

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  $\text{Au}^{198}$  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  $t_{\text{eff}}$  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  $\Delta H$  was calculated for each pressure from the relation

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

where  $\Delta H_0$  was taken as 41.7 kcal/mole,<sup>23</sup>  $\Delta V$  was approximated as 7 cm<sup>3</sup>/mole, and  $\alpha$ , 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  $\Delta G$ , the diffusion coefficient may be written

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

where  $\gamma$  is a constant depending on the crystal structure,  $a$  is the lattice constant,  $\nu$  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  $\gamma_G$  is the Grüneisen constant.

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

$$860^\circ\text{C}: \log_{10} D = (0.9215 \pm 0.0217) P - (0.02750 \pm 0.00380) P,$$

$$910^\circ\text{C}: \log_{10} D = (1.2525 \pm 0.0127) P - (0.03372 \pm 0.00221) P,$$

$$960^\circ\text{C}: \log_{10} D = (1.5675 \pm 0.0234) P - (0.02569 \pm 0.00536) P,$$

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

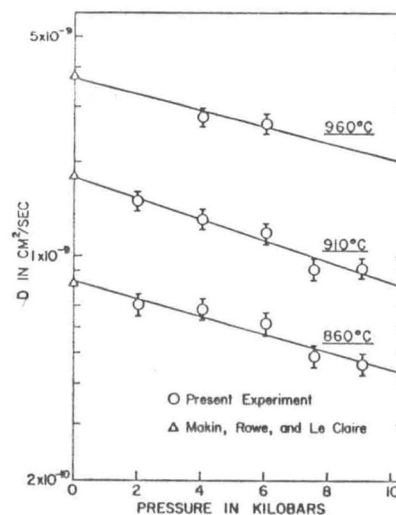


FIG. 6. Variation with pressure of the diffusion coefficient at 860, 910, and 960°C.