

FIG. 2. Variation of diffusivity with inverse temperature for Pd in Pb along selected isobars.

Because of the temperature dependence of the pressure calibration no two high-pressure samples were annealed at exactly the same pressure. Hence the high-pressure data were corrected to isobars for displaying in the graph. This adjustment, which was in all cases less than 1.7 kbar, was accomplished using the best-fit parameters from all the data and the expansion of Eq. (1). The somewhat larger scatter in the atmospheric pressure data was the result of having to use a less sophisticated temperature control system as compared to that used for the high-pressure data.

The diffusion coefficients for Pd in Pb as a function of pressure are shown along the 600-K isotherm in Fig. 3. Corresponding diffusion data for Cu, Ni, Zn, Au, Ag, Cd, and Hg in Pb, along with the results for Pb self-diffusion,<sup>20,21,28</sup> are

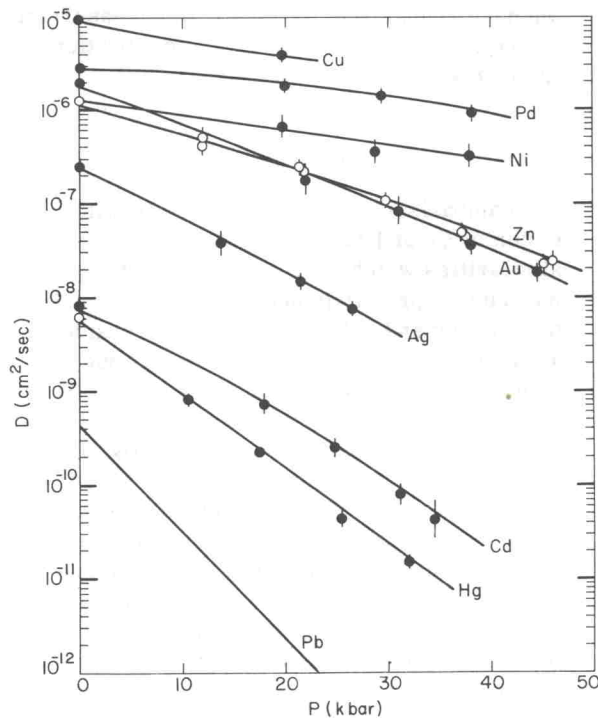


FIG. 3. Variation of diffusivity with pressure at 600 K for Cu, Pd, Au, Ni, Zn, Ag, Cd, Hg, and Pb in Pb.

also shown. The solid lines represent this isotherm calculated from the best fit to all the data to Eq. (1).

Table I shows the experimental values for the pre-exponential factor  $D_0$ , the activation energy  $\Delta H$ , and activation volume per atomic volume  $\Delta V/V_0$ , and the pressure and temperature derivatives of the activation volume for the diffusion of Pd in Pb. Note that  $D_0$ ,  $\Delta H$ , and  $\Delta V$  are functions of temperature and/or pressure and have been tabulated for various temperatures and pressures. Recently, we have determined the pressure increase in our liquid cell as the temperature of the cell is increased to the diffusion-anneal temperature at constant press load.<sup>24</sup> This result differs from that estimated in our earlier work<sup>10-13</sup>; so

TABLE I. Measured parameters for the diffusion of palladium in lead.

$(P, T)$ (kbar, K)	$D_0(P, T)$ ( $10^{-3} \text{cm}^2/\text{sec}$ )	$\Delta H(P, T)$ (eV)	$\Delta V/V_0$	$\frac{\partial(\Delta V/V_0)}{\partial P}$	$\frac{\partial(\Delta V/V_0)}{\partial T}$
				( $10^{-3}/\text{kbar}$ )	( $10^{-4}/\text{K}$ )
(0 600)	$3.4 \pm 0.6$	$0.367 \pm 0.009$	$0.038 \pm 0.013$	$2.6 \pm 0.5$	$0.9 \pm 0.4$
(25 600)	2.4	0.375	0.103		
(25 775)	2.4	0.375	0.117		
(50 600)	1.5	0.414	0.168		
(50 925)	1.5	0.414	0.197		

we have reanalyzed all our former measurements using a more accurate pressure calibration. A summary is given in Table II.

### V. DISCUSSION

A comparison of the diffusion of Pd with the diffusion of Cu and Ni impurities in Pb show several similarities which suggest a pure interstitial mechanism primarily because of their small activation energy and volume. However, considering the accumulated results shown in Fig. 3, one is struck with the fact that the diffusivities of Cu, Pd, Ni, Zn, Au, Ag, Cd, Hg, and Pb in Pb are almost continuously distributed in regard to activation energy and volume between the extremes of Cu in Pb and Pb self-diffusion. It is difficult to imagine a single mechanism being responsible for this great variation in diffusivity, which ranges over more than four orders of magnitude. Even those impurities which have a relatively small activation volume and energy differ enough to question the concept of one responsible mechanism. Comparing Ni and Pd, which are in the same column of the Periodic Table, one finds a smaller activation energy for Pd and an activation volume about  $\frac{1}{3}$  as large as for Ni. The pressure derivative of  $\Delta V$  is also of opposite sign. This last fact is interesting in light of Weyland's<sup>29</sup> observation that, from Frank and Turnbull's<sup>30</sup> dissociative mechanism, the sign of the derivative of  $\Delta V$  was dependent on the ratio of interstitial to substitutional impurities. Therefore, an attempt was made to correlate the high pressure data for the diffusivities of Ni and Pd, along with the noble metals in Pb, with the dissociative model by varying the equilibrium ratio of interstitial and substitutional impurities. No consistent result could be obtained for all of these impurities.

Miller,<sup>18</sup> in an attempt to understand the diffusion of Cd in Pb, extended Frank and Turnbull's

dissociative model to include bound interstitial-vacancy pairs. He concluded that Cd in Pb diffused primarily by interstitial-vacancy pairs with little or no contribution from substitutional or interstitial defects. Miller's calculations were valid only for the case where the fraction of impurities as free interstitials  $q$ , and as pairs  $p$ , was much less than unity. Decker and Vanfleet<sup>26</sup> extended the calculations to include all values of  $p$  and  $q$ . The high-pressure diffusion data were fit to this later model. Following Miller one has

$$D = (1 - q - p)D_s + qD_i + pD_p, \quad (3)$$

where  $q$  and  $p$  are the equilibrium fractions of impurities as free interstitials and pairs, respectively, and the subscripts  $s$ ,  $i$ , and  $p$  refer to pure substitutional, interstitial and pair diffusion. In terms of energy states, the fractions  $p$  and  $q$  can be expressed by

$$p = 6e^{-Q/kT} / (1 + e^{-I/kT} + 6e^{-Q/kT}), \quad (4)$$

$$q = e^{-I/kT} / (1 + e^{-I/kT} + 6e^{-Q/kT}),$$

where  $I$  is the energy of a free interstitial and  $Q$  is the energy of an interstitial-vacancy pair relative to a substitutional impurity. Note that  $Q = I + g_v + B$  in Miller's notation, where  $g_v$  is the energy to form a vacancy, and  $B$  is the binding energy between the interstitial and vacancy.

The effective activation energy and volume are found by taking logarithmic derivatives of the effective diffusion coefficient with respect to temperature and pressure and are given by

$$\Delta H = (1 - p - q)(\Delta H_s - qI - pQ)D_s/D + p[\Delta H_p - qI + (1 - p)Q]D_p/D + q[\Delta H_i + (1 - q)I - pQ]D_i/D, \quad (5)$$

$$\Delta V = (1 - p - q)(\Delta V_s - q\Delta V_{is} - p\Delta V_{ps})D_s/D + p[\Delta V_p - q\Delta V_{is} + (1 - p)\Delta V_{ps}]D_p/D + q[\Delta V_i + (1 - q)\Delta V_{is} - p\Delta V_{ps}]D_i/D, \quad (6)$$

TABLE II. Summary of high-pressure measurements of diffusion in lead evaluated at zero pressure and 600 K.

Isotope	$D$ ( $10^{-8}$ cm <sup>2</sup> /sec)	$D_0$ ( $10^{-2}$ cm <sup>2</sup> /sec)	$\Delta H$ (eV)	$\Delta V/V_0$	$\frac{\partial(\Delta V/V_0)}{\partial P}$ ( $10^{-3}$ /kbar)	$\frac{\partial(\Delta V/V_0)}{\partial T}$ ( $10^{-4}$ /K)
<sup>64</sup> Cu	912	0.86 ± 0.09	0.354 ± 0.007	0.16 ± 0.02	-2.9 ± 1.7	0.8 ± 0.8
<sup>109</sup> Pd	280	0.34 ± 0.06	0.367 ± 0.009	0.04 ± 0.02	2.5 ± 0.9	0.9 ± 0.7
<sup>197</sup> Au	182	0.58 ± 0.07	0.417 ± 0.006	0.27 ± 0.02	0.7 ± 1.6	-1.8 ± 0.7
<sup>63</sup> Ni	133	1.9 ± 0.8	0.495 ± 0.029	0.13 ± 0.02	-1.0 ± 1.3	1.4 ± 1.3
<sup>65</sup> Zn	112	1.65 ± 0.2	0.496 ± 0.007	0.21 ± 0.01	1.2 ± 0.6	-0.7 ± 0.4
<sup>110</sup> Ag	24.8	4.8 ± 0.5	0.630 ± 0.006	0.35 ± 0.02	1.9 ± 1.7	-2.7 ± 0.8
<sup>109</sup> Cd	0.75	42 ± 9	0.924 ± 0.010	0.32 ± 0.02	4.9 ± 1.5	2.2 ± 1.2
<sup>203</sup> Hg	0.57	143 ± 17	1.000 ± 0.005	0.51 ± 0.03	-0.3 ± 0.6	0.2 ± 0.3