THE EFFECT OF HYDROSTATIC PRESSURE ON THE CHEMICAL DIFFUSION RATE OF SILVER INTO LEAD

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INTRODUCTION

The diffusion (interpenetration)of metals into lead was first reported by Roberts-Austen,[1] who measured the diffusion coefficients of Au into Pb. Since that time, the diffusion coefficients of a number of metals into lead have been measured and tabulated, including that for self-diffusion (see, for instance, Barrer).[2] Of the many systems studied, the two with the highest diffusion rates are Au in Pb[3] and Ag into Pb[4]--the former being the greater.

Although there has been a great deal of data taken for various systems at atmospheric pressure, there has been very little done to determine the effect of high pressures on diffusion. Self-diffusion in lead has been studied to 10 kb. by Nachtrieb and Rice,[5] and to 40 kb. by Hudson and Hoffman[6] with some disagreement in the interpretation of the results.

There have been several theories advanced relating to diffusion that either directly or indirectly involve a pressure dependence. The Dushman-Langmuir equation[7] is related to a pressure study through its ability to be tested against results for the same system at various pressures. Braune and Van Liempt[8] and Rice and Nachtrieb[9] have postulated linear relations between the melting point of the solvent and the activation energy of diffusion which may be compared against a known fusion curve.

Also of interest is the actual atomic mechanism involved in a particular diffusing system. Many of the postulated mechanisms, along with possible means of identification are discussed by Chalmers,[10] Mehl,[11] Barrer,[2] and Le Claire.[12] In particular, a good discussion of interstitial diffusion (which is what Au and Ag into Pb is assumed by many to be), is contained in Diffusion In Solids by Shewmon.[13] Also of possible interest along this line are the calculations of Stern and Eyring[14] pertaining to the change of diffusion constant with pressure for a lead solvent system.

Lead was chosen as a solvent material for this study because of the rapid rates of diffusion of materials in it, and because reliable data at atmospheric pressure existed for comparison.[4] Ag was chosen as a solute over Au because the former possesses advantages of experimental technique (compare the present work with that of Ascoli, Germagnoli, and Mongini).[3] Another influencing factor in the choice of the chemical system was the possibility that if Ag did diffuse interstitially, the diffusion rate might increase with pressure.[31]

THEORY

1. The Diffusion Problem

There are two basic approaches to the diffusion problem. The first, or atomic approach, is through the solution of a random walk problem. This method considers, statistically, the probability of an atom migration from one site in a crystal lattice to another by a series of random jumps over some potential barrier. The second, or macroscopic approach, is through the solution of Fick's law for various boundary conditions.[14] Of the two, the random walk approach comes closer to dealing with the actual physical situation; but in doing so, is much more complicated mathematically than the second. However, problems of this type have been solved for special geometries (see, for instance, Ree[15] or Shewmon).[13] Both approaches lead to the same asymptotic form for the equations involving observable properties of the diffusion system.

2. Criteria for Diffusion

Chemical diffusion, in a macroscopic sense, is the mechanism by which a heterogeneous chemical system approaches equilibrium. Thermodynamically, the criteria that such a system be in equilibrium is that the chemical potential of each component of the system be constant throughout the system.[16]

If we have a chemical system in which there is a concentration gradient of material A, the above criteria is sufficient to require: (1) material A to diffuse from a region of higher concentration to a region of lower concentration, (2) the system to be in equilibrium despite the presence of a concentration gradient, (3) material A to diffuse from a region of lower concentration to a region of higher concentration.[17] Case 1 is by far the most common, and is the one that applies to a silver-lead system.

3. Diffusion Equations

In the case of an isothermal, isobaric diffusion process, the chemical potential is a function of the entropy and volume of the system. These in turn are solely dependent upon the solute distribution. In particular, the differential equation governing the approach to equilibrium of an interdiffusing metallic system is[18]

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x_i}\left(D_{ij}\,\frac{\partial c}{\partial x_j}\right) \qquad i, j = 1, 2, 3 \qquad (1)$$

where c is the concentration of the solute material, D_{ij}s are the components of the diffusion tensor, t is the time, and x_i are the position coordinates. In general, the D_{ij}s are functions of the concentration c.[19] However, in the case of extremely low solute concentrations, the D_{ij}s are approximately constants. Furthermore, if a principle axes system is used, equation 1 reduces to the much simpler Fick's law equation:

$$\frac{\partial c}{\partial t} = D_i\,\frac{\partial^2 c}{\partial x_i^2} \qquad (2)$$

Equation 2 is still three dimensional with three independent diffusion constants, D_1, D_2 and D_3 corresponding to the three crystalline axes. However, if the material has cubic symmetry, it can be shown that the bulk diffusion is isotropic; that is, independent of crystalline direction with $D_1 = D_2 = D_3 = D$ where D is called the diffusion constant. If the geometry is such that the concentration is a function only of a single cartesian coordinate and time, equation 2 reduces to the usual one dimensional diffusion equation:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \tag{3}$$

Solutions of equation 3 for various initial conditions are tabulated and discussed by Crank.[14] The solution for a semi-infinite rod with a delta-function source on the end is given by equation 4:

$$C = \frac{\alpha}{2\sqrt{\pi D t}} \exp\left(\frac{-x^2}{4Dt}\right) \tag{4}$$

where α is a constant associated with the strength of the source, t is the anneal time at constant pressure and temperature, and x is the penetration distance measured from the source. A rule of thumb for determining the length of rod needed in order for equation 4 to be a good approximation for the solution of the diffusion equation for a finite rod is $\ell > 2\sqrt{Dt}$.

If we take the log of both sides of equation 4,

$$\ln C = \frac{-x^2}{4Dt} + \ln\left(\frac{\alpha}{2\sqrt{\pi D t}}\right) \tag{5}$$

we see that $-1/4Dt$ is the slope of the log of the concentration vs the square of the penetration distance curve.

As might be expected, what is represented by an experimentally determined diffusion constant will depend upon the experimental situation. We have already mentioned that diffusion is concentration dependent. In addition to this, it may be enhanced by grain boundary and surface diffusion[22,23] and either enhanced or reduced by an oxide or non-crystaline layer between the solvent and the solute.[4,8] It may also vary with the purity of the solvent material.[3] Many reported diffusion constants represent some average of these several effects.

The most meaningful diffusion constant should be that for pure lattice diffusion of a pure solute material of low concentration in a pure, single crystal solvent.[12] Care should be taken to approach this situation as closely as possible. In general, diffusion constants for temperatures near the melting point approach those for pure lattice diffusion more closely than lower temperature ones do.

4. Theoretical Equations

From a phenomonological point of view, there are many theories advanced,[2,5,8,9,11,26] all of which (for the ideal case where D is not a function of concentration) take the form

$$D = D_o \exp\left(\frac{-Q}{RT}\right) \tag{6}$$

where R is the gas constant, T is the absolute temperature and Q is called the activation energy, the difference in the various mechanisms being in the interpretation of Q and D_o. One of the prime objectives of this investigation is to determine the pressure dependence of these terms for our silver-lead system. It is thought that this dependence might help in the interpretation of the mechanisms involved.

Empirically, Q is usually obtained from a plot of log D vs 1/T, and D_o by extrapolation of this plot. Another way of obtaining Q, used by many authors for comparison, is to calculate Q from the Dushman-Langmuir equation;[7]

$$D = \frac{d^2 Q}{N h} \exp\left(\frac{-Q}{RT}\right) \tag{7}$$

consequently,

$$D_o = \frac{d^2 Q}{N h} \tag{8}$$

where N is Avogadro's number, h is Plank's constant, and d is the interatomic spacing. The two approaches agree quite well in most cases.[27] However, Van Liempt[28] points out that this agreement is no proof of equation 7 due to the insensitivity of values of Q obtained to changes as large as a factor of 10 in D_o. This objection may not be too serious in light of the statement made by Nowick[29] in defense of a similar equation by Zener " that values of D_o obtained from conventional plots of ln D vs 1/T often appear to be in error by factors as great as 10^8. "

Braun and Van Liempt, using Lindemann's theory of melting, derived an equation relating the activation energy to the melting temperature (T_m) of the solvent;

$$Q = 3 b^2 R T_m \tag{9}$$

where b is a number characteristic of the solvent material, approximately equal to 2 for all materials. This equation shows fairly good agreement with the results of work done for many systems at atmospheric pressure.[30]

It would appear that the best check of this relationship would be by comparing it with the results obtained for a single system studied over a wide pressure (melting point) range. This has been done by Rice and Nachtrieb[5] for self-diffusion in lead up to 12 kilobars, and by Hudson and Hoffman[6] to 40 kilobars (Bridgman's resistance scale). The former investigators report a functional dependence of Q on T_m similar to that of equation 9. The latter claim that although this relation may appear to hold below 10 kilobars, it does not appear to be valid at higher pressures. It is hoped that the present study might shed more light on this matter.

A quantity of considerable interest, which may be derived[31] through the use of quasi-equilibrium thermodynamics, is the activation volume, ΔV_a.

$$\left[\frac{\partial \ln (D/D_0)}{\partial P}\right]_T \equiv \frac{\Delta V_a}{RT} \tag{10}$$

The activation volume, as reported by Hudson and Hoffman for self-diffusion in lead ranges from 13 cm^3/mole at 770°K to 10.4 cm^3/mole at 475°K. Although there is considerable scatter in their data, the ratio $\Delta V_a / V_m$ (where V_m is the molar volume) is approximately equal to .64. It may be possible to gain some insight into the mechanism of diffusion of Ag in Pb by examining this ratio for our system.

EXPERIMENTAL METHOD

1. Synopsis

Lead crystals, .1" long and 1/8" diameter, plated on one end with radioactive silver, were used in this investigation. The samples were prepared by growing 1 1/2" long by 1/8" diameter single crystals from pure lead. The crystals were grown ten at a time in a graphite mold in an evacuated furnace by the Bridgman method. Without removing the crystals from the mold, a surface perpendicular to the axis of the lead rods was ground smooth. The freshly-ground lead was then cleaned by ion bombardment, and vacuum plated with Ag^{110}. One-tenth inch was then sawed off of the plated end of the crystals.

The plated crystals were mounted inside a specially designed high-pressure sample holder and annealed in silicone oil at various pressures and temperatures.

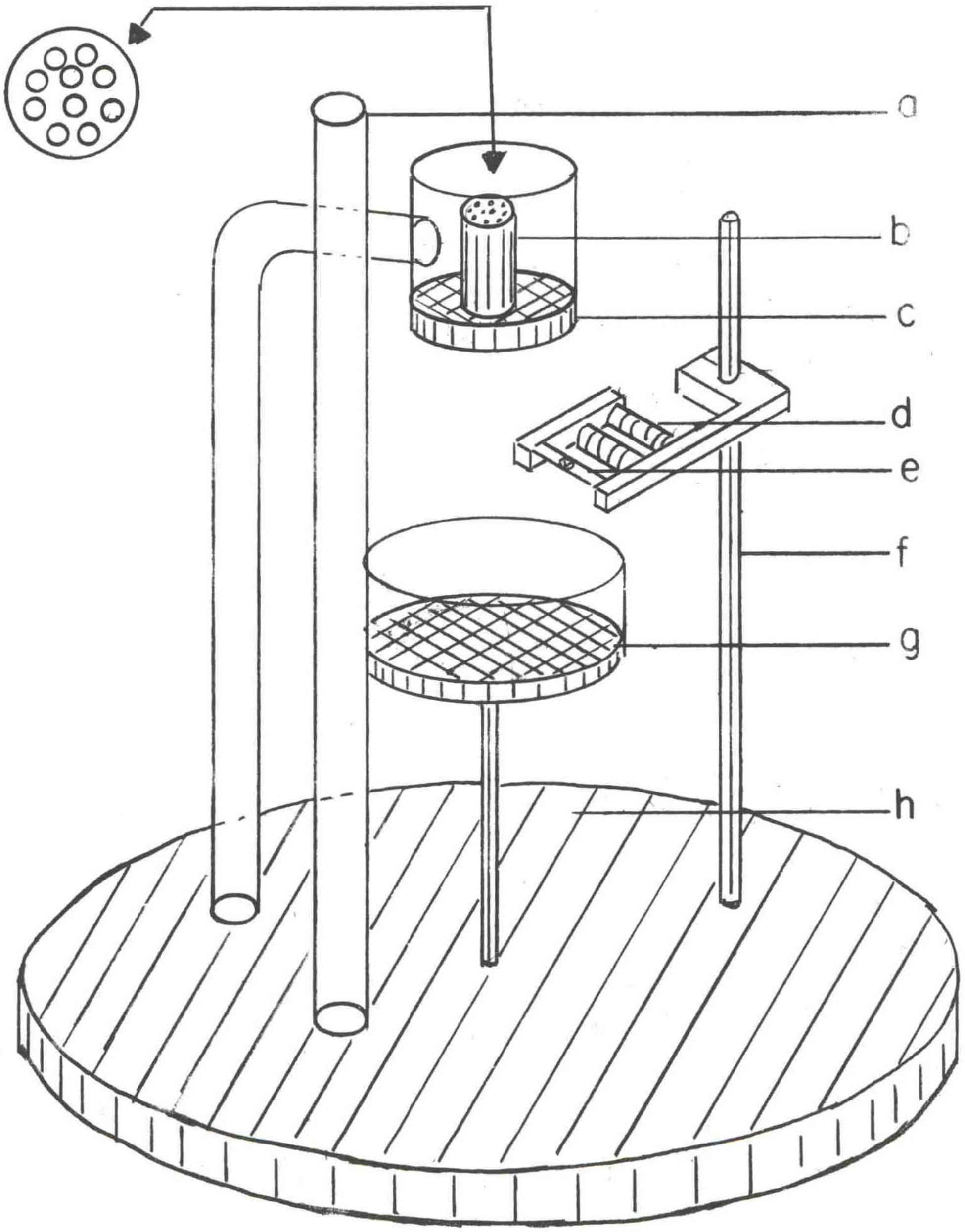
After the samples had been annealed, they were analyzed by slicing off thin layers parallel to the plated surface with a sliding microtome and counting the activity of these slices with a scintillation counter.

2. Sample Preparation

Lead rod (99.999% pure) obtained from A. D. Mackay, Inc. (New York, New York) was first trimmed on a lathe to remove the oxidized surface layer. The lead was then placed in the reservoir of a clean graphite mold (see Figure 1), and single crystals were grown ten at a time by means of an evacuated gradient furnace.[31] The bottom of the mold containing the crystals was then sawed off square, by means of a mitre box, and ground on successively finer grades of silicon carbide paper placed on plate glass. In grinding, care was taken to draw the crystals only over unused portions of the paper to avoid contamination of the surface. The final grinding was on #600 grit silicon carbide paper using Methyl alcohol as a lubricant to minimize the depth of amorphous layer that results from such a grinding operation.[32] The freshly-ground surface was rinsed in alcohol and the mold placed in a drying oven at 110°C for six to twenty-four hours.

In order to remove the amorphous film which resulted from the grinding operation, along with any other surface contamination that might inhibit diffusion, the samples were ion bombarded immediately prior to plating. An apparatus, as shown in Figure 1, was constructed, which made it possible to ion bombard and plate samples without removing them from the vacuum system. It was found that the ion bombarding procedure would dislodge material from any exposed metal surface in the region of the ion discharge and that some of this material would be plated onto the lead surfaces. In order to minimize this problem, glass was used wherever possible within the bell jar.

It is to be noted that during the entire operation, the lead crystals were contained in the same mold in which they were grown. The reason for this is threefold. First, the fact that carbon has a lower conductivity



a. Glass tube for introducing Argon gas
b. Lead crystals contained in graphite mold
c. Graphite washer
d. Ceramic insulator
e. Tantalum strip, dimpled in center
f. Steel rod which may be rotated or elevated from outside of the bell jar
g. Graphite plate, at ground potential
h. Steel base plate

Figure 1. Ion Bombarding, and Vacuum Plating Apparatus

than lead causes the surfaces of the lead crystals to be at a slightly higher (negative) potential than the surrounding material, thus giving more effective ion cleaning. Second, the very good fit of the crystals, due to never having been removed from the mold, made it possible to plate the entire surface with no fear of silver plating the cylindrical sides of the crystals. Third, leaving the crystals in the mold protected them from deformation and general contamination due to handling.

Prior to putting the lead in the vacuum system, the system was pumped down overnight and outgassed by turning on the ion bombarding apparatus for twenty minutes. The strip furnace for evaporating silver and the ion gauge were also outgassed. The system was then opened. The lead was put in place and a 1 mg pellet of Ag^{110}, specific activity .012 mC/mg, was placed in the dimple of the strip furnace (see Figure 1). The system was pumped down to 30 micro-torr before the cold trap was filled with liquid nitrogen and to approximately 3 micro-torr before Argon was introduced into it. The bell jar was flushed for one-half hour with Argon entering at the top and being pumped out the bottom. The amount of Argon flowing through the system was regulated by means of a needle valve and limited by the ability of the forepump to keep up with the diffusion pump--the forepump pressure being maintained at less than 100 torr.

When the flush was completed, the pressure in the bell jar was raised to 18-20 torr by partially closing a baffle valve between the diffusion pump and the bell jar, meanwhile still maintaining maximum

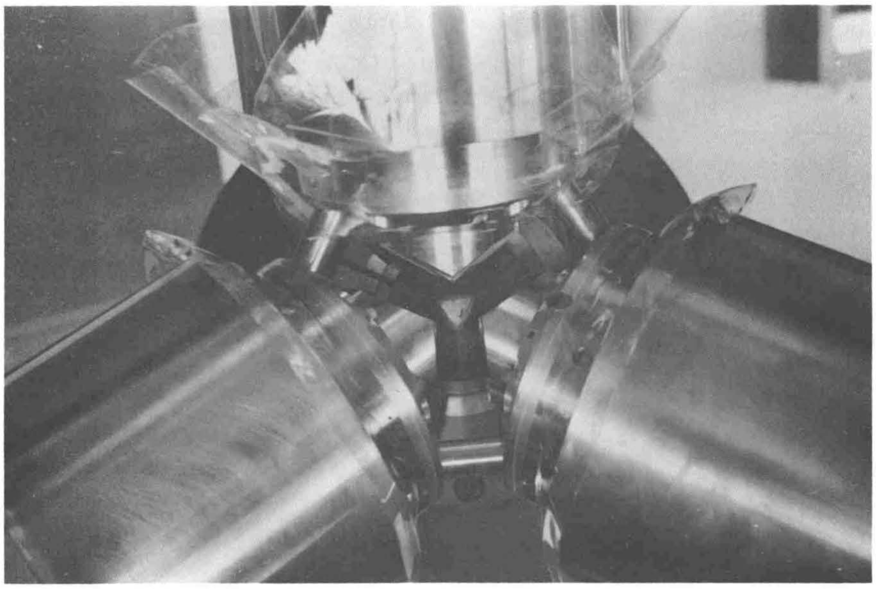
Argon flow through the system. The crystals were ion bombarded for twenty minutes at 2000 volts and 0.6 ma current. The system was then immediately pumped down to a pressure of 5 micro-torr. The strip furnace was then heated to outgas the silver and swung into place approximately 1 cm from the surface of the lead. It took approximately ten minutes to pump down, at which time the silver was evaporated onto the lead. The system was vented slowly to ambient, and the mold containing the crystals removed.

One tenth of an inch was sawed off the silver-plated end of the mold containing the crystals. The crystals were removed from the mold by cooling to liquid nitrogen temperature. The difference in coefficients of the thermal expansion between graphite and lead allowed the plated samples to drop from the mold without damage.

As the original crystals were about 1 1/2" long, it was possible to obtain about 50 samples from one mold (5 cuttings). It was thought advisable to use only the lower 1/3 of the 1 1/2" long crystals to avoid possible regions of imperfect crystal growth.

3. Anneal Procedure

The study of chemical diffusion at high pressure at this university is conducted in a large volume (1" anvils) Tetrehedral-Anvil Press designed by Dr. Tracy Hall[33, 34] as shown in Figure 2. This press is similar to the X Ray Tetrehedral-Anvil Press previously reported by Barnett and Hall[35] with the exceptions that it contains no x ray apparatus and is mounted oppositely (upside down) from the latter.



Close up
of Sample
Chamber

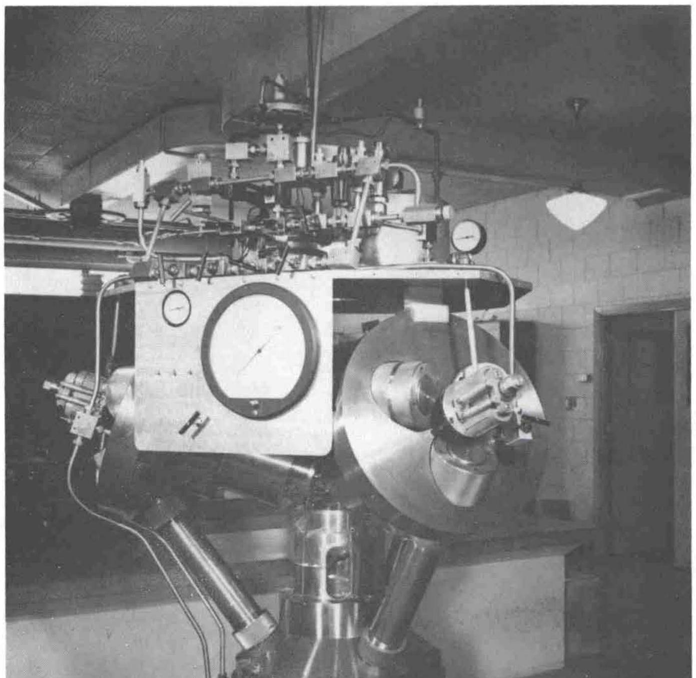
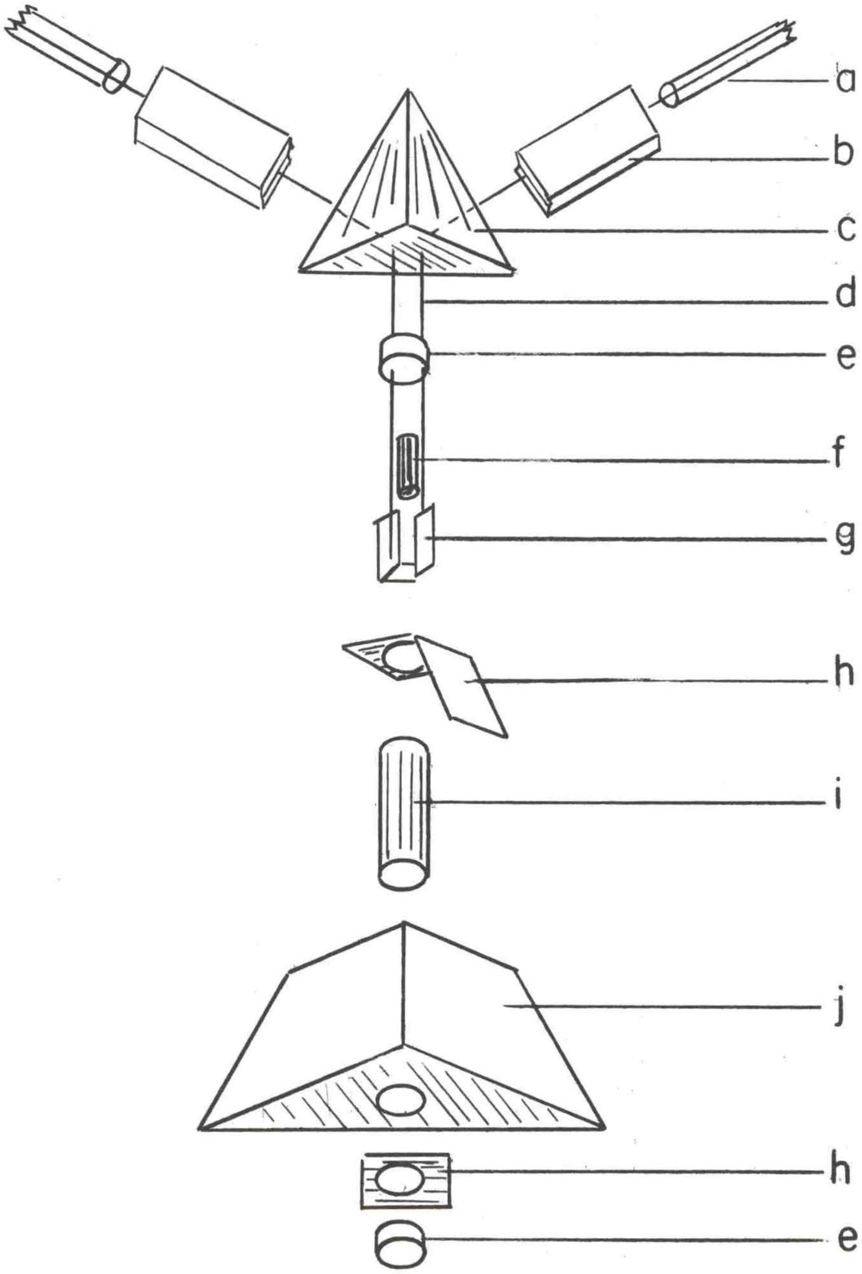


Figure - 2
Tetrahedral
Anvil Press



a. Teflon insulating tube
b. Pyrophyllite gasket
c. Pyrophyllite tetrahedron top
d. Chromel-alumel thermocouple wire
e. Teflon plug
f. Lead sample
g. .001" steel shim stock
h. Tab for electrical contact to heater
i. 3/16" monel heater tube
j. Pyrophyllite tetrahedron base, .45" deep

Figure 3. High Pressure Sample Chamber Geometry

The samples were annealed in General Electric Viscasil 100,000 cs silicone fluid contained inside a specially designed tetrahedral high-pressure sample holder as shown in Figure 3. It is to be noticed that this design puts the thermocouple (30 gauge chromel-alumel) in intimate contact with the lead. This was necessary because of the large temperature gradient associated with such a short furnace. Experiments using multiple thermocouples have shown that there was probably not more than a 5 C° temperature differential in the lead itself, and probably much less.

In order to insure that the system remained hydrostatic (i.e., the Viscasil did not solidify), the system was raised to 150°C at 6 kilobars and maintained there until the pressure was reached at which the sample was to be annealed.

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 R 820, 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 .05 mv. Using this procedure, equilibrium could usually be obtained in less than ten seconds.

4. Sample Analysis

After removal from the press, the pyrophyllite tetrahedron was broken open and the monel heating tube removed. By gripping the edge that overlapped the heater tab with a pair of long-nosed pliers and gently twisting outward, it was possible to peel open the tube, leaving the lead crystal exposed and undamaged. 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 securily mounted in paraffin for slicing with a sliding microtome.

The sample was sliced in layers 10 microns thick--the slices being collected, either 2 or 6 at a time, on pieces of gummed paper. The activity of each group was counted by means of a Tracerlab, type sc-57, well scintillation counter and Tracerlab, sc-73 versa/matic 11, scaler.

RESULTS

Figures 4 through 8 display the data taken from samples annealed at various temperatures at 25 kilobars pressure. These five plots are included to represent the more than 90 diffusion runs made to date in this study.

It would be extremely difficult to accurately account for the diffusion which takes place during the time between when a sample is plated and when it is annealed, and while it is being taken to and returned from the anneal pressure; therefore, an experiment was conducted to see if such extraneous diffusion could be neglected. A sample was subjected to the extremes of the experimental technique. It sat at room temperature for one month prior to being annealed and was heated to a temperature greater than 210°C for one hour while being pumped to a pressure of 38 kilobars, but it was not annealed. The results of this experiment are displayed in Figure 9. The coordinate representing the square of the penetration distance is expanded to ten times that of Figures 4 through 8.

The results of many of the runs were questionable because of one experimental difficulty or another. The results of all runs for which there was no apparent experimental difficulty are displayed in the conventional log D vs 1/T form in Figure 10. Included also on this plot (Figure 10) are values reported by Seith and Keil[4] 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.

In order to obtain a sufficient range of values along isotherms to make a plot of log D vs pressure (Figure 11), the isobars of Figure 10 were extrapolated graphically. Many of the points included in Figure 11 range beyond the region in which data was actually taken.

In Figure 12 the log of each diffusion constant is plotted as a function of the ratio of the melting point of lead at the anneal pressure to the anneal temperature. The melting points used are those reported by Butuzov[36] and Christensen.[37] The pressure calibration used in these two determinations of the lead fusion curve is different than that of the present work; therefore, it was necessary to convert the reported pressure scale to that used in this study.

Calculated activation energies and activation volumes along with other quantities of interest such as melting points and diffusion constants are tabulated in Tables 1 and 2.

Figure 13 shows the pressure calibration[38] for the sample geometry used in this study. Included also on this plot are calibration points for the same sample design with the exception of length of the tube heater.

Figure 14 shows calibration phase transitions for Bi, Hg and Yb made in the same sample design and material as the diffusion runs, with the exception that these runs were made at room temperature.

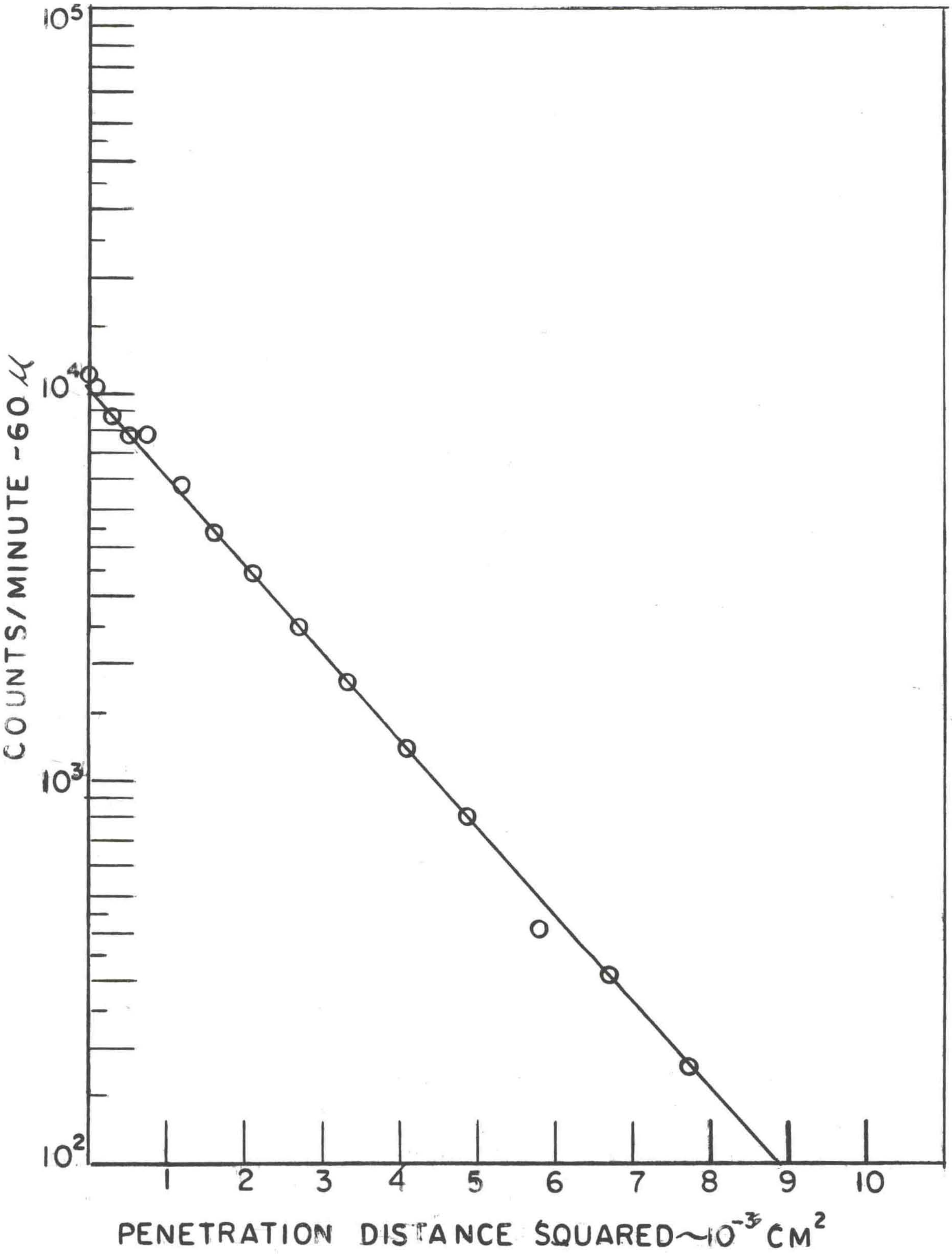


Figure 4. Solute Penetration Curve, Sample No. 59--
Annealed at 24 kb. pressure and 713°K for 3.6 X 10^3 sec

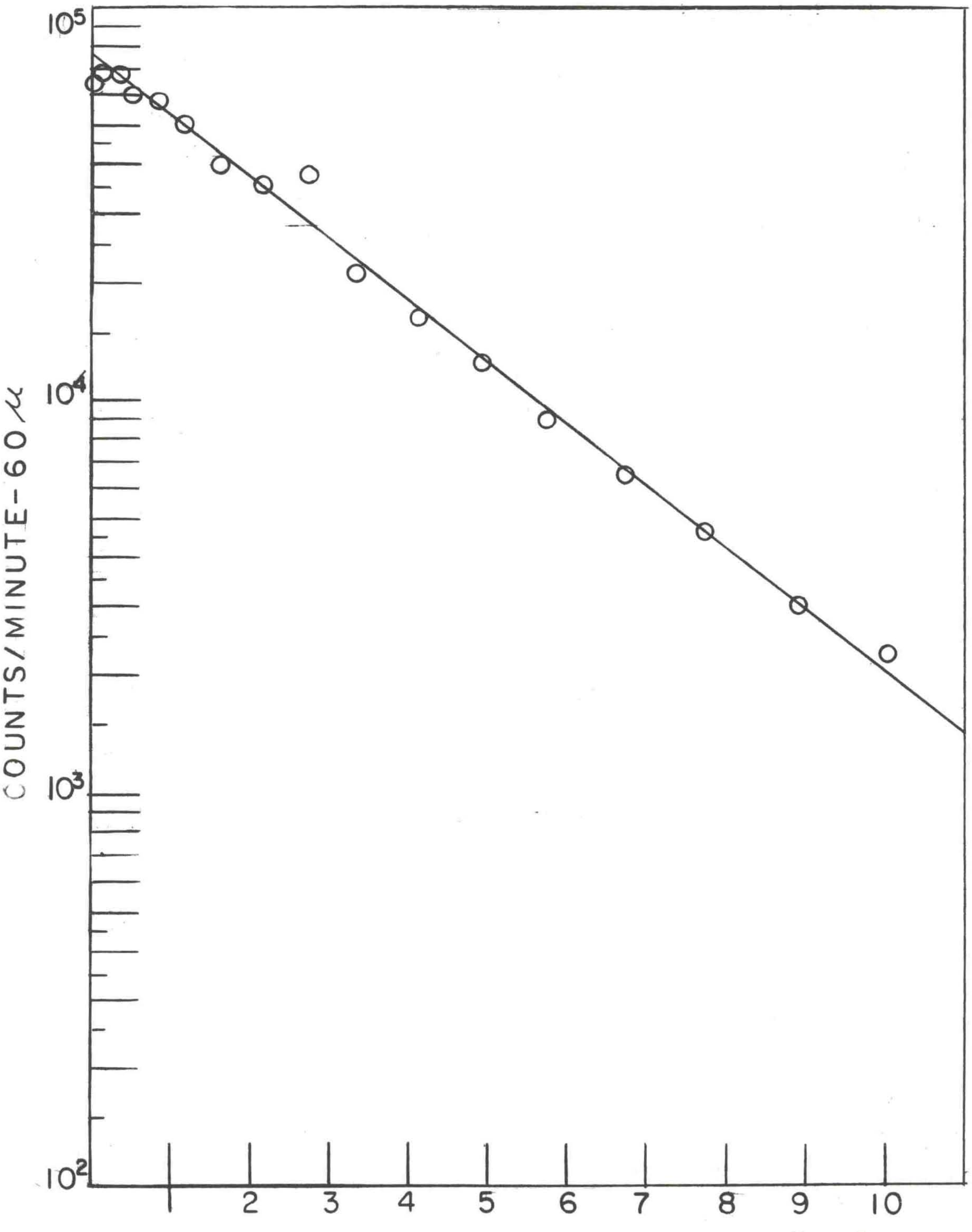


Figure 5. Solute Penetration Curve, Sample No. 68--
Annealed at 24 kb. pressure and 763°K for 3.18 X 10^3 sec

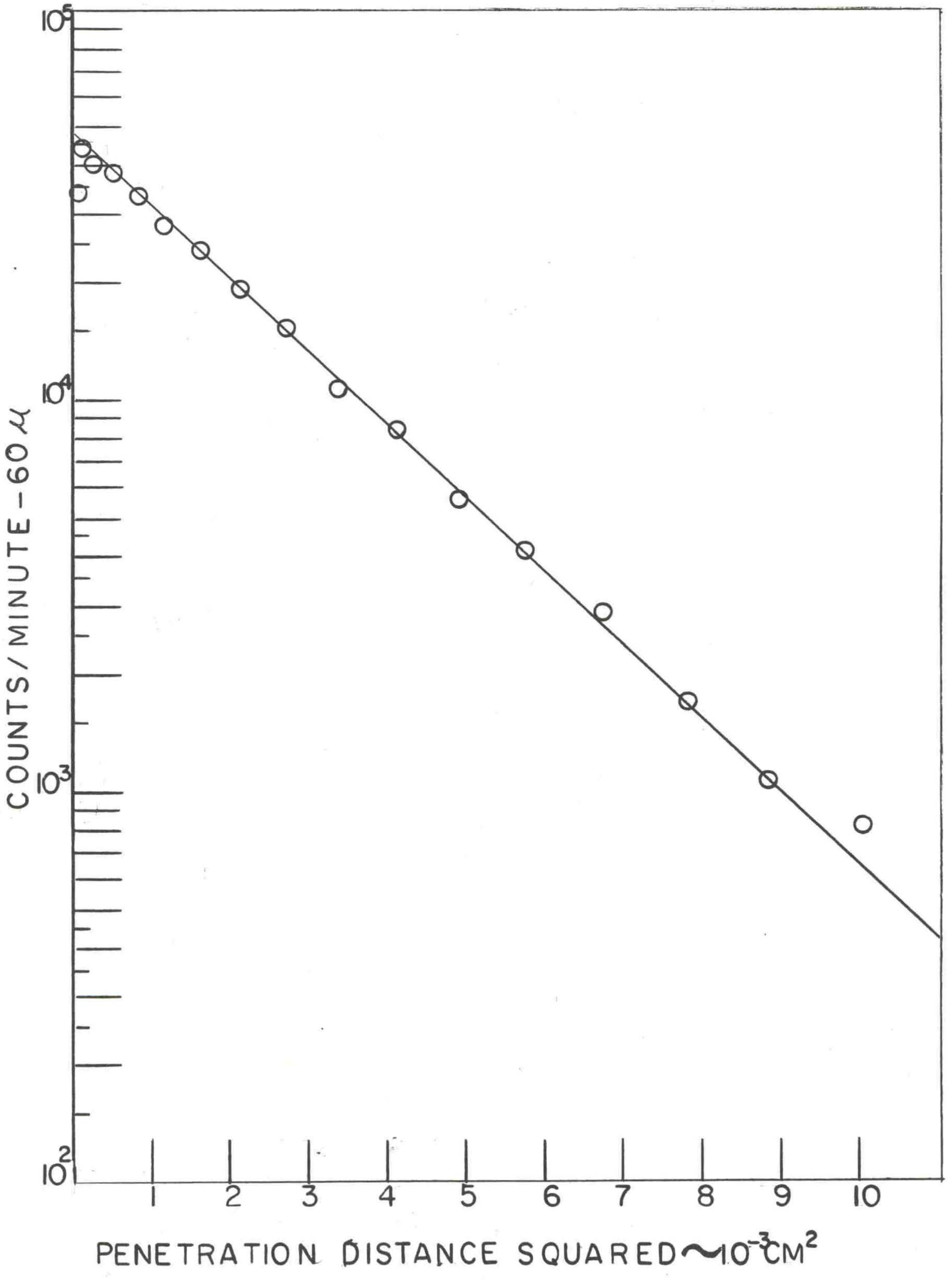


Figure 6. Solute Penetration Curve, Sample No. 72--
Annealed at 24 kb. pressure and 625°K for 4.4 X 10^4 sec

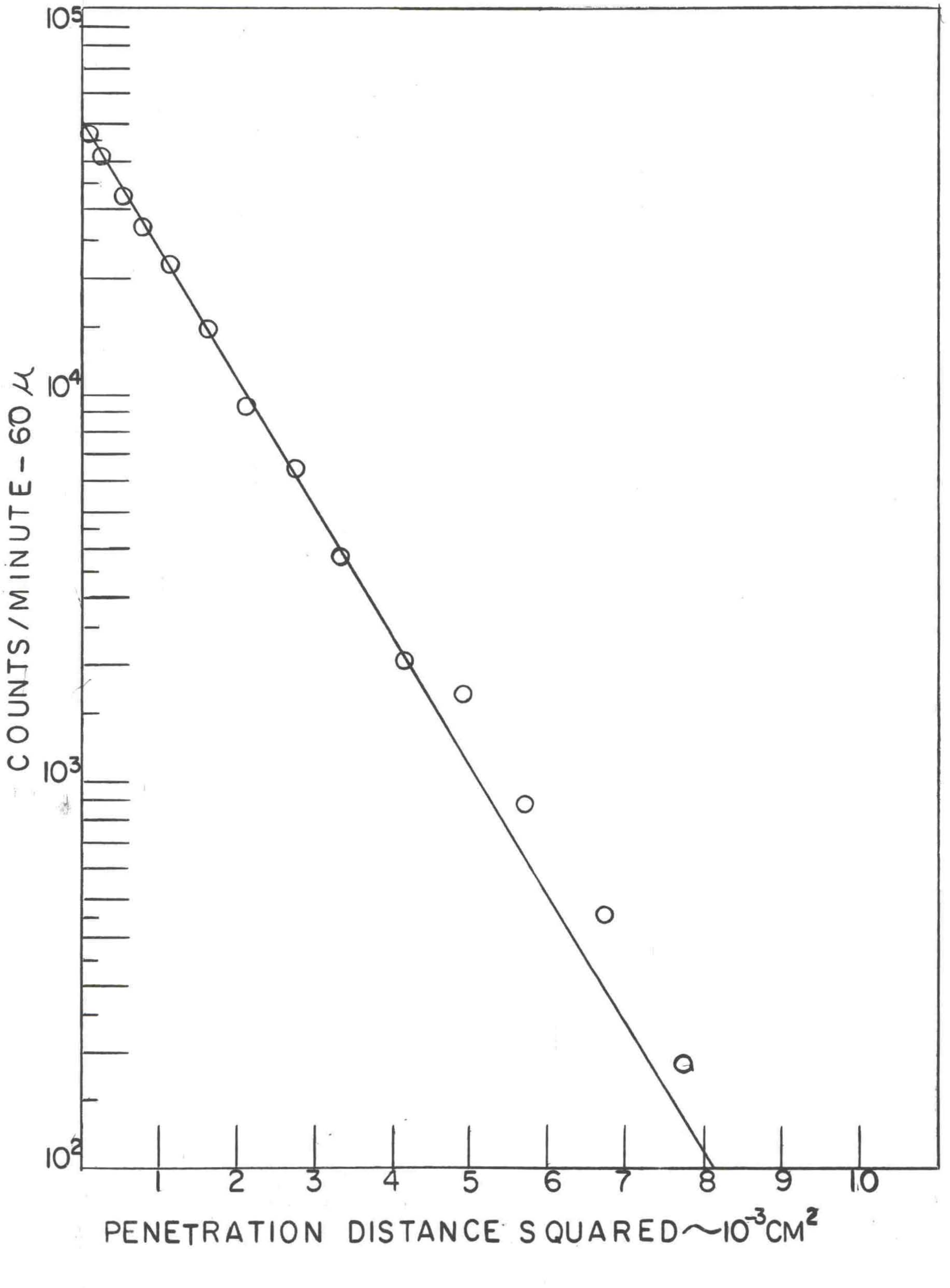


Figure 7. Solute Penetration Curve, Sample No. 77--
Annealed at 24 kb. pressure and 590°K for 5.13 X 10^4 sec

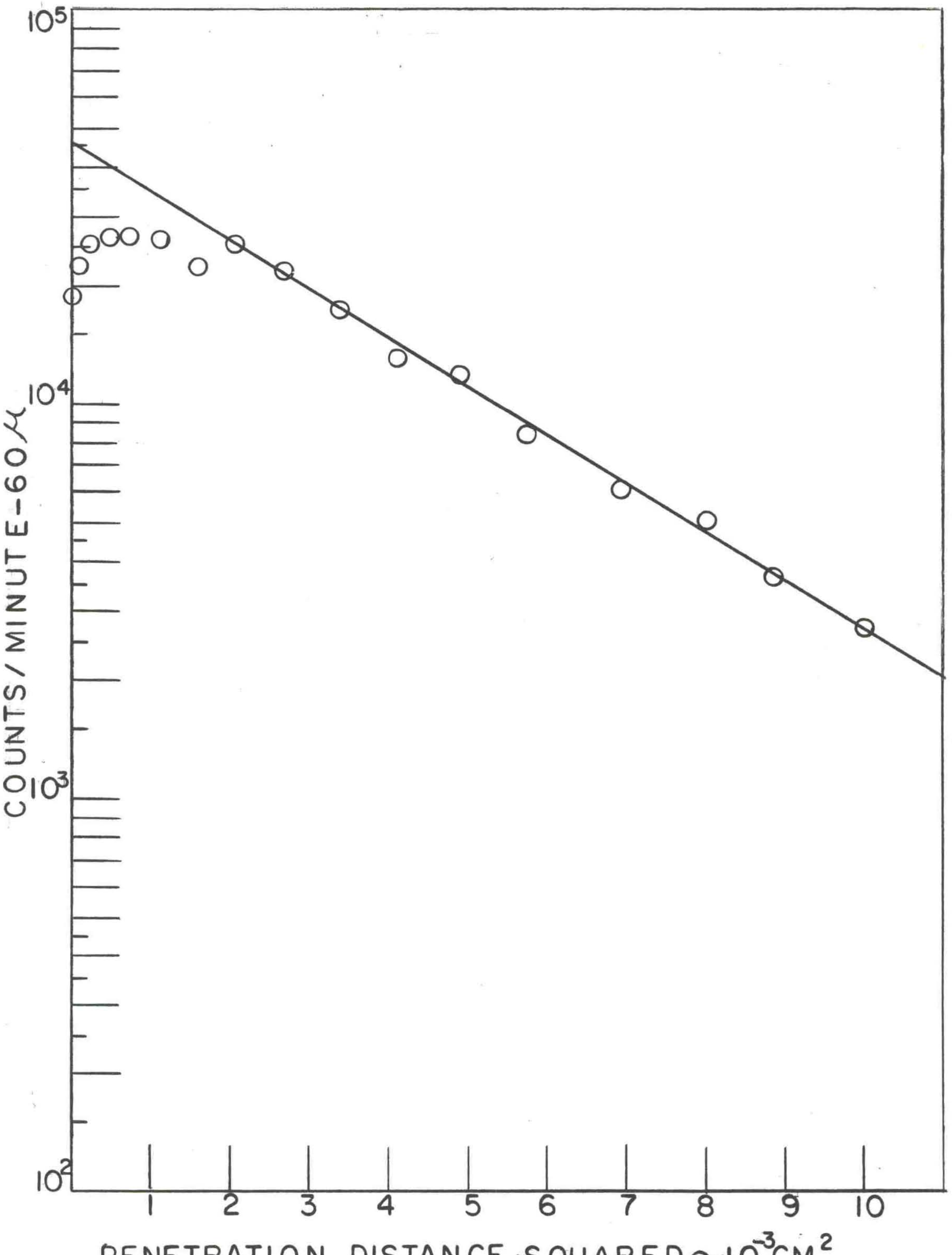


Figure 8. Solute Penetration Curve, Sample No. 88--
Annealed at 24 kb. pressure and 694°K for 1.63 X 10^4 sec

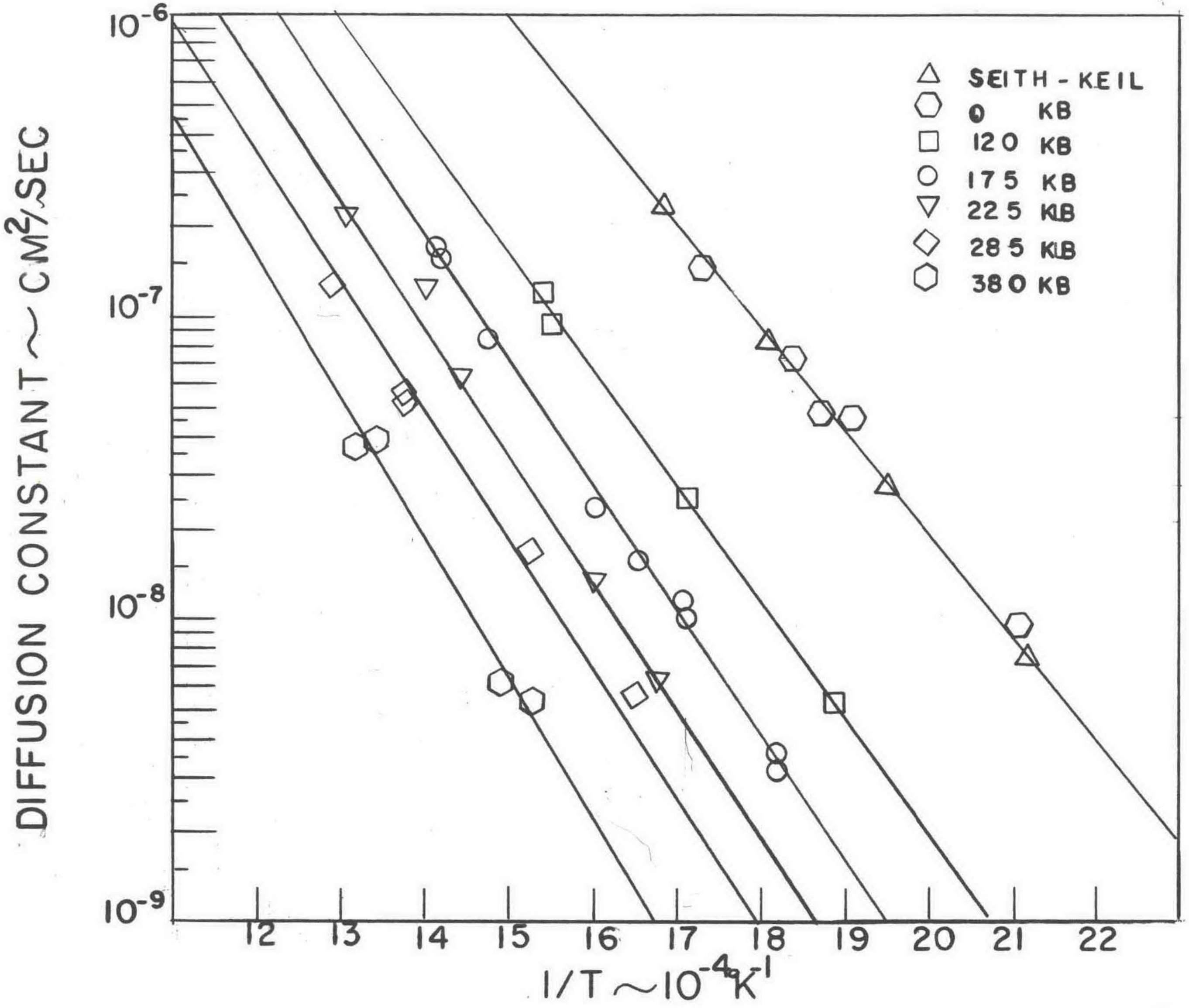


Figure 10. Plot of The Diffusion Constant versus The Reciprocal of The Anneal Temperature--Plotted in Isobars

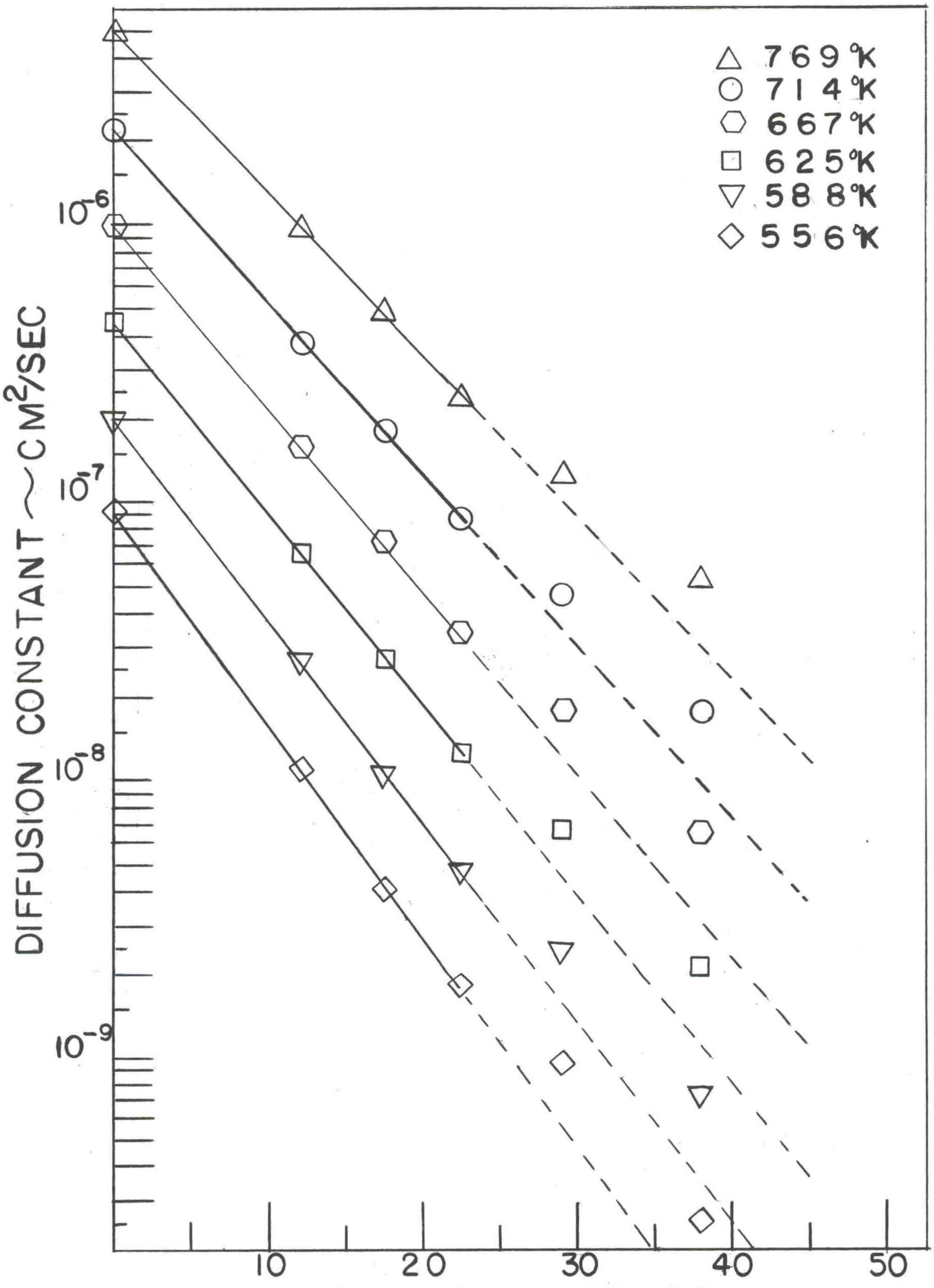


Figure 11. Plot of The Diffusion Constant as a Function of Pressure--Plotted in Isotherms

TABLE 1

CALCULATED ACTIVATION ENERGIES, ACTIVATION VOLUMES AND RELATED QUANTITIES

Pressure in kilobars	0	12.0	17.5	22.5	28.5	38.0
Activation energy $\sim$ kcal/mole, determined graphically	15.83	18.45	19.10	19.30	19.60	21.04
Activation energy $\sim$ kcal/mole, determined by least squares	15.20*	17.18	18.66	19.44	17.54	20.59
$D_o \sim cm^2/second$, determined graphically	0.160	0.165	0.135	0.081	0.048	0.051
$D_o \sim cm^2/second$, determined by least square	0.075*	0.087	0.103	0.086	0.009	0.039
Diffusion constant at the melting point $\sim 10^{-6} cm^2/sec.$	2.70	2.50	2.48	2.45	2.42	2.50
Diffusion constant 10^9 at 352 $^oC \sim cm^2/second$	460.	66.0	28.0	13.5	6.7	2.2
Melting temperature of Pb, ^oK	600	689	728	765	803	865
Geometrical constant (d) in Dushman Langmuir equation determined from experimental values of the activation energy Å	3.08	3.10	2.64	1.98	1.56	1.55
Activation energy $\sim$ kcal/mole, self diffusion **	24.8	26.0			26.0	27.0

* Seith and Keil[4]
** Hudson and Hoffman[6]

TABLE 2

CALCULATED ACTIVATION VOLUMES

Temperature ^{o}K	Activation Volume ΔV_{α}, cm^3/mole	Ratio Activation Volume/Molar Volume
769	8.51	.454
725	8.28	.438
667	8.31	.442
625	8.14	.432
588	8.11	.431
556	8.06	.428
769*	13.0*	.715*
525*	10.4*	.572*

*Hudson and Hoffman[6] (values for self-diffusion)

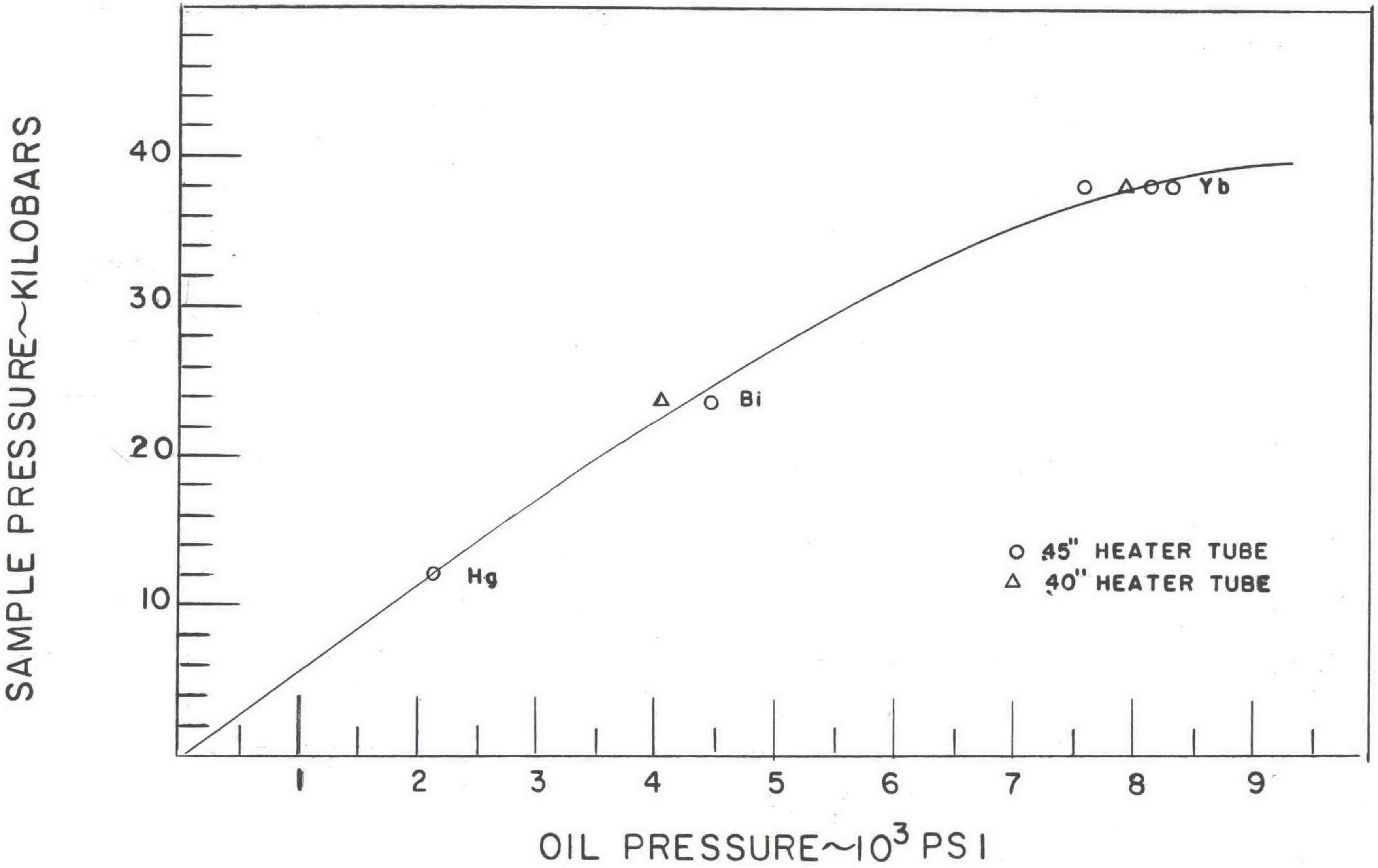


Figure 13. Calibration Curve for The Sample Geometry of This Investigation, Using The NaCl Pressure Scale

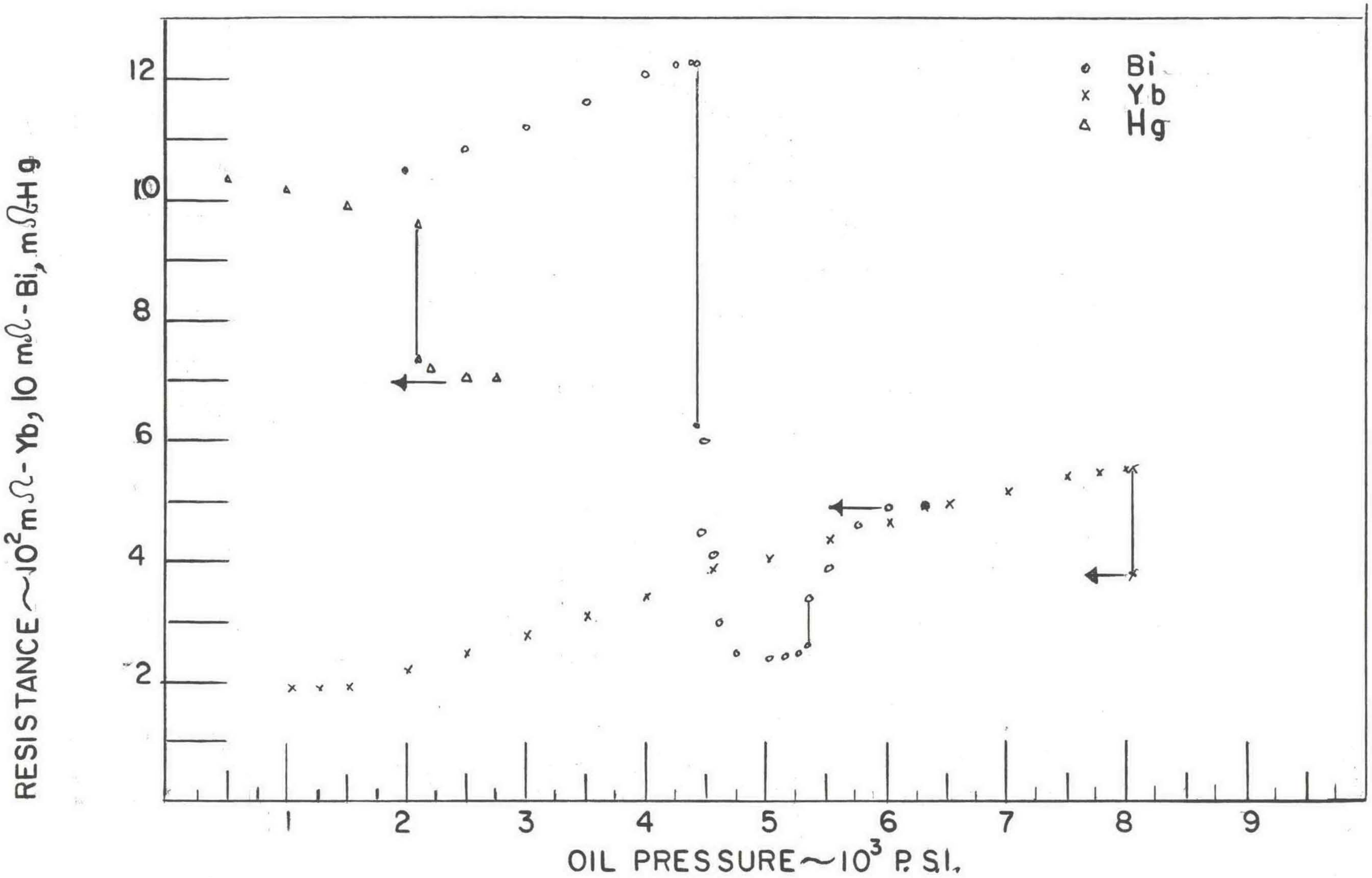


Figure 14. Calibration Phase Transitions for Bi, Hg, and Yb (for increasing pressure)

DISCUSSION

1. General

The data obtained from the first forty runs, with the exception of those made at ambient pressure, were rendered essentially useless by the large amount of experimental scatter. It is believed that this scatter came about from three primary causes:

1. The error in temperature measurement due to not having the thermocouple in contact with the sample crystal.
2. The lack of correlation between the oil pressure to the rams and the actual pressure applied to the crystal due to a lack of uniformity in sample design.
3. Too short of anneal times due to a lack of knowledge of the order of magnitude of the diffusion constant at high pressures.

In the later runs, the uncertainty in the temperature of the anneal was reduced to an estimated plus or minus 5 C^{o} by improvements in the sample design (Figure 3) and temperature regulating device. The effect of the sample design on the pressure calibration is seen in Figure 13. The change in calibration here is caused by samples that differed only in length of tube heater. This problem was a result of the apparently high compressibility of the pressure transmitting media. In later runs care was taken to insure uniformity of sample design.

If the anneal time is too short, the uncertainty in the diffusion constant is high due to the extraneous diffusion that occurs during storage (see Figure 9). This was the case for many of the early samples. Figures 4 through 8, on the other hand, show that the penetration in the latter runs was sufficient to render the extraneous diffusion negligible.

The high degree of consistency of the plotted and tabulated results indicate that the major sources of error were satisfactorily overcome.

2. Activation Energies and Activation Volumes

Figure 10 shows that our system has a temperature dependence of the type suggested by equation 6 for all pressures covered in this study. The values for the activation energies (Q) given in Table 1 tend to increase with increasing pressure from 15.8 kcal/mole at atmospheric pressure to 21.0 kcal/mole at 38 kb. This is in accord with the interpretation of Q being an energy of activation, it being expected that energy required to form an activated state would increase with pressure.

Figure 11 shows that, for our system, the term ΔV_a defined by equation 10 is independent of pressure for pressures below 23 kilobars; but it tends to decrease at higher pressures. There is not enough data at these higher pressures to be certain that this effect is real. However, Hudson and Hoffman[6] reported a similar effect in the case of self-diffusion in lead. For their pressure calibration, Hudson and Hoffman apparently used Bridgman's resistance scale which assigns much higher pressures to the calibration transitions than does Decker's[38] sodium chloride scale, which was used in this study. However, the reported effect persists, though to a lesser degree, when corrections are made for the difference in calibration.

Values of ΔV_a for pressures below 23 kilobars show a tendency to increase with increasing temperature (Table 2) varying from 8.058 cm^3/mole at 536°K, to 8.506 cm^3/mole at 769°K. Assuming that both pressure and temperature effects are real, it would appear that factors that tend to loosen the lattice (i.e., increasing temperature and decreasing pressure) increase ΔV.

3. Diffusion Mechanism

It has been generally supposed that silver diffuses through lead by an interstitial mechanism. The low activation energies and activation volumes, as well as the large diffusion constants obtained in this study, tend to support this supposition.

Stern and Eyring[25] calculated that the pressure required to reduce the diffusion constant by a faction of two for lead at 560°K would be of the order of 11 kb., assuming that the increase in volume required for an impurity jump resulted in an equivalent increase in the total volume of the system. On the other hand, if the increase in volume is absorbed by the surrounding lattice with no increase in the total volume of the system, the pressure required to reduce the diffusion constant for lead at 560°C by a factor of two is the order of 2.6 kb. Figure 11 of the present paper shows that at 555°C a pressure of 4 kilobars is required to reduce the diffusion constant by a factor of two. If we take Eyring's calculations at face value, the present study would indicate that most of the increase in volume is absorbed by the lattice, and a smaller part results in an increase in the total volume of the system.

4. Correlation of Results With Theoretical Equations

The results of plotting log D vs T_m/T (Figure 12) appear to support, or at least fail to refute, a relation of the form Q/T_m=constant $\approx$26.4 cal/mole °K (equation 9). This agrees with the work of Nachtrieb and Rice,[5,9] and disagrees with that of Hudson and Hoffman.[6] Hudson and Hoffman reported that when data for self-diffusion in lead was plotted in this manner, all points lay along a single line for pressures below 10 kilobars, but tended to lower values of D at higher pressures. This trend to lower values of D was not observed in the present investigation. Because the experimental error appears to be much less for the present study than for either of the former, and because the diffusion constant at the melting point (Table 1) appears to be very nearly a constant, we would have to conclude that an equation of the form of equation 9 is at least approximately valid for diffusion of Ag in lead at pressures below 38 kilobars.

In order to test the Dushman-Langmuir equation for D_o (equation 8), the geometric constant d was calculated from the experimentally determined values of the activation energies. Table 1 shows that although these values are of the same order of magnitude as the distance between interstitial sites (3.48 Å), they vary by a factor of two over the pressure range of this study. Since a geometric factor will not change this much over the pressure range investigated, it is apparent that D_o must depend on some parameter not explicitly contained in equation 8.

Another equation for D_o has been proposed by Zener[39] who treated the impurity jump as an equilibrium thermodynamic process:

$$D_o = \gamma a^2 \nu \exp\left(\frac{\Delta S}{R}\right) \tag{11}$$

In this equation, a is the lattice constant, ν is a characteristic frequency which is not well defined but usually taken to be the Debye frequency, γ is a geometric constant equal to 1 for both interstitial and vacancy diffusion in a fcc lattice, and ΔS represents the entropy increase of the system due to adding one mole of activated complexes.

Using equation 11 and a known value of the isothermal compressibility (K), it can be shown that, to first order:

$$\frac{D_o(P)}{D_o(0)} = \left(1 - \frac{K}{3}P\right)^{3/2} \exp\left(\frac{\Delta S(P) - \Delta S(0)}{R}\right) \tag{12}$$

Using the graphically determined values of D_o, along with Zener's expression for ΔS at zero pressure:

$$\Delta S = \lambda \beta \frac{Q}{T_m} \tag{13}$$

(Where β is a dimensionless quantity equal to .5 for lead; and λ is an empirical constant equal to .55 for vacancy diffusion in a fcc lattice, and equal to 1 for interstitial diffusion), the following values are obtained:

Pressure Kilobars	$\Delta S(P)-\Delta S(0)$ cal/mole °K	$\Delta S(P)$ * cal/mole °K	$\Delta S(P)$ ** cal/mole °K
0.0	0.0	7.26	13.22
12.0	+ 0.03	7.29	13.25
17.5	- 0.27	6.99	12.95
22.5	- 1.24	6.02	11.98
24.5	- 2.01	5.25	11.21
38.0	- 2.08	5.18	11.14

* vacancy mechanism
** interstitial mechanism

Of particular interest would be a study of chemical or self-diffusion for a solvent metal whose melting temperature decreases with pressure. The results of the present investigation would seem to predict an increase in diffusion rate with pressure for such a system.

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THE EFFECT OF HYDROSTATIC PRESSURE ON THE CHEMICAL DIFFUSION RATE OF SILVER INTO LEAD

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