

$[(0.7734 r_s)/(21+r_s)]$. Here $g(x)$ is a multiplicative correction to the usual Lindhard dielectric function, r_s is the electron spacing in Å, and q is the magnitude of the change in electron wave number. This parametrization of γ was determined from the electron gas compressibility in the long-wavelength limit; it should be reasonably valid for $q < 2k_F$, but it is questionable for larger q . In the

case of potassium, $\gamma=1.084$.

²⁵See, for example, J. M. Ziman, *Electrons and Photons* (Oxford U.P., Oxford, England, 1960), Chap. 9, pp. 369 and 370; or F. J. Blatt, *Physics of Electronic Conduction in Solids* (McGraw-Hill, New York, 1968), Chap. 7, p. 193.

Effect of Pressure on the Diffusion of Gold in Lead to 50 kbar*†

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We have measured the diffusion of gold in lead to pressures of 46 kbar and temperatures of 420 °C using a radioactive-tracer technique. The data were analyzed assuming a single effective mechanism of diffusion with a temperature- and pressure-dependent activation volume. The earlier data on the diffusion of silver in lead by Curtin, Decker, and Vanfleet were also analyzed in a similar manner. The activation energy and activation volume at the melting point and atmospheric pressure are, respectively, $\Delta H=9.48 \pm 0.30$ kcal per mole, $\Delta V/V_0=0.28 \pm 0.03$ for Au in Pb; $\Delta H=14.63 \pm 0.24$ kcal per mole, $\Delta V/V_0=0.34 \pm 0.04$ for Ag in Pb. Although no definite conclusion as to the specific nature of the diffusion mechanism can be drawn, the results are not inconsistent with an interstitial-substitutional double mechanism.

I. INTRODUCTION

The diffusion of noble metals in lead has been of interest since the early work of Roberts-Austen¹ and Seith and Keil.² It was noted that these materials diffuse in lead at a rate which is several orders of magnitude more rapid than the self-diffusion of lead and that the activation energy for the diffusion of noble metals in lead is very small. The question to be considered is then by what mechanism does this rapid diffusion take place.

Nowick³ suggested that the high rate of diffusion for gold and silver in lead was due to diffusion along internal surfaces. However, Ascoli⁴ and Kidson⁵ demonstrated that there is no important contribution to the diffusion of gold in lead from grain boundaries, dislocations, or the crystalline surface for diffusion anneals above 190 °C.

Because of the rapidity of the diffusion, Wagner⁶ proposed that gold dissolved in lead interstitially and diffused via an interstitial mechanism. Ascoli and Damask⁷ proposed that gold dissolves substitutionally in lead and diffuses by a vacancy mechanism with a strong binding between the gold atoms and the vacancies. Kidson⁵ considered both of these models and concluded that neither of them is consistent with the experimental observations. He suggested, along the lines of that proposed by Frank and Turnbull⁸ for the diffusion of copper in germanium, that gold dissolved in lead both substitutionally and interstitially and that the interstitial component diffuses very rapidly. His analysis as-

sumes also that the concentration of substitutional gold is much larger than the concentration of interstitial gold. Curtin *et al.*⁹ made a similar proposal of a possible double mechanism to interpret their data on the diffusion of silver in lead at high pressures. Dyson, Anthony, and Turnbull¹⁰ concluded that rapid diffusion of copper and silver in lead must be principally due to interstitial diffusion with both substitutional and interstitial noble-metal atoms present.

Measurements of the effect of pressure on these diffusion couples adds another dimension of information which should help to distinguish between the proposed mechanisms. Pressure dependence on self-diffusion in lead was studied by Nachtrieb, Resing, and Rice¹¹ to 8 kbar and also by Hudson and Hoffman¹² to 33 kbar. The latter results are somewhat clouded by their pressure calibration which is greatly in error at the higher pressures, but from these results we see that the activation volume of self-diffusion in lead is 0.66 ± 0.07 atomic volumes. This value can be considered as typical of diffusion by a vacancy-controlled mechanism. Curtin *et al.*⁹ measured the effect of hydrostatic pressure on the diffusion of silver in lead to 40 kbar. Their results indicated a reduction of the activation volume from 0.5 atomic volumes at atmospheric pressure to 0.38 atomic volumes at and above 12 kbar. They felt that this indicated a change from one diffusion mechanism to another as one progressed to higher pressures. Ascoli *et al.*¹³ measured the effect of pressure on the dif-

fusion of gold in lead to 10 kbar. This is the only previous work on the subject of this research. They also invoked a double-mechanism idea to interpret their results and predicted that the activation volume above 10 kbar would be zero, which they thought to correspond to pure interstitial diffusion. Since the "kink" in their diffusion parameters, on which many of their conclusions were based, came so near their maximum pressure, and their technique did not allow them to know whether their sample actually attained the desired pressure, we felt it appropriate to repeat their experiment and extend it to higher pressures. This work was also undertaken because the extension of the work of Ascoli *et al.* to high pressures predicted results for the diffusion of gold into lead which differed greatly from the measured diffusion of silver in lead at high pressures.

Nachtrieb¹⁴ and his collaborators proposed a law of corresponding states for diffusion in that $\ln D$ vs T_m/T is independent of pressure where T_m is the melting temperature at each pressure. This proposal was further investigated by Rapoport.¹⁵ Hudson and Hoffman's¹² data were not in agreement with the law of corresponding states but their data are too scattered to completely reject it. The results of Curtin *et al.* on the diffusion of silver in lead was in reasonable agreement with this law. The present results can also be used to examine the law of corresponding states proposed by Nachtrieb.

II. EXPERIMENTAL PROCEDURE

Lead crystals, 4.8 mm diam, were grown from 99.9999% pure lead in graphite molds in a vacuum of 10^{-5} Torr. Sections, about 3 mm long, were cut from the crystals. A surface was defined perpendicular to the axis by slicing with a sliding microtome. This surface was then etched in acetic acid and hydrogen peroxide. A layer of about 100 Å of gold was plated on the surface from a commercial gold plating solution obtained from Lea-Ronal Inc. The lead was then reduced to 3.2 mm diam in a lathe to remove any surface contamination.

These samples were placed in pressure cells similar to those described by Curtin *et al.*,⁹ the major differences being that our heater can was made of Inconel and the hydrostatic fluid was petroleum ether. The samples were taken to the desired pressure in a tetrahedral anvil press, and after the anneal cycle the pressure was slowly returned to atmospheric pressure. The anneal temperature was monitored using a chromel-alumel thermocouple and was held constant to within $\pm 0.03^\circ\text{C}$ over the period of the anneal. The control circuit, described by Decker,¹⁶ allowed the small-capacity furnace to be heated to the anneal temperature and under control in less than 3 min. The

cooling time was less than 10 sec. The measurement was corrected for heat-up and cool-down times which in the worst cases amounted to less than 4% of the total anneal cycle. After lowering the pressure, the undistorted lead crystals were removed from the hydrostatic chamber for analysis. Samples were not used if they were deformed because of improper sealing of the liquid chamber. The pressure of the anneal was determined from the ram load of the press, which was calibrated against the Bi I-II and Tl II-III phase transitions on increasing pressure, which were taken as 25.6 and 38 kbar, respectively.¹⁷

The measured temperature and pressure must be corrected for pressure effects on the thermocouple emf and for expansion effects on the pressure calibration due to heating of the sample chamber within the pressure cell. Neither of these corrections is known very precisely but they only slightly alter the final diffusion results as reported here. Thermocouple corrections have been studied by Hanneman, Strong, and Bundy,¹⁸ and by Getting and Kennedy.¹⁹ Hanneman *et al.* indicate that the correction for chromel-alumel thermocouples increases with increasing pressure and temperature, giving a correction of about $+3.1^\circ\text{C}$ at 50 kbar and 500°C , while Getting and Kennedy indicate that the correction increases and then decreases with both increasing pressure and temperature. Over the range covered by this experiment their correction would always be less than $\pm 1.5^\circ\text{C}$. Thus in the worst case there is a difference of 4.7°C in the temperature using these two results. We have used the results of Getting and Kennedy in the measurements reported, but the uncertainties quoted here will span the results analyzed with either of these thermocouple corrections. Aside from possible systematic errors we believe our temperatures are accurate to $\pm 3^\circ\text{C}$.

A more difficult problem is the correction to the pressure due to thermal expansion of the internally heated pressure chamber. We endeavored to measure this pressure rise in the following manner. A heat-treated manganin coil was placed in the liquid chamber in place of the lead diffusion sample and its electrical resistance was measured versus pressure and temperature using a four-lead measurement. The results were analysed by comparing them with atmospheric-pressure data over the same range of temperature and with the 4-kbar measurements of Wang²⁰ on the electrical resistance of manganin. From these measurements we concluded that the pressure rise with increasing temperature was independent of pressure above 15 kbar and in rough qualitative agreement with results estimated using x-ray measurements at high pressures and elevated temperatures in solid pressure-transmitting medium.²¹ This pressure correction

amounted to 7 kbar at 500°C.

After the diffusion anneal the samples were again reduced by about 0.03 mm diam in a lathe and then oriented in the microtome using a He-Ne laser for alignment. The alignment was better than 0.6°. Slices of 20- μ thickness were removed with the microtome and collected in polyethylene bags with four to seven slices per bag. These were sent to General Atomics for irradiation and counting or to Idaho Nuclear Corp., who irradiated them with neutrons and returned them to us for counting the activation in the 410-keV peak of gold using a multi-channel analyzer and a Tracerlab well counter. The minimum detectable amount of gold in these samples was about 3×10^{-4} μ g or a sensitivity of 0.05 ppm.

A more detailed description of the experimental procedure has been given by Weyland.²² We also made a set of measurements near atmospheric pressure with the rams of the press just contacting the tetrahedron so that the pressure on the sample was less than 0.5 kbar. These measurements were to check the technique against atmospheric-pressure results which are quite well established. Values of the diffusion constant at atmospheric pressure were in reasonable agreement with results reported by Kidson⁵ and Ascoli⁴ and indicate that no significant discrepancy can be attributed to the high-pressure diffusion results because of experimental technique, i. e., annealing in petroleum ether, machining before and after annealing.

III. ANALYSIS

The analysis of diffusion over a range of pressure and temperature is relatively straightforward if one assumes a reaction-rate activation theory with an effective single diffusion mechanism and applies thermodynamics. The standard analysis is given in many reference works. The usual experimental approach to obtain the activation energies is to graph the data along isobars as $\ln D(P, T)$ vs $1/T$. From the slope of these curves one obtains the activation energy ΔH at each pressure. To obtain activation volumes one now graphs the diffusion constant along isotherms, i. e., $\ln D(P, T)$ vs P , and determines ΔV from the slope of these curves:

$$\frac{\Delta V}{RT} = - \left(\frac{\partial \ln(D/a^2 f \nu)}{\partial P} \right)_T. \quad (1)$$

The quantity $[\partial(\ln a^2 f \nu)/\partial P]_T$ will make a small correction to the graphical results. The symbols in this expression are defined following Eq. (2).

Because of the effects of pressure on the thermal emf, and thermal expansion on the pressure calibration, the raw data were not taken along exact isotherms or isobars and would have to be adjusted in order to follow the above approach. A better

method is to consider all the data simultaneously and determine the best value for ΔH and ΔV that would yield the entire set of results $D(P, T)$. One can consider just the high-pressure results or include atmospheric-pressure results as well in this analysis.

We begin by considering the equation

$$D(P, T) = f a^2(P, T) \nu(P, T) e^{-\Delta G(P, T)/RT}, \quad (2)$$

where $D(P, T)$ is the diffusion constant, f is the product of a geometric and correlation factor, $a(P, T)$ is the lattice parameter, $\nu(P, T)$ is some average frequency of oscillation, $\Delta G(P, T)$ is the Gibbs free energy per mole of activated complexes for the thermodynamic potential barrier opposing the individual jumps, and R is the molar gas constant. Since the measurement of the impurity distribution is made at atmospheric pressure and room temperature, the measured diffusion corresponds to²³

$$D_m(P, T) = f a^2(0, T_0) \nu(P, T) e^{-\Delta G(P, T)/RT}. \quad (3)$$

We now expand $\ln \nu(P, T)$ and $\Delta G(P, T)$ about $P=0$ and $T=T_0$:

$$\begin{aligned} \ln \nu(P, T) = & \ln \nu + \gamma \kappa P - \gamma \beta (T - T_0) + \frac{1}{2} \gamma \frac{\partial \kappa}{\partial P} P^2 \\ & + \gamma \frac{\partial \kappa}{\partial T} P (T - T_0) - \frac{1}{2} \gamma \frac{\partial \beta}{\partial T} (T - T_0)^2 + \dots, \quad (4) \end{aligned}$$

where κ is the isothermal compressibility, β is the volume coefficient of thermal expansion, and γ is the Grüneisen parameter, which is assumed to be independent of P and T in this approximation. All symbols without specific functional dependence are to be evaluated at $T=T_0$ and $P=0$. Similarly,

$$\begin{aligned} \Delta G(P, T) = & \Delta H + P \Delta V - T \Delta S + \frac{1}{2} \frac{P^2}{\partial P} \frac{\partial \Delta V}{\partial P} \\ & + \frac{P(T - T_0)}{\partial T} \frac{\partial \Delta V}{\partial T} - \frac{1}{2} \frac{(T - T_0)^2}{T_0} \frac{\partial \Delta C_p}{\partial T} + \dots, \quad (5) \end{aligned}$$

where $\Delta H = \Delta G + T_0 \Delta S$ is the activation energy, $\Delta V = \partial \Delta G / \partial P$ is the activation volume, $\Delta S = -\partial \Delta G / \partial T$ is the entropy difference between a mole of the diffusing species at the activated complex compared to their equilibrium positions, and $\Delta C_p = T_0 (\partial \Delta S / \partial T)_p$ is the difference in specific heats at constant pressure for the diffusing species at the activated complex compared to their equilibrium positions.

We now substitute (4) and (5) into (3) and rearrange terms to obtain

$$\begin{aligned} \ln D_m(P, T) = & A - \frac{B}{RT} - \frac{CP}{RT} + EP - FT + \frac{JP^2}{RT} \\ & + LP^2 + MPT + NT^2, \quad (6) \end{aligned}$$

where

$$\begin{aligned}
 A &= \ln D_0 + \gamma T_0 \left(\beta - \frac{1}{2} T_0 \frac{\partial \beta}{\partial T} \right) - \frac{\Delta C_p}{R}, \\
 B &= \Delta H - \frac{1}{2} \Delta C_p T_0, \quad C = \Delta V - \frac{T_0 \partial \Delta V}{\partial T}, \\
 E &= \gamma \left(\kappa - \frac{T_0 \partial \kappa}{\partial T} \right) - \frac{1}{R} \frac{\partial \Delta V}{\partial T}, \\
 F &= \gamma \left(\beta - \frac{T_0 \partial \beta}{\partial T} \right) - \frac{\Delta C_p}{2 R T_0}, \\
 J &= -\frac{1}{2} \frac{\partial \Delta V}{\partial P}, \quad L = \frac{1}{2} \frac{\gamma \partial \kappa}{\partial P}, \\
 M &= \frac{\gamma \partial \kappa}{\partial T}, \quad N = -\frac{1}{2} \frac{\gamma \partial \beta}{\partial T}.
 \end{aligned} \tag{7}$$

The experimental diffusion values were fitted to Eq. (6) by a least-squares technique to give best values for A , B , C , E , F , and J as well as a standard deviation for each parameter. These values can then be used in the set of Eq. (7) and from which one solves for ΔH , ΔV , $\ln D_0$, $\partial \Delta V / \partial T$, $\partial \Delta V / \partial P$, and ΔC_p which are all evaluated at $P=0$ and $T=T_0$. In order to accomplish the above calculation one must assign values to γ , β , κ , $\partial \beta / \partial T$, $\partial \kappa / \partial T$, and $\partial \kappa / \partial P$.

We should point out that this approach does not predict a necessarily linear Arrhenius curve for it allows $\Delta H(P, T)$ to be a function of T as well as $D_0(P, T)$. We calculate, from the above, expressions for the activation energy and D_0 as functions of P and T with the following results:

$$\begin{aligned}
 \Delta H(P, T) &= \Delta H + P V_0 \left(\frac{\Delta V}{V_0} + \frac{P}{2} \frac{\partial (\Delta V / V_0)}{\partial P} \right. \\
 &\quad \left. - T_0 \frac{\partial (\Delta V / V_0)}{\partial T} \right) + \frac{R(T^2 - T_0^2)}{2 T_0} \frac{\Delta C_p}{R} \tag{8}
 \end{aligned}$$

and

$$\begin{aligned}
 \ln D_0(P, T) &= \ln D_0 - \gamma (T - T_0) \left(\beta + \frac{1}{2} \frac{(T - T_0) \partial \beta}{\partial T} \right) \\
 &\quad + \gamma P \left(\kappa + \frac{(T - T_0) \partial \kappa}{\partial T} + \frac{1}{2} \frac{P \partial \kappa}{\partial P} \right) \\
 &\quad - \frac{P V_0}{R} \frac{\partial (\Delta V / V_0)}{\partial T} + \frac{(T - T_0) \Delta C_p}{R T_0}. \tag{9}
 \end{aligned}$$

V_0 is the atomic volume of lead at atmospheric pressure and room temperature with a value of $18.26 \text{ cm}^3/\text{mole}$.

IV. RESULTS

Figure 1 gives examples of the penetration curves. The horizontal region at large penetration is likely due to background from the gold impurity in the original lead. Our evidence for this statement comes from the observation that the level of

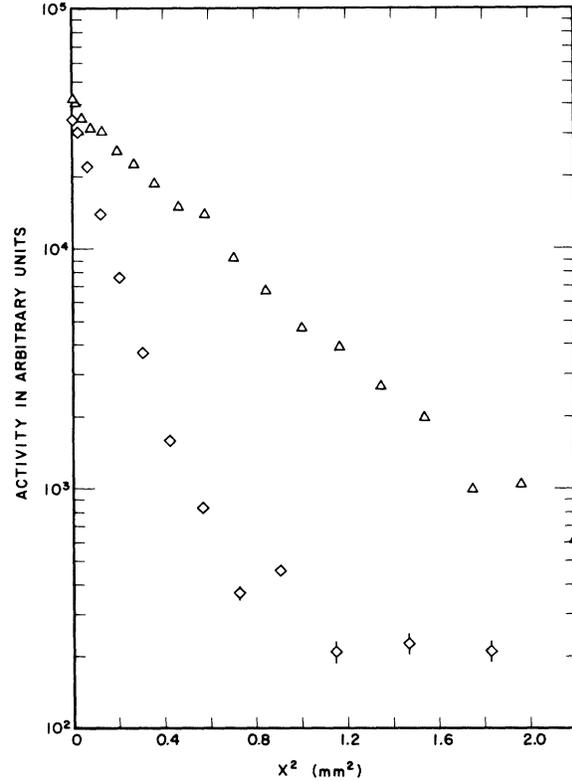


FIG. 1. Solute penetration curve of Au diffusing in Pb for two representative samples. Δ : sample annealed at 21.8 kbar pressure and 288.6 °C for 1.5 h. \diamond : sample annealed at 30.5 kbar pressure and 253.1 °C for 5.9 h.

this region decreased substantially when using 99.9999% pure lead rather than 99.999%. For the purest lead this background concentration of gold was less than 0.2 ppm. It cannot be completely ruled out, however, that the gold found at large penetration distances may arise in part from a small concentration diffusing very rapidly along dislocations.²⁴ The concentration was corrected by subtracting the average background from each point. Then the slope in the initial linear region was calculated by a least-squares fit to $\ln c$ vs x^2 , where x is the penetration depth measured from the surface, and was used to determine the diffusion constant. An effective anneal time was determined by correcting for heating and cooling times using an estimate of D . The values of $D(P, T)$ are estimated to be accurate to about 15% for temperatures above 200 °C. Two of the penetration profiles for anneals below 200 °C seemed to have no linear region but were continuously curved. $D(P, T)$ calculated from these points is likely no better than 50% accurate.

The measured diffusion constants $D_m(P, T)$ were fit to Eq. (6) by a least-squares technique and val-

TABLE I. Measured parameters for the diffusion of Au in Pb and Ag in Pb. Analyzed using data from Ref. 9.

Solute	(P, T) (kbar, °C)	D_0 (cm ² /sec)	ΔH (kcal/mole)	$\Delta V/V_0$	$\frac{\partial(\Delta V/V_0)}{\partial P}$ (10 ⁻³ kbar ⁻¹)	$\frac{\partial(\Delta V/V_0)}{\partial T}$ (10 ⁻⁴ °K ⁻¹)
Au	(0, 25)	0.0056 ± 0.0015	9.48 ± 0.30	0.324 ± 0.022	1.0 ± 0.5	-1.4 ± 0.4
	(0, 250)	0.0053 ± 0.0015	9.48 ± 0.30	0.290 ± 0.030		
	(0, 327)	0.0052 ± 0.0015	9.48 ± 0.30	0.28 ± 0.03		
	(30, 350)	0.016 ± 0.007	14.5 ± 0.9	0.31 ± 0.05		
Ag	(0, 25)	0.059 ± 0.013	14.63 ± 0.24	0.395 ± 0.030	3.0 ± 0.8	-1.9 ± 0.4
	(0, 250)	0.056 ± 0.013	14.63 ± 0.24	0.35 ± 0.04		
	(0, 327)	0.055 ± 0.013	14.63 ± 0.24	0.34 ± 0.04		
	(30, 350)	0.23 ± 0.14	21.1 ± 1.0	0.42 ± 0.07		

ues of A , B , C , E , F , and J were determined along with a standard deviation for each. For this calculation we took $\gamma = 2.65$, $\kappa = 2.39 \times 10^{-3}$ kbar⁻¹, $\partial\kappa/\partial P = -3.26 \times 10^{-5}$ kbar⁻², $\partial\kappa/\partial T = 8.1 \times 10^{-7}$ kbar⁻¹ deg⁻¹,²⁵ $\beta = 8.73 \times 10^{-5}$ deg⁻¹, $\partial\beta/\partial T = 3.0 \times 10^{-8}$ deg⁻².²⁶ Since the diffusion measurements have been made at temperatures well above the Debye temperature where the law of equipartition should hold, the change in the number of degrees of freedom for the impurity at the activated complex compared to its equilibrium position would not be expected to differ by more than one, and $|\Delta C_p/R| \leq \frac{1}{2}$. It was also noted by the χ^2 test that the results were insensitive to ΔC_p , so a most probable value of $\Delta C_p = 0$ was chosen. The uncertainties in Table I are consistent with an uncertainty of $\pm \frac{1}{2}$ in $\Delta C_p/R$. From the measurements, using Eq. (7), one calculates D_0 , ΔH , $\Delta V/V_0$, $\partial(\Delta V/V_0)/\partial P$, and $\partial(\Delta V/V_0)/\partial T$ all at $T = T_0 = 298$ °K and $P = 0$. These values, as well as values for $D_0(P, T)$, $\Delta H(P, T)$, and $\Delta V(P, T)/V_0$ at selected pressures and temperatures, are given in Table I along with an uncertainty for each. We also analysed the Ag in Pb diffusion data of Curtin *et al.*⁹ by this same technique and included these results in Table I.

The results of $\log_{10} D$ vs $1/T$ at four pressures nearest which the data were taken are displayed in Fig. 2. The atmospheric-pressure data were taken from Kidson.⁵ Figure 3 gives $\log_{10} D$ vs P along selected isotherms. These curves come directly from the computer but the relative scatter of the measurements will be similar to that in Fig. 2. The activation energies for Ag and Au diffusing in Pb is displayed vs pressure in Fig. 4. Again these are taken from the least-squares fits but points are added at the measured pressures to indicate the relative precision of this measured quantity. The results of Ascoli *et al.*¹³ below 10 kbar are also shown in this figure along with Kidson's zero-pressure result. Finally, using the melting tempera-

ture T_m of lead vs pressure, measured by Millet,²⁷ we have plotted $\log_{10} D$ vs T_m/T in Fig. 5.

V. DISCUSSION AND CONCLUSIONS

We analyzed our measurements assuming a single effective diffusion mechanism characterized

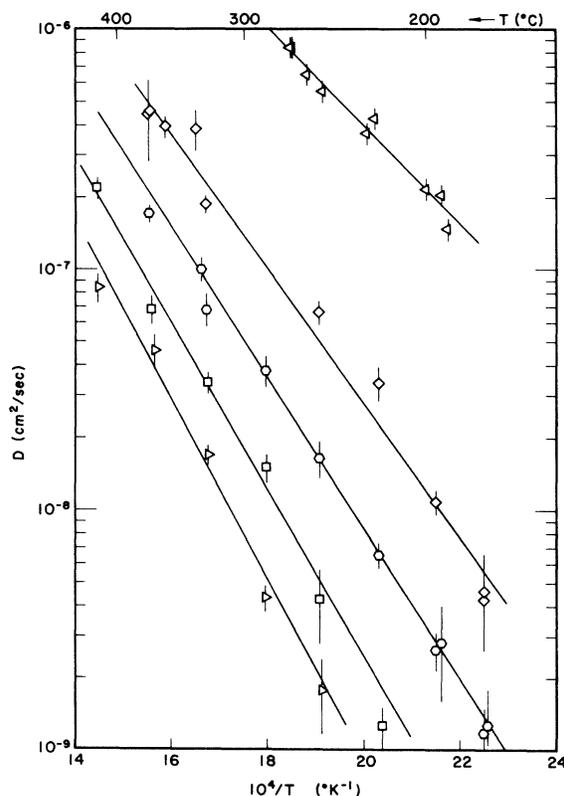


FIG. 2. Variation of the diffusion constant D with temperature at constant pressure. Δ : atmospheric-pressure data of Kidson (Ref. 5); \diamond : 21 kbar; \circ : 30 kbar; \square : 39 kbar; \triangle : 46 kbar.

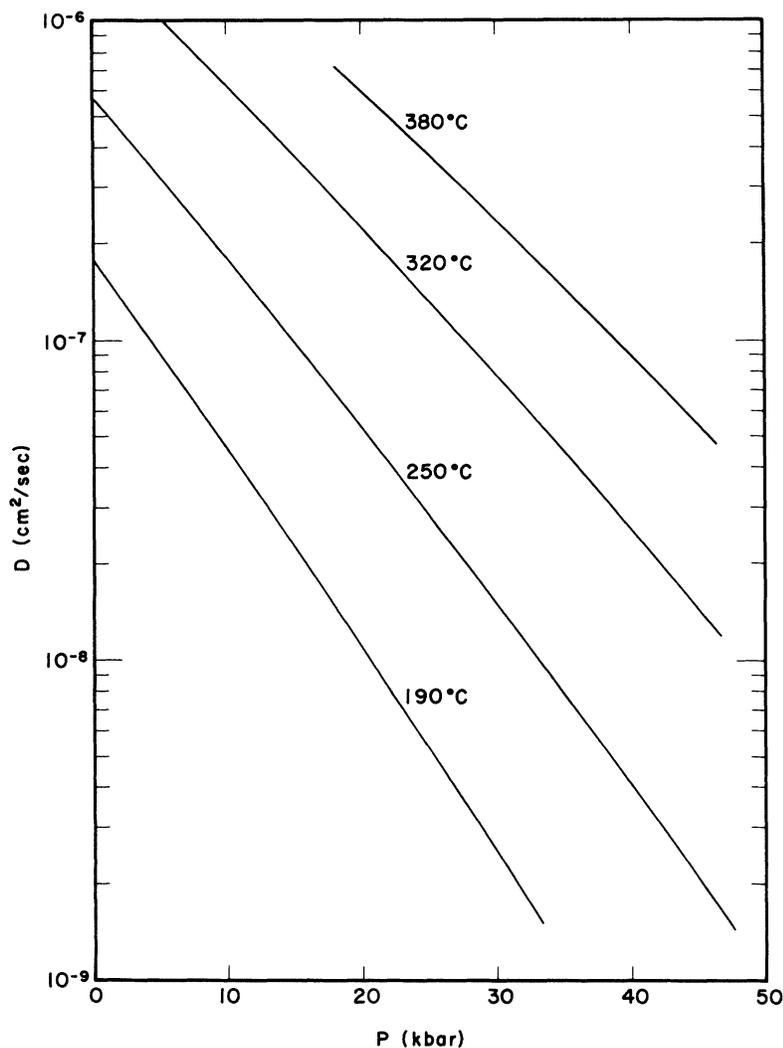


FIG. 3. Variation of the diffusion constant D with pressure at constant temperature. Curves obtained from best fit of all data to Eq. (6).

by a possible pressure- and temperature-dependent activation energy and preexponential frequency factor. One notes from Eq. (8) that the only temperature-dependent term in the activation energy involves a factor ΔC_p , which we chose to be equal to zero as explained above. A temperature-independent ΔH coupled with the fact that the observed temperature dependence of D_0 [see Eq. (9)] is very small leads to linear Arrhenius curves. A double mechanism characterized by two different activation energies would tend to show curvature in the Arrhenius lines. Such curved Arrhenius lines in our analysis would require ΔC_p to be different from zero and would also not allow one to give it the physical interpretation of an activation specific heat. This type of double mechanism would lead to a positive curvature of the $\ln D$ vs $1/T$ plot. If one frees the parameter ΔC_p in the least-squares fit to our measured data it indicates a slight negative curvature to the best fit thus giving no evidence

of two separate diffusion mechanisms. This same tendency is found in the analysis of Curtin's data on the diffusion of Ag in Pb.

This analysis, which considers all the data simultaneously, smooths the scatter in the individual diffusion measurements and selects a best set of least-squares fit curves as shown in Fig. 2. This is equivalent to making more measurements along a given Arrhenius line to improve one's statistics. Thus one can get meaningful numbers for such terms as $\partial(\Delta V V_0^{-1})/\partial P$ and $\partial(\Delta V V_0^{-1})/\partial T$. In fact, the fit to the data is significantly worsened by taking these values outside the range given for them in Table I. There may be systematic errors in these quantities however which must be considered.

First let us consider the temperature uncertainty due to temperature gradients in the relatively small furnace and the effects of pressure on the emf of the thermocouples. In spite of a temperature uncertainty of $\pm 3^\circ\text{C}$, we could still measure meaning-

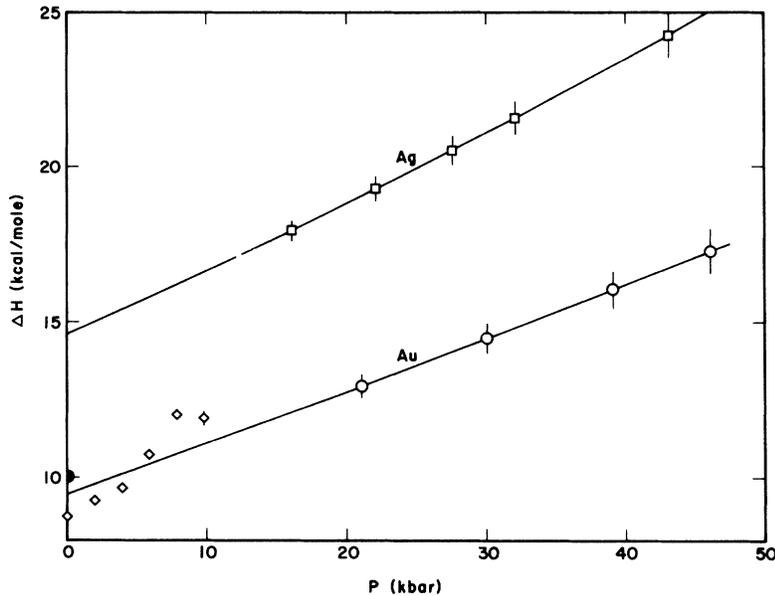


FIG. 4. Dependence of the activation energy ΔH [obtained from Eq. (8)] on the annealing pressure for diffusion of gold in lead and silver in lead. \diamond : measurements of Ascoli *et al.* (Ref. 13). The solid half-circle from atmospheric-pressure measurements by Kidson (Ref. 5).

ful pressure and temperature derivatives of the activation volume, principally because of the number of data points, the method of analysis, and the large range of pressure and temperature available. To get a feeling as to the errors that might be introduced by the temperature uncertainty, we analyzed the data using emf pressure corrections on the thermocouple reported by Hanneman, Strong, and Bundy¹⁸ to compare with our results when using the thermocouple corrections given by Getting and Kennedy.¹⁹ These temperatures differ by as much as 4 °C but the effect on the determined quantities in Table I was considerably less than the quoted standard deviations. We further used the original emf correction measurements by Hanneman and Strong,²⁰ which differ from Getting and Kennedy's by as much as 10 °C in the pressure and temperature range of this experiment, and yet the analyzed results were still within the quoted standard deviation. Thus the temperature measurement is not a serious problem.

A more serious problem comes from the uncertainty in the pressure calibration. The pressures were calibrated against fixed points on the pressure scale, but the interpolation between these points is subject to some ambiguity. In addition to this, the pressure rises by a hard to determine amount as one increases the temperature from room temperature at which the calibration was made. The difference between our reanalysis of the work of Curtin *et al.* and their original publication of that work (see Fig. 6) is due only to our method of determining the pressure, which included a measurement of the pressure increase due to heating of the pressure cell. Our present method

gives results which are in good agreement with measurements of Gilder²⁰ for the initial value of $\Delta V/V_0$ for the diffusion of Ag in Pb measured in a

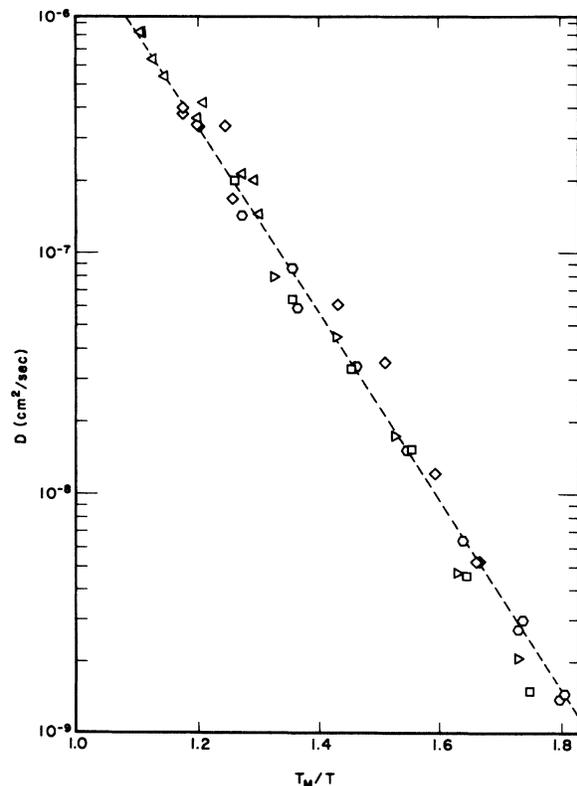


FIG. 5. Diffusion constant D as a function of the ratio of the melting to the annealing temperature for all of the data. Symbols used are the same as in Fig. 2.

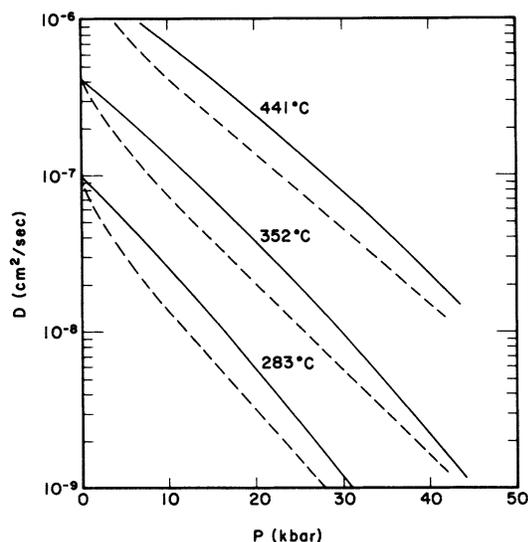


FIG. 6. $\log_{10}D$ vs pressure for the diffusion of Ag in Pb. The dotted line was obtained previously (Ref. 9) and does not take into account the effect of temperature on sample pressure. The solid line represents same data analyzed by the techniques presented in this paper.

low-pressure gas system. The present analysis however removes the basis from which Curtin's earlier work argued that the diffusion of Ag in Pb was a two-mechanism process, one of which mechanisms was quenched by pressure. One notes in Fig. 6 that there is now no positive curvature in the plot of $\log_{10}D$ vs pressure as there was in the original paper. Our analysis of $\log_{10}D$ vs P shows a slight negative curvature for both Ag and Au diffusion in Pb. This result is consistent with the sign predicted by Anthony, Dyson, and Turnbull.³⁰ It should be pointed out, however, that if one retained all the terms in their theory one finds a negative curvature for a range $0 < K < (D_s/D_i)^{1/2}$ and positive curvature for $(D_s/D_i)^{1/2} < K < \infty$, where $K = C_s/C_i$ and the subscripts s and i refer to substitutional and interstitial quantities, respectively. Our measured curvature, however, is very dependent on the pressure calibration and cannot be considered seriously until we can pin down the pressure measurement more accurately.

The Zener relation for diffusion in fcc metals is written³¹

$$\Delta S/R \approx b\Delta H/RT_m, \quad (10)$$

where $b = 0.5$ for Pb, ΔS is an activation entropy, and T_m is the melting temperature. $\Delta S/R$ is determined from the measurement of D_0 by using

$$\Delta S/R = \ln(D_0/a^2\nu), \quad (11)$$

where $\nu = (\Delta H/ma^2)^{1/2}$ as given by Wert and Zener,³² with m as the mass of the impurity and a as the lattice parameter. $\Delta S/R$ and $b\Delta H/RT_m$ for our experiment and also the data of Curtin *et al.* are given in Table II along with their ratio λ . The fact that $\lambda \neq 1$ may indicate that the diffusion is not by interstitial motion only. We might further ask whether the Zener relation will hold as one increases the pressure, changing ΔH and T_m relatively rapidly. To answer this question we differentiated Eqs. (9) and (11) with respect to pressure and compared the measured $\partial D_0/\partial P$ with its value calculated from the Zener relation:

$$\frac{\partial \ln D_0}{\partial P} = \kappa\gamma + \frac{b}{RT_m} \left(\frac{\partial \Delta H}{\partial P} - \frac{\Delta H}{T_m} \frac{\partial T_m}{\partial P} \right). \quad (12)$$

Using the measurements of Millet²⁷ for the melting temperature vs pressure and assuming that the small noble-metal concentration does not alter T_m , we evaluated both sides of Eq. (12). These results are also given in Table II and it is noted that the Zener relation is reasonably well satisfied for Au in Pb.

The activation energies for Au and Ag diffusion in Pb are considerably smaller than that for self-diffusion of Pb. In fact, the activation energy for these materials is of the order of the energy of motion of vacancies in Pb, which was measured as 11 ± 2 kcal/mole by Feder and Nowick.³³ Thus these impurities move as rapidly through Pb as do vacancies. The activation energy for the diffusion of Cu in Pb, 6 kcal/mole,³⁴ is even smaller than for Ag or Au. If we suppose that Cu diffuses by an interstitial mechanism then one might think that the diffusion of Au and Ag in Pb would not be purely interstitial. Kidson gives the relation⁵ for interstitial-substitutional dissociative diffusion:

TABLE II. Comparison of $\Delta S/R$ with $b\Delta H/RT_m$ for diffusion of Au in Pb and Ag in Pb.

Solute	$\Delta S/R$	$b\Delta H/RT_m$	λ^a	$\frac{\partial D_0}{\partial P}$	$\frac{\partial D_0}{\partial P}$
				(10^{-4} cm ² /sec kbar) measured	(10^{-4} cm ² /sec kbar) calculated [Eq. (12)]
Au	0.93 ± 0.23	3.97 ± 0.13	0.23 ± 0.06	2.1 ± 0.7	1.3 ± 0.6
Ag	2.77 ± 0.20	6.14 ± 0.10	0.45 ± 0.03	29 ± 8	8 ± 8

^a $\lambda = \Delta S/(b\Delta H/T_m)$.

$$\Delta H = \Delta H_m^{\ddagger} + \Delta G_{1s}, \quad (13)$$

where ΔH is the measured activation energy, ΔH_m^{\ddagger} for the motion of interstitials, and ΔG_{1s} is related to the equilibrium between substitutional and interstitial components, i. e., $c_s/c_i = e^{\Delta G_{1s}/RT}$. If we let $\Delta H_m^{\ddagger} = 6$ kcal/mole for Au and Ag also, then $c_s/c_i = 18$ for Au in Pb and 1300 for Ag in Pb. The ratio of the total solubility of Ag and Au in lead is given by

$$\frac{(c_s + c_i)_{Ag}}{(c_s + c_i)_{Au}} = \frac{c_i(Ag)(1 + c_s/c_i)_{Ag}}{c_i(Au)(1 + c_s/c_i)_{Au}}, \quad (14)$$

which yields for this ratio about 20 using $c_i(Ag)/c_i(Au) = \frac{1}{3}$ as inferred from measurements of Westbrook and Aust³⁵ on the relative hardness increase at grain boundaries for extremely dilute solutions of Ag and Au in Pb. The experimental solubility of Au in Pb has not been reliably measured but from the best available work the ratio of the solubility of Ag in Pb to that of Au in Pb is about 3.³⁶ This is not very strong correlation but within reason considering the uncertainties involved.

The activation volumes are both too large for representative interstitial diffusion and too small for substitutional diffusion. A relation, similar to the above, based on the interstitial-substitutional dissociative model of Frank and Turnbull,⁹ can be found for the activation volumes³⁰:

$$\Delta V/V_0 = \Delta V_m^{\ddagger}/V_0 + \Delta V_{1s}/V_0. \quad (15)$$

This relation assumes $D_i \gg D_s$ and $c_s \gg c_i$. ΔV_m^{\ddagger} is the activation volume for motion of interstitials and $\Delta V_{1s} = \partial \Delta G_{1s} / \partial P$. Candland³⁴ has recently measured the diffusion of Cu in Pb at high pressure, and finds $\Delta V/V_0 = 0.04$. If we assume this is characteristic of interstitial diffusion then we find $\Delta V_{1s}/V_0$ equal to 0.25 and 0.32, respectively, for Au and Ag. These are not unreasonable values since ΔV_{1s} involves the dilatation of the lattice about an interstitial minus the contraction of the lattice about the vacancy formed when a Au or Ag atom leaves a substitutional position.

The Nachtrieb relation¹⁴ seems to be valid for the diffusion of Au in Pb as evidenced by Fig. 5. This was also satisfied by the diffusion of Ag in Pb.⁹ The requirement suggested by Rapoport¹⁵ for this relationship to hold is also satisfied, within the accuracy of the data, i. e.,

$$\Delta H = Ac\Delta V, \quad (16)$$

with $A = 63$ kbar and $c = 1.3$ for the Simon's equation

parameters along the melting curve of Pb.²⁷ The right-hand side of Eq. (16) is 10.1 ± 1.3 kcal/mole compared to $\Delta H = 9.48 \pm 0.30$ kcal/mole.

The pressure and temperature dependence of the activation volume is somewhat surprising in that the change is of opposite sign to that of the compressibility and coefficient of thermal expansion. That is to say, for the diffusion of Au and Ag in Pb, the activation volume increases for increasing pressure and decreases for increasing temperature. This is in contrast to the recent results of Gilder and Chhabildas³⁷ which show a rather large increase in ΔV with increasing temperature for self-diffusion in zinc. The results for Au and Ag in Pb can qualitatively be explained in terms of the relative thermal expansion and compressibility between the solvent and solute. For example, if the solvent is much more compressible than the solute one would expect the activation volume of motion to increase with pressure. Similarly, if the thermal expansion of the solvent is greater than the local expansion near the solute ions one would expect the activation volume of motion to decrease with increasing temperature. However, in the case of self-diffusion where the solvent and solute are the same, and in the absence of strong correlation effects one would expect activation and atomic volumes to be nearly proportional.

The above results give some interesting information concerning the diffusion of the noble metals in Pb, but they do not clearly specify the mechanism for diffusion. The magnitudes of the activation volumes for diffusion of Ag in Pb and Au in Pb appear to reject the purely interstitial and purely substitutional mechanisms. The results reported here are not in contradiction with predictions obtainable with the interstitial-substitutional dissociative mechanism. Indeed, if the curvature of $\log_{10} D$ vs P plots could be determined more definitely this type of experiment could be used to test the validity of this type of double-mechanism theory. However, the uncertainty of our pressure calibration at the present time prevents such a determination.

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Theory of Work-Function Changes Induced by Alkali Adsorption

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Changes of the work function due to adsorption of alkali atoms by a high-work-function substrate are studied using a very simple ("jellium") model of the metallic substrate-adsorbate system. A self-consistent quantum-mechanical analysis of the model leads to a work-function-vs-coverage curve with a minimum at a coverage below that of a single full adsorbed layer, and a maximum at completion of the layer. Good agreement with the results of recent measurements is obtained for these extremal values; and, though not designed to treat very low coverages, the model yields an initial dipole moment in satisfactory agreement with experiment. The computed full-layer work function is very nearly equal to that obtained theoretically for the corresponding bulk sample. A study of limiting cases provides a framework for viewing the results of the calculation in a coherent way.

I. INTRODUCTION

As alkali metal atoms are adsorbed onto the surface of a metal such as W or Ni, the measured work function decreases rapidly from its initially high value. With continued adsorption, the work function reaches a minimum, and then rises to approximately the bulk alkali value with completion of the first full layer of adsorbate atoms.

Some of the earliest observations of this behavior were reported by Ives,¹ Langmuir and Kingdon,² and Becker.³ Since the time of this early work, there have been many such experimental studies. One of the chief reasons for this effort stems from

interest in alkali adsorption as a way of enhancing the electron-emission properties of a surface. Another is the strong theoretical interest in this process as one of the simplest examples of chemisorption.

The first explanation for these observed changes of work function appears to be due to Langmuir.⁴ His picture is as follows: When the alkali atoms are adsorbed, they lose their valence electrons to the substrate. (This loss was ascribed to the fact that the adatom ionization potential is less than the substrate work function.) The resulting positive ions induce images in the substrate, producing dipoles which lower the work function by an amount