

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; Ht, 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 Ag<sup>110</sup> concentration was insignificant for penetration distances beyond 1000 μ. 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 ±5°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 μ 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 versamatic 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 ±5°C even though the thermocouple is accurate to ±2°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

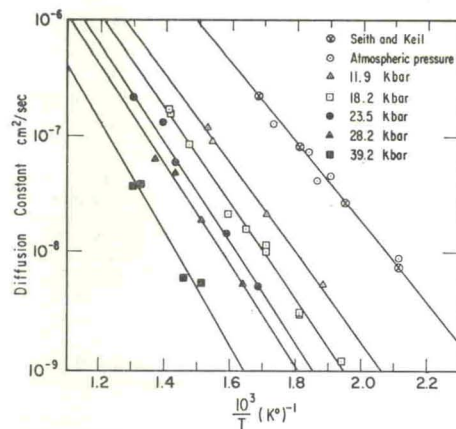


FIG. 2. Variation with temperature of the diffusion coefficient at constant pressure.

<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.

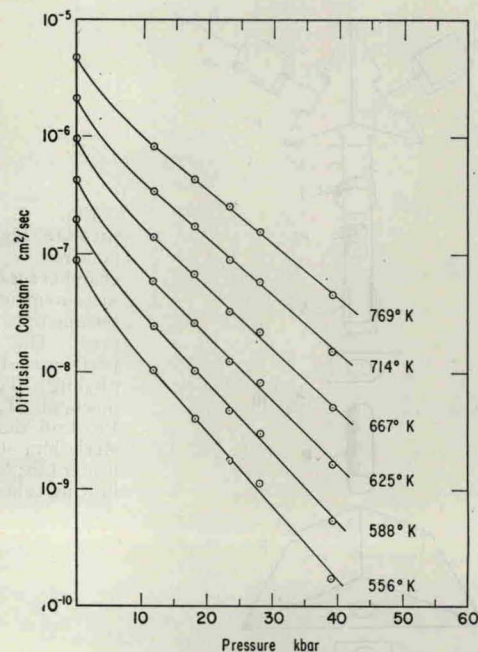


FIG. 3. Variation with pressure of the diffusion coefficient at constant temperature.

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).