

FIG. 5. Extrapolated relative equilibrium vacancy concentration at a given temperature as a function of pressure in gold. Numbers by points show sequence in which points were taken on a given isotherm.

activation volume corresponding to the least-squares straight line along with the least-squares error is shown for each specimen. Weighting each value by the reciprocal of the least-squares error (and taking the error of Γ_4 to be ± 1 cm^3/mole since so few points are involved), an average value for ΔV_f is found to be

$$\Delta V_f = 6.8 \pm 0.4 \text{ cm}^3/\text{mole}.$$

This is $0.65 V_m$, where V_m is the 640°C molar volume of gold.

B. Aluminum

Of 19 aluminum specimens constructed and placed in the pressure vessel, only two remained intact long enough to obtain data at more than two pressures. Of these, the results for Al 14 are shown in Fig. 6. The pre-quench temperature stability as indicated by the K3 potentiometer was better than $\pm 1^\circ\text{C}$. This stability is reflected in the reproducibility and small scatter of the data. The intercepts of Fig. 6 are plotted in Fig. 7. The results for the other specimens, where more than one isobar was obtained, were consistent with the results for Al 14. If there was any trend in these other data, it was toward a smaller formation volume. However, in those cases there was a large baseline shift between quenches so that those results cannot be given much consideration. None of the aluminum specimens was observed to sag as in the case of gold. Some did appear to discolor, however, which was not the case for gold. The resistance base shift in aluminum may therefore be due to impurities introduced during the anneals.

Unfortunately it has not been possible to measure the residual resistivity of the specimens after the series of quenches.

Quench rates were constant to below 0°C for the aluminum specimens. High-pressure fast quenches were also found to be consistent with the slower quenches. Several quenches were also made from a lower temperature (375°C) and were in agreement with, but had larger error than, Al 14. Thus, for aluminum

$$\Delta V_f = 6.38 \pm 0.15 \text{ cm}^3/\text{mole}.$$

The error indicates only the least-squares fit to the plot of the intercepts versus pressure. The value is $0.62 V_m$, where V_m is the 420°C molar volume of aluminum.

V. DISCUSSION

A. Gold

1. Formation Volumes

Several formation volumes for vacancies in gold have been reported. They have been discussed in the quenching papers^{2,3} and the BLB paper.⁷ All are in fair agreement within their respective experimental errors. The present value agrees with the BLB value within the stated errors but is considerably higher than the earlier quenching values. There are several reasons for this discrepancy.

The earlier quenches did not have at hand the BLB resistance-versus-pressure data. They used the ambient temperature resistance of the specimen at the quench pressure along with the atmospheric-pressure temperature coefficient to determine the specimen resistance at quench pressure and temperature. A simple calculation shows that the ratio of the resistance using the BLB data to that used by the earlier quenches goes to 1 as

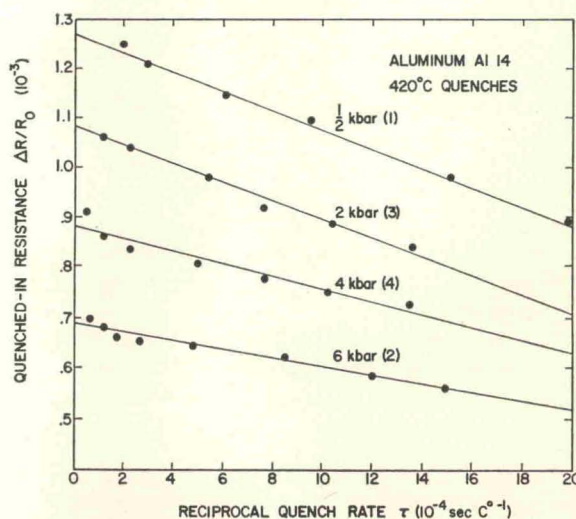


FIG. 6. Isobars of quenched-in resistance versus reciprocal quench rate for aluminum. Numbers in parentheses show sequence in which isobars were made.

P goes to zero, whereas at 10 kbar and temperatures from 600 to 700°C it may be 1.01. Thus, the earlier experimenters were quenching from 6 to 8°C too high at their 10-kbar quenches thereby cancelling part of the pressure effect. Indeed, application of this correction to the Huebener and Homan data yields a value of 6.8 cm³/mole, in remarkable agreement with the present value.

Huebener and Homan assume that a fixed quench rate will produce a fixed fractional loss of vacancies. The present results show that this is not the case. However, for their quench rates, the effect is small compared with their temperature error. Even for the 640°C quenches a measurable fraction was lost at a linear quench rate of 10⁴°C sec⁻¹. Finally, the previous experimenters had to apply relatively large corrections to their data to reduce it to a fixed quench temperature. In the present experiment the precision of the temperature control eliminated the need for such corrections. It is therefore not necessary to assume a formation energy in determining ΔV_f .

The sum of the present value of ΔV_f and the earlier ΔV_m value⁴ of 1.50 ± 0.15 cm³/mole is 8.3 ± 0.5 cm³/mole. This is about 80% of the molar volume. Dickerson *et al.*⁵ find 7.2 ± 0.4 cm³/mole while Beyeler and Adda⁶ report 7.3 cm³/mole. The agreement between the present value and that of Dickerson *et al.* is just within the limits of error. Dickerson⁵ mentions considerable difficulty with chromel-alumel thermocouple deterioration during the diffusion anneals. Subsequent improvements have been made on the temperature-correction procedure used by Dickerson, but extreme care is required to keep the temperature error as small as ±5°C. Adda does not mention temperature-measurement procedure. The agreement between the present value of ΔV_f , the corrected Huebener and Homan value, and the BLB value along with the fact that ΔV_m contributes a small absolute error makes it appear that the self-diffusion values are low.

Even though the value of ΔV_{act} inferred from the quenching experiments is somewhat larger than the self-diffusion value, it is still small when compared with the values found for other fcc metals. The values for copper⁶ and silver¹⁹ are 0.91 and about 0.89 molar volumes, respectively. Theoretically, Schottky *et al.*²⁰ find 0.93, 0.97, and 0.99 molar volumes for copper, silver, and gold, respectively.

Thus, the agreement between formation, motion, and diffusion activation volumes is rather poor. Part of the discrepancy may arise from the fact that the measurements were made at three different tempera-

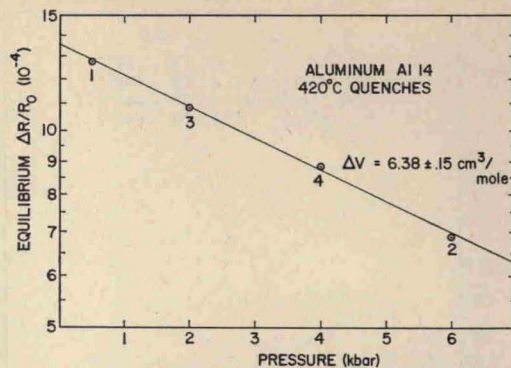


FIG. 7. Extrapolated relative equilibrium vacancy concentration at 420°C as a function of pressure in aluminum. Numbers by points show sequence in which points were taken on a given isotherm.

tures, so that different multiple vacancy components would be present. Part may be due to the temperature-measurement difficulties in the diffusion experiments. It would be desirable to redo the latter experiments using improved techniques.

2. Vacancy-Loss Mechanisms

Kino and Koehler¹⁰ conclude that the temperature dependence of the fractional loss eliminates migration to grain boundaries as a possible loss mechanism. They conclude that both dislocations and impurity clusters can act as important sinks for vacancies in a quenched specimen. For the dislocation mechanism, Kino and Koehler find

$$(c_0 - \bar{c})/c_0 = 0.8\pi\nu\tau_Q a^2 N_d e^{-E_m^1/kT_Q}, \quad (4)$$

where c_0 is the equilibrium concentration at the quench temperature T_Q , \bar{c} is the actual amount quenched in from T_Q at time taken to quench τ_Q , ν is the atomic vibration frequency, a is the interatomic distance, and N_d is the dislocation density. For the gold specimens used in this experiment, assuming $\nu = 3 \times 10^{13}$ sec⁻¹, the values of N_d are 1 to 3×10^5 cm⁻². This value is 1 to 2 orders of magnitude smaller than observed in most quenching experiments and may reflect the fact that the specimen is not moved once it has been mounted in the vessel.

If we define Σ to be the slope of a plot of $(c_0 - \bar{c})/c_0$ versus τ_Q , then differentiating (4) we find

$$\left(\frac{\partial \ln \Sigma}{\partial P}\right)_{T_Q} = \left(\frac{\partial \ln(\nu a^2 N_d)}{\partial P}\right)_{T_Q} - \frac{1}{kT_Q} \left(\frac{\partial E_m^1}{\partial P}\right)_{T_Q}. \quad (5)$$

But

$$\Delta V_m^1 = (\partial E_m^1 / \partial P)_{T_Q}, \quad (6)$$

where E_m^1 is now interpreted as the Gibbs free energy of motion so that substituting (6) into (5) and re-

¹⁹ C. T. Tomizuka, R. C. Lowell, and A. W. Lawson, *Bull. Am. Phys. Soc.* **5**, 181 (1960); M. Beyeler and Y. Adda, *Physics of Solids at High Pressures* (Academic Press Inc., New York, 1965), p. 349.

²⁰ G. Schottky, A. Seeger, and G. Schmid, *Phys. Status Solidi* **4**, 419 (1964).