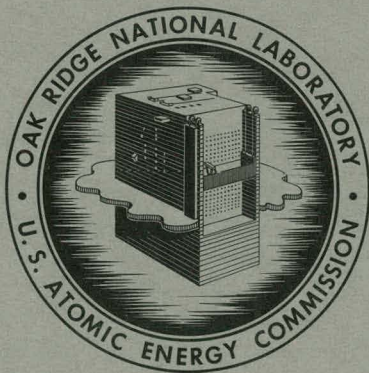


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DIFFUSION OF  $Zr^{95}$  IN BODY-CENTERED  
CUBIC IODIDE ZIRCONIUM

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**OAK RIDGE NATIONAL LABORATORY**

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Oak Ridge, Tennessee  
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T. S. Lundy and J. I. Federer

ABSTRACT

Chemically purified Zr<sup>95</sup> has been used in determining self-diffusion coefficients in the body-centered cubic phase of iodide zirconium over the temperature range of 900 to 1750°C. In order to minimize effects of build-in of the daughter isotope Nb<sup>95</sup>, all heat treatments were completed within 48 hr after the purification. The temperature dependence of the diffusion coefficients could not be described by the usual Arrhenius-type equation. Instead, apparent values of the frequency factor D<sub>0</sub> and the activation energy Q varied from 4.8 × 10<sup>-6</sup> to 2.5 × 10<sup>-2</sup> cm<sup>2</sup>/sec and 20,700 to 46,900 cal/mole, respectively, between the lower and upper extremities of the temperature range. Empirical treatment of the data indicated that Q is a linear function of temperature and that D<sub>0</sub> varies with a power of the temperature. The data may be described in terms of the α to β transition temperature of 1136°K and the absolute temperature of the heat treatments by the following equation:

$$D = 3 \times 10^{-6} \left( \frac{T}{1136} \right)^{15.6} \exp \left( - \frac{19,600 + 31(T - 1136)}{RT} \right) \text{ cm}^2/\text{sec}$$

## INTRODUCTION

Several studies on the diffusion of Zr<sup>95</sup> in zirconium have been reported.<sup>1-5</sup> The values of the constants contained in the usual Arrhenius-type equation for describing the temperature dependence of the diffusion coefficient

$$D = D_0 \exp\left(-\frac{Q}{RT}\right)$$

are summarized in Table 1. The reported values of  $D_0$ , the frequency factor, and  $Q$ , the activation energy, are seen to vary by factors of about 60 and 1.6, respectively. Examination of the data from any one study indicated reasonable consistency of experimental measurements. The large discrepancies of overall results, therefore, cannot be explained on the basis of experimental scatter. One possible explanation for the differences in results could be a varying impurity content of the zirconium. Another possibility is that the radioactive daughter Nb<sup>95</sup> influenced the values of some of the determined diffusion coefficients. Therefore, one purpose of this study was to explain the large differences in diffusion results that have been obtained.

Several empirical relations have been proposed to relate the diffusion coefficients in solids with physical properties, such as the absolute melting point, the heat of fusion, and the heat of sublimation. In face-centered cubic metals the activation energy of diffusion can be predicted to within about 10% by such relations.<sup>6</sup> However, except for

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<sup>1</sup>G. B. Fedorov and V.D. Gulyakin, Met. i Metalloved. Christykh Metal. Sbornik Nauch, Rabot 1959, No. 1, pp 170-78.

<sup>2</sup>G. Kidson and J. McGurn, Can. J. Phys. 39, 1146-57 (1961).

<sup>3</sup>V. S. Lyashenko et al., Phys. Metals and Metallog. 8(3), 362-69 (1959).

<sup>4</sup>D. Volokoff et al., Compt. Rend. 251, 2341-43 (1960).

<sup>5</sup>Ye. V. Borisov et al., "Study of Diffusion in Zirconium and in Certain Alloys with a Zirconium Base," pp 196-209 in Metallurgiya i Metallovedeniye, Izdatel'stvo Akademii Nauk USSR, Moscow, 1958 (NP-TR-448, F-TS-9849/V).

<sup>6</sup>R. E. Hoffman et al., Trans. Met. Soc. AIME 206, 483-86 (1956).

Table 1. Summary of Previous Studies of the Diffusion of Zr<sup>95</sup> in Body-Centered Cubic Zirconium

Frequency Factor (cm <sup>2</sup> /sec)	Activation Energy (kcal/mole)	Temperature Range (°C)	Reference
<u>Experimental</u>			
4 × 10 <sup>-5</sup>	26.0	1000-1250	a
2.4 × 10 <sup>-4</sup>	30.1	1170-1500	b
2.4 × 10 <sup>-3</sup>	38.0	900-1500	c
4.2 × 10 <sup>-5</sup>	24.0	900-1240	d
1 × 10 <sup>-4</sup>	27.0	900-1200	e
<u>Empirical</u>			
Q = 40T <sub>m</sub> = 85.0		(T <sub>m</sub> = 2125°K)	
Q = 16.5 ΔH <sub>f</sub> = 90.8		(ΔH <sub>f</sub> = 5.5 kcal/mole)	
Q = 0.67 ΔH <sub>s</sub> = 73.7		(ΔH <sub>s</sub> = 110.0 kcal/mole)	

<sup>a</sup>G. B. Fedorov and V. D. Gulyakin, Met. i Metalloved. Christykh Metal. Sbornik Nauch, Rabot 1959, No. 1, pp 170-78.

<sup>b</sup>G. Kidson and J. McGurn, Can. J. Phys. 39, 1146-57 (1961).

<sup>c</sup>V. S. Lyashenko et al., Phys. Metals and Metallog. 8(3), 362-69 (1959).

<sup>d</sup>D. Volokoff et al., Compt. Rend. 251, 2341-43 (1960).

<sup>e</sup>Ye. V. Borisov et al., "Study of Diffusion in Zirconium and in Certain Alloys with a Zirconium Base," pp 196-209 in Metallurgiya i Metallovedeniyc, Izdatel'stvo Akademii Nauk USSR, Moscow, 1958 (NP-TR-448, F-TS-9849/V).



the diffusion of Nb<sup>95</sup> in niobium,<sup>7</sup> the relations do not correlate with observed results for diffusion in body-centered cubic metals.<sup>2</sup> Specifically, the empirical relations predict that the activation energy for the diffusion of Zr<sup>95</sup> in zirconium should be about 80 kcal/mole. As shown in Table 1, experimentally determined values have ranged from 24 to 38 kcal/mole. Therefore, a second purpose of this study was to determine the validity of these empirical relationships as applied to zirconium.

The fact that large diffusion coefficients of Zr<sup>95</sup> in zirconium exist throughout the body-centered cubic range of temperatures (863-1852°C) makes possible a study over a very wide temperature range. A third purpose of this study was therefore to provide basic diffusion data in a body-centered cubic metal over as large a temperature range as possible.

#### MATERIALS AND PROCEDURE

The zirconium used in these experiments was reactor-grade 1 crystal-bar ingot of 99.94% minimum purity. The ingot was arc-melted, forged to a 1½-in.-diam rod, and swaged to ¾-in. diam from which ½-in.-long by 5/8-in.-diam specimens were machined. The major impurities in the zirconium are shown in the following analysis:

<u>Element</u>	<u>Content, ppm</u>
C	50
Cu	25
Fe	242
H	53
Hf	135
N	10
Ni	24
O	19
Si	22

The machined specimens were degreased with acetone, heavily etched with 46 HNO<sub>3</sub>-46 H<sub>2</sub>O-8 HF solution, homogenized at 1150°C for 48 hr in a

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<sup>7</sup>R. Resnick and L. S. Castleman, Trans. Met. Soc. AIME 218, 307-10 (1960).

vacuum of  $3 \times 10^{-5}$  torr or better, and furnace cooled. To prevent possible contamination by the mullite furnace tube, the specimens were completely enclosed in a tantalum box which, in turn, was placed within a tantalum tube. An example of the large  $\beta$  grain size produced by the heat treatment (body-centered cubic  $\beta$  exists above  $865^\circ\text{C}$ , close-packed hexagonal  $\alpha$  below) is shown in Fig. 1 and the room-temperature macrostructure is shown in Fig. 2. The specimens were probably quite coarse grained at all temperatures in the  $\beta$  phase. It is also probable that the hydrogen content of the zirconium was decreased to less than 10 ppm by the vacuum anneal, although no additional analysis was obtained.

Following the vacuum anneal, the specimens were abraded through 0000-grit emery polishing papers to produce a smooth, flat surface and heavily etched in 46  $\text{HNO}_3$ -46  $\text{H}_2\text{O}$ -8  $\text{HF}$  solution to remove the cold-worked surface layer. Another light polishing with 0000-grit emery paper followed by etching completed the preparation of the specimens.

The  $\text{Zr}^{95}$  isotope used in these experiments was obtained as an oxalate complex in oxalic acid solution which was then diluted with a sufficient amount of distilled water to yield a specific activity of about 120 counts/ $\lambda \cdot \text{sec}$  ( $1\lambda = 10^{-6}$  liters). Fifteen  $\lambda$  of solution were placed on the surface of each specimen and evaporated to dryness under a heat lamp, leaving a residue which was probably a zirconium oxalate compound. Upon heating to the diffusion temperature, the oxalate decomposed to an oxide from which  $\text{Zr}^{95}$  atoms diffused into the metal. The maximum oxygen contamination produced by dissolution of the oxide was less than 1 ppm if all oxygen were confined to the layers sampled. The initial activity of each specimen was about 1800 counts/sec and no significant loss of activity occurred during any diffusion anneal.

The  $\text{Zr}^{95}$  isotope decays (65-day half-life) to  $\text{Nb}^{95}$  which decays (35-day half-life) to stable  $\text{Mo}^{95}$  with 0.75- and 0.76-Mev gamma emissions, respectively, preventing discrimination by gamma spectrometry. For this reason, the  $\text{Zr}^{95}$  was purified of  $\text{Nb}^{95}$  just prior to these experiments and all diffusion anneals were completed within two days from the time of purification. The maximum activity due to  $\text{Nb}^{95}$ , therefore, did not exceed 3.8% of the total activity at the termination of the anneals.

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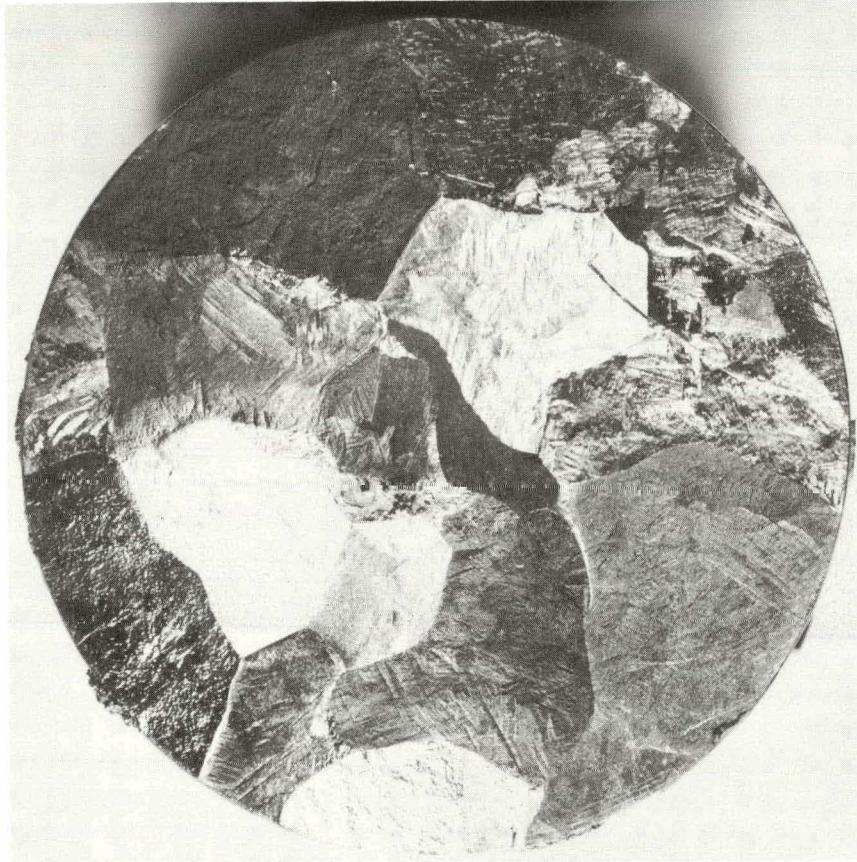


Fig. 1. Typical Zirconium Specimen After Vacuum Annealing at 1150°C for 48 hr. 7X.

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Fig. 2. Same Zirconium Specimen Shown in Fig. 1 After Polishing and Etching. 7X.

For diffusion anneals up to and including 1150°C, the specimens were wrapped with three layers of tantalum foil, sealed in fused quartz ampoules under a vacuum of  $8 \times 10^{-5}$  torr or better, and inserted into furnaces previously set at the desired temperature. The furnaces were controlled within  $\pm 1^\circ\text{C}$  and temperatures were measured with Pt vs Pt-10% Rh thermocouples which had been calibrated with a standard thermocouple (calibrated at the melting points of gold, silver, aluminum, and zinc). All diffusion anneals above 1150°C were performed in a tantalum filament furnace under 5 psig of 99.995% pure argon. Temperatures were measured with a Pyro micro-optical pyrometer calibrated for the particular sighting conditions (identical for all specimens) with a Pt vs Pt-10% Rh thermocouple. The accuracy of temperature measurements made with the pyrometer was estimated to vary from  $\pm 5^\circ\text{C}$  at 1200°C to  $\pm 10^\circ\text{C}$  at 1750°C. After the diffusion anneals, all the specimens were bright and shiny with a macrostructure similar to that shown in Fig. 1.

Each specimen was aligned in a lathe and the diameter decreased about 0.08 in. to eliminate effects of surface diffusion. Between 12 and 15 sections, each approximately 2 mils thick, were then removed from each specimen and the turnings of each section were quantitatively collected and weighed. The section thicknesses expressed in weight units were then used to determine the average distance of each section from the original isotope layer.

The turnings from each section were transferred to counting cards and secured with paper tape, making the counting geometry constant for all sections of all specimens. Gamma counting was performed using a single-channel analyzer and a 3 in.  $\times$  3 in. NaI (Tl) scintillation crystal enclosed in a lead container.

The boundary conditions for these specimens conformed to the case of unidirectional diffusion from a plane source into an infinitely long medium for which the following equation<sup>8</sup> is applicable:

$$A(x) = \frac{M}{\sqrt{\pi Dt}} \exp\left(-\frac{x^2}{4Dt}\right),$$

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<sup>8</sup>J. Crank, The Mathematics of Diffusion, 1st ed., p 9, Oxford University, 1956.

where

$A(x)$  = the activity at a distance  $x$  into the specimen,

$M$  = the activity initially deposited at  $x = 0$ ,

$D$  = the diffusion coefficient,

$t$  = the time of isothermal diffusion annealing.

Taking the natural logarithm of this equation yields a convenient form for treating sectioning data, for the equation indicates that  $\ln A(x)$  should be a linear function of  $x^2$  with a slope of  $-\frac{1}{4Dt}$ . In all penetration plots which follow,  $x$  has units of weight (milligrams) rather than distance. The diffusion coefficients then had units of square milligrams per second which were converted to square centimeters per second using the specimen diameter and density. Corrections were made for densities at the various annealing temperatures by using the data of Krikorian.<sup>9</sup>

## RESULTS

The penetration plots, or activity profiles, for specimens annealed at temperatures from 901 to 1098°C are shown in Fig. 3. Slight deviations from linearity were noted for these five specimens. The initial data points appear to lie on a smooth curve concave upwards; however, the radius of curvature is sufficiently large so that each curve may be treated as two straight-line segments of slightly different slope. From the slopes of the two straight lines "composing" each curve, the two diffusion coefficients,  $D_{\max}$  and  $D_{\min}$  presented in Table 2, were calculated.

The penetration plots for all specimens annealed above 1100°C are presented in Figs. 4, 5, and 6. No deviations from linearity were noted for any of these specimens. The diffusion coefficients calculated from the slopes of the straight lines, temperatures, times, and  $Dt$  values are given in Table 2.

The temperature dependence of the self-diffusion coefficient is shown in an Arrhenius-type plot in Fig. 7. The lack of scatter in the

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<sup>9</sup>O. H. Krikorian, Thermal Expansion of High-Temperature Materials, UCRL-6132 (Sept. 1960).

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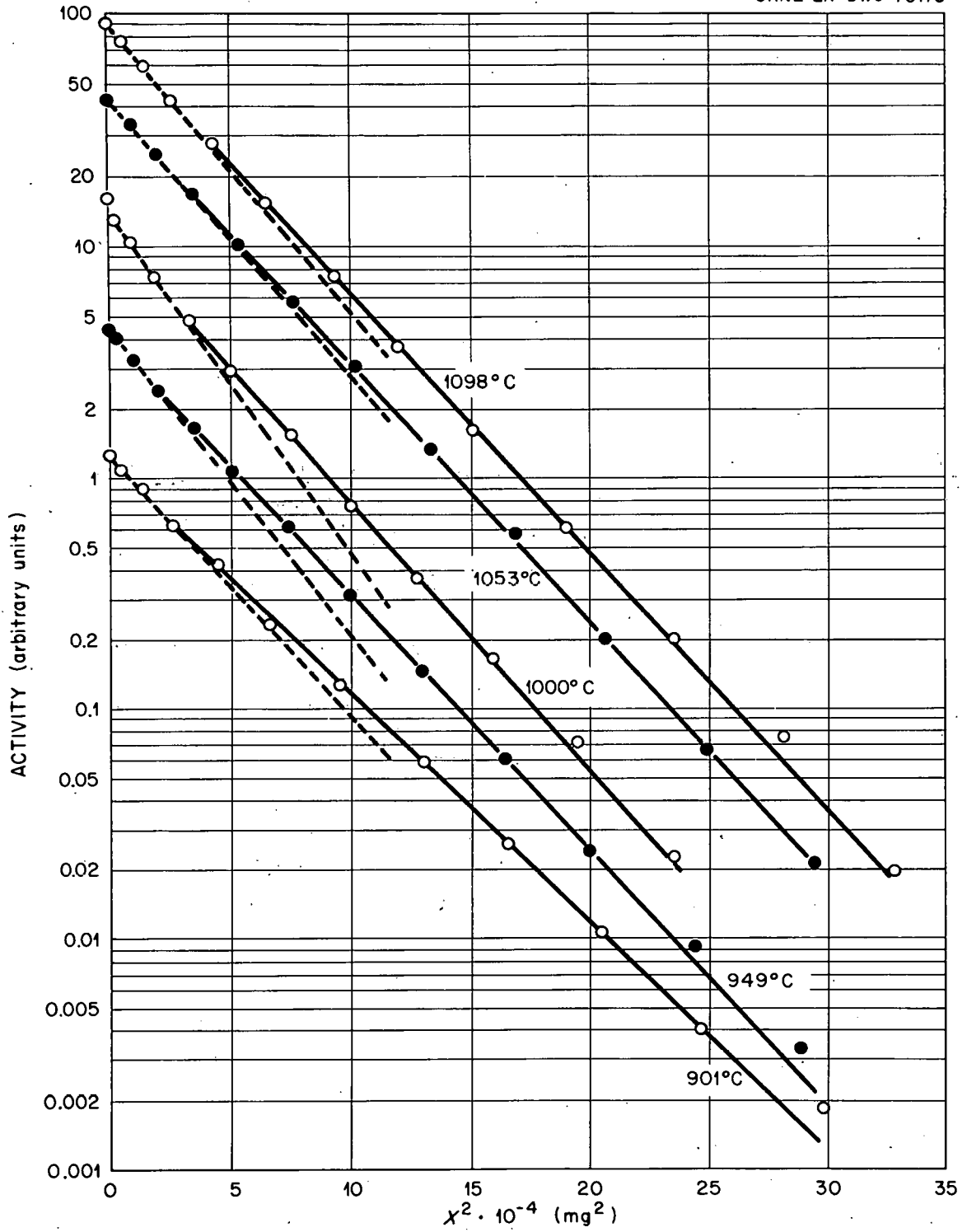


Fig. 3. Activity Profiles for Diffusion of  $Zr^{95}$  in Body-Centered Cubic Zirconium.

Table 2. Results of Diffusion of Zr<sup>95</sup> in  
Body-Centered Cubic Zirconium

Temperature		$10^4$	Time	Diffusion Coefficient		$Dt \cdot 10^4$
(°C)	(°K)	T°K	(sec)	(cm <sup>2</sup> /sec)		(cm <sup>2</sup> )
				Minimum	Maximum	
901	1174	8.518	172,800	$6.25 \times 10^{-10}$	$7.27 \times 10^{-10}$	1.17 av
949	1222	8.183	129,600	$8.50 \times 10^{-10}$	$1.03 \times 10^{-9}$	1.20 av
1000	1273	7.855	86,400	$1.19 \times 10^{-9}$	$1.44 \times 10^{-9}$	1.13 av
1053	1326	7.542	57,600	$2.20 \times 10^{-9}$	$2.26 \times 10^{-9}$	1.28 av
1098	1371	7.294	39,120	$2.86 \times 10^{-9}$	$3.06 \times 10^{-9}$	1.16 av
1148	1421	7.037	25,200	$4.38 \times 10^{-9}$		1.10
1200	1473	6.789	18,000	$6.81 \times 10^{-9}$		1.23
1252	1525	6.557	14,520	$8.81 \times 10^{-9}$		1.28
1302	1575	6.349	10,800	$1.38 \times 10^{-8}$		1.49
1355	1628	6.143	9,000	$1.74 \times 10^{-8}$		1.57
1403	1676	5.967	7,260	$2.45 \times 10^{-8}$		1.78
1457	1730	5.780	5,400	$3.40 \times 10^{-8}$		1.84
1504	1777	5.627	3,600	$4.62 \times 10^{-8}$		1.66
1551	1824	5.482	3,600	$6.09 \times 10^{-8}$		2.19
1605	1878	5.325	2,700	$8.44 \times 10^{-8}$		2.28
1647	1920	5.208	2,760	$1.09 \times 10^{-7}$		3.02
1698	1971	5.074	1,920	$1.51 \times 10^{-7}$		2.90
1747	2020	4.951	1,920	$2.05 \times 10^{-7}$		3.94





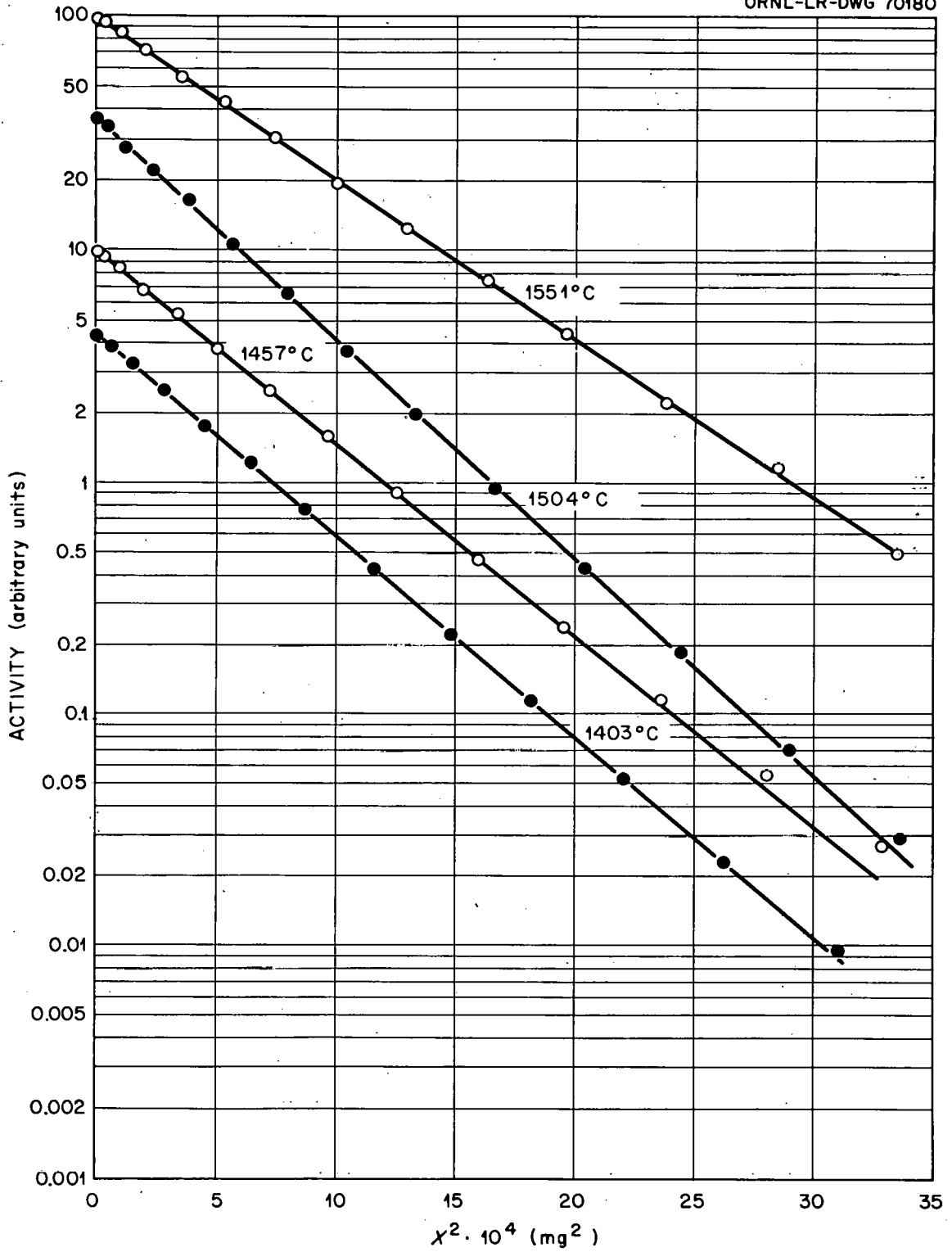


Fig. 5. Activity Profiles for Diffusion of  $Zr^{95}$  in Body-Centered Cubic Zirconium.

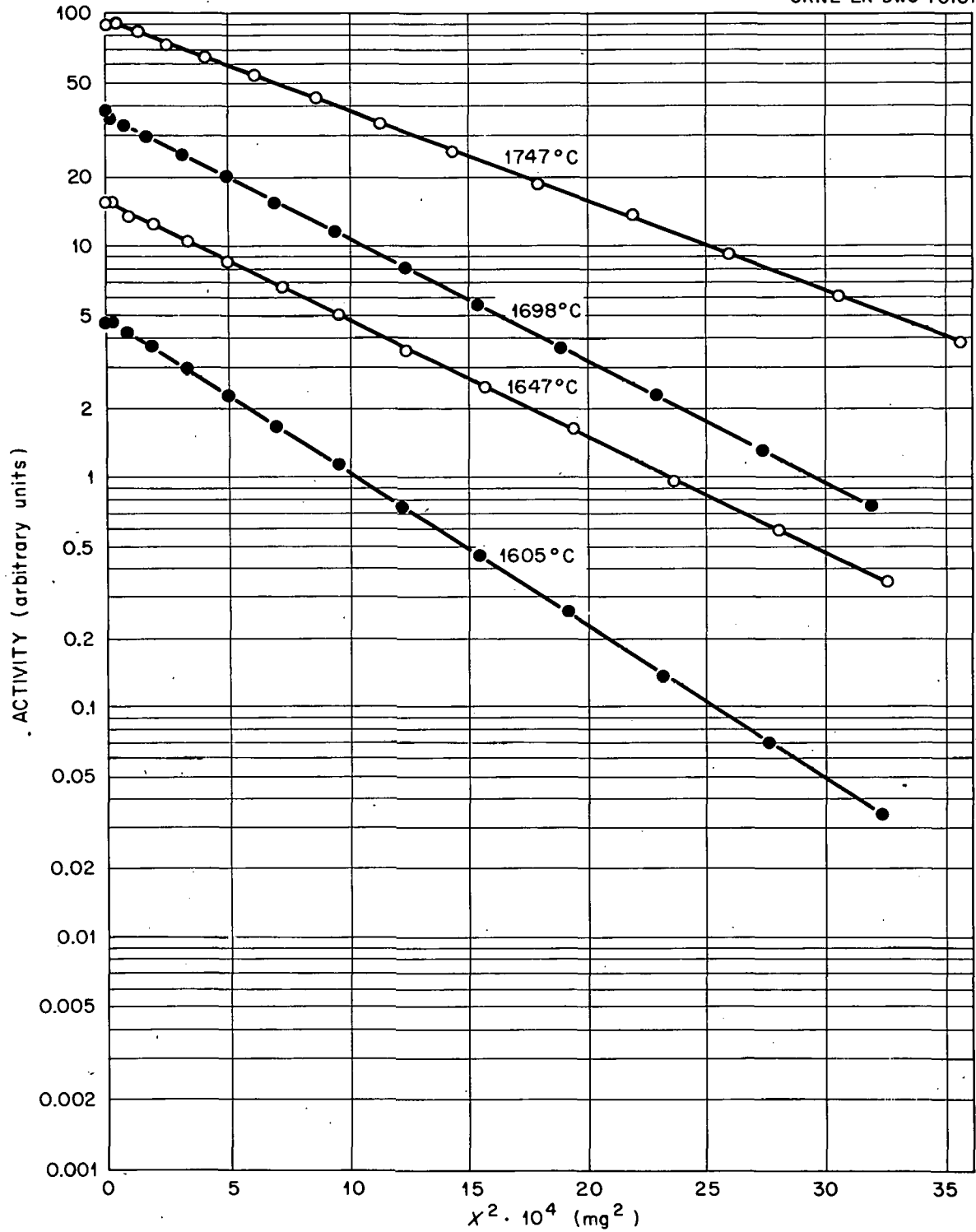


Fig. 6. Activity Profiles for Diffusion of  $Zr^{95}$  in Body-Centered Cubic Zirconium.

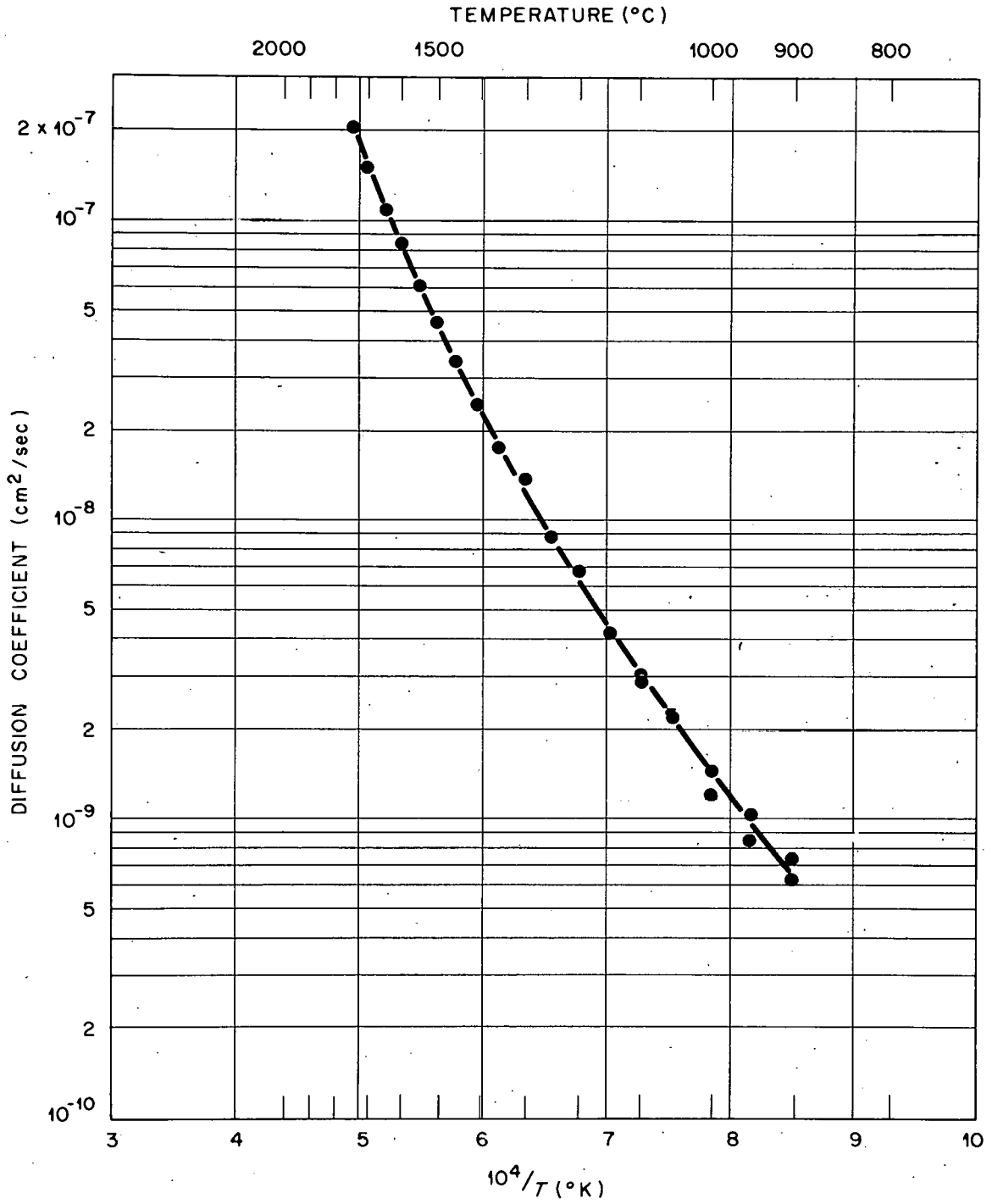


Fig. 7. Temperature Dependence of Diffusion of  $Zr^{95}$  in Body-Centered Cubic Zirconium.

data indicated that the data points were best fitted by a line of small, but continuous, curvature over the entire temperature range that was investigated.

#### DISCUSSION OF RESULTS

The diversity in the data obtained by other investigators can now be explained in terms of the curvature found in the Arrhenius-type plot shown in Fig. 7. The curved line representing the data obtained in the present study, but omitting the data points, is shown in Fig. 8 with the data obtained by other investigators. Several observations may be made: (1) the temperature range included in the present study was larger than that for any previous study; (2) with one exception, which may be due to a difference in the impurity content of the zirconium, the data previously obtained are in very good agreement with the results of the present study; and (3) the apparent activation energy for self-diffusion is a function of temperature (to be discussed in more detail later). The frequency factor and activation energy reported by each previous investigator appear to be dependent in a qualitative manner on the temperature range of study (refer to Table 1) such that, in general, the higher the temperature the higher are the values of frequency factor and activation energy.

A slight amount of curvature was observed in the penetration plots for specimens annealed in the temperature range 901 to 1098°C (Fig. 3). Such curvature is sometimes attributed to short-circuit or grain-boundary diffusion. If grain-boundary diffusion is predominant, i.e., if the ratio of grain-boundary diffusion rate to lattice diffusion rate is high, then the activity plotted on a logarithmic scale vs the penetration distance should yield a straight line.<sup>10</sup> This was not the case, however, for the specimens referred to above; rather, curved lines concave downwards were obtained from such plots. The analytical procedure seemed to substantiate the belief that a significant amount of grain-boundary diffusion did not occur in the coarse-grained specimens.

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<sup>10</sup>J. C. Fisher, J. Appl. Phys. 22, 74-77 (1951).

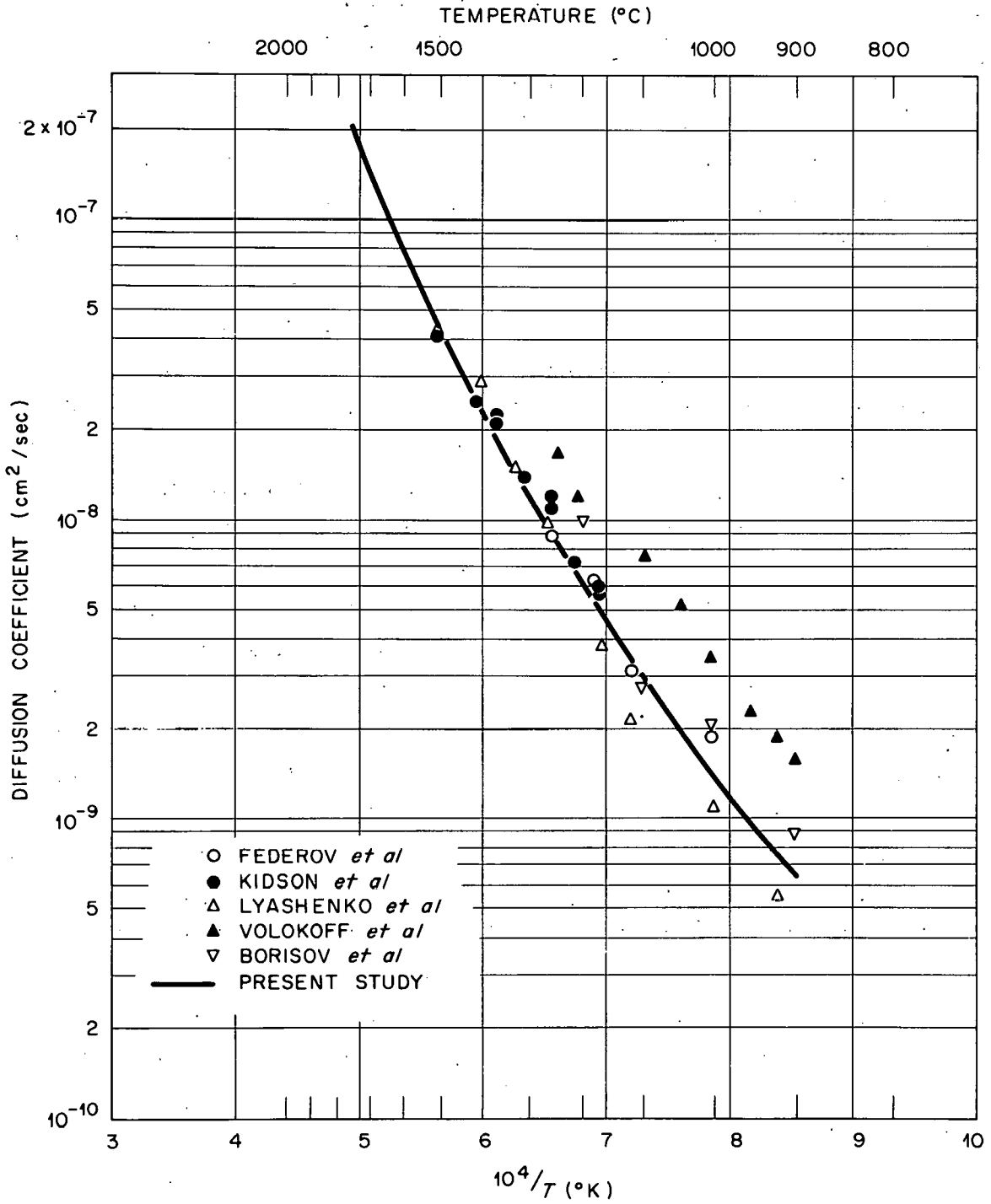


Fig. 8. Comparison of Present Results with Results Obtained by Other Investigators.

Another possible explanation of the curvature is that a chemical diffusion barrier existed at the surface on which the isotope was initially deposited. This possibility is discounted for three reasons: (1) the initial data point for each of the penetration plots shown in Fig. 3 is in line with the trend of the next four or five data points rather than much higher as would be expected if a significant diffusion barrier existed; (2) the curvature extends to depths of 0.006 to 0.010 in. which are unrealistic thicknesses for surface barriers; and (3) the surface oxide is rapidly dissolved in the specimen under the experimental conditions.

A third possibility is that the outer layers of the specimens became contaminated during the diffusion anneals. For these anneals, the specimens were wrapped in degassed tantalum foil and sealed in evacuated fused quartz ampoules. The only other source of contamination was the oxalate compound containing the  $Zr^{95}$  isotope. However, conservative calculations indicated that the maximum amount of impurities (hydrogen, carbon, and oxygen) available from this source was extremely low ( $\ll 1$  ppm).

A metallographic examination of specimens diffusion annealed at the lowest, intermediate, and highest temperatures revealed a second phase existing as platelets in the matrix. The method of selective anodization<sup>11</sup> was used to show that this phase was not zirconium hydride. The phase may be an intermetallic of iron and zirconium. Contamination by oxygen was not indicated in any of the microstructures examined.

Maximum and minimum diffusion coefficients were calculated from the curved and straight portions of each of the penetration plots discussed. Although there is no ready explanation for the curvature of the penetration plots, the maximum and minimum values for a particular temperature differ by no more than 20%. The effect of the maximum and minimum values on the Arrhenius-type plot (Fig. 7), therefore, is small.

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<sup>11</sup>M. L. Picklesimer, Anodizing as a Metallographic Technique for Zirconium-Base Alloys, ORNL-2292 (April 26, 1957).

Data obtained in this work are best fitted by a continuously curving line, as shown in Fig. 7. The curvature, however, is sufficiently small that the usual Arrhenius-type equation

$$D = D_0 \exp\left(-\frac{Q}{RT}\right)$$

adequately represents the data over temperature ranges of 100 to 200°C. Thus, for any small temperature range there is an apparent activation energy  $Q$  and frequency factor  $D_0$  as defined by the Arrhenius-type equation. Accordingly, the slope of the  $\ln D$  vs  $\frac{1}{T}$  plot equals  $-\frac{Q}{R}$ ; and, having obtained  $Q$  in this manner,  $D_0$  is readily calculated. Tangent lines drawn at specific temperatures on the Arrhenius-type plot in Fig. 7 were used to calculate apparent activation energies and frequency factors (Table 3). The apparent activation energy  $(Q)_A$  was found to be a linear function of temperature as shown in Fig. 9. The temperature dependence of the apparent activation energy may be represented by the equation

$$(Q)_A = a + b(T - T_t) ,$$

where

$$a = 19,600 \text{ cal/mole}$$

$$b = 31 \text{ cal/mole-deg}$$

$$T_t = \text{temperature of transformation of } \alpha \text{ to } \beta \text{ zirconium} = 1136^\circ\text{K}.$$

The apparent frequency factor  $(D_0)_A$  was found to obey the following relation:

$$(D_0)_A = c \left(\frac{T}{T_t}\right)^n ,$$

where

$$c = 3 \times 10^{-6} \text{ cm}^2/\text{sec}$$

$$n = 15.6.$$

The fit of  $(D_0)_A$  to this equation is demonstrated by the linearity of the plot shown in Fig. 10.



Table 3. Apparent Activation Energy and Frequency Factor Values for Diffusion of  $Zr^{95}$  in Body-Centered Cubic Zirconium

$10^4$ T°K	Temperature (°K)	Apparent Activation Energy (kcal/mole)	Apparent Frequency Factor ( $cm^2/sec$ )
8.52	1174	21.0	$4.82 \times 10^{-6}$
8.20	1220	22.1	$8.96 \times 10^{-6}$
8.00	1250	23.1	$1.27 \times 10^{-5}$
7.80	1282	24.2	$2.01 \times 10^{-5}$
7.60	1316	25.6	$3.02 \times 10^{-5}$
7.40	1351	26.5	$4.58 \times 10^{-5}$
7.20	1389	27.9	$7.09 \times 10^{-5}$
7.00	1429	29.2	$1.10 \times 10^{-4}$
6.80	1471	30.1	$1.68 \times 10^{-4}$
6.60	1515	31.7	$2.73 \times 10^{-4}$
6.40	1563	32.8	$4.47 \times 10^{-4}$
6.20	1613	34.2	$7.13 \times 10^{-4}$
6.00	1667	35.6	$1.21 \times 10^{-3}$
5.80	1724	37.4	$1.99 \times 10^{-3}$
5.60	1786	39.0	$3.54 \times 10^{-3}$
5.40	1852	42.2	$6.13 \times 10^{-3}$
5.20	1923	44.9	$1.15 \times 10^{-2}$
4.95	2020	46.9	$2.46 \times 10^{-2}$

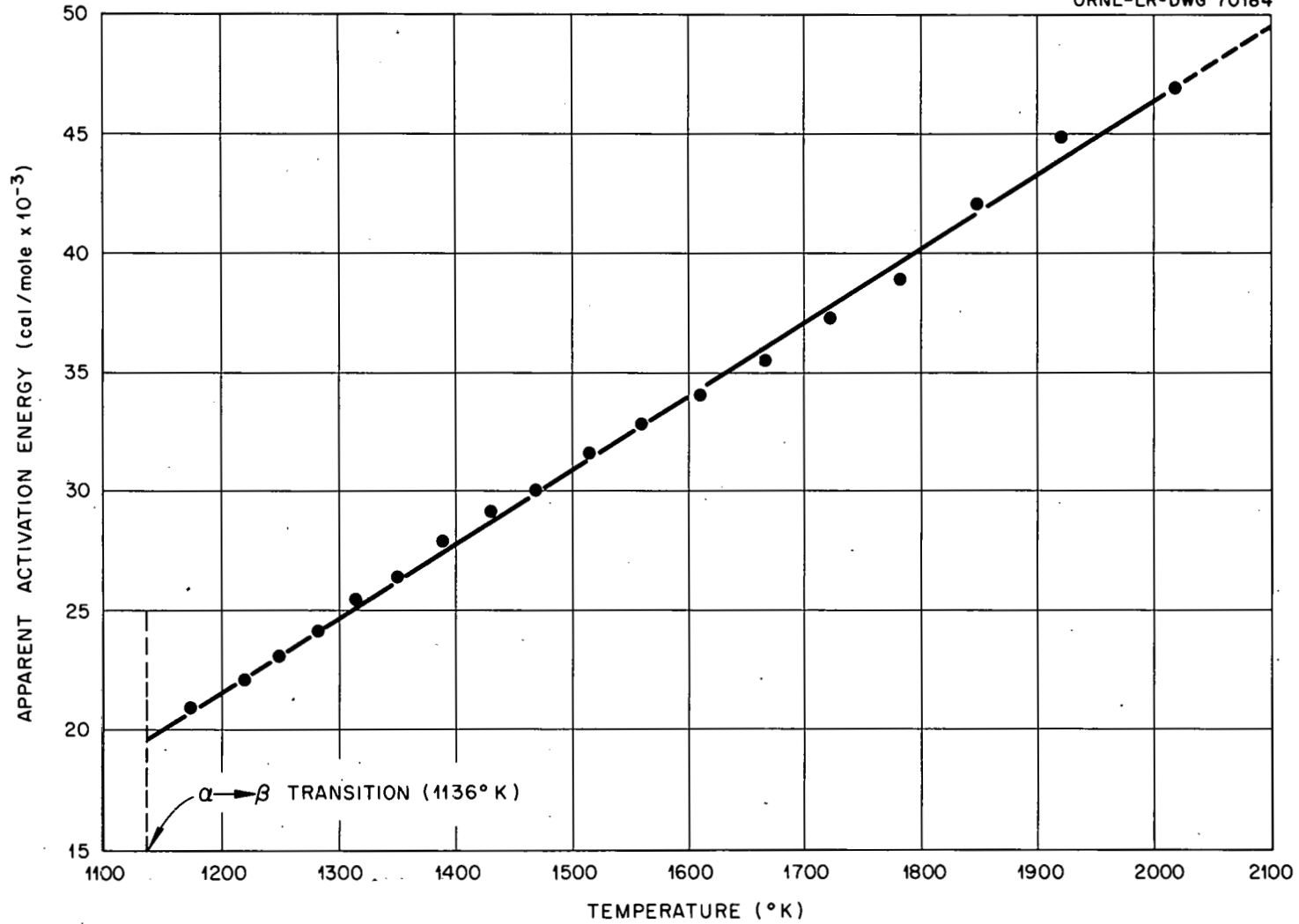


Fig. 9. Temperature Dependence of the Apparent Activation Energy for Diffusion of Zr<sup>95</sup> in Body-Centered Cubic Zirconium.

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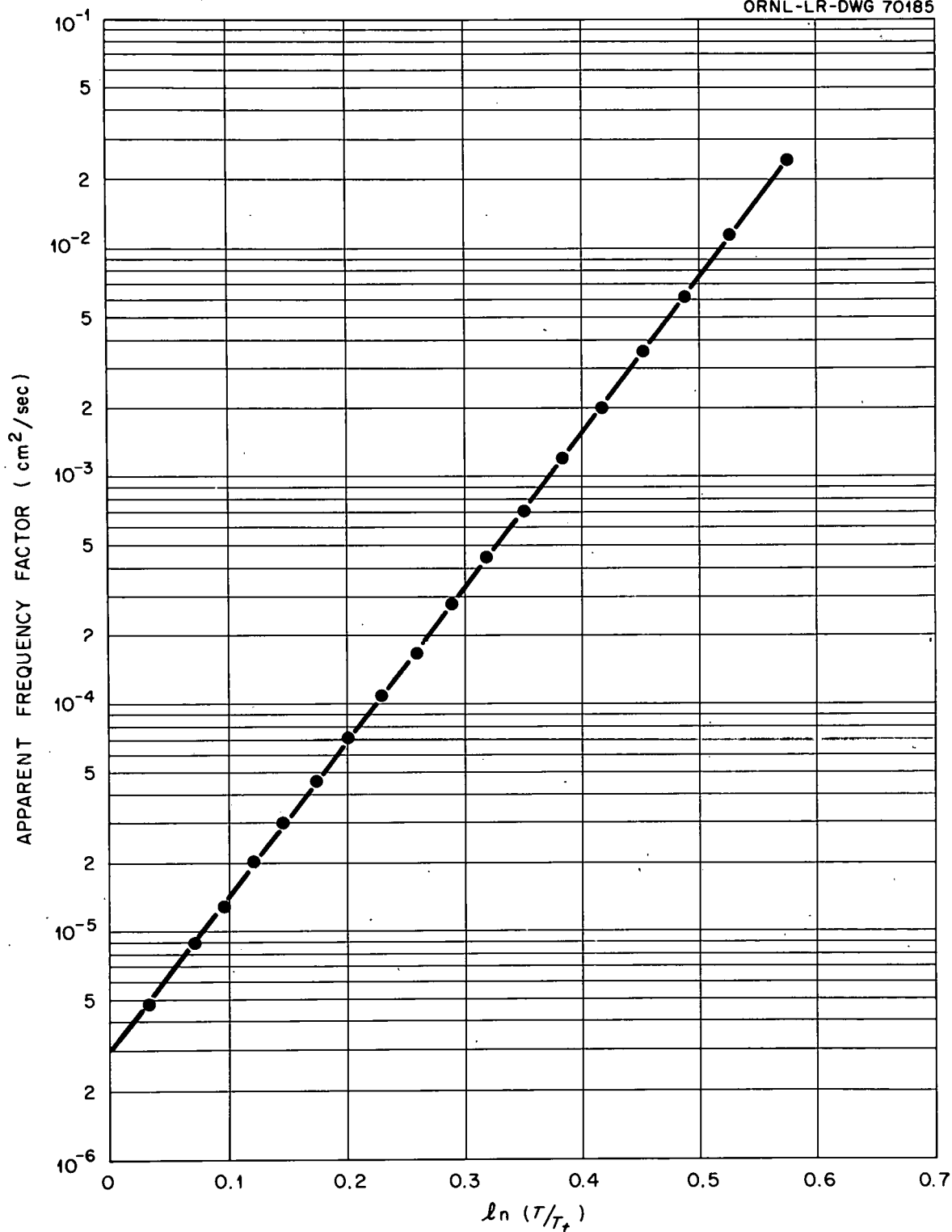


Fig. 10. Temperature Dependence of the Apparent Frequency Factor for Diffusion of Zr<sup>95</sup> in Body-Centered Cubic Zirconium.

Thus, the results of the present work can be described by the following equation:

$$D = 3 \times 10^{-6} \left( \frac{T}{1136} \right)^{15.6} \exp \left( - \frac{19,600 + 31(T - 1136)}{RT} \right) \text{ cm}^2/\text{sec}$$

which describes the data over the entire temperature range investigated. Recalling that the Arrhenius-type equation is valid for small temperature ranges, the data are well described by an equation of the same form where the usual constants  $D_0$  and  $Q$  are temperature dependent.

The present data might also be described analytically in other ways. The curvature in Fig. 7 could be produced if either the activation energy or frequency factor were constant and the other continuously changing. However, the present data do not permit an individual evaluation of either  $D_0$  or  $Q$  - rather, one is uniquely determined by the other. The curvature could also be obtained by the addition of three straight lines, i.e.,

$$D = (D_0)_1 \exp \left( - \frac{Q_1}{RT} \right) + (D_0)_2 \exp \left( - \frac{Q_2}{RT} \right) + (D_0)_3 \exp \left( - \frac{Q_3}{RT} \right) ,$$

where the components represent competing diffusion mechanisms. There are undoubtedly other methods of describing the data; however, the results of the various curve-fitting methods attempted are best represented by the equation having the power of temperature in the pre-exponential factor and having a linear variation with temperature of the activation energy.

A temperature-dependent pre-exponential factor of temperature is not without precedent in describing diffusion results. Swets et al.,<sup>12</sup> described their results on the diffusion of helium in fused silica by two intersecting straight lines on a  $\ln D$  vs  $\frac{1}{T}$  plot. Doremus,<sup>13</sup> however, found that plotting the data of Swets et al. as  $\ln \frac{D}{T}$  vs  $\frac{1}{T}$  resulted in a single straight line over the entire temperature range investigated, giving an equation having the form of

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<sup>12</sup>D. E. Swets et al., J. Chem. Phys. 34, 17 (1961).

<sup>13</sup>R. H. Doremus, J. Chem. Phys. 34, 6 (1961).

$$D = cT \exp\left(-\frac{Q}{RT}\right)$$

Other departures from linearity in Arrhenius-type plots of diffusion data have been reported for beryllium in BeO,<sup>14</sup> iron in  $\alpha$ -Fe,<sup>15</sup> and carbon in  $\alpha$ -Fe.<sup>16</sup>

### CONCLUSIONS

The present study has revealed that results of past experiments<sup>17-21</sup> on the diffusion of Zr<sup>95</sup> in zirconium are in good agreement with one another and with present results if the activation energy and frequency factors are not constant but vary with temperature. The previously reported empirical relations involving melting point, heat of fusion, and heat of sublimation do not predict the correct activation energies for diffusion in zirconium. The temperature dependence of the coefficient of diffusion of Zr<sup>95</sup> in zirconium can best be described by an equation involving a power of the absolute temperature in the pre-exponential term and an activation energy that is a linear function of temperature. This equation is

$$D = 3 \times 10^{-6} \left(\frac{T}{1136}\right)^{15.6} \exp\left(-\frac{19,600 + 31(T - 1136)}{RT}\right) \text{ cm}^2/\text{sec}$$

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<sup>14</sup>S. B. Austermann, Diffusion of Beryllium in Beryllium Oxide, Part II, NAA-SR-5893 (May 1961).

<sup>15</sup>R. J. Borg and C. E. Birchenall, Trans. Met. Soc. AIME 218, 980-84 (1960).

<sup>16</sup>R. P. Smith, Trans. Met. Soc. AIME 224, 105-11 (1962).

<sup>17</sup>G. B. Fedorov and V. D. Gulyakin, Met. i Metalloved. Christykh Metal. Sbornik Nauch, Rabot 1959, No. 1, pp 170-78.

<sup>18</sup>G. Kidson and J. McGurn, Can. J. Phys. 39, 1146-57 (1961).

<sup>19</sup>V. S. Lyashenko et al., Phys. Metals and Metallog. 8(3), 362-69 (1959).

<sup>20</sup>D. Volokoff et al., Compt. Rend. 251, 2341-43 (1960).

<sup>21</sup>Ye. V. Borisov et al., "Study of Diffusion in Zirconium and in Certain Alloys with a Zirconium Base," pp 196-209 in Metallurgiya i Metallovedeniyc, Izdatel'stvo Akademii Nauk USSR, Moscow, 1958 (NP-TR-448, F-TS-9849/V).

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