

Effect of Hydrostatic Pressure on the Self-Diffusion Rate in Single Crystals of Gold*†

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The rate of self-diffusion in gold was measured by the radioactive-tracer-lattice sectioning technique at 860, 910, and 960°C. and at hydrostatic pressures from 2.00 to 9.08 kbar. The diffusion rate was observed to decrease with increasing pressure, and the activation volume for self-diffusion was determined to be 7.2 ± 0.4 cm³/mole. This value is in good agreement with the sum of the experimental values of the activation volumes of formation and motion in gold, the experimental values of the activation volumes in other face-centered metals, and many of the theoretical values calculated for copper. The present value also is in fair-to-excellent agreement with the various expressions relating the activation volume to other experimentally derived quantities. The limiting source of error in pressure-diffusion experiments of the present type was found to be in controlling the measurement, reproducibility, and uniformity of the temperature.

I. INTRODUCTION

MANY experiments have been carried out in recent years in an effort to clarify the nature of atomic defects in metals. A series of such experiments by Simmons and Balluffi¹⁻⁴ has convincingly established that the predominant thermally-generated defects in the noble metals and aluminum are vacant sites, reinforcing the already general belief that diffusion-limited phenomena proceed by the vacancy mechanism in these metals. However, many of the details pertaining to the nature of these defects are still not well defined, and there are some important gaps in the experimental values of some of the basic properties of vacancies in metals.

Of particular use in clarifying the detailed nature of the defects in metals are the values of the total activation energy and the total activation volume of the defects, as well as the independently determined values of the energies and volumes of formation and motion. Self-diffusion experiments are appropriate for measuring the values of the total activation energy and volume. The radioactive tracer and sectioning technique may be used for most metals in such measurements, although other techniques are sometimes used, such as measurements of anelastic relaxation in certain alloys, or nuclear-magnetic-resonance techniques in certain metals. Diffusion rates have been measured for many of the pure metals at atmospheric pressure,

yielding values of the activation energy for these metals. Relatively few of these metals have been subjected to self-diffusion studies at elevated pressures because of the technical difficulties involved. For the lower melting-point metals, liquid pressure systems and external furnaces may be utilized. Nachtrieb and co-workers have thus determined the activation volumes for sodium,⁵ alpha-white phosphorus,⁷ and lead.⁸ Hudson and Hoffman⁹ used a "belt"-type pressure system¹⁰ in their determination of the activation volume in lead; they used silicone oil as the pressure fluid and an internal heater to maintain the diffusion temperature. However, self-diffusion measurements of the high-melting-point metals, such as the noble metals, require the use of a gas pressure system to insure both hydrostaticity, and chemical stability of the pressure medium at high temperatures. An internal heater also is required in order to make it possible to maintain the temperature of the pressure vessel sufficiently low by forced external cooling. Tomizuka¹¹ used such an arrangement to determine the activation volume of silver, and Albrecht and Tomizuka,¹² with the apparatus in this laboratory, have recently completed a determination of the activation volumes for diffusion of gold and silver tracers in a gold-34 atomic percent silver alloy.

Most of the theoretical calculations on point defects have been done for copper,¹³ which is representative of the face-centered cubic crystal structure, but for which

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¹ R. O. Simmons and R. W. Balluffi, *Phys. Rev.* **117**, 52 (1960).

² R. O. Simmons and R. W. Balluffi, *Phys. Rev.* **119**, 600 (1960).

³ R. O. Simmons and R. W. Balluffi, *Phys. Rev.* **125**, 862 (1962).

⁴ R. O. Simmons and R. W. Balluffi, *Phys. Rev.* **129**, 1533 (1963).

⁵ See, for example, F. Seitz, in *Phase Transformations in Solids*, edited by R. Smoluchowski *et al.* (John Wiley & Sons, Inc., New York, 1951), p. 77.

⁶ N. H. Nachtrieb, J. A. Weil, E. Catalano, and A. W. Lawson, *J. Chem. Phys.* **20**, 1189 (1952).

⁷ N. H. Nachtrieb and A. W. Lawson, *J. Chem. Phys.* **23**, 1193 (1955).

⁸ N. H. Nachtrieb, H. A. Resing, and S. A. Rice, *J. Chem. Phys.* **31**, 135 (1959).

⁹ J. B. Hudson and R. E. Hoffman, *Trans. Met. Soc. AIME* **221**, 761 (1961).

¹⁰ H. T. Hall, *Rev. Sci. Instr.* **31**, 125 (1960).

¹¹ 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.

¹² E. D. Albrecht and C. T. Tomizuka, *J. Appl. Phys.* (to be published).

¹³ For a list of references see R. A. Johnson and E. Brown, *Phys. Rev.* **127**, 446 (1962).

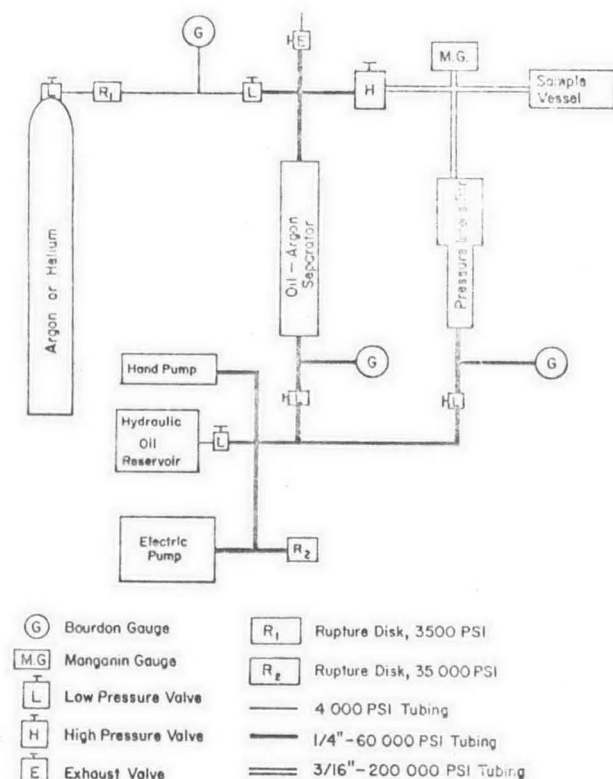


FIG. 1. Schematic drawing of the pressure system.

many of the experiments are difficult to perform because of oxidation problems. Gold has been the most extensively studied fcc metal in the experimental investigations, and it is the only one of the noble metals for which independent measurements have been made of the volumes of formation and motion. Emrick¹⁴ determined the volume of motion ΔV_m by measuring the effect of pressure on the annealing rate of quenched-in resistivity. DeSorbo¹⁵ derived a value of the volume of formation ΔV_f by combining his calorimetric measurement of the total energy released during the annealing out of quenched-in vacancies with the resistivity data of Bauerle and Koehler.¹⁶ Simmons and Balluffi³ likewise derived a value of ΔV_f by combining their vacancy-concentration data with the data of Bauerle and Koehler, and also with the data of Takamura,¹⁷ both combinations yielding the same value, but differing from DeSorbo's value. A more direct determination of ΔV_f was accomplished by Huebener and Homan,¹⁸ who measured the effect of pressure on the quenched-in resistivity of gold. The purpose of the

¹⁴ R. M. Emrick, *Phys. Rev.* **122**, 1720 (1961).

¹⁵ W. DeSorbo, *Phys. Rev.* **117**, 444 (1960).

¹⁶ J. E. Bauerle and J. S. Koehler, *Phys. Rev.* **107**, 1493 (1957).

¹⁷ J. Takamura, *Acta Met.* **9**, 547 (1961).

¹⁸ R. P. Huebener and C. G. Homan, *Phys. Rev.* **129**, 1162 (1963).

present investigation is to provide an independent determination of the total activation volume, $\Delta V = \Delta V_f + \Delta V_m$, by measuring the effect of hydrostatic pressure on the rate of self-diffusion in gold.

II. EXPERIMENTAL PROCEDURE

A. Preparation of Specimens

A single crystal of 99.99% pure gold (Sigmund Cohn Corporation), approximately $\frac{3}{8}$ in. in diameter and 4 in. in length, was grown under a vacuum of at least 5×10^{-6} mm of mercury in a furnace similar to that described by Lazarus and Chipman.¹⁹ The usual precautions were taken to clean and bake out the high-purity graphite crucible used for the crystal growth.

The single crystal was sectioned with a jeweler's saw, and the standard metallographic procedure was used to polish, etch, and anneal the cylindrical specimens. The final size of the specimens was 0.410 in. in diameter and 0.210 in. in thickness. A light etch after annealing showed that some recrystallization had occurred in some of the specimens, but the stray grains were few and large enough to preclude competitive grain-boundary diffusion.

The Au¹⁹⁸ isotope was obtained from Oak Ridge National Laboratory in the form of a very high-specific-activity solution of AuCl₃ in a mixture of HCl and HNO₃. An active layer of Au¹⁹⁸ was electroplated on each specimen just prior to the diffusion anneal. It was estimated that the thickness of the plated layer could not have exceeded 100 Å.

B. Apparatus and General Procedure

A gas pressure system similar to the one described by Goldsmith and Heard²⁰ was used in the present experiment. A schematic drawing appears in Fig. 1. A mixture of argon and helium was used, the helium being added in a small amount to make possible the use of a mass spectrometer leak detector tuned for helium. Gas leaking from connections or other possible leakage sites was trapped and carried outside the safety barricade by a set of polyethylene tubes. A sniffer attachment to the leak detector was then used to find the locations and magnitudes of any leaks that existed.

Pressures up to 2 kbar could be reached with the separator alone. Higher pressures were attained with the Harwood intensifier. Inevitable leaks during the diffusion anneals limited the runs to 9 kbar.

The sample vessel itself was machined from Bethlehem "Omega" tool steel and hardened to Rockwell C-52. The volume available for the internal furnace

¹⁹ D. Lazarus and D. R. Chipman, *Rev. Sci. Instr.* **22**, 211 (1951).

²⁰ J. R. Goldsmith and H. C. Heard, *J. Geol.* **69**, 45 (1961).

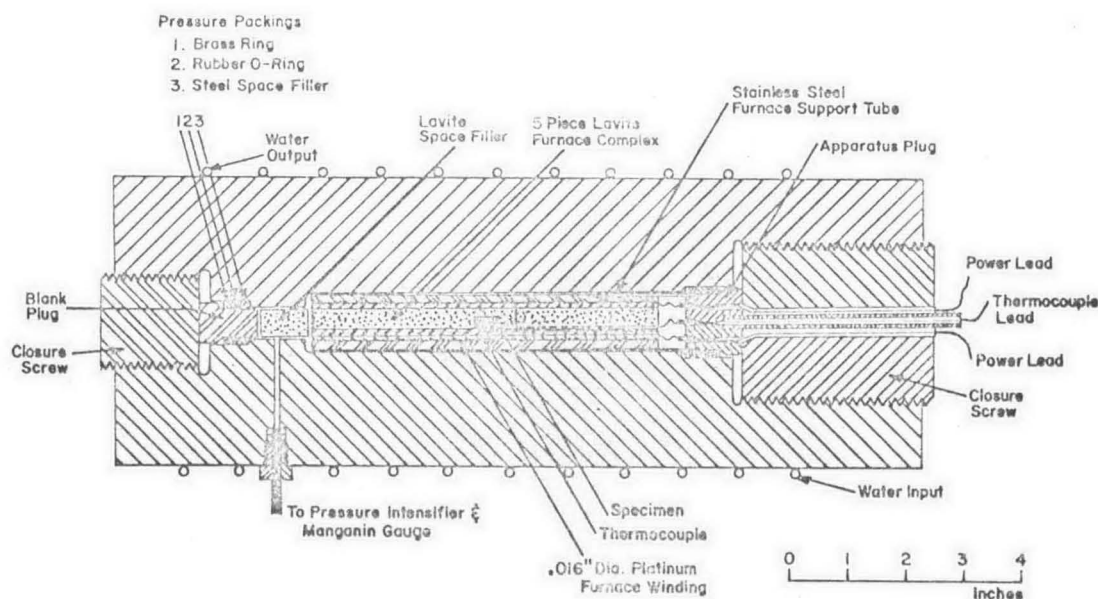


Fig. 2. Cross-sectional view of the assembled high-pressure vessel and the high-temperature internal furnace.

was 1 in. in diameter by $6\frac{1}{2}$ in. in length. The vessel was water-cooled during each of the runs.

Thermocouple and power leads were conducted from the vessel through Chromel, Alumel, and steel cones seated in the pressure plug with unfired lava A (American Lava Corporation) conical insulators. Chromel and Alumel (B. & S. gauge No. 24) were selected as the thermocouple materials because of the small pressure effect on the emf output reported by Bundy.²¹ The high-pressure side of the plug was covered with Eccobond 76 epoxy to fill the gaps between the plug and the metal cones. These gaps were caused by a crumbling away of the insulating cones when the metal cones were pressed in initially with an arbor press. This application of the epoxy virtually eliminated electrical arcing of the power lead cones to the plug, which had frequently occurred prior to this modification.

The internal furnace consisted of a $\frac{1}{2}$ -in. inside-diameter-threaded core closely wound (16 turns per in.) with 0.016-in. platinum wire, an insulating sheath surrounding this core, and a three-piece sample holder and thermocouple support assembly. All five pieces were machined from lava A. Figure 2 shows a cross-sectional view of the internal furnace and pressure vessel.

The diffusion specimen was situated near the center of the furnace with its axis of symmetry normal to the horizontal axis of symmetry of the furnace. Its bottom face, the face to be sectioned, rested on a platinum disk 0.003 in. thick. Chromel and Alumel wires were spot-welded to the bottom side of this platinum disk, creating a large thermocouple junction

spread across the face of the specimen. This type of thermocouple was adopted for several reasons. Early tests with spot-welded Chromel-Alumel junction thermocouples indicated that temperature gradients of several degrees existed near the center of the furnace over a region as small as the extent of the specimen diameter. Also, large vertical temperature gradients were observed between a specimen and a Chromel-Alumel junction when the specimen and junction were separated by a thin mica sheet. Furthermore, the early Chromel-Alumel junction thermocouples, used primarily in conjunction with mica sheets, showed large and irregular deteriorations in their emf characteristics in subsequent calibrations. The platinum disk thermocouple assembly was found to reduce greatly the magnitude of the thermocouple deterioration which had been observed with the previously used thermocouple assemblies. The disk also provided a means to eliminate the vertical temperature gradients and to give a better indication of the average temperature of the face of the specimen to be sectioned.

After most diffusion anneals, the platinum disk was found to be adhered slightly to the face of the specimen, but it was always possible to remove it with little or no discernable damage to the specimen face. A new thermocouple, including platinum disk, was used for each run.

A special calibration furnace was built in an effort to approximate the steep temperature gradient in the internal furnace from the center of the furnace to the plug. Each thermocouple was calibrated in this furnace after the diffusion anneal against new Chromel and Alumel from the same spools which were spot-welded symmetrically with the original wires on the opposite

²¹ F. P. Bundy, *J. Appl. Phys.* **32**, 483 (1961).

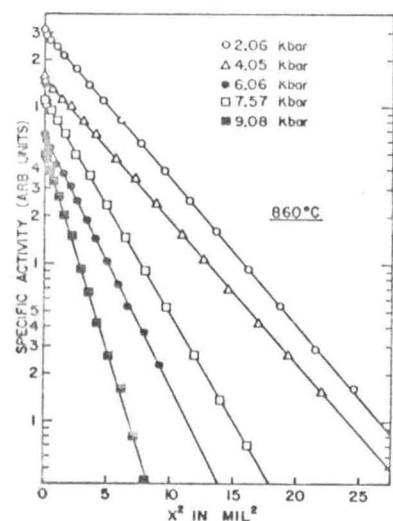


FIG. 3. Penetration curves for self-diffusion in gold at 860°C.

side of the platinum disk. Various portions of the spools were calibrated against a standard Pt-10%-Rh-Pt thermocouple which had been previously calibrated against the melting points of several NBS metals. Final calibrations of the thermocouples used in these runs also showed the deterioration to be irregular, but to a much smaller degree than any of the previous thermocouple configurations.

During the diffusion anneals, the temperature was controlled manually. It was possible to maintain the thermocouple emf reading at the desired value to within 0.02 mV, which would ordinarily correspond to 0.5°C. However, since some runs indicated a gradual thermocouple deterioration, maintaining a constant thermocouple emf was not equivalent to maintaining a constant temperature for these runs. The amount of deterioration was determined by subsequent calibration of the thermocouple. Warm-up time was always 5 min or less, and cooling time was 3 min or less. Corrections, described in Part IV, were made for both. The total effective times for each diffusion anneal are listed in Table I.

The pressure was maintained constant to within 10 bars during warm-up, the extent of the run, and cooling. The pressure was measured with a coil of manganin wire calibrated against the freezing point of mercury at 0°C (7490 bar).

The usual lathe-sectioning and weighing techniques described by Tomizuka²² were employed. After much trial and error, a lathe tool was ground which made possible the cutting of sections as thin as 0.0002 in., often in the form of a single lathe turning, and leaving behind a mirror-like surface with no burr.

An RIDL model 34-12B 400-channel analyzer and NaI(Tl) scintillation counter were used to count the

²² C. T. Tomizuka, in *Methods of Experimental Physics*, edited by K. Lark-Horovitz and V. A. Johnson (Academic Press Inc., New York, 1959), Vol. 6, p. 364.

TABLE I. Self-diffusion coefficients for gold.

Pressure (kbar)	Temperature (°K)	t_{eff} (sec)	D_T (cm ² /sec)	D_i (cm ² /sec)
0.00	1133	...	8.20×10^{-10}	8.20×10^{-10}
2.06	1132	10826	6.94	7.06
4.05	1136	10875	7.11	6.82
6.06	1131	7289	5.95	6.15
7.57	1132	10830	4.79	4.87
9.08	1131	6183	4.46	4.61
0.00	1183	...	1.80×10^{-9}	1.80×10^{-9}
2.00	1194	10917	1.75	1.50
4.05	1184	10834	1.34	1.32
6.06	1182	10845	1.16	1.18
7.57	1182	10858	8.94×10^{-10}	9.08×10^{-10}
9.08	1181	10860	8.90	9.18
0.00	1233	...	3.73×10^{-9}	3.73×10^{-9}
4.05	1231	7202	2.70	2.78
6.06	1236	7240	2.77	2.66

gamma activity, at the 0.411-MeV peak, of the lathe sections. The live-time counting mode automatically corrected for dead-time, and the usual corrections for background were made.

III. EXPERIMENTAL RESULTS

Twelve successful diffusion anneals were completed. Penetration plots for each run are shown in Figs. 3-5, and they show that the specific activity decreases exponentially as the square of the penetration distance. The values determined for the diffusion coefficients at each temperature and pressure are listed in Table I, together with temperature-corrected values of the diffusion coefficient D_i , and values from the data of Makin, Rowe, and LeClaire.²³ Figure 6 shows a semilogarithmic plot of the temperature-corrected values of

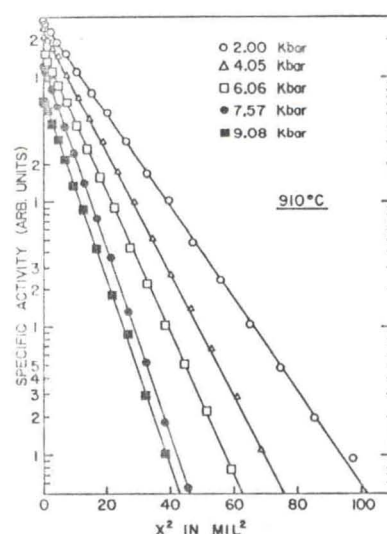


FIG. 4. Penetration curves for self-diffusion in gold at 910°C.

²³ S. M. Makin, A. H. Rowe, and A. D. LeClaire, Proc. Phys. Soc. (London) B70, 545 (1957).

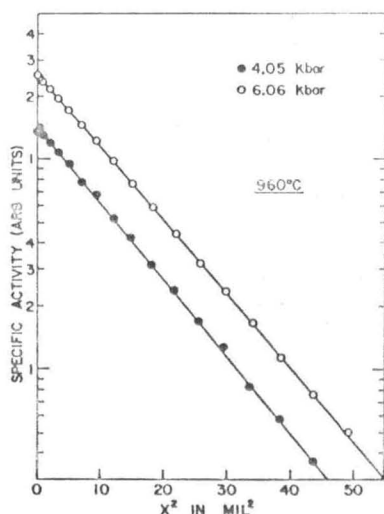


FIG. 5. Penetration curves for self-diffusion in gold at 960°C.

the diffusion coefficient versus pressure. The error limits of D shown in the figure correspond to the estimated uncertainty in the temperature correction of $\pm 5^\circ\text{C}$.

IV. DISCUSSION

The geometry and initial conditions for the present diffusion analysis give the specific activity $c(x,t)$ at a distance x from the initial plated surface after a diffusion anneal time t as

$$c(x,t) = [c(0,0)/(\pi Dt)^{1/2}] \exp(-x^2/4Dt),$$

where D is the diffusion coefficient.

The specific activity of each section was computed from the observed counting rate and the mass of the section. Each was corrected for the radioactive decay of the Au^{198} isotope. The midpoint x of each section was calculated in the usual way, and the slope of the straight line for each penetration plot was determined by a least-squares analysis. The effective time t_{eff} of each diffusion anneal was calculated from

$$t_{\text{eff}} = \left[\int \exp[-\Delta H/RT(t)] dt \right] / \exp(-\Delta H/RT_A).$$

In this expression, the integral was approximated by a sum of several terms during warm-up and cooling, plus the measured time at the diffusion anneal temperature T_A . A value of ΔH was calculated for each pressure from the relation

$$\Delta H = \Delta H_0 + P\Delta V(1 - T\alpha),$$

where ΔH_0 was taken as 41.7 kcal/mole,²³ ΔV was approximated as 7 cm³/mole, and α , the volume coefficient of thermal expansion, was approximated as $6 \times 10^{-5} \text{ } ^\circ\text{C}^{-1}$ for the high temperatures involved.

The temperature of each run was determined from the calibration procedure described in Part II. The deterioration which took place during some of the

diffusion anneals was assumed to be approximately linear, and one-half the magnitude of this deterioration was used to arrive at the final temperature. Each value of D_T was then corrected for one of the isotherms of interest by

$$D_i = D_T \exp(\Delta H[T_i - T]/RTT_i),$$

where D_i is the corrected diffusion coefficient on the isotherm T_i .

Considering diffusion to be an activated process with an activation free energy ΔG , the diffusion coefficient may be written

$$D = \gamma a^2 \nu f \exp(-\Delta G/RT),$$

where γ is a constant depending on the crystal structure, a is the lattice constant, ν is a vibrational frequency, and f is the correlation factor. The activation volume is then given by

$$\begin{aligned} \Delta V &= (\partial \Delta G / \partial P)_T \\ &= -RT [(\partial \ln D / \partial P)_T - (\partial \ln a^2 / \partial P)_T \\ &\quad - (\partial \ln \nu / \partial P)_T] \\ &= -RT [(\partial \ln D / \partial P)_T + \frac{2}{3} K_T - \gamma_G K_T], \end{aligned}$$

where K_T is the isothermal compressibility and γ_G is the Grüneisen constant.

The straight lines shown in Fig. 6 were determined by least-squares analyses and are expressed by the following equations:

$$\begin{aligned} 860^\circ\text{C}: \log_{10} D &= (0.9215 \pm 0.0217) \\ &\quad - (0.02750 \pm 0.00380)P, \\ 910^\circ\text{C}: \log_{10} D &= (1.2525 \pm 0.0127) \\ &\quad - (0.03372 \pm 0.00221)P, \\ 960^\circ\text{C}: \log_{10} D &= (1.5675 \pm 0.0234) \\ &\quad - (0.02569 \pm 0.00556)P, \end{aligned}$$

where the pressure P is expressed in kbar and D is in

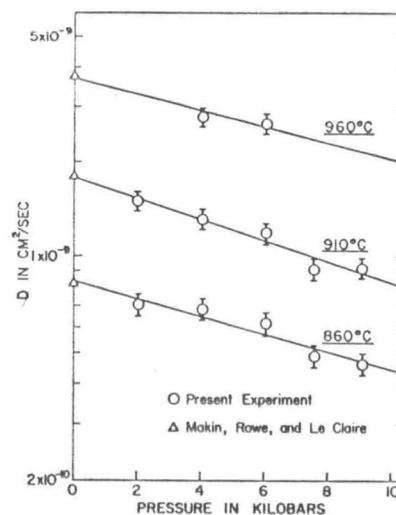


FIG. 6. Variation with pressure of the diffusion coefficient at 860, 910, and 960°C.

TABLE II. Activation volumes for gold. V_M : molar volume of gold, 10.2 cm³/mole.

ΔV_f (cm ³ /mole)	ΔV_m (cm ³ /mole)	ΔV (cm ³ /mole)	$\Delta V/V_M$	$\Delta V_f/V_M$
...	...	7.2 ^a	0.71	...
5.6 ^b	1.5 ^a	7.1	0.70	0.55
5.8 ^c	1.5	7.3	0.72	0.57
4.6 ^d	1.5	6.1	0.60	0.45

- ^a Present experiment.
- ^b Huebener and Homan (Ref. 18).
- ^c DeSorbo (Ref. 15).
- ^d Simmons and Balluffi (Ref. 3).
- ^e Emrick (Ref. 14).

cm²/sec. The error limits shown are the standard deviations.

Combining the slopes of these lines with the much smaller terms involving K_T and γ_G in the expression for ΔV above, one obtains the following values of ΔV :

$$860^\circ\text{C}: \Delta V = 6.1 \pm 0.8 \text{ cm}^3/\text{mole},$$

$$910^\circ\text{C}: \Delta V = 7.7 \pm 0.5 \text{ cm}^3/\text{mole},$$

$$960^\circ\text{C}: \Delta V = 6.2 \pm 1.4 \text{ cm}^3/\text{mole},$$

where the error limits here are derived from the standard deviations of the slopes.

It was assumed that the temperature dependence of the activation volume, if any, is very small compared to the uncertainties in the present results, and a weighted average of ΔV was computed from the 860 and 910°C values. The result is

$$\Delta V = 7.2 \pm 0.4 \text{ cm}^3/\text{mole},$$

where the error limit here is the standard deviation of the weighted average. The difficulties encountered in making successful runs at the highest temperature, 960°C, limited the data to such an extent that the uncertainty in ΔV for that temperature was great enough to produce a negligible effect on the value of the weighted average.

Table II shows values of ΔV_f for gold determined by other experimental investigations. These are combined with Emrick's value for ΔV_m to give a total value for the

TABLE III. Activation volumes for fcc metals.

Metal	ΔV (cm ³ /mole)	V_M (cm ³ /mole)	$\Delta V/V_M$
Au ^a	7.2	10.2	0.71
Ag ^b	9.2	10.3	0.89
Au in AuAg ^c	7.5	10.3	0.73
Ag in AuAg ^c	7.2	10.3	0.70
AgZn ^d	5.4	10.0	0.54
Pb ^e	13.0	18.2	0.71
Pb ^f	11.6	18.2	0.64

- ^a Present experiment.
- ^b Tomizuka (Ref. 11).
- ^c Albrecht and Tomizuka (Ref. 12).
- ^d Tichelaar and Lazarus (Ref. 24).
- ^e Nachtrieb, Resing, and Rice (Ref. 8).
- ^f Hudson and Hoffman (Ref. 9).

activation volume. Comparison of these values with the result of the present investigation shows good agreement.

Experimental results for activation volumes in several of the fcc metals are collected in Table III. The radioactive tracer and sectioning technique was used in all but one of these investigations: Tichelaar and Lazarus²⁴ determined the activation volume for AgZn by measuring the effect of pressure on the anelastic relaxation in that alloy.

The values given for the activation volumes in Tables II and III indicate that considerable relaxation occurs about a vacant lattice site in an fcc crystal. Many theoretical calculations are in disagreement with this finding. For example, Kanzaki²⁵ and Nardelli and Repanai²⁶ predict a volume contraction about a vacancy in an fcc lattice of less than 1% of an atomic volume. Negligible relaxations also are predicted by calculations of static lattice energies and configurations by Hall²⁷ and by Girifalco and Streetman.²⁸ Lawson, Rice, Corneliussen, and Nachtrieb²⁹ argue that the above calculations could not have correctly predicted the relaxation, since they did not include the anharmonic forces which are responsible for relaxation. They perform a calculation which includes such anharmonic terms, and predict a volume relaxation of 33% about a vacant lattice site in a cubic crystal.

Many detailed calculations of energies and lattice distortions of various defects in copper have been made during the past few years. Although Gibson, Goland, Milgram, and Vineyard³⁰ find the volume relaxation about a vacant site to be quite small—10% at most—others have calculated much larger relaxations. Calculations by Tewordt,³¹ Tewordt and Bennemann,³² Seeger and Mann,³³ Bennemann,³⁴ and Johnson and Brown¹³ yield values of $\Delta V_f/V_M$ which are in good agreement with the experimental indications of considerable volume relaxation about vacancies in fcc metals. Table IV contains most of the results of these calculations, in the form of $\Delta V_f/V_M$. It should be noted that these calculations of the lattice distortion take into account an important effect first pointed out by Eshelby.³⁵ He showed that the stress-free surface of a finite crystal gives rise to an image term in the displacement about a point imperfection; this term has a large effect upon the magnitude of the volume relaxa-

²⁴ G. W. Tichelaar and D. Lazarus, Phys. Rev. **113**, 438 (1959).

²⁵ H. Kanzaki, Phys. Chem. Solids **2**, 24 (1957).

²⁶ G. Nardelli and A. Repanai, Physica **24**, S182 (1958).

²⁷ G. L. Hall, Phys. Chem. Solids **3**, 210 (1957).

²⁸ L. A. Girifalco and J. R. Streetman, Phys. Chem. Solids **4**, 182 (1958).

²⁹ A. W. Lawson, S. A. Rice, R. D. Corneliussen, and N. H. Nachtrieb, J. Chem. Phys. **32**, 447 (1960).

³⁰ J. B. Gibson, A. N. Goland, M. Milgram, and G. H. Vineyard, Phys. Rev. **120**, 1229 (1960).

³¹ L. Tewordt, Phys. Rev. **109**, 61 (1958).

³² K. H. Bennemann and L. Tewordt, Z. Naturforsch. **15a**, 772 (1960).

³³ A. Seeger and E. Mann, Phys. Chem. Solids **12**, 326 (1960).

³⁴ K. H. Bennemann, Z. Physik **165**, 445 (1961).

³⁵ J. D. Eshelby, J. Appl. Phys. **25**, 255 (1954).

the about a vacancy, and it must be included before the theoretical calculation of the relaxation about a vacancy site in an infinite lattice may be directly compared with experimental results.

It is also possible to compare the result of the present experiment with expressions relating the activation volume to other known quantities. Nachtrieb, Resing, and Rice⁸ and Rice and Nachtrieb³⁶ showed that

$$\Delta V = (\Delta H / \Delta H_m) \Delta V_m,$$

where ΔH_m and ΔV_m are the enthalpy and volume change upon melting. Using 42 kcal/mole²³ for ΔH , 3.0 kcal/mole³⁷ for ΔH_m , and 0.51 cm³/mole³⁷ for ΔV_m , one finds that ΔV is equal to 7.1 cm³/mole, in startling agreement with the present results.

Keyes³⁸ noted that many materials follow the semi-empirical relationship

$$\Delta V = 4K_T \Delta H.$$

Using 6.0×10^{-7} bar⁻¹ for K_T , and 42 kcal/mole for ΔH , one obtains the value 4.2 cm³/mole for ΔV . In a later paper³⁹ Keyes derived the expression

$$\Delta V = 2(\gamma_G - \frac{2}{3}) K_T \Delta G.$$

There is some doubt about the correct value of γ_G for gold.⁴⁰ A compromise between the value of γ_G derived from compressibility data and from shock-wave experiments suggests the value 2.0. With this value, and with $\Delta G \approx \Delta H = 42$ kcal/mole, ΔV is equal to only 2.8 cm³/mole. However, a derivation of γ_G from the heat capacity at constant volume gives a value of 3.0. If this is used in the above equation, then ΔV is equal to 4.9 cm³/mole.

Lawson *et al.*²⁹ also derived an approximate relation between the activation volume of formation ΔV_f and the molar volume

$$\Delta V_f / V_M = 1 / (\gamma_G - \frac{1}{3}).$$

With $\gamma_G = 3.0$, ΔV_f is 3.8 cm³/mole, but with $\gamma_G = 2.0$, ΔV_f is 6.1 cm³/mole.

Many of the calculations cited are but rough approximations. However, many of the experimental results cited also are quite limited in their certainty by large experimental errors. In the present investigation,

³⁶ S. A. Rice and N. H. Nachtrieb, *J. Chem. Phys.* **31**, 139 (1959).

³⁷ C. J. Smithells, *Metals Reference Book* (Butterworths Scientific Publications Ltd., London, 1962), 3rd ed., Vol. 2, p. 618.

³⁸ R. W. Keyes, *J. Chem. Phys.* **29**, 467 (1958).

³⁹ R. W. Keyes, in *Solids Under Pressure*, edited by W. Paul and D. M. Warschauer (McGraw-Hill Book Company, Inc., New York, 1963), p. 71.

⁴⁰ K. A. Gschneidner, Jr., *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York), Vol. 16 (to be published).

TABLE IV. Theoretical values for volume relaxation about vacancies in copper. Potentials a , b , V_1 , and V_2 are Born-Mayer repulsive potentials. The explicit form of V_1 is due to Huntington,^a and that of V_2 is due to Huntington and Seitz.^b V_3 is a Morse repulsive potential whose explicit form is due to Girifalco and Weizer.^c The constant δ is the Eshelby factor (Ref. 35), which is equal to $3(1-\sigma)/(1+\sigma)$, where σ is Poisson's ratio.

Source	Nearest-neighbor potential	Fractional volume relaxation	$\Delta V_f / V_M$
Tewordt ^d ($\delta = 1.5$)	V_1	-0.53	0.47
	V_2	-0.45	0.55
Seeger and Mann ^e ($\delta = 1.5$)	a	-0.09	0.91
	b	-0.19	0.81
	V_1	-0.29	0.71
Bennemann and Tewordt ^f ($\delta = 1.2$)	V_1	-0.38	0.62
	V_2	-0.32	0.68
	V_3	-0.44	0.56
	V_1	-0.46	0.54
($\delta = 1.5$)	V_2	-0.39	0.61
	V_3	-0.53	0.47
	V_1	-0.40	0.60
Bennemann ^g ($\delta = 1.2$)	V_1	-0.40	0.60
Johnson and Brown ^h ($\delta = 1.5$)	V_1	-0.48	0.52

^a H. B. Huntington, *Phys. Rev.* **91**, 1092 (1953).

^b H. B. Huntington and F. Seitz, *Phys. Rev.* **61**, 315 (1942).

^c L. A. Girifalco and V. G. Weizer, *Phys. Rev.* **114**, 687 (1959).

^d See Ref. 31.

^e See Ref. 33.

^f See Ref. 32.

^g See Ref. 34.

^h See Ref. 13.

limitations in accuracy of the experimental data made it impossible to draw any conclusions with respect to the temperature dependence of the activation volume or the pressure dependence of the activation energy. These limitations are due to the difficulties involved in the measurement, reproducibility, and control of the temperature. A reasonable value for the error in the temperature measurement was estimated to be $\pm 5^\circ\text{C}$, and the error limits in Fig. 6 are based upon this estimate. It is probable that the cause of the irregular thermocouple deteriorations which were observed was due to contamination of the thermocouple wires by uncontrollable impurities in the gas, furnace parts, or vessel parts, although precautions were taken to minimize this possibility. Measurement of an accurate temperature in a small furnace of the type used in this experiment also is limited by the presence of temperature gradients. Once these difficulties are overcome, more reliable data can be obtained from measurements of the type made in this investigation.

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