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EFFECT OF HYDROSTATIC PRESSURE ON THE VACANCY-IMPURITY  
INTERACTION IN PURE METALS

by

Frederick Ramon Bonanno

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A Dissertation Submitted to the Faculty of the  
DEPARTMENT OF METALLURGICAL ENGINEERING  
In Partial Fulfillment of the Requirements  
For the Degree of  
DOCTOR OF PHILOSOPHY  
In the Graduate College  
THE UNIVERSITY OF ARIZONA

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THE UNIVERSITY OF ARIZONA

GRADUATE COLLEGE

I hereby recommend that this dissertation prepared under my direction by Frederick Ramon Bonanno entitled Effect of Hydrostatic Pressure on the Vacancy-Impurity Interaction in Pure Metals be accepted as fulfilling the dissertation requirement of the degree of Doctor of Philosophy

Carl E. Tomizuka  
Dissertation Director

Aug. 17, 1964  
Date

After inspection of the dissertation, the following members of the Final Examination Committee concur in its approval and recommend its acceptance:\*

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27 Aug 1964

\*This approval and acceptance is contingent on the candidate's adequate performance and defense of this dissertation at the final oral examination. The inclusion of this sheet bound into the library copy of the dissertation is evidence of satisfactory performance at the final examination.



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## ABSTRACT

The rate of self-diffusion in silver and the rate of diffusion of indium-114 and of antimony-124 in silver were measured at 910°C and at hydrostatic pressures up to 9.00 kilobars by the radioactive tracer - lathe-sectioning technique. The diffusion rates were observed to decrease with increasing pressure and the activation volumes were determined to be 9.6 cm<sup>3</sup>/mole for self-diffusion, 9.1 cm<sup>3</sup>/mole for indium-114, and 8.5 cm<sup>3</sup>/mole for antimony-124. Thus the activation energies for self-diffusion and for electropositive impurity diffusion in silver should increase by approximately 0.2 kcal/mole per kilobar. It was found that the difference in these values of activation volume could be explained by the Lazarus theory of impurity diffusion as modified by Le Claire. The limiting source of error was found to be the accuracy of the determination of the temperature of the diffusion anneal at high pressures.

## INTRODUCTION

Current developments in high-pressure techniques make it possible to perform prolonged diffusion runs at high hydrostatic pressures and at high temperatures. As a result, pressure effects on the self-diffusion rate have been successfully measured in some noble metals and alloys. These results along with the earlier work by Nachtrieb and his co-workers on the pressure effect on low melting point crystals such as sodium,<sup>1</sup> phosphorus,<sup>2</sup> and lead<sup>3</sup> presented a different viewpoint from which the point defects in metals can be investigated. The concept of activation volume is frequently employed to describe the pressure-sensitive phenomena of this type. For self-diffusion the activation volume is interpreted as the measure of the volume of a vacancy. The difference between the atomic volume and the activation volume per atom gives the amount of relaxation present around a vacancy in an actual solid. For impurity diffusion the concept of activation volume can be utilized as a measure of the impurity ion-vacancy interaction and of the difference between this interaction and that between the solvent ion and the vacancy.

It was proposed by Lazarus<sup>4</sup> that the observed difference between the activation enthalpy of self-diffusion

and that of impurity diffusion in the same matrix (most frequently, noble metals) can be described in terms of the screening potential in the neighborhood of the impurity atoms. This model was later modified by Le Claire<sup>5</sup> to yield consistently good agreement with the experimental results. The concept of screening must then offer an adequate description for the pressure effect on the diffusion rates of foreign atoms in an otherwise pure crystal. The purpose of this investigation was to test the Lazarus-Le Claire theory by determining the effect of hydrostatic pressure on the diffusion of indium-114 and of antimony-124 in silver and by comparing this effect to that on self-diffusion in silver.

## EXPERIMENTAL

Single crystals of 99.99% silver (Handy and Harman) were grown in an evacuable, vertical crystal-growing furnace similar to that described by Lazarus and Chipman.<sup>6</sup> Ingots were cast in high-purity graphite crucibles which had been boiled in aqua regia followed by repeated boiling in distilled water. The single crystals were prepared in a vacuum of the order of  $10^{-6}$  torr and degassed by repeated cycling to 1200°C. Afterwards the single crystals were cut, polished, and etched to a final diameter of 0.40 inch and a height of 0.20 inch.

Silver-110, silver-111, indium-114, and antimony-124 radioisotopes were obtained from the Oak Ridge National Laboratory and were electroplated on the well-annealed specimens. It was estimated that the thickness of the plated layer was less than 100 angstroms. (Details of electroplating are in Appendix A.)

A gas pressure system similar to that of Goldsmith and Heard<sup>7</sup> was used to obtain pressures between 1 and 9 kilobars. The pressure medium was Linde high-purity argon (99.995%). The pressure, measured with a manganin gauge calibrated at the freezing pressure (7640 bars) of mercury at 0°C, was maintained constant to within  $\pm 10$  bars during heating, the diffusion anneal, and until 600°C during the quench.

The specimen was placed in contact with the thermocouple within a platinum-wound lavite furnace similar to that described by Albrecht and Tomizuka.<sup>8</sup> The furnace assembly had previously been cleaned by baking in vacuo at 1000°C for 24 hours. In order to prevent any contamination (especially by oil) the specimen and furnace were handled with gloved hands.

The temperature was controlled manually to within  $\pm \frac{1}{2}^{\circ}\text{C}$  through the use of a chromel-alumel thermocouple so chosen because of its small pressure effect as reported by Bundy.<sup>9</sup> The hot junction of the thermocouple consisted of a 3 mil platinum disk  $\frac{3}{8}$  inch in diameter to which B and S No. 24 chromel and alumel wires had been spot-welded. A new thermocouple was used for each specimen. The length of each diffusion run was limited to  $2\frac{1}{2}$  hours.

Each thermocouple was calibrated after the diffusion anneal against new chromel and alumel from the same spools which were spot-welded to the hot junction of the specimen thermocouple. Appropriate portions from the spools were calibrated against a standard platinum-platinum 10% rhodium thermocouple which had previously been calibrated against the melting points of several NBS metals.

After the diffusion anneal each specimen was sectioned on a precision lathe according to the standard technique described by Tomizuka.<sup>10</sup> A RIDL Model 34-12B

400-channel analyzer and a NaI(Tl) well-type scintillation counter were used to determine the gamma activity of each section. (Photographs and diagrams of equipment are in Appendix B.)

## RESULTS

Fifteen successful diffusion runs were performed at high pressures. Typical penetration plots are shown in Fig. 1. Effective diffusion time was calculated including the warm-up and cool-down corrections after which diffusion coefficients were determined by the method of least squares. The diffusion coefficients at each temperature,  $D_T$ , together with the temperature-corrected value,  $D_{906}$ , are given in Table I. The pressure dependence of the diffusion coefficients is shown in Fig. 2.

## DISCUSSION

Diffusion coefficients may be normalized by the relation

$$D_{T_1} = D_{T_2} \exp \left[ - \frac{H}{R} \left( \frac{T_2 - T_1}{T_1 T_2} \right) \right] ,$$

where  $D_{T_1}$  and  $D_{T_2}$  are the diffusivities at temperatures  $T_1$  and  $T_2$ , respectively, and  $H$  is the enthalpy of activation at atmospheric pressure. All the results obtained were normalized to 906°C. Experimental results indicated that the entire emf changes of the thermocouple caused by the high temperature-high pressure took place shortly after the beginning of each run. In determining the actual temperature of the diffusion anneal, the temperature correction was applied accordingly.

It is believed that the limiting source of error in any experiment of this type is the measurement of temperature. In order to make an attempt to reduce this error special care was taken in handling the furnace to prevent contamination and high-purity argon was used as the pressure medium. The result of these precautions was a slight reduction in the magnitude of the emf changes at high

temperature-high pressure from that found on thermocouples used earlier in the course of this work when these precautions were not taken.

The diffusion coefficient  $D$  can be expressed as

$$D = \gamma a^2 \nu f \exp \frac{-\Delta G}{RT} ,$$

where  $\gamma$  is a numerical constant of order unity depending on lattice geometry;  $a$ , the lattice parameter;  $\nu$ , a vibration frequency;  $f$ , the correlation factor; and  $\Delta G$ , the Gibbs free energy change associated with diffusion. It is convenient to consider pressure effects in terms of an activation volume  $\Delta V$  which is defined as

$$\Delta V = \left( \frac{\partial \Delta G}{\partial P} \right)_T .$$

Then the activation volume for diffusion processes can be expressed as

$$\begin{aligned} \Delta V &= -RT \left( \frac{\partial \ln D}{\partial P} \right)_T + RT \left( \frac{\partial \ln \gamma a^2 \nu f}{\partial P} \right)_T \\ &= -RT \left( \frac{\partial \ln D}{\partial P} \right)_T + RT K_T \left( \gamma_G - \frac{2}{3} \right) , \end{aligned}$$

where  $\gamma_G$  is the Grüneisen constant and  $K_T$  is the isothermal compressibility. The effect of pressure on the correlation

factor was neglected. If one uses the values of 3.3 for  $\gamma_G$  at 906°C,<sup>11</sup>  $1.6 \times 10^{-12}$  cm<sup>2</sup>/dyne for  $K_T$  at 906°C,<sup>12</sup> and the values of  $(\frac{\partial \ln D}{\partial P})_T$  from Fig. 2, the activation volumes for diffusion in silver are found to be

$$\begin{aligned}\Delta V_{\text{self}} &= 9.6 \pm 0.1 \text{ cm}^3/\text{mole} \\ \Delta V_{\text{In}} &= 9.1 \pm 0.6 \text{ cm}^3/\text{mole} \\ \Delta V_{\text{Sb}} &= 8.5 \pm 0.5 \text{ cm}^3/\text{mole} ,\end{aligned}$$

where the error limits shown are the standard deviations.

Table II gives these values as well as that of silver self-diffusion independently determined earlier by Tomizuka<sup>13</sup> with an entirely different pressure system and furnace. The result of the present work on self-diffusion in silver is in good agreement with that of the earlier work.

One approach to calculating a theoretical value of the difference between the activation volume for impurity and self-diffusion is to assume that correlation effects are independent of pressure and take the pressure derivative of the difference in activation enthalpies,  $\Delta H$ . Based on the model by Lazarus,<sup>4</sup> Le Claire<sup>5</sup> has derived an expression for this energy difference by assuming that the effect of size difference is negligible and that the energy of any configuration in the metal containing solute differs from that in the pure metal only by a term due to the interaction between the vacancy and the screened effective charge difference between solute and solvent ion cores. This interaction is

calculated in the Thomas-Fermi approximation with the vacancy regarded as a half-vacancy behaving as a point charge of  $-\frac{1}{2}e$  on each side of the migrating atom when that atom is in the saddle-point configuration. Le Claire's calculations yield

$$\Delta H = - \frac{N_0 Z e^{2\delta}}{\frac{11}{16} r} \exp \left( - \frac{11qr}{16} \right) ,$$

where  $N_0$  is Avogadro's number;  $Ze$ , the difference in charge between the solute and solvent ions;  $\delta$ , a constant dependent on  $Z$  only;  $r$ , the interatomic distance; and  $q$ , the screening parameter given by

$$q^2 = \frac{16\pi^2 m e^2}{h^2} \left( \frac{3n_0}{\pi} \right)^{1/3} ,$$

where  $m$ ,  $e$ , and  $n_0$  are the mass, charge, and number per unit volume of electrons, respectively. Differentiation yields

$$\left( \frac{\partial \Delta H}{\partial P} \right)_T = \frac{16}{11} N_0 Z e^{2\delta} \left[ \left( \frac{1}{r^2} + \frac{11q}{16r} \right) \left( \frac{\partial r}{\partial P} \right)_T + \frac{11}{16} \left( \frac{\partial q}{\partial P} \right)_T \right] \exp \left( - \frac{11}{16} qr \right) .$$

Since

$$\left( \frac{\partial r}{\partial P} \right)_T = - \frac{1}{3} K_T r ,$$

and

$$\left(\frac{\partial q}{\partial P}\right)_T = \frac{1}{6} K_T q ,$$

it follows that

$$\left(\frac{\partial \Delta H}{\partial P}\right)_T = - \frac{N_o Z e^2 \delta K_T}{44} \left(\frac{16}{r} + \frac{11q}{2}\right) \exp\left(-\frac{11}{16} qr\right) .$$

(Details of derivation are in Appendix C.)

Corless and March<sup>14</sup> evaluated the interaction energies between impurities and vacancies in a free-electron model. The result of this calculation is identical to that of Le Claire's except the factor  $\delta$  is absent in the formula calculated. Thus the resulting expression for  $\left(\frac{\partial \Delta H}{\partial P}\right)_T$  is

$$\left(\frac{\partial \Delta H}{\partial P}\right)_T = - \frac{N_o Z e^2 K_T}{44} \left(\frac{16}{r} + \frac{11q}{2}\right) \exp\left(-\frac{11}{16} qr\right) .$$

From either one of the foregoing expressions the difference in activation volumes  $\Delta \Delta V$  can be calculated by the relation

$$\left(\frac{\partial \Delta H}{\partial P}\right)_T = \Delta \Delta V (1 - \alpha T) ,$$

where  $\alpha$  is the volume expansivity. Values of  $\Delta \Delta V$  thus calculated are tabulated in Table III. The value at 906°C for

$r$  is  $2.95 \text{ \AA}$ ; <sup>15</sup> for  $q$ ,  $1.70 \text{ \AA}^{-1}$ ; and for  $\alpha$ ,  $7.97 \times 10^{-5} \text{ } ^\circ\text{C}^{-1}$ .<sup>11</sup> It can be seen that, within the experimental error and the approximation inherent in the theory, the theoretical values agree well with the experimental results.

It is possible to estimate the value of the activation enthalpy at pressure from the above relation, i.e.,

$$H_P = H_0 + \Delta V \Delta P (1 - \alpha T).$$

At  $906^\circ\text{C}$ ,  $\Delta V \Delta P (1 - \alpha T)$  is 0.21, 0.20 and 0.19 kcal/mole per kilobar, respectively for silver self-diffusion and indium and antimony diffusion. The activation enthalpy thus increases very slightly with increasing pressure. The effect of pressure is greater on the interatomic distance than on the screening radius ( $\frac{1}{q}$ ) by a factor of  $2rq$  which is approximately 10 for silver. The ion, therefore, finds itself further inside the screening potential thus requiring less energy to form a vacancy. However, due to the decrease in the interatomic distance around a saddle point with pressure, the energy to move a vacancy increases significantly to offset the change in the formation energy.

The activation volume of  $9.6 \text{ cm}^3/\text{mole}$  corresponds to 86.5 percent of the molar volume ( $11.1 \text{ cm}^3/\text{mole}$  at  $906^\circ\text{C}$ <sup>16</sup>) which implies a significantly smaller atomic relaxation

around a vacancy compared to the results obtained for gold.<sup>17</sup> Since no experimental values of the individual activation volumes for the formation and for the motion are available, the present results for silver cannot be compared adequately with a theoretical calculation of the relaxation around a vacancy. If one assumes, however, that the activation volume for the motion of vacancies in silver is similar to the value obtained for gold by Emrick,<sup>18</sup> the activation volume for the vacancy formation in silver can be estimated as 73 percent of the molar volume. This value is significantly larger than the theoretical calculation of Tewordt.<sup>19</sup>

Nachtrieb, Resing, and Rice<sup>3</sup> and Rice and Nachtrieb<sup>20</sup> showed that

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

where  $H_m$  and  $\Delta V_m$  are the enthalpy and volume change upon melting, respectively. Using 44.1 kcal/mole for  $H$ ,<sup>21</sup> 2.73 kcal/mole for  $H_m$ ,<sup>22</sup> and 0.50 cm<sup>3</sup>/mole for  $\Delta V_m$ ,<sup>23</sup> one obtains a value of 8.1 cm<sup>3</sup>/mole for  $\Delta V$  which is 16 percent smaller than the result of this investigation.

## CONCLUSIONS

This investigation has shown that (1) the activation volume for diffusion in silver is a positive quantity and, therefore, the activation enthalpy increases with increasing pressure, and that (2) the activation volume for the diffusion of electropositive impurities is less than that for self-diffusion, the difference being proportional to the difference in ionic charge. It is found that the screening model developed by Lazarus and Le Claire offers a semi-quantitative explanation of the experimental results.

Figure 1. Typical penetration plots.

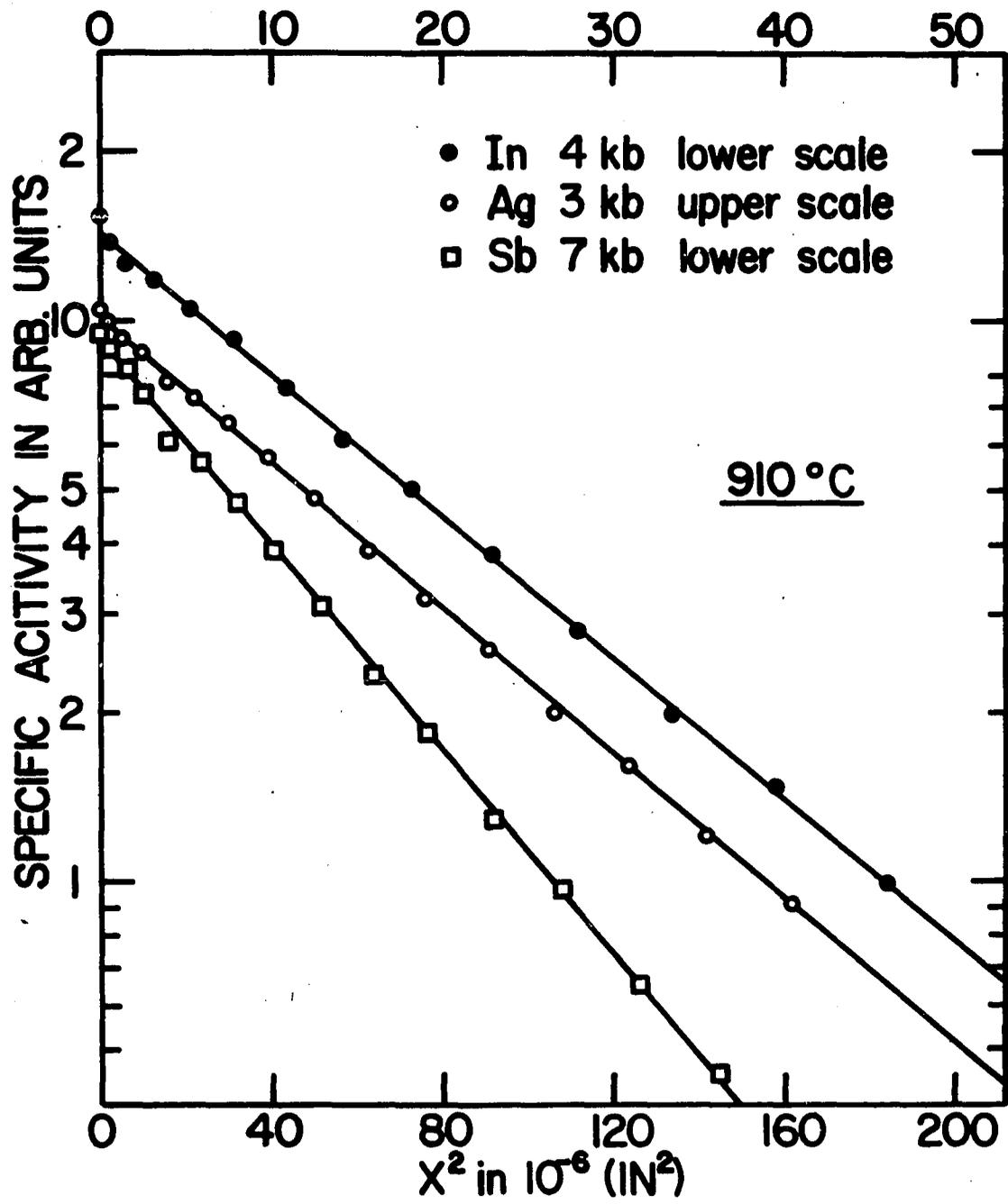


TABLE I  
Diffusion Coefficients

Tracer	Pressure (kbars)	$D_T$ ( $\text{cm}^2/\text{sec}$ )	$D_{906}$ ( $\text{cm}^2/\text{sec}$ )
Ag <sup>110</sup>	1	$3.23 \times 10^{-9}$	$2.65 \times 10^{-9}$
Ag <sup>110</sup>	3	$2.97 \times 10^{-9}$	$2.20 \times 10^{-9}$
Ag <sup>111</sup>	7	$2.22 \times 10^{-9}$	$1.49 \times 10^{-9}$
Ag <sup>110</sup>	8	$1.51 \times 10^{-9}$	$1.39 \times 10^{-9}$
Ag <sup>111</sup>	9	$1.73 \times 10^{-9}$	$1.25 \times 10^{-9}$
In <sup>114</sup>	1	$1.34 \times 10^{-8}$	$1.15 \times 10^{-8}$
In <sup>114</sup>	2	$1.28 \times 10^{-8}$	$1.06 \times 10^{-8}$
In <sup>114</sup>	4	$1.21 \times 10^{-8}$	$8.95 \times 10^{-9}$
In <sup>114</sup>	6	$8.12 \times 10^{-9}$	$6.82 \times 10^{-9}$
In <sup>114</sup>	8	$7.49 \times 10^{-9}$	$6.29 \times 10^{-9}$
Sb <sup>124</sup>	1	$1.23 \times 10^{-8}$	$1.21 \times 10^{-8}$
Sb <sup>124</sup>	3	$1.22 \times 10^{-8}$	$1.09 \times 10^{-8}$
Sb <sup>124</sup>	5	$1.05 \times 10^{-8}$	$9.60 \times 10^{-9}$
Sb <sup>124</sup>	7	$8.45 \times 10^{-9}$	$7.62 \times 10^{-9}$
Sb <sup>124</sup>	8	$7.22 \times 10^{-9}$	$6.97 \times 10^{-9}$

Figure 2. Pressure dependence of  
the diffusion coefficients.

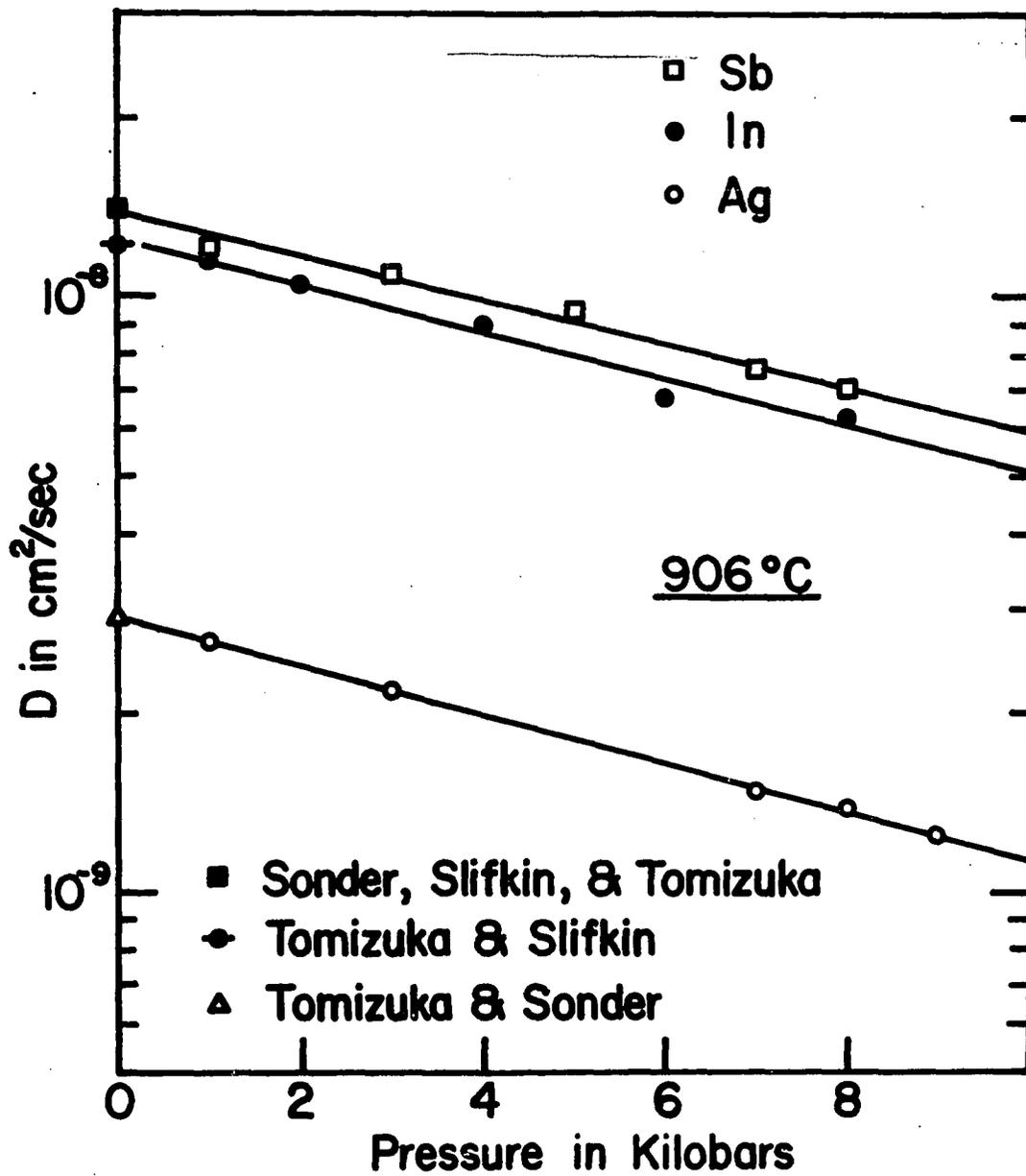


TABLE II

Activation Volumes for Diffusion in Silver

Tracer	$-RT\left(\frac{\partial \ln D}{\partial P}\right)_T$ cm <sup>3</sup> /mole	$\Delta V$ cm <sup>3</sup> /mole
Ag	9.2	9.6
Ag <sup>a</sup>	9.3	9.7
In	8.7	9.1
Sb	8.1	8.5

a: Tomizuka<sup>13</sup>

TABLE III

Comparison between  $\Delta\Delta V_{\text{exp}}$  and  $\Delta\Delta V_{\text{cal}}$ 

Tracer	$\Delta\Delta V_{\text{cal}}$ (Le Claire) cm <sup>3</sup> /mole	$\Delta\Delta V_{\text{cal}}$ (C&M) cm <sup>3</sup> /mole	$\Delta\Delta V_{\text{exp}}$ cm <sup>3</sup> /mole
In	0.3	0.5	0.5
Sb	0.5	1.0	1.1

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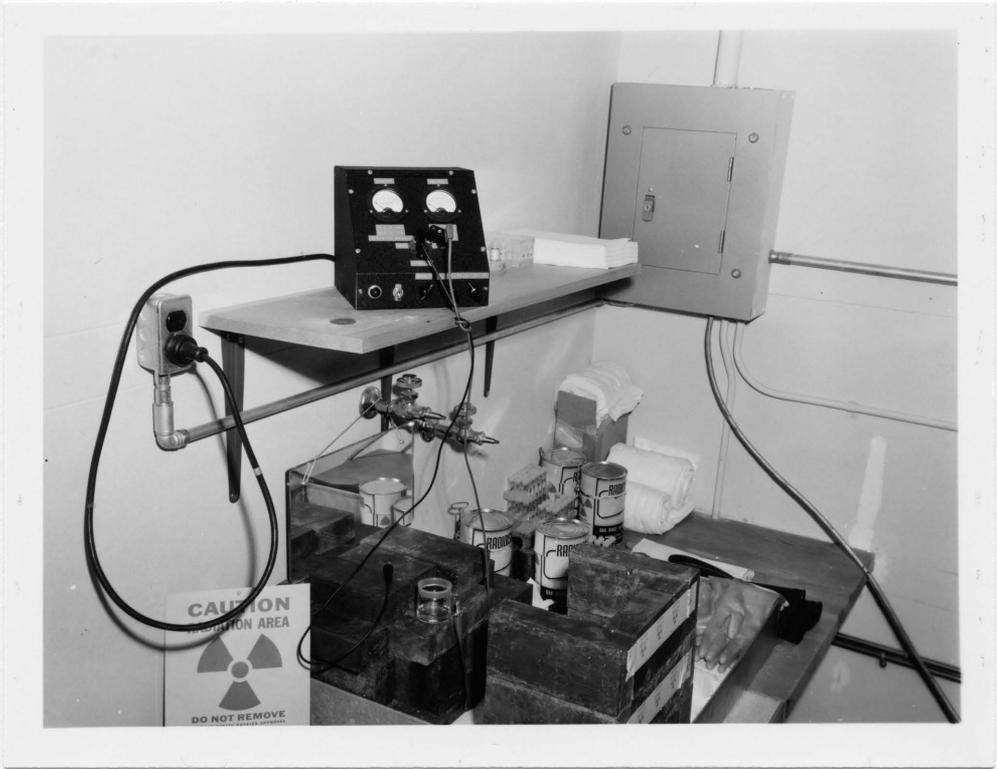
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## APPENDIX A

### Electroplating

The plating baths for the isotopes of silver and indium were prepared by adding two or three drops from the isotope solution to 25 ml of distilled water. Antimony-124 was plated from a 1M HCl bath to which a trace of the isotope had been added. In each case the anode was platinum wire formed in the shape of a flat spiral, and the cathode was the silver specimen around which platinum wire had been wound to suspend the specimen in the bath. The plating current was approximately 10  $\mu$ A for silver, 15  $\mu$ A for indium, and 0.2 A for antimony. The time varied from several seconds to 30 minutes depending upon the strength of the solution. The plating facility is shown in Fig. 3.

Figure 3. Electroplating and radioisotope  
handling facility.



## APPENDIX B

### Photographs and Diagrams of Equipment

Photographs and diagrams of equipment pertinent to this investigation are shown here in an attempt to illustrate the description given in the text.

Figure 4. Crystal-growing furnace.



Figure 5. Disassembled internal  
furnace.

Figure 6. Pressure system showing,  
from left to right, separator, small  
manganin gauge vessel, intensifier,  
and horizontal specimen vessel  
housed within the safety barricade.

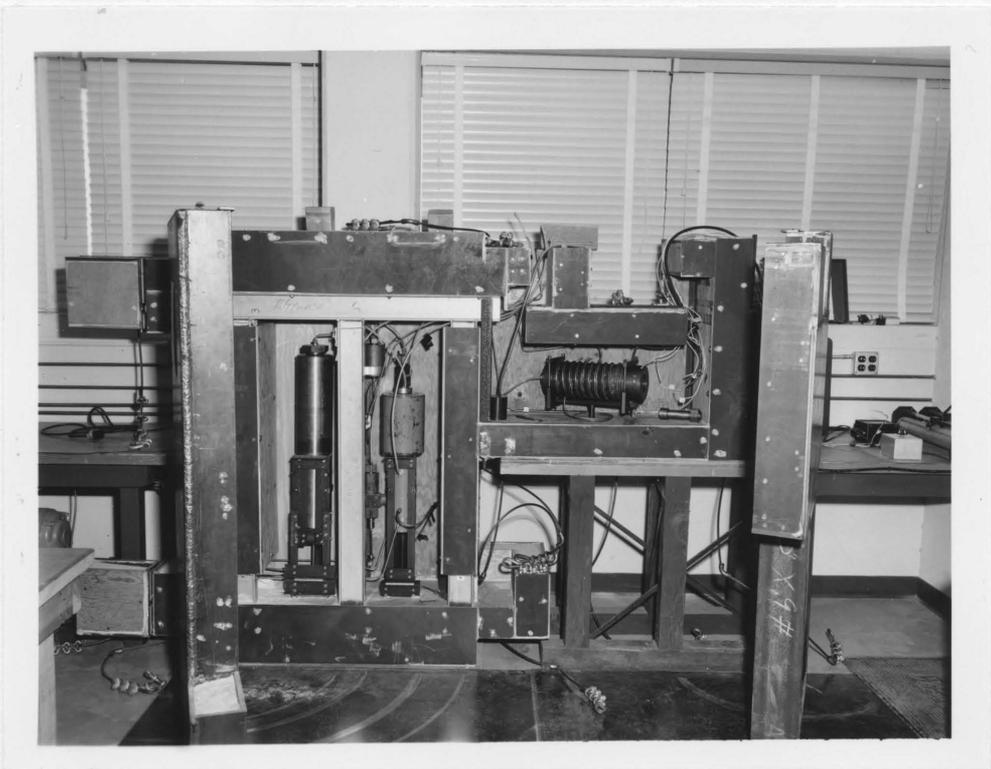
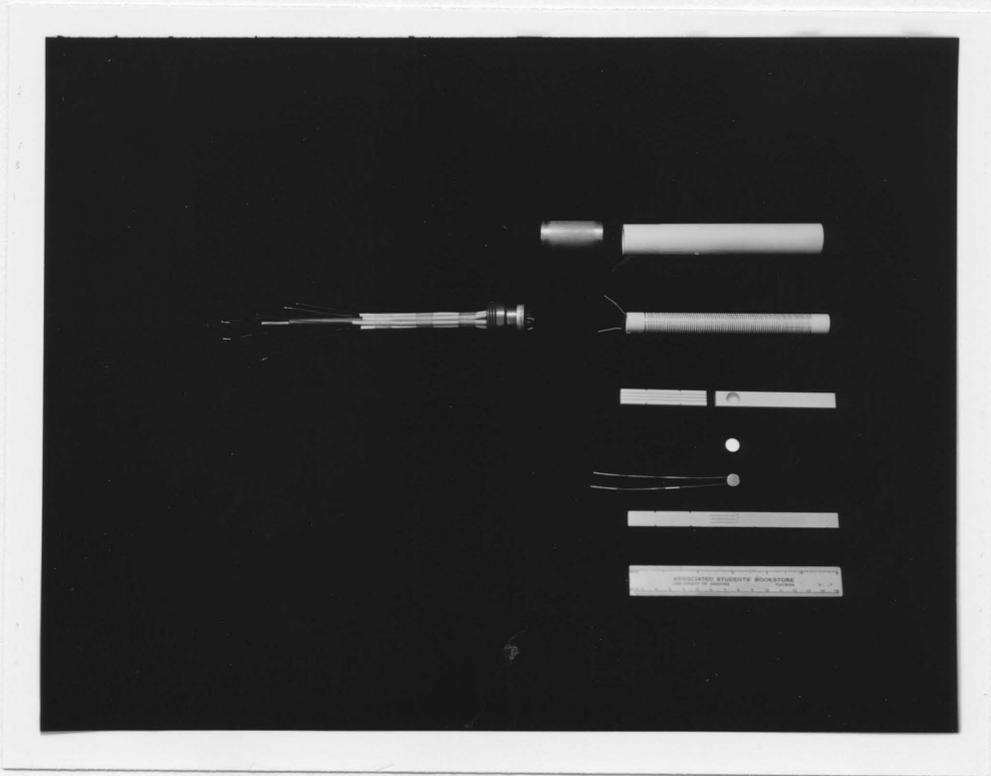
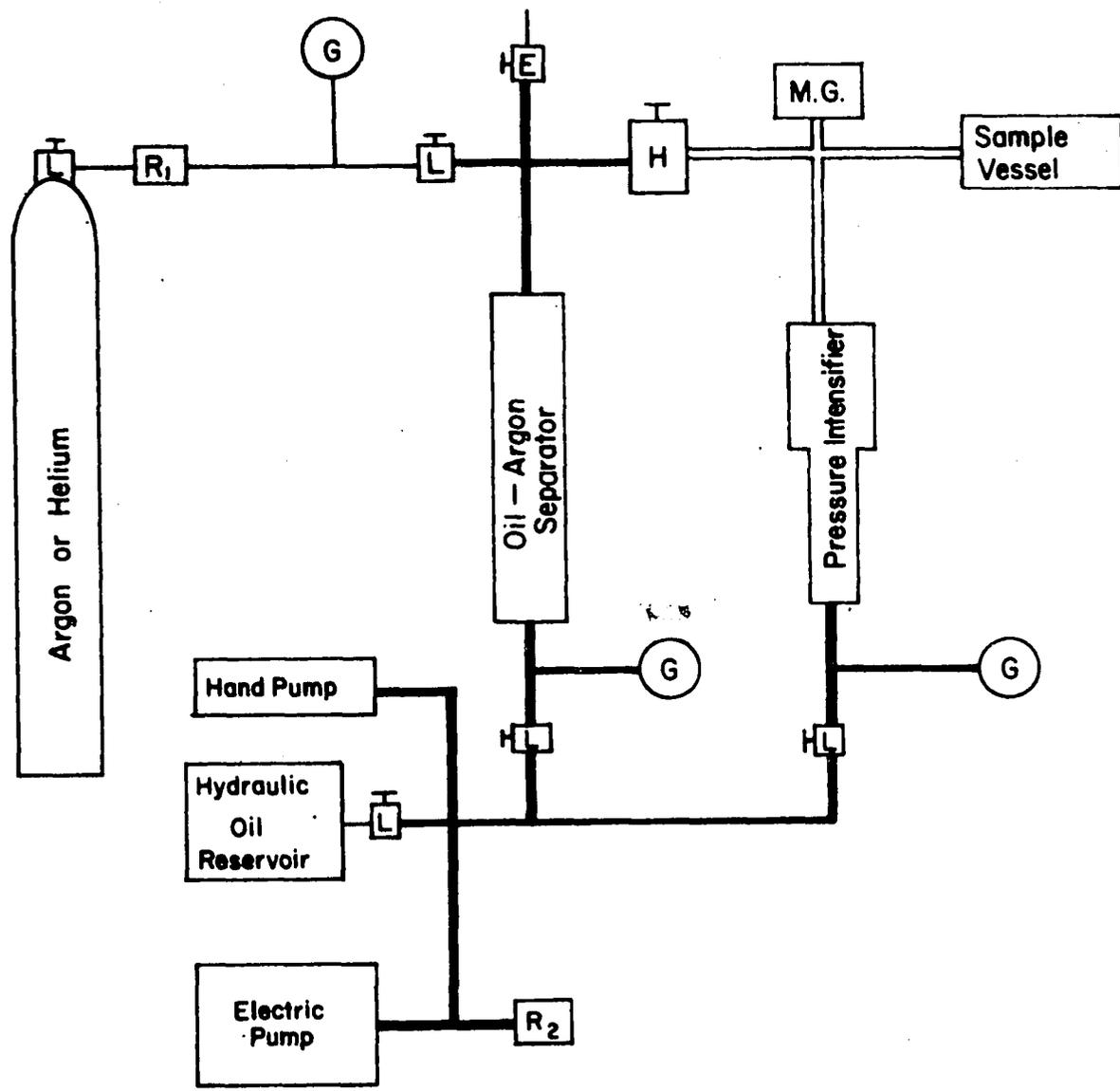


Figure 7. Schematic drawing of  
the pressure system.



- |                              |   |
|------------------------------|---|
| <b>(G)</b> Bourdon Gauge     | <b>R<sub>1</sub></b> Rupture Disk, 3500 PSI   |
| <b>M.G.</b> Manganin Gauge   | <b>R<sub>2</sub></b> Rupture Disk, 35,000 PSI |
| <b>L</b> Low Pressure Valve  | — 4,000 PSI Tubing                            |
| <b>H</b> High Pressure Valve | — 1/4" - 60,000 PSI Tubing                    |
| <b>E</b> Exhaust Valve       | ≡ 3/16" - 200,000 PSI Tubing                  |

Figure 8. Cross section of the assembled vessel and internal furnace.

- Pressure Packings**
1. Brass Ring
  2. Rubber O-Ring
  3. Steel Space Filler

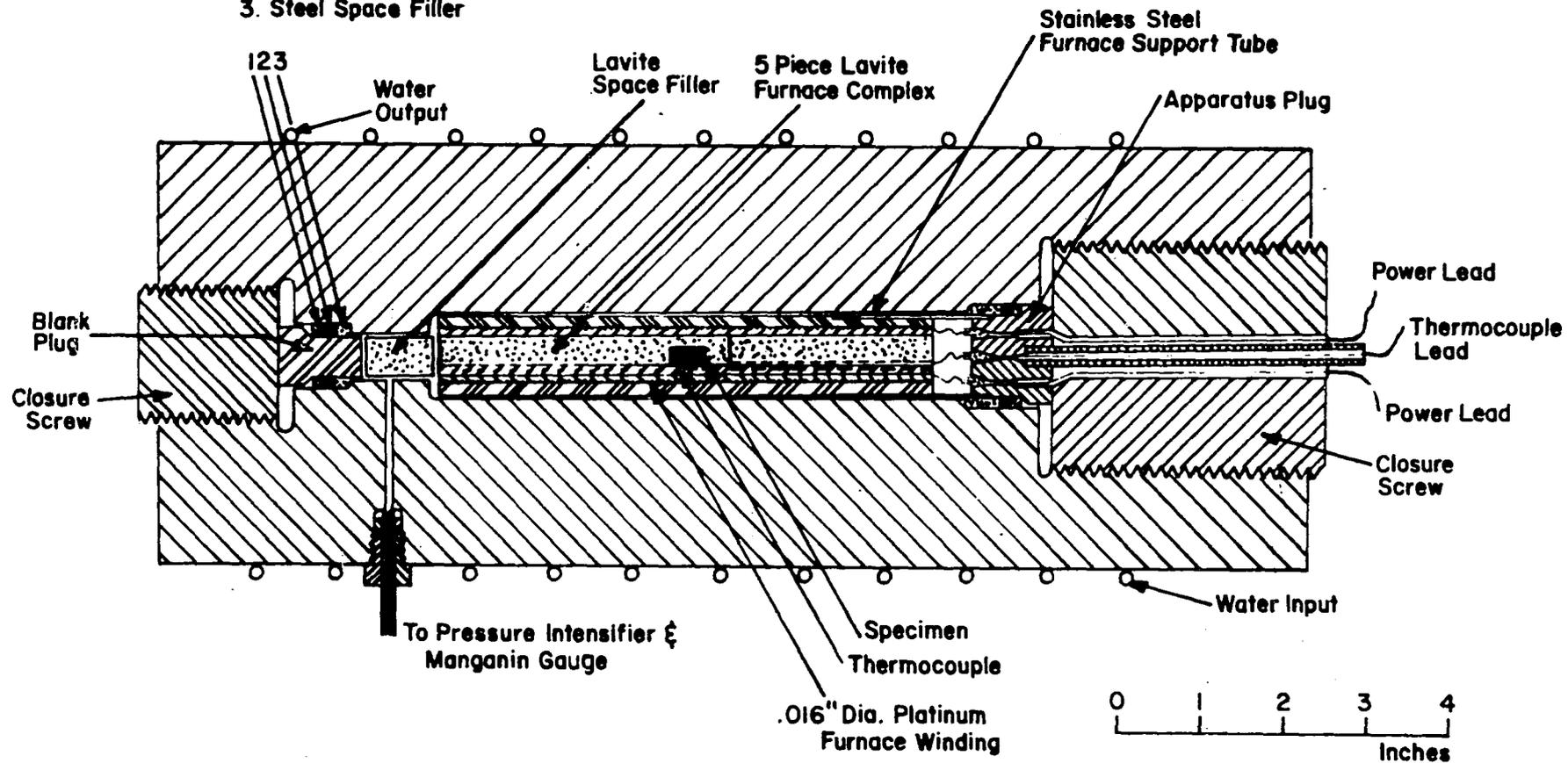


Figure 9. Temperature-control system.

Figure 10. Close-up of adjustable chuck and sectioning set-up on the precision lathe.



APPENDIX C

Derivation of  $(\frac{\partial \Delta H}{\partial P})_T$

Le Claire's expression for  $\Delta H$  is

$$\Delta H = - \frac{16N_0 Z e^2 \delta}{11 r} \exp \left( - \frac{11}{16} q r \right) .$$

Differentiation yields

$$\left( \frac{\partial \Delta H}{\partial P} \right)_T = \frac{16N_0 Z e^2 \delta}{11} \left[ \left( \frac{1}{r^2} + \frac{11q}{16r} \right) \left( \frac{\partial r}{\partial P} \right)_T + \frac{11}{16} \left( \frac{\partial q}{\partial P} \right)_T \right] \exp \left( - \frac{11}{16} q r \right) .$$

For the f.c.c. lattice,  $r = cV^{1/3}$ , where  $V$  is the volume of the cube and  $c$ , a constant, then

$$\left( \frac{\partial r}{\partial P} \right)_T = c \left( \frac{\partial V^{1/3}}{\partial P} \right)_T = \frac{1}{3} c V^{-2/3} \left( \frac{\partial V}{\partial P} \right)_T = - \frac{1}{3} c V^{1/3} K_T = - \frac{1}{3} K_T r ,$$

and

$$\begin{aligned} \left( \frac{\partial q}{\partial P} \right)_T &= \left[ \frac{\partial}{\partial P} \frac{4\pi m^{1/2} e}{h} \left( \frac{3Nr^{-3}}{4c\pi} \right)^{1/6} \right] = - \frac{2\pi m^{1/2} e}{h} \left( \frac{3N}{4c\pi} \right)^{1/6} r^{-3/2} \left( \frac{\partial r}{\partial P} \right)_T \\ &= \frac{1}{6} K_T q . \end{aligned}$$

Substituting and simplifying yields

$$\left(\frac{\partial \Delta H}{\partial P}\right)_T = - \frac{N_o Z e^2 \delta K_T}{44} \left(\frac{16}{r} + \frac{11q}{2}\right) \exp\left(-\frac{11}{16} qr\right) .$$