuring ion current at 27 AMU versus total milligrams of aluminum lost due to vaporization. Such experiments lasted 1 to 3 weeks, and 20 to 50% weight-loss rates were obtained for calibration of the mass spectrometer. Special *in situ* annealing at temperatures giving a low rate of weight loss was found to be necessary, especially near single-phase compositions, and samples could not be left at constant higher temperatures for extended time or else the ion current would continually drop with time even in the two-phase regions. Near 82 wt% zirconium numerous experimental difficulties were encountered. The aluminum vapor pressures at and beyond this point were sufficiently low to give ion intensities at 27 AMU near the background level of the residual gas in the vacuum system and rates of weight loss inordinately slow except near the melting point of the sample. Also, according to the phase diagram commonly published in the various handbooks, Zr_4Al_3 (81.6 wt% Zr) should be observed in residues near this composition. We observed instead what appeared to be the high-temperature compound Zr_5Al_4 (80.8 wt% Zr) reported by Pötschke and Schubert. The phases in this part of system are also sufficiently close in composition that when attempts were made to push beyond 82 wt% Zr it was never completely clear which phases were coexisting in the solid sample despite the low rate of weight loss.

These experimental difficulties were overcome to as great an extent as possible in the following ways. To determine which of the phases Zr_5Al_4 or Zr_4Al_3 was participating in the vaporization processes at high temperature numerous Guinier powder photographs of effusion run residues, as-cast and annealed samples of composition 78 to 83 wt% Zr were examined. Samples from this composition range, when quenched from high temperature, seem to be rather poorly crystallized. It was some-

times necessary to expose the Guinier films up to 20 hr (2 to 4 is average) to get diffraction lines of measurable intensity. In all cases the compound Zr_4Al_3 was absent in as-cast samples or samples annealed at temperatures above about 1050°C, while annealing at less than 1000°C resulted in formation of Zr_4Al_3 . A phase that could be indexed as Zr_5Al_4 (Ti₅Ga₄-type, as per Schubert) appeared in samples quenched from temperatures at or above the same temperature that Zr_4Al_3 disappeared. These results agree well with those of Schubert.

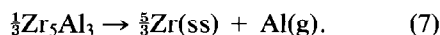
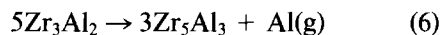
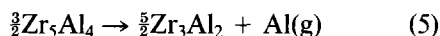
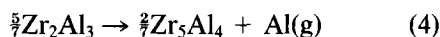
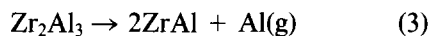
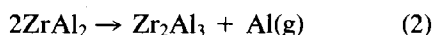
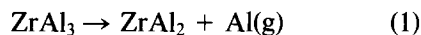
To obtain aluminum vapor pressures in equilibrium with two-phase alloys of composition beyond 82 wt% Zr separate samples of nominal composition 82.2, 84.2, and 87.1 wt% Zr were prepared. These were shown by their X-ray powder patterns to be mixtures of $Zr_5Al_4 + Zr_3Al_2$, $Zr_3Al_2 + Zr_5Al_3$, and $Zr_5Al_3 + Zr$, respectively. The extremely low vapor pressures over these samples were measured by using a computer to signal average the quadrupole mass spectrometer ion current at 27 AMU. The signal was averaged in exactly the same manner with the shutter open and then closed and the differences recorded. Near the end of each of these experiments the temperature was raised to near the melting point of the solid sample and 1 to 3 mg of aluminum were volatilized while the rate of weight loss and ion currents were recorded, thus providing data for the calibration of the mass spectrometer. The computer control system we have recently added to this system provides for automated control of the temperature set point and shutter, and digitizes the output of the Cahn balance, mass spectrometer, and control thermocouple. The program ramped the temperature back and forth between an upper and lower limit in increments of 5 or 10 degrees, and stopped to average the signal from the mass spectrometer at each point. Use of this procedure extended the lowest aluminum pressure that could be measured with high pre-

cision from about 10^{-8} to about 10^{-9} atm. The X-ray powder patterns of residues of the experiments performed in this manner showed the same phases as present at the beginning, verifying the measurement of univariant systems.

Finally, to obtain some information on the solid solution of aluminum in bcc zirconium a sample of ~91.8 wt% Zr ("Zr₃Al") was loaded and heated to 1310°C, and the ion current at 27 AMU was followed versus total weight loss. Even with the largest orifice available it took 2 weeks for this sample to lose ~4 mg of aluminum at this temperature. As the composition of the sample drifted toward pure zirconium the temperature was raised from 1310 to 1400°C. Attempts to measure Al partial pressures at temperatures higher than 1400°C were unsuccessful as the Zr-rich sample began to slowly react with the tungsten crucible to form W_2Zr .

Thermodynamic Calculations

By measuring the vapor pressure of aluminum over the various two-phase ranges in the Zr-Al system, and neglecting any effects of possible nonstoichiometry of the intermetallic compounds, the heats of the following decomposition reactions were determined by second- and third-law methods:



The equilibrium constant for each of the above reactions is $K = P_{Al}$. Second-law enthalpy changes at the median temperatures

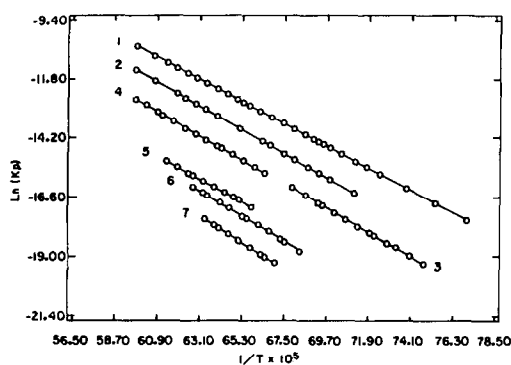


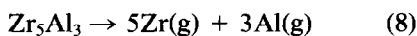
FIG. 2. Second-law plots. Numbers refer to reactions given in text. Not all data points are shown because of crowding.

were obtained by least-squares fitting of $R \ln(K)$ versus $1/T$ and evaluating the slope of the line (Fig. 2). Third-law enthalpies at 298 K were derived by averaging the quantities

$$(R \ln(K) + \Delta_{\text{fef}}) * T = \Delta H_{298}^{\circ}$$

obtained at each experimental temperature. Assuming Neumann-Kopp's rule the Δ_{fef} change for each of the above reactions reduces to that for the vaporization of pure aluminum at the same temperature. Second-law enthalpies at 298 K were evaluated from the slope of the line obtained by plotting $(R \ln(K) + \Delta_{\text{fef}})$ versus $1/T$ (16).

In order to determine the enthalpies of formation of the compounds listed in reactions (1)–(7) above, some data were collected for Zr(ss). The aluminum partial pressure at 1310°C was obtained as a function of composition across the bcc solid solution range, and the zirconium pressure at the two-phase Zr_5Al_3 , Zr(ss) boundary was calculated from a graphical integration of the Gibbs–Duhem equation. From these pressures a value for the equilibrium constant for



was calculated. The enthalpy change for this reaction as derived by the third-law method (from $T = 1583$ K, the only temper-

TABLE II
SECOND AND THIRD-LAW RESULTS FOR THE
DECOMPOSITION REACTIONS

Reaction	ΔH_f° (kcal)	ΔS_f° (cal)	$\Delta H_{298}^{\text{II}}$ (kcal)	$\Delta H_{298}^{\text{III}}$ (kcal)	Temp range (°K)
1	81.6(2)	28.0(1)	86.5(2)	84.8(1)	1299–1673
2	87.5(4)	29.6(3)	92.7(4)	88.3(2)	1406–1673
3	89.1(8)	28.3(5)	93.5(8)	92.1(1)	1338–1473
4	88.3(3)	27.6(2)	93.8(3)	92.0(1)	1503–1673
5	82.6(5)	20.6(3)	88.0(5)	97.5(2)	1519–1629
6	91.7(6)	25.4(4)	96.8(6)	98.9(1)	1464–1594
7	96.6(2)	26.5(1)	101.8(3)	102.20(2)	1493–1578

ature measured) is 1038.2 kcal. This leads to a heat of formation of Zr_5Al_3 of -74.6 kcal. This value was coupled with the data of reactions (1) to (6) above to determine the heats of formation of the remaining compounds. The thermodynamic data for the pure elements used in the calculations were taken from Hultgren (17).

Results and Discussion

The measured aluminum partial pressures over the various two-phase ranges are available from the authors upon request. Second-law plots ($R \ln(K)$ vs $1/T$) are shown in Fig. 3. The results of second- and third-law treatments for the decomposition reactions (1)–(7) are given in Table II. Second- and third-law enthalpies at 298 K are

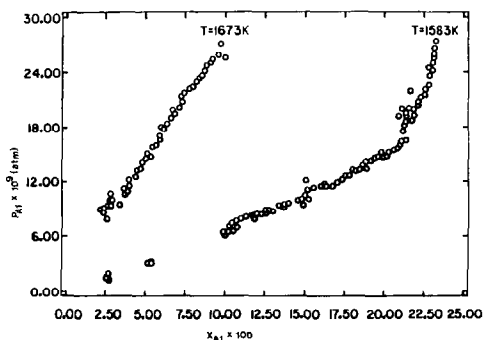
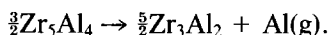


FIG. 3. Aluminum partial pressures over the bcc Zr solid solution.

in fairly good agreement except for reaction (5)



It is somewhat difficult to account for this difference. It is possible that in making the temperature-dependent measurements that the temperature was inadvertently being cycled back and forth across a phase-transition temperature of some sort. Although the X-ray powder pattern of the sample used to study the above reaction showed a mixture of Zr_5Al_4 and Zr_3Al_2 , it is possible that when the temperature was raised to the point necessary to make vapor pressure measurements the sample became single-phase Zr_5Al_4 or Zr_3Al_2 instead of a mixture, and the vapor pressure changed sufficiently with composition drift to cause problems since the system was no longer univariant. This sample was also in the composition range for which it was difficult to obtain sharp powder diffraction patterns despite repeated annealing, so sluggish diffusion or kinetic problems in the vapor pressure measurements cannot be ruled out. Only third-law values have been used in the calculation of the enthalpies of formation of the compounds. In view of the narrow temperature ranges and low pressures to which the vapor pressure data correspond, the second-law heats for the decomposition reactions should be considered approximate even when the agreement with third-law values is fairly good.

It should be mentioned that during the course of these experiments effusion cells with different orifice areas were used. The orifice areas were chosen to be progressively larger as the aluminum pressures to be measured became lower. Measurements were made over certain two-phase regions with orifices of three different areas, ranging from 0.00676 to 0.0580 cm^2 and the aluminum pressures obtained in these separate experiments agreed to within about $\pm 15\%$ and showed no systematic orifice depen-

dence. The $\pm 15\%$ scatter between experiments probably arises from problems with the calibration of the temperature-measuring thermocouple, the accurate measurement of the cell orifices, and inherent problems ("chemistry") in the different samples used. Sufficient overlap between experiments performed with and without the computer automation was also obtained to demonstrate that there were no systematic differences.

We have tabulated the various phases and lattice parameters observed during the course of this study in Table III, along with notes on the heat treatment history of the sample and coexisting phases. The phase Zr_4Al_3 does not exist at temperatures above 1100°C according to our results. The phase diagram modification proposed by Schubert *et al.* appears to be in keeping with our observations, however, we would not be able to emphatically say that the proposed structure of Zr_5Al_4 is correct since we obtained relatively poor powder patterns of this phase. We note that a single crystal study of Zr_5Al_4 has been reported (20). All our attempts to find crystals of either Zr_5Al_4 or Zr_4Al_3 failed. Powder patterns of samples in the composition range 78 to 83 wt% zirconium also often show the presence of a hexagonal Mn_5Si_3 type phase which Edshamar (1) believes to be a ternary, $\text{Zr}_5\text{Al}_3\text{O}_x$.

The variation of lattice parameters of the various phases with composition appears to be rather small, at least for phases for which we have sufficient data. This is indicative of relatively narrow single-phase widths. We have not had much success in trying to measure single-phase widths in the effusion experiments, kinetic effects which occur near single-phase compositions require careful *in situ* annealing of the sample before continuing with vapor pressure measurements, and the composition drifts during the process of cycling from the annealing temperature to a temperature at which pressure measurements can be made, and

TABLE III
 PHASES OBSERVED

Phase	Lattice parameters (Å)			Comments
ZrAl ₃	<i>a</i> = 4.0074(6)	<i>c</i> = 17.286(4)		Single phase, annealed ~1100°C
lit.	<i>a</i> = 4.013	<i>c</i> = 17.320		
ZrAl ₂	<i>a</i> = 5.2792(7)	<i>c</i> = 8.747(2)		Trace ZrAl ₃ , annealed 1 week at 1000°C
	<i>a</i> = 5.2807(5)	<i>c</i> = 8.749(1)		Single phase ~1200°C
	<i>a</i> = 5.2880(5)	<i>c</i> = 8.760(1)		Coex Zr ₂ Al ₃ , annealed at ~1200°C
lit.	<i>a</i> = 5.2824	<i>c</i> = 8.7482		
Zr ₂ Al ₃	<i>a</i> = 9.603(4)	<i>b</i> = 13.927(5)	<i>c</i> = 5.578(2)	Coex ZrAl ₂ , annealed ~1200°C
	<i>a</i> = 9.617(3)	<i>b</i> = 13.934(3)	<i>c</i> = 5.584(2)	Single phase ~1200°C
	<i>a</i> = 9.609(3)	<i>b</i> = 13.917(6)	<i>c</i> = 5.575(3)	Coex Zr ₅ Al ₄ , 76 wt% Zr as-cast sample
lit.	<i>a</i> = 9.601	<i>b</i> = 13.906	<i>c</i> = 5.574	
ZrAl	<i>a</i> = 3.362(1)	<i>b</i> = 10.892(3)	<i>c</i> = 4.274(2)	77 wt% Zr, annealed 1200°C, trace Zr ₂ Al ₃
	<i>a</i> = 3.362(2)	<i>b</i> = 10.903(3)	<i>c</i> = 4.281(2)	81 wt% Zr, annealed 935°C, coex Zr ₄ Al ₃
lit.	<i>a</i> = 3.353	<i>b</i> = 10.866	<i>c</i> = 4.266	
Zr ₄ Al ₃	<i>a</i> = 5.424(1)	<i>c</i> = 5.405(2)		81 wt% Zr, annealed 800°C, 2 weeks, trace Zr ₅ Al ₃ O _x ; 81 wt% Zr, annealed at 935°C,
	<i>a</i> = 5.432(1)	<i>c</i> = 5.396(1)		4 days, coex ZrAl, Zr ₅ Al ₃ O _x ; 82.2 wt% Zr,
	<i>a</i> = 5.428(1)	<i>c</i> = 5.387(1)		annealed 750°C, coex with Zr ₃ Al ₂ , Zr ₅ Al ₃ O _x
lit.	<i>a</i> = 5.433	<i>c</i> = 5.390		
Zr ₅ Al ₄	<i>a</i> = 8.459(4)	<i>c</i> = 5.784(4)		81 wt% as-cast
	<i>a</i> = 8.432(2)	<i>c</i> = 5.791(2)		81 wt% Zr, annealed 800°C, 2 weeks, 1200°C, 24
lit.	<i>a</i> = 8.447	<i>c</i> = 5.810		hr coexisting with ZrAl, Zr ₅ Al ₃ O _x
Zr ₃ Al ₂	<i>a</i> = 7.6333(8)	<i>c</i> = 6.996(2)		82.2 wt% Zr, coex with Zr ₅ Al ₄ , annealed
lit.	<i>a</i> = 7.6342(8)	<i>c</i> = 6.989(2)		1150°C; 84.2 wt% Zr, coex with Zr ₅ Al ₃ ,
	<i>a</i> = 7.630	<i>c</i> = 6.998		annealed 1150°C
Zr ₅ Al ₃	<i>a</i> = 11.043(2)	<i>c</i> = 5.392(2)		Coex with Zr ₃ Al ₂ , annealed 1100°C
lit.	<i>a</i> = 11.049	<i>c</i> = 5.396		

as a consequence relatively few measurements can be made over the single-phase region. The only phases upon which we can comment are ZrAl₂ and Zr₂Al₃, these both appear to have a homogeneity range between 1 and 2 at.-%.

The measured aluminum partial pressure versus composition across the bcc zirconium solid solution range is shown in Fig. 3. The 1583 K isotherm, when extrapolated back to the pressure measured over the Zr₅Al₃, Zr(ss) region indicates the position of the two-phase boundary to be 23.5 at.-% Al, a value which is in excellent agreement with the phase diagram work of McPhersen and Hansen. The zirconium partial pressure over a 23.5 at.-% Al alloy at 1583 K, calculated by a Gibbs–Duhem integration, is 1.14–13 atm. This value was used along

with the measured aluminum pressure to calculate a value for the equilibrium constant for the atomization of Zr₅Al₃ at this temperature, and a third-law enthalpy change at 298 K of 1038.2 kcal. Assuming Raoult's law behavior for zirconium up to 23.5 at.-% Al would yield a value of 1036 kcal. The enthalpy of formation of Zr₅Al₃ calculated by subtracting the enthalpies of vaporization of the pure elements from the above is 74.6 kcal (72.2 kcal, assuming Raoult's Law). This value, used with the data for reactions (1)–(7), gives the enthalpy of formation of the remaining compounds. The results are presented in Table IV and Fig. 4. Enthalpies of formation at selected compositions in the solid solution range were calculated using the Henry's law constant obtained from the linear por-

TABLE IV
 ENTHALPIES OF FORMATION OF ZIRCONIUM (AND HAFNIUM) ALUMINIDES $\frac{1}{2} + y M(s) + y/1 + y Al(s) \rightarrow \frac{1}{2} + y MAl_3(s)$, $\Delta H_{f,298}^{\circ}$ (kcal/g-ATOM)

	I ^a	II ^b	III ^c	
ZrAl ₃	-9.74	-14.28	-9.99	HfAl ₃
ZrAl ₂	-10.95	-17.83	-11.54	HfAl ₂
Zr ₂ Al ₃	-11.22	-19.53	-11.35	Hf ₂ Al ₃
ZrAl	-10.68	-19.79	-11.06	HfAl
Zr ₅ Al ₄	-10.42	-18.84	-10.6	Hf ₄ Al ₃
Zr ₃ Al ₂	-9.76	-17.61	-10.4	Hf ₃ Al ₂
Zr ₅ Al ₃	-9.32	-16.76	-9.8	Hf ₂ Al
			-7.95	Hf ₃ Al

^a This work.

^b Miedema (Ref. (18)).

^c Kaufmann and Nesor (HF-Al), Ref. (19).

tion of the 1583 K isotherm (Fig. 3) and Raoult's law for zirconium.

The possible uncertainties in the calculated enthalpies of formation deserve comment. The error in the measured aluminum partial pressures is probably on the order of $\pm 20\%$, while the error in the free energy function changes estimated by the Neumann-Kopp rule is probably on the order of ± 0.5 cal/ $^{\circ}$ K mole. A worse case estimate of the uncertainty in the heat of formation of Zr₅Al₃ would then be around ± 6 kcal (74.6 ± 6.0), or 9.32 ± 0.75 kcal/g-

atom. Since the estimated error in the other measured enthalpies of reaction are substantially smaller than this value, and the enthalpies of formation of the remaining compounds depend on the value obtained for Zr₅Al₃, the uncertainty in all of the enthalpies of formation are estimated to be about ± 0.75 kcal/g-atom at the most.

The experimental heats of formation calculated as above are compared to values predicted by Miedema's (18) empirical model (Fig. 4 and Table IV). The model values are higher than the experimental values by nearly a factor of 2. It seems the model seriously overestimates the bonding capability of aluminum with zirconium. The enthalpies of formation of several hafnium aluminum compounds were estimated by Kaufman and Nesor (19) by a fitting of the Hf-Al phase diagram, and these values are also plotted in Fig. 4. It is reassuring to see that these values are in fairly close agreement with the values we calculate for the Zr-Al compounds.

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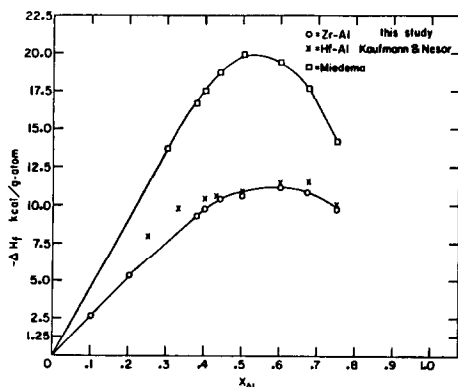


FIG. 4. Enthalpies of formation of Zr-Al compounds.

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