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## Effect of Pressure on the Intermetallic Diffusion of Silver in Lead\*

H. R. CURTIN,<sup>†</sup> D. L. DECKER,<sup>‡</sup> AND H. B. VANFLEET

Brigham Young University, Provo, Utah

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The diffusion of silver-110 into lead has been investigated using radioactive-tracer techniques in a temperature range within 200°C of the melting point of lead for six pressures between 0 and 40 kbar. The activation energy was found to increase from 15.2 to 21.9±0.3 kcal/mole as the pressure increased from atmospheric to 39.2 kbar. The activation volume for pressures below 11.9 kbar ranged from 0.54±0.06 to 0.48±0.05 atomic volumes as the temperature decreased from 769 to 556°K. Above 11.9 kbar the activation volume was nearly constant at 0.38±0.03 atomic volumes over the same temperature interval. As a result of the large decrease in the activation volume that occurs between 0 and 11.9 kbar it is suggested that the diffusion process for silver into lead changes from a composite of interstitial plus vacancy to an interstitial mechanism. Therefore the activation volume of 0.38±0.03 atomic volumes as measured for pressures above 11.9 kbar represents the activation volume of motion  $\Delta V_m$  characterizing the interstitial mechanism. Within the accuracy of the experimental data for  $\ln D$  versus  $T_m/T$  the results suggest that  $\Delta H(P)/T_m(P)$  is independent of pressure to 40 kbar.

### I. INTRODUCTION

THE diffusion of silver-110 in lead has been investigated using radioactive-tracer techniques in a temperature range within 200°C of the melting point of lead for six pressures between 0 and 40 kbars. The pressure effect on diffusion has generally been interpreted in terms of the "activated-state theory" of absolute reaction rates using equilibrium thermodynamics. The theory<sup>1</sup> leads to an expression for the diffusion coefficient of the form

$$D = \alpha a^2 \nu w e^{-\Delta G_m/RT}, \quad (1)$$

where  $\Delta G_m$  is the increase in free energy necessary to move one mole of diffusing atoms from their equilibrium positions to the so-called "activated positions,"  $a$  is the lattice constant,  $\nu$  is the mean vibrational frequency of the diffusing atoms,  $\alpha$  is a geometrical constant, and  $w$  is the probability of finding a vacant site adjacent to the diffusing atom into which it can jump. For interstitial diffusion, in the limit of low concentrations,  $w$  is approximately unity. For vacancy diffusion  $w$  is the mole fraction of vacant lattice sites, i.e.,

$$w = e^{-\Delta G_f/RT}, \quad (2)$$

where  $\Delta G_f$  is the free energy necessary to form one mole of vacancies. One can show that Eqs. (1) and (2) are equivalent to the usual Arrhenius equation

$$D = D_0 e^{-\Delta H/RT},$$

where

$$D_0 = \alpha a^2 \nu e^{\Delta S/R}. \quad (3)$$

Differentiation of Eqs. (1) and (3) with respect to pressure and inverse temperature gives the equations for the activation volume and activation energy.

$$\Delta V = (\partial \Delta G / \partial P)_T = -RT(\partial \ln D / \partial P)_T + (\gamma - \frac{2}{3})K_T RT, \quad (4)$$

$$\Delta H = \Delta G + T\Delta S = -R(\partial \ln D / \partial (1/T))_P + (\gamma - \frac{2}{3})R\beta T^2. \quad (5)$$

The activation volume  $\Delta V$ , as defined by Eq. (4), is the sum of the volume of formation  $\Delta V_f$  and the volume of motion  $\Delta V_m$  for the vacancy mechanism and equal to  $\Delta V_m$  only for interstitial diffusion. Physically the volumes  $\Delta V_m$  and  $\Delta V_f$  represent the volume increase of the system which would result from the addition of one mole of activated complexes and one mole of vacancies, respectively. The activation energy or enthalpy  $\Delta H$  from Eq. (5) can be separated in a manner similar to that for  $\Delta V$ . The quantities  $\gamma$ ,  $\beta$ ,  $K_T$  are the Grüneisen constant, coefficient of thermal expansion, and the isothermal compressibility.

In recent years chemical diffusion in metals has been studied at high pressures by a number of investigators. The results of these investigations have yielded the activation volume of self diffusion for a number of metals. The activation volume of sodium,<sup>2</sup> alpha-white phosphorus,<sup>3</sup> and lead<sup>4</sup> have been determined by Nachtrieb and co-workers in a high-pressure bomb utilizing pressures up to 8 kbar. Hudson and Hoffman<sup>5</sup> using a "belt"<sup>6</sup> apparatus measured the activation volume of lead at pressures up to 40 kbar. Tomizuka and co-workers have measured activation volumes of

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<sup>†</sup> Present address: Batelle Memorial Institute, Pacific Northwest Laboratories, Richland, Washington.

<sup>‡</sup> Temporary address until September 1965: University of California, Los Alamos Scientific Laboratory, Los Alamos, New Mexico.

<sup>1</sup> C. A. Wert, Phys. Rev. **79**, 601 (1950).

<sup>2</sup> N. H. Nachtrieb, J. A. Weil, E. Catalano, and A. W. Lawson, J. Chem. Phys. **20**, 1189 (1952).

<sup>3</sup> N. H. Nachtrieb and A. W. Lawson, J. Chem. Phys. **23**, 1193 (1955).

<sup>4</sup> N. H. Nachtrieb, H. A. Rising, and S. A. Rice, J. Chem. Phys. **31**, 135 (1959).

<sup>5</sup> J. B. Hudson and R. E. Hoffman, Trans. AIME **221**, 761 (1961).

<sup>6</sup> H. T. Hall, Rev. Sci. Instr. **31**, 125 (1960).



self diffusion for silver<sup>7</sup> and gold<sup>8</sup> and activation volumes for silver and gold<sup>9</sup> tracers in a gold 34 at. % silver alloy using a gas-pressure system to 9 kbar.

The values for the activation volume as measured by self diffusion at high pressure have generally been in good agreement with corresponding data obtained from quenching experiments.<sup>8</sup> This substantiates other evidence that self diffusion takes place primarily by the vacancy mechanism. Activation volumes measured for systems characterized by interstitial diffusion should be considerably different (smaller) than for self diffusion.

On a hard-sphere model one would expect  $\Delta V_f$  to be of the order of one atomic volume for close packed structures and as small as 0.386 atomic volumes for relaxed bcc structures. Theoretical calculations by Johnson and Brown,<sup>10</sup> Tewordt,<sup>11</sup> and Bennerman<sup>12</sup> for lattice relaxation about a vacancy in copper (fcc) however yields values for  $\Delta V_f$  ranging from 0.47 to 0.60 atomic volumes. These values correlate well with the experimental value of  $0.53 \pm 0.04$  atomic volumes obtained by Huebener and Homan<sup>13</sup> from high-pressure quenching experiments on gold. The contribution  $\Delta V_m$  might be expected to be small in comparison to  $\Delta V_f$  inasmuch as it represents the momentary volume increase of the system as the diffusing atom passes from one equilibrium position to another. From an investigation of the pressure effects on the annealing rate of vacancies quenched into gold Emrick<sup>14</sup> found  $\Delta V_m = 0.15 \pm 0.014$  atomic volumes.

It is evident that there exists a possibility of determining the mechanism of diffusion by comparing measured activation volumes with those of known processes. As a result of the abnormally large relative value of  $D$  for the diffusion of gold<sup>15,16</sup> and silver<sup>15</sup> into lead it is suggested that the diffusion may occur by the interstitial mechanism, and hence one would expect a relatively small activation volume. The purpose of this investigation is to measure the activation volume for the diffusion of silver into lead and to correlate the measured value with a mechanism of diffusion.

<sup>7</sup> C. T. Tomizuka, in *Progress in Very High Pressure Research*, edited by F. Bundy *et al.* (John Wiley & Sons, Inc., New York, 1961), p. 266.

<sup>8</sup> R. H. Dickerson, R. C. Lowell, and C. T. Tomizuka, *Phys. Rev.* **137**, 613 (1965).

<sup>9</sup> E. D. Albrecht and C. T. Tomizuka, *J. Appl. Phys.* **35**, 3560 (1964).

<sup>10</sup> R. A. Johnson and E. Brown, *Phys. Rev.* **127**, 446 (1962).

<sup>11</sup> L. Tewordt, *Phys. Rev.* **109**, 61 (1958).

<sup>12</sup> K. H. Bennemann, *Z. Physik* **165**, 445 (1961).

<sup>13</sup> R. P. Huebener and C. G. Homan, *Phys. Rev.* **129**, 1162 (1963).

<sup>14</sup> R. M. Emrick, *Phys. Rev.* **122**, 1720 (1961).

<sup>15</sup> W. Seith and A. Keil, *Physik Chemie* **22**, 350 (1933).

<sup>16</sup> A. Ascoli, E. Germagnoli, and L. Mongin, *Nuovo Cimento* **4**, 123 (1956).

## II. EXPERIMENTAL PROCEDURE

### 1. Sample Preparation

Lead, 99.999% pure, supplied by A. D. Mackay, Inc., New York, was placed in a graphite mold and single crystals  $1\frac{1}{2}$  in. long and  $\frac{1}{8}$  in. in diameter were grown 10 at a time by the Bridgman method. The mold was then sawed off perpendicular to the axes of the lead cylinders and the surface ground on successively finer grades of silicon carbide paper. The final grinding was on No. 600 grit paper using methyl alcohol as a lubricant to minimize the depth of the amorphous layer which results from the grinding.<sup>17</sup> The freshly-ground surface was then rinsed in alcohol and the mold containing the exposed lead cylinders was placed in a drying oven at 110°C for at least 6 h. This treatment served to remove the alcohol and water which might have been absorbed by the mold and to recrystallize and strain anneal the damaged lead surfaces.

In order to remove any surface contamination from the lead that may enhance or impede diffusion the lead surfaces were bombarded with argon ions prior to vacuum deposition of Ag<sup>110</sup>. Using a movable vacuum probe it was possible to ion bombard and then vacuum deposit the Ag without opening the vacuum system. Approximately 1  $\mu$ Ci of Ag<sup>110</sup> was plated on the face of each lead cylinder.

It is to be noted that during the entire operation, the lead crystals were contained in the same mold in which they were grown. The reason for this is threefold. First, the fact that carbon has a lower conductivity than lead causes the surfaces of the lead crystals to be at a slightly higher (negative) potential than the surrounding material, thus giving more effective ion cleaning. Second, by leaving the crystals in the original casting mold it was possible to plate the entire surface with no fear of silver plating the cylindrical sides of the crystals. Third, this procedure protected the crystals from deformation and general contamination due to handling.

One-tenth of an inch was then sawed off the silver-plated end of the mold containing the crystals. The crystals were removed from the mold by cooling to liquid-nitrogen temperature. The difference in coefficients of thermal expansion between graphite and lead allowed the plated samples to drop from the mold without damage.

### 2. Diffusion Anneal

The lead samples were diffusion-annealed in General Electric Viscasil 100 000-centistoke silicone fluid contained inside a specially designed tetrahedral high-pressure sample holder as shown in Fig. 1. It is to be noted that this design puts the thermocouple in intimate contact with the lead. This was necessary because of

<sup>17</sup> B. W. E. Avient and H. Wilman, *Brit. J. Appl. Phys.* **13**, 521 (1962).



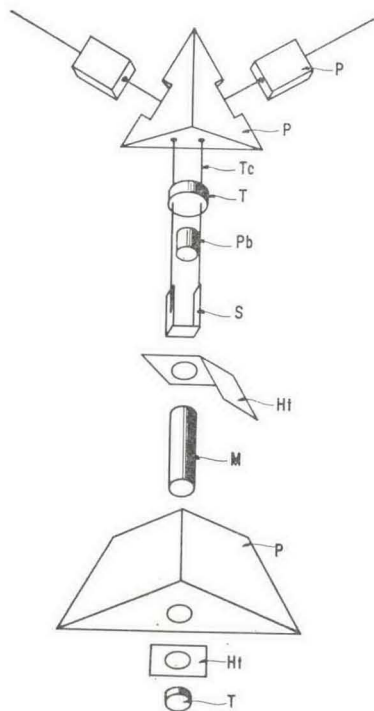


FIG. 1. High-pressure high-temperature sample chamber for diffusion measurements in the tetrahedral anvil press. The lettered parts are: P, pyrophyllite; Tc, thermocouple; T, Teflon; Pb, lead sample; S, steel shim stock; HI, heater tab; M, monel heating tube.

the large temperature gradients associated with such a short furnace. Experiments using multiple thermocouples have shown that there was not more than a 5°C temperature differential in the lead itself.

In order to ensure that the system remained hydrostatic, i.e., the Viscasil did not solidify, the system was raised to 150°C at 6 kbar and maintained there until the pressure was reached at which the sample was to be annealed. The anneal times were approximated for each temperature and pressure such that the  $\text{Ag}^{110}$  concentration was insignificant for penetration distances beyond 1000  $\mu$ . This ensured that the one-dimensional solution of the diffusion equation would satisfactorily describe this experimental arrangement.

High-current, low-voltage power was supplied by a combined "inducteral" and step-down transformer. The power was controlled by a solid-state dimmer device manufactured by Hunt Electronics, Dallas, Texas, which was driven from a Leeds and Northrup, type R820, amplifier. The power was advanced manually and equilibrium obtained before switching to automatic control. The regulating system compared the thermocouple with a reference voltage developed by a Honeywell, type 2745, portable potentiometer and controlled to within 0.05 mV. Using this procedure, equilibrium could usually be obtained in less than 10 sec. The long term stability was better than  $\pm 5^\circ\text{C}$  in a 24-h period.

The ram loading was calibrated to indicate pressure by measuring the resistance transitions in Hg (12.8 kbar, liquid to solid at 25°C), Bi (25.4 kbar) and Yb

(39.5 kbar), and interpolating between these points with a smooth curve.

After removal from the press, the pyrophyllite tetrahedron was broken open and the sample removed from the monel heating tube. The Viscasil was removed from the surface of the lead crystal by cleaning it in carbon tetrachloride and rinsing in water and alcohol. This was necessary so that the crystal could be securely mounted in paraffin for slicing with a sliding microtome.

The sample was sliced in layers 10  $\mu$  thick and collected, either 2 or 6 at a time. The activity of each group was counted by means of a Tracerlab, type sc-57, well scintillation counter and Tracerlab, sc-73 versatile 11, scaler. By plotting the logarithm of the activity, which is proportional to the concentration of silver, versus the square of the mean penetration for each group, straight lines were obtained from which the diffusion coefficient for a given temperature and pressure was calculated. These curves were generally very linear for count rates above 100 counts/min.

### III. EXPERIMENTAL RESULTS

Diffusion coefficients were measured for various annealing temperatures at six pressures. The temperature at each pressure was measured using a calibrated chromel-alumel thermocouple whose emf was corrected for pressure using the correction deduced by Hanneman and Strong.<sup>18</sup> This correction amounted to less than 9°C at the maximum temperature and pressure. It is estimated that as a result of temperature drift in the control system with time, the temperature measurements are accurate only within  $\pm 5^\circ\text{C}$  even though the thermocouple is accurate to  $\pm 2^\circ\text{C}$  at atmospheric pressure.

As a result of experimental difficulty in not resetting the pressure exactly from one diffusion anneal to the next there was a mean deviation in pressure at each

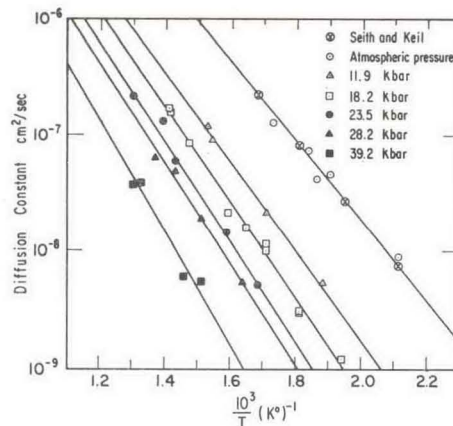


FIG. 2. Variation with temperature of the diffusion coefficient at constant pressure.

<sup>18</sup> R. E. Hanneman and H. M. Strong, J. Appl. Phys. 36, 523 (1965).



TABLE I. Activation energies and  $D_0$  for the diffusion of Ag into Pb as a function of pressure.

Pressure kbar	$\Delta H$ activation energy kcal/mole	$D_0$ cm <sup>2</sup> /sec
Atmospheric	15.2 <sup>a</sup>	0.075 <sup>a</sup>
11.9	17.3 $\pm$ 0.12	0.066 $\pm$ 0.009
18.2	18.6 $\pm$ 0.10	0.084 $\pm$ 0.007
23.5	19.4 $\pm$ 0.19	0.069 $\pm$ 0.013
28.2	19.6 $\pm$ 0.18	0.058 $\pm$ 0.013
39.2	21.9 $\pm$ 0.25	0.073 $\pm$ 0.017

<sup>a</sup> Seith and Keil (Ref. 15).

pressure of as much as 0.75 kbar. To correct for this effect activation energies were calculated using Eq. (3) and the raw data. These approximate activation energies were then used to correct each diffusion coefficient for its appropriate mean pressure. A third type of correction that should be applied to the raw data is a pressure correction that results from thermal expansion within the pressure cell. This increase in sample pressure that results from thermal expansion is usually not observed as an increase in gauge pressure because of the hysteresis and internal friction of the pyrophyllite. No pressure correction for thermal expansion was made however because it was felt that the thermocouple correction of Hanneman and Strong actually represents an effective pressure-temperature correction. This temperature or emf correction appears to be similar to the effective pressure correction used by Decker and Vanfleet<sup>19</sup> in their high-pressure measurements on the melting temperature of gold.

The corrected data is shown in Fig. 2. Included also in Fig. 2 are values reported by Seith and Keil<sup>15</sup> for diffusion of silver into lead at atmospheric pressure. The anneal temperature for the atmospheric pressure runs of the present work was controlled by a different, far less sophisticated system, than that used for the ones at high pressure. Consequently, this data is only suitable for comparison with previous work.

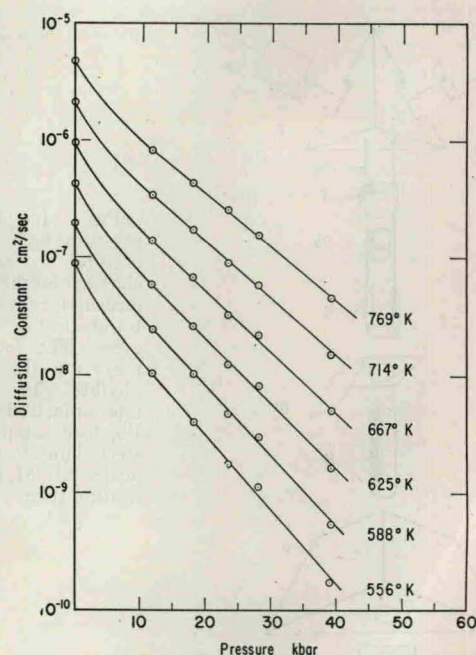


FIG. 3. Variation with pressure of the diffusion coefficient at constant temperature.

In order to obtain a sufficient range of values along isotherms for curves of  $\ln D$  versus pressure as shown in Fig. 3, the isobars of Fig. 2 were extrapolated. Many of the points included in Fig. 3 range beyond the region in which data was actually taken.

Values for the activation energy and activation volume as calculated from the data of Figs. 2 and 3 using Eqs. (4) and (5) are summarized in Tables I and II. Measurements by Hudson and Hoffman<sup>5</sup>, and Nachtrieb *et al.*<sup>4</sup> on the activation volume for self diffusion of lead are also given in Table II for comparison. It should be noted that the correction term  $(\gamma - \frac{2}{3})R\beta T^2$ , in Eq. (5), was of order 0.01% of the activation energy and consequently could be neglected.

TABLE II. Activation volumes for the diffusion of Ag into Pb for various temperatures.

$10^3/T$ (°K) <sup>-1</sup>	$\Delta V^a$ cm <sup>3</sup> /mole	$\Delta V^b$ cm <sup>3</sup> /mole	$\frac{\Delta V^a}{V_M}$	$\frac{\Delta V^b}{V_M}$	$\frac{\Delta V^c}{V_M}$	$\frac{\Delta V^d}{V_M}$
1.3	9.87 $\pm$ 1.14	7.07 $\pm$ 0.60	0.540 $\pm$ 0.062	0.387 $\pm$ 0.034	0.715	
1.4	9.54 $\pm$ 1.10	6.94 $\pm$ 0.58	0.522 $\pm$ 0.060	0.380 $\pm$ 0.033		
1.5	9.33 $\pm$ 1.05	6.95 $\pm$ 0.55	0.511 $\pm$ 0.057	0.381 $\pm$ 0.031	0.670	
1.6	9.00 $\pm$ 1.01	6.86 $\pm$ 0.54	0.492 $\pm$ 0.055	0.376 $\pm$ 0.030		
1.7	8.87 $\pm$ 0.98	6.88 $\pm$ 0.52	0.485 $\pm$ 0.054	0.377 $\pm$ 0.029	0.632	
1.74					0.615	0.715
1.8	8.69 $\pm$ 0.95	6.96 $\pm$ 0.51	0.476 $\pm$ 0.052	0.381 $\pm$ 0.028		
1.9					0.599	0.846

<sup>a</sup> Calculated values using the atmospheric and 11.9-kbar points from Fig. 2.<sup>b</sup> Calculated values for pressures greater than 11.9 kbar.<sup>c</sup> Hudson and Hoffman's values for self diffusion in lead (Ref. 5).<sup>d</sup> Nachtrieb's values for self diffusion in lead (Ref. 4).<sup>19</sup> D. L. Decker and H. B. Vanfleet, Phys. Rev. 138, A129 (1965).



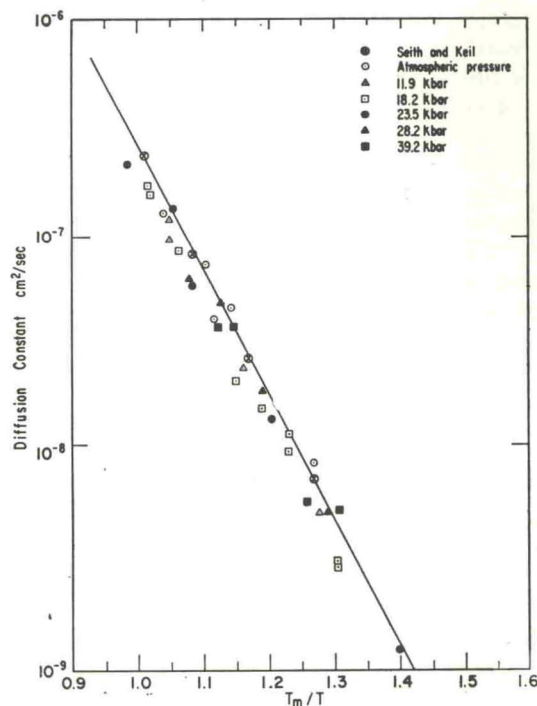


FIG. 4. The diffusion coefficient as a function of the ratio of the melting to the annealing temperature for all of the data.

However, the correction  $(\gamma - \frac{2}{3})RTK_T$  to the activation volume, in Eq. (4), ranged from about 3 to 5% for temperatures between 556 and 769°K for all pressures between 0 and 40 kbar. The correction terms in Eqs. (4) and (5) were approximated using  $\gamma = 3.0$ , the coefficient of thermal expansion as tabulated in standard tables<sup>20</sup> for atmospheric pressure and 100°C, and Bridgman's<sup>21</sup> isothermal-compressibility data extrapolated to the temperatures of interest.

The logarithm of the diffusion coefficient is plotted in Fig. 4 as a function of the ratio of the melting temperature at the annealing pressure to the annealing temperature. The values for the melting temperature of lead were obtained from work performed in this laboratory by Dudley and Millet,<sup>22</sup> and subsequently pressure corrected for thermal expansion using the correction obtained by Decker and Vanfleet<sup>19</sup> on their work with gold.

#### IV. DISCUSSION

The activation energies  $\Delta H$  shown in Table I increase monotonically with pressure from 15.2 kcal/mole at atmospheric pressure to 21.9 kcal/mole at 39.2 kbar. This is in accord with the interpretation of  $\Delta H$  being an energy of activation, it being expected that the

energy required to form a vacancy and/or move a defect from one equilibrium position to an adjacent one should increase with increasing pressure.

The activation volume  $\Delta V$  as can be seen from the slopes of the curves of Fig. 3 is independent of the pressure for each temperature above 11.9 kbar. Below 11.9 kbar, however, it is evident that  $\Delta V$  increases with decreasing pressure. This effect can be explained if one assumes that at some pressure both the vacancy and interstitial mechanism contribute significantly to the diffusion. The ratio of the diffusion constant  $D_v$  for vacancy diffusion to that for interstitial diffusion  $D_i$  is proportional to  $\exp[-(\Delta G_v - \Delta G_i)/RT]$ , where  $\Delta G_v$  and  $\Delta G_i$  are the free energies for diffusion by the vacancy and interstitial mechanism, respectively. If the activation volume for the vacancy mechanism  $\Delta V_v$  is large in comparison to  $\Delta V_i$  for an interstitial, it is evident that  $D_v/D_i$  will decrease rapidly with increasing pressure. A calculation has been made assuming that the linear portions of the  $\ln D$  versus pressure curves of Fig. 3 are characteristic of interstitial diffusion. These curves were extrapolated to atmospheric pressure for each isotherm. The resulting values of  $D$  were taken to represent the interstitial contribution to the diffusion at atmospheric pressure for each temperature. By subtracting the interstitial contribution from Seith and Keil's<sup>15</sup> data the vacancy contribution at atmospheric pressure is obtained. Analysis of these data gave atmospheric pressure activation energies of 15.4 and 15.7 kcal/mole for the interstitial and vacancy contributions to the diffusion. Good agreement with the isotherms of Fig. 3 was made by using Hudson and Hoffman's<sup>5</sup> low-pressure activation volumes for  $\Delta V_v$  and the high-pressure activation volume from this experiment for  $\Delta V_i$  in conjunction with the atmospheric-pressure values of  $D_i$  and  $D_v$  as discussed above. Hence, if the diffusion mechanism changes with pressure, as it is seen that it may do, one would expect the observed decrease in the measured activation volume. However, since the proposed mechanism involves a diffusion constant with two terms with different temperature dependency some curvature in the  $\ln D$  versus  $1/T$  curves for pressures below about 10 kbar should be apparent. Data in this pressure range would do much to confirm or refute the proposed mechanism.

Hudson and Hoffman<sup>5</sup> observed a decrease in the activation volume for self diffusion in lead at about 30 kbar which is probably similar to the effect at atmospheric pressure observed in this experiment.

It has been proposed by Braune<sup>23</sup> and Van Liempt<sup>24</sup> using Lindemann's theory of melting that

$$\Delta H(P)/T_m(P) = \Delta H(0)/T_m(0), \quad (6)$$

where  $\Delta H(P)$  and  $T_m(P)$  are the activation energy and melting temperature of the solvent at the pressure  $P$ .

<sup>20</sup> Landolt-Börnstein Tables, edited by H. Borchers and E. Schmidt (Springer-Verlag, Berlin, 1964), Vol. IV, Part 2a, p. 934.

<sup>21</sup> P. W. Bridgman, *The Physics of High Pressure* (G. Bell and Sons, Ltd., London, 1949), p. 161.

<sup>22</sup> J. D. Dudley and L. E. Millet (private communication).

<sup>23</sup> H. Braune, *Z. Physik Chem.* **110**, 147 (1924).

<sup>24</sup> J. A. M. Van Liempt, *Rec. Trav. Chim.* **51**, 114 (1932).



