Intermolecular Potentials of Argon, Krypton, and Xenon*

E. Whalley and W. G. Schneider
National Research Council, Ottawa, Canada
(Received October 27, 1954)

The intermolecular potentials of argon, krypton, and xenon are investigated using the recently measured second virial coefficients and the crystal properties at 0°K. The potential functions considered are the 9:6, 12:6, and exp:6. The methods of determination of parameters are reviewed and the method of least squares used in this paper described. All the potentials fitted the second virial coefficient very well, but with the same parameters fitted the crystal properties only moderately well.

I. INTRODUCTION

Accurate information about the forces between molecules can be obtained from physical properties only if the theory of the physical property is sufficiently well known that comparison of experimental and theoretical values serve to test the force law rather than the theory. Such properties are few in number. They are (a) the second and third virial coefficients and related properties; (b) transport properties of the dilute gas; (c) crystal properties at 0°K.

The third virial coefficient measurements are not accurate enough for more than a rough comparison with theory. It is well known that the agreement is not very good1,2 and little more information is obtainable with present measurements. They are therefore not discussed in this paper.

Measurements of the viscosity of the dilute gas are accurate and are available over a wide temperature range. The property is well suited to an investigation of intermolecular potentials; detailed discussions of the data have been given in previous papers.3,4 Good fits were not obtained over a wide temperature range using any of the potentials considered below.

In this paper we discuss the second virial coefficient of the gas and the crystal properties at 0°K. This has been done recently for the gases we are considering by Corn4 for argon and by Mason and Rice5 for argon, krypton, and xenon. Recently experimental values of the second virial coefficients of these gases have been measured in this laboratory over a wider temperature range than hitherto available. We have consequently re-examined the intermolecular potentials using the new data.

All the potentials used in this study, and in fact all potentials which are at present seriously considered as applicable to more than one gas, are of the form

$$u = u_0(r_0/r), \quad (1)$$

where $u$ is the potential energy of two molecules separated by a distance $r$, $\epsilon$ is an energy which will usually be the depth of the potential energy minimum, and $r_0$ a length which will usually be either the value of $r$ for which $u = 0$ or the value of $r$ for which $u$ is a minimum; in the latter case it will be called $r_m$. The more important of the potentials which have been considered are

1. 12:6 potential: $f = 4(r_0/r)^2 - (r_0/r)^4$, \quad (2)

2. 9:6 potential: $f = 2(r_m/r)^2 - 3(r_m/r)^4$, \quad (3)

3. exp:6 potential:

$$f = \frac{1}{1 - 6/\alpha} \left[ \frac{6}{\alpha \left(1 - \frac{r}{r_m}\right)^{-\alpha}} \right]. \quad (4)$$

It is well known1,2 that the second virial coefficient can be quite well fitted by any of these potentials. Therefore in order to obtain the maximum useful information from the data it is necessary to use a more critical method of fitting than employed in discussing the viscosity. Graphical comparison of reduced viscosity = reduced temperature curves were found to be adequate to show clearly the relative degrees of fit.

The object of this investigation was to determine whether any of the foregoing potentials is a significantly better fit to the experimental second virial coefficient than the others. The best fit to available data may give some information about the force law and would provide probably the best available method of extrapolating the measured virial coefficients to higher temperatures.

The procedure used in fitting the potentials differs from that used by Corner4 and Mason and Rice5. These authors used the zero degree crystal properties to determine the potential parameters and calculated second virial coefficients and other properties from this. We have preferred to start with the virial coefficients and have used these to determine the potential parameters. The zero degree crystal properties were then calculated from the parameters obtained. The reasons for adopting this procedure are: (1) Crystal data depend
only on that part of the potential from near the minimum of the potential energy curve to large values of \( r \), whereas the virial coefficients also reflect the potential energy curve at much smaller values of \( r \). (ii) Virial coefficient data have now been extended to cover a wide temperature range. (iii) The theory of the crystal properties involves the principle of superposition of potentials, an assumption which may not be strictly valid.  

II. DETERMINATION OF PARAMETERS

1. The Virial Coefficients and Transport Properties

An excellent review of the theory of the compressibility and the transport properties of dilute gases is given by Hirschfelder, Curtiss, and Bird.\(^1\) For potentials of type (1) the second and third virial coefficients and the coefficients of viscosity, thermal conductivity, and concentration diffusion, are given by equations of the kind

\[
\xi = \rho \varphi(\tau),
\]

where \( \xi \) is the coefficient concerned perhaps multiplied by some power of the temperature, \( \rho \) is dependent on \( r_0 \) or \( r_m \), the mass of the molecules etc., but not on \( \epsilon \) or the temperature \( T \), and \( \varphi(\tau) \) is a function of \( \tau = kT/\epsilon \) only and not of \( r_0 \) or \( r_m \). Values of \( \xi, \rho, \) and \( \varphi \) are given in reference 1. In principal only two values of \( \xi \) are necessary to determine \( \epsilon \) and \( r_0 \) or \( r_m \). In practice one usually has more than two values of \( \xi \) available, usually over a fairly wide temperature range and the problem arises of finding the parameters which give the best fit over a part or the whole of the temperature range. Several methods are available and are discussed below.

(a) Lennard-Jones Method\(^8\)

Log \( \xi \) vs log \( T \) is plotted on transparent paper and superposed on a plot of log\( \varphi(\tau) \) vs log \( \tau \) on the same scale by shifting parallel to both axes. The shift along the log\( \varphi(\tau) \) axis gives \( \log \rho \) and that along the log axis gives log\( \epsilon/\kappa \). This method is rather rapid and permits quick comparison of several potentials if they are plotted on the same graph. It is, however, not sufficiently sensitive for a detailed comparison of several potentials which agree approximately with the data.

(b) Buckingham Method\(^9\)

The quantities

\[
\begin{align*}
\log X &= \log \xi - \log \varphi, \\
\log Y &= \log T - \log \tau,
\end{align*}
\]

are calculated at each temperature for several values of \( \tau \) around that expected. The intersection of two curves for two values of \( \xi \) gives values of \( \epsilon/\kappa \) and \( \rho \)

\[
\begin{align*}
\log X &= \log \xi, \\
\log Y &= \log \epsilon/\kappa,
\end{align*}
\]

which satisfy the two values of \( \xi \). The mean of all the intersections will give a “best” value of \( \rho \) and \( \epsilon/\kappa \). However, when this method was tried for the second virial coefficients for the gases and potentials considered here it was possible readily to adjust the “best” values so obtained to reduce the deviations of the experimental from the calculated values of the second virial coefficient. It was concluded that a “best” fit in no accepted sense is given by this method and it has no advantage over method (a). A modification of the Buckingham method which is sometimes used involves adjusting \( \epsilon/\kappa \) until the ratio of two experimental values of \( \xi \) at two temperatures is equal to the ratio of the corresponding \( \varphi \) values.

(c) Least Squares Method

As pointed out above the Lennard-Jones method is adequate for a quick comparison of various potentials; if two or more potentials agree quite well with the experimental data a more critical comparison is necessary. For this the method of least mean squares was chosen. The method of fitting is that described by Deming.\(^10\)

Approximate values of \( \rho \) and \( \epsilon/\kappa \), say \( \rho_0 \) and \( (\epsilon/\kappa)_0 \), are chosen, usually by method (a) above. Then if

\[
\begin{align*}
\epsilon/\kappa &= (\epsilon/\kappa)_0 - K, \\
\rho &= \rho_0 - L,
\end{align*}
\]

the normal equations for computing the small correction terms \( K \) and \( L \) are, written with detached coefficients,

\[
\begin{align*}
\sum F_{x,t}^2 &= \sum F_{x,t}F_p + \sum F_{x,t}F_0, \\
\sum F_p^2 &= \sum F_p F_0, \\
\text{where}
F_p &= \xi - \rho \varphi(kT/\epsilon), \\
F_{x,t} &= -\frac{\partial \varphi}{\epsilon/\kappa} \frac{\partial \varphi}{\partial \tau}, \\
F_0 &= \varphi(kT/\epsilon),
\end{align*}
\]

\( F_0, F_{x,t}, \) and \( F_p \) are to be calculated using the approximate values of \( \epsilon/\kappa \) and \( \rho \). The standard deviation from the measurements and the standard error of the parameters are readily obtained. If the approximate values of \( \epsilon/\kappa \) and \( \rho \) were more than a few percent different from the final values the fitting was done using the better approximations.


2. Crystal Data

The heats of sublimation and the lattice spacing at 0°K are simply related to the intermolecular potential. The heat of sublimation is dependent mainly on that part of the potential from the minimum outwards to larger values of \( r \). The equations for the lattice spacing, including the effect of the zero point energy have been given by Corner for an n=6 and exp:6 potential and for the potentials here considered reduce to

\[
9:6 \quad C_8 \left( \frac{r_m}{a_0} \right)^8 + \left( \frac{\hbar^2}{8 \pi^2 m r_m^2} \right) \left[ \frac{3}{4 C_{14} (r_m/a_0)} \right] ^{1/2} 11 C_{12} (r_m/a_0)^2 - 5 C_8 \right) \left( \frac{4 C_{16} (r_m/a_0)^2}{2 C_{14} (r_m/a_0)^2} \right) \left( \frac{77 C_{14} (r_m/a_0)^4}{22 C_{14} (r_m/a_0)^2} \right) = C_6, \quad (5)
\]

\[
12:6 \quad 2 C_{12} \left( \frac{r_m}{a_0} \right)^4 + \left( \frac{\hbar^2}{8 \pi^2 m r_m^2} \right) \left[ \frac{3}{2 \pi^2 m r_m^2} \right] \left[ \frac{3}{4 C_{14} (r_m/a_0)} \right] ^{1/2} 12 \left( \frac{\alpha - \frac{r_m}{a_0}}{r_m} \right) \exp \left( 1 - \frac{a_0}{r_m} \right) = 0, \quad (7)
\]

where \( C_8, C_9, C_{11}, C_{12}, C_{14} \), and \( C_{16} \) are numerical constants calculated by Lennard-Jones and Ingham, involved in summing inverse power interactions over an infinite crystal lattice; \( \theta \) is a function of \( a_0/r_m \) tabulated by Corner similarly concerned in summing an exponential interaction and \( \theta ' \) is \( \theta / \theta (a_0/r_m) \).

Equations (5), (6), and (7) are readily solved for \( a_0 \) either graphically or by successive approximations.

The heats of sublimation including the zero point energy \( \Delta H_s(0) \) are calculated from the equations

\[
9:6 \quad \Delta H_s(0) = \frac{N \epsilon}{2} \left[ 2 C_8 \left( \frac{r_m}{a_0} \right)^8 - 3 C_8 \left( \frac{r_m}{a_0} \right)^6 \right], \quad (8)
\]

\[
12:6 \quad \Delta H_s(0) = 2 N \epsilon \left[ C_{12} \left( \frac{r_m}{a_0} \right)^4 - C_6 \left( \frac{r_m}{a_0} \right)^6 \right], \quad (9)
\]

\[
\exp:6 \quad \Delta H_s(0) = \frac{N \epsilon}{2 (1 - 6/\alpha)} \times \left\{ \frac{72 \theta}{\alpha} \exp \left( 1 - \frac{a_0}{r_m} \right) - C_6 \left( \frac{r_m}{a_0} \right)^6 \right\}. \quad (10)
\]

The standard errors were calculated by the usual methods of statistics.

The kind of packing in the crystal should be determined by the intermolecular force law. Recently T.
Table III. Parameters and crystal data for krypton from second virial coefficients.

<table>
<thead>
<tr>
<th>Potential</th>
<th>(b_6) ml mole(^{-1})</th>
<th>(r_6) (\text{a} \text{ngstroms})</th>
<th>(e/\ell \text{K})</th>
<th>(d_6) (\text{a} \text{ngstroms})</th>
<th>(\Delta H'(0)) cal mol(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>9:6</td>
<td>125.07±0.33</td>
<td>107.76±0.75</td>
<td>3.043±0.009</td>
<td>0.35</td>
<td>3.776±0.009</td>
</tr>
<tr>
<td>12:6</td>
<td>166.67±0.47</td>
<td>132.92±0.44</td>
<td>4.130±0.009</td>
<td>0.36</td>
<td>4.041±0.009</td>
</tr>
<tr>
<td>exp:6 (\alpha = 12)</td>
<td>144.67±0.56</td>
<td>132.65±1.08</td>
<td>4.054±0.006</td>
<td>0.46</td>
<td>4.127±0.006</td>
</tr>
<tr>
<td>(\alpha = 15)</td>
<td>183.66±0.56</td>
<td>86.04±0.70</td>
<td>3.626±0.011</td>
<td>0.42</td>
<td>3.904±0.011</td>
</tr>
<tr>
<td>Expt.</td>
<td>183.64±0.56</td>
<td>86.01±0.70</td>
<td>3.93±0.03</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Kihara and S. Koba\(^{12}\) have investigated the relative energies of hexagonal and cubic close packing and find that for the 12:6 and exp:6 potentials the hexagonal close packed structure is more stable by about 0.01%. Apart from helium the inert gases all crystallize in cubic close packing. They conclude from this that the energy well must be wider than given by the 12:6 potential to explain the stability of the cubic structure. The difference is so small, however, that little weight should be placed on this conclusion.

(c) Procedure in Fitting Potentials

The procedure followed in fitting the potentials was in all cases the same.

The fit of the various potentials to the second virial data was examined by least mean squares and the parameters obtained were used to calculate the lattice spacing and the heat of sublimation at 0\(^\circ\)K. These were compared with experimental values. The experimental values were recalculated from all the available experimental data and are given in the appendix.

III. RESULTS

1. Argon

The data for the virial coefficients were taken from a previous paper.\(^{13}\) They were converted to values of \(B_6\) in ml mole\(^{-1}\) by the relation

\[
B_6 = V_N B_p,
\]

where \(V_N\) is the volume occupied by one mole of gas at NTP. The \(B_6\) values were fitted to 9:6, 12:6, and exp:6 potentials by the method of least mean squares. The "best" parameters are given in Table I together with their standard error and the standard deviation of the calculated from the experimental virial coefficients. For the exp:6 potential graphical comparison by method (a) above showed that only \(\alpha = 15\) agreed with all the points moderately well and only this potential was used. In Table II the experimental and calculated values of \(B_6\) are compared. The calculated values of the heat of sublimation at 0\(^\circ\)K and the lattice spacings are given in Table I and compared with the experimental values. The calculation of the experimental value of \(\Delta H'(0)\) is given in the appendix. The experimental value of \(d_6\) is extrapolated from the value at 40\(^\circ\)K of 3.83±0.02 A\(^4\) and at 20\(^\circ\)K of 3.82 A\(^4\).

The integrals \(e/\ell\) for the viscosity are calculated only for the 12:6 and exp:6 potentials. The 12:6 potential is a better fit to the experimental viscosity data over a wide temperature range but a close fit is not obtained\(^{14}\) and above about 850\(^\circ\)K no real solution for \(e/\ell\) for argon is possible from the viscosity data.\(^{14,16}\)

2. Krypton

The second virial coefficient data were obtained from a recent paper\(^{17}\) and were treated in the same way as argon. The exp:6 potentials with \(\alpha = 12, 13, 14,\) and 15, appeared equally good by graphical comparison and least squares were used for each potential. The parameters and crystal data are given in Table III and the virial coefficient and their deviations in Table IV. The lattice spacing has been measured by Nasini and Natta\(^{18}\) as 4.09 A at 77\(^\circ\)K, by Keesom and Mooy\(^{19}\) as 3.95 at 20\(^\circ\)K and by Ruhemann and Simon\(^{20}\) as 4.03 at 88\(^\circ\)K. The best value of \(d_6\) is probably 3.93±0.03 A. The calculation of the experimental value of \(\Delta H'(0)\) is given in the appendix.

Table IV. Comparison of experimental and calculated second virial coefficients of krypton.

| \(T^\circ\) | \(B_6\) ml \(\text{mole}^{-1}\) | \(B_6\) (exp.) = \(B_6\) (calc) |
|----------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 9:6      | \(273.169\)     | \(237.169\)     | \(237.169\)     | \(237.169\)     | \(237.169\)     |
| 12:6     | \(273.169\)     | \(237.169\)     | \(237.169\)     | \(237.169\)     | \(237.169\)     |
| exp:6 \(\alpha = 12\) | \(273.169\)     | \(237.169\)     | \(237.169\)     | \(237.169\)     | \(237.169\)     |
| \(\alpha = 13\) | \(273.169\)     | \(237.169\)     | \(237.169\)     | \(237.169\)     | \(237.169\)     |
| \(\alpha = 14\) | \(273.169\)     | \(237.169\)     | \(237.169\)     | \(237.169\)     | \(237.169\)     |
| \(\alpha = 15\) | \(273.169\)     | \(237.169\)     | \(237.169\)     | \(237.169\)     | \(237.169\)     |


3. Xenon

The second virial coefficient data were obtained from a recent paper. The parameters and the crystal data are given in Table V and the second virial coefficients and their deviations in Table VI. The lattice spacing has been measured by Natta and Nasini as 4.37±0.02 Å at 77°K and by Ruhemann and Simon as 4.41 Å at 88°K. The best value of \( a_0 \) will be about 4.30±0.04. More accurate crystal data on argon, krypton, and xenon would be very useful. The calculation of the experimental value of \( \Delta H_s(0) \) is given in the appendix.

IV. DISCUSSION

From an examination of Tables I–VI the following facts are evident.

1. The standard deviation of the experimental from the calculated values of the second virial coefficient using the various potentials is always less than three times, and mostly less than twice the standard error of the experimental data. Thus all the potentials tried fit quite well and none of the potentials is a very much better fit than the rest.

2. The several potentials obtained from the same measurements can be very different; for example, for argon there is a spread of 42° in \( \epsilon/k \), for krypton 58°, and for xenon 81°. This is rather surprising in view of the close similarities in the curves of \( f \) of Eq. (1). This is readily seen in Fig. 1 where \( f = u/\epsilon \) is plotted against \( r/r_0 \) for the 9:6 and exp:6, \( a = 15 \) potentials. The 12:6 and other exp:6 potentials fall between these two lines.

3. In spite of the large variation in \( \epsilon/k \) the calculated values of \( \Delta H_s(0) \) are not very dissimilar. The crystal properties are moderately well predicted using any of the potentials obtained from second virial data and one can usually be chosen which will fit either \( a_0 \) or \( \Delta H_s(0) \) very well, but not both together; the potentials are too simple to fit all three properties exactly.

It has been shown previously that good fits to the viscosity data were not obtained by any potential which is a reasonable approximation to the true potential. The comparison of viscosity data, therefore, is a more critical evaluation of potential curves than the second virial coefficient.

One concludes from all this that a potential which best fits even several gas properties is not necessarily closely related to the true potential. The depth of the actual potential minimum could differ by more than 20% from the values derived in this paper. However,

<table>
<thead>
<tr>
<th>Potential</th>
<th>( \epsilon/k )</th>
<th>( a_0 )</th>
<th>( \sigma )</th>
<th>( \Delta H_s(0) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>9:6</td>
<td>168.4±1.2</td>
<td>147.8±2.2</td>
<td>4.594±0.024</td>
<td>1.20</td>
</tr>
<tr>
<td>12:6</td>
<td>225.1±1.1</td>
<td>194.9±0.84</td>
<td>4.586±0.013</td>
<td>0.82</td>
</tr>
<tr>
<td>exp:6 ( \alpha = 12 )</td>
<td>196.1±1.1</td>
<td>140.3±1.6</td>
<td>4.782±0.018</td>
<td>0.88</td>
</tr>
<tr>
<td>exp:6 ( \alpha = 14 )</td>
<td>233.3±1.0</td>
<td>121.1±1.0</td>
<td>4.579±0.013</td>
<td>0.70</td>
</tr>
<tr>
<td>exp:6 ( \alpha = 15 )</td>
<td>248.9±1.0</td>
<td>114.7±1.0</td>
<td>4.497±0.013</td>
<td>0.62</td>
</tr>
</tbody>
</table>

**Table V.** Parameters and crystal data for xenon from second virial coefficients.

---

**Table VI.** Comparison of experimental and calculated second virial coefficients of xenon.

<table>
<thead>
<tr>
<th>( T^\circ \text{K} )</th>
<th>( B_s ), ( \text{ml mole}^{-1} )</th>
<th>( B_s(\text{exp}) - B_s(\text{calc}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>273.16</td>
<td>-154.74</td>
<td>-2.77</td>
</tr>
<tr>
<td>298.16</td>
<td>-130.21</td>
<td>-0.26</td>
</tr>
<tr>
<td>323.16</td>
<td>-110.62</td>
<td>+0.99</td>
</tr>
<tr>
<td>348.16</td>
<td>-95.04</td>
<td>+1.42</td>
</tr>
<tr>
<td>373.16</td>
<td>-82.13</td>
<td>+1.25</td>
</tr>
<tr>
<td>423.16</td>
<td>-62.10</td>
<td>+0.80</td>
</tr>
<tr>
<td>473.16</td>
<td>-46.74</td>
<td>+0.46</td>
</tr>
<tr>
<td>573.16</td>
<td>-25.06</td>
<td>-0.15</td>
</tr>
<tr>
<td>673.16</td>
<td>-10.77</td>
<td>-0.72</td>
</tr>
<tr>
<td>773.16</td>
<td>-0.13</td>
<td>-0.68</td>
</tr>
<tr>
<td>873.16</td>
<td>+7.95</td>
<td>-0.45</td>
</tr>
<tr>
<td>973.16</td>
<td>+14.22</td>
<td>+0.16</td>
</tr>
</tbody>
</table>

Standard deviation \( \sigma \) 1.20 0.82 0.88 0.70 0.62

---


potentials derived using the same model for several gases will be approximately relatively correct.

For extrapolating experimental second virial coefficients to high and low temperatures either the 12:6 or the exp:6 potential appears to be equally good. One would perhaps prefer the 12:6 because it is rather simpler to use. Some caution in extrapolation is, however, necessary, particularly when the potential parameters have been derived from experimental data extending only over a very limited temperature range.

ACKNOWLEDGMENTS

We wish to thank Mr. G. David and Mr. G. Kell for help with the computations.

APPENDIX. HEATS OF SUBLIMATION AT 0°K

The heat of sublimation at 0°K $\Delta H_s(0)$ can be calculated from the equation

$$\Delta H_s(0) = \Delta H_s(T) + \int_0^T C_p dT - \int_0^T C_v g(T) dT + \Delta H_{JT},$$

(11)

where $\Delta H_s(T)$ is the heat of sublimation at temperature $T$, $C_p$ is the heat capacity at constant pressure of the solid or liquid, $C_v g(T)$ is the heat capacity of the ideal gas and $\Delta H_{JT}$ is the isothermal heat of expansion of the gas (Joule-Thomson effect) from the vapor pressure at temperature $T$ to zero pressure. The change in heat content on expansion is small and can be calculated from the equation of state. This we write in the form

$$PV = RT + BP.$$

Then

$$\Delta H_{JT} = H(P,T) - H(0,T) = \left( B - \frac{T dB}{dT} \right) P.$$ (12)

It has been shown that the value of $B$ for vapors is calculated with fair accuracy from the equation

$$B = \frac{9}{128} \frac{RT_s}{P_s} \left( 1 - \frac{T_s}{T} \right)^2.$$

This formula agrees well with a 12:6 formula over the temperature range $T/T_s = 0.25$ to 1.6 and is quite adequate for calculating the relatively small term $\Delta H_{JT}$. Insertion of this into (12) gives

$$\Delta H_{JT} = \frac{9}{128} \frac{RT_s}{P_s} \left( 1 - \frac{T_s}{T} \right)^2 P.$$ (13)

Critical data for the gases were taken from the compilation of Kobe and Lynn.

1. Argon

Several measurements have been reported which can be used to derive $\Delta H_s(0)$ for argon. It is most convenient to choose the temperature $T$ as the melting point. For $\Delta H_s(T)$ for solid argon the following direct values have been obtained:

- Calorimetric, Eucken $^{24}$ 1739 cal mole$^{-1}$
- Vapor pressure of solid argon, Crommelin $^{26}$ calculated by Nernst $^{27}$ 1819 cal mole$^{-1}$
- Vapor pressure of solid argon, Born $^{28}$ 1830 cal mole$^{-1}$

$\Delta H_s(T)$ can also be obtained from the heat of vaporization of the liquid and the heat of melting. The following values for the heat of melting are given:

- Eucken $^{27}$ 267.9 cal mole$^{-1}$
- Eucken and Hanck $^{29}$ 265.2 cal mole$^{-1}$
- Clusius $^{30}$ 280.8 cal mole$^{-1}$
- Mean 271.3 cal mole$^{-1}$

Using the mean value and the heats of vaporization of the liquid obtained by various workers we find the following values for the heat of vaporization of solid argon at the melting point:

- V.P. of liquid argon, Crommelin $^{26}$ calculated by Nernst $^{27}$ 1830 cal mole$^{-1}$
- V.P. of liquid argon Born $^{28}$ 1842 cal mole$^{-1}$

The mean of all values of $\Delta H_s(T)$ for solid argon is $1823 \pm 18$ cal mole$^{-1}$.

The heat capacity of solid argon has been measured by Eucken $^{24}$ and by Clusius. $^{30}$ From Eucken's results Born $^{30}$ found $\int_0^{\infty} C_p dT = 406$ cal mole$^{-1}$. From Clusius' results by graphical interpolation we find $\int_0^{\infty} C_p dT = 395$ cal mole$^{-1}$. The data of Clusius are the more extensive so this value will be used. The heat of expansion $\Delta H_{JT}$ is from Eq. (13) $17$ cal mole$^{-1}$. For the heat of sublimation at 0°K we obtain therefore $\Delta H_s(0) = 1818$ cal mole$^{-1}$. As a rough estimate of the standard error 40 cal mole$^{-1}$ seems reasonable. For calculations of $\Delta H_s(0)$ from the intermolecular potential we need to allow for the zero point energy. This is $9/8R\theta$ where $\theta$ is the Debye characteristic temperature. The Clusius value of $\theta$ gives 178 cal mole$^{-1}$, is probably the most accurate, and will be used. The heat of vaporization including the zero point energy is therefore $1998 \pm 40$ cal mole$^{-1}$.

$^{26}$ W. Nernst, Z. Electrochem. 22, 185 (1916).
2. Krypton

The only data for obtaining the heat of vaporization are the density and vapor pressure measurements of Mathias, Crommelin, and Meihuizen. The empirical equation proposed to represent the results is

\[ \Delta H_s(T) = 0.01896T(209.39 - T)^4 + 0.3837T - 0.004346T^2 + 1.212 \times 10^{-3}T^3, \quad (14) \]

based on measurements down to 126°C. The specific heat measurements extend only to 123°C, so Eq. (13) was extrapolated to this value giving

\[ \Delta H_s(123) = 2052 \text{ cal mole}^{-1}. \]

The value of \( \int_{0}^{123} C_P \, dT \) is 252.5 cal mole\(^{-1}\). The heat of expansion to zero pressure from Eq. (13) at 123°C is 28 cal mole\(^{-1}\), the \( \int_{0}^{123} \rho C_P(\rho) \, dT \) is 611 cal mole\(^{-1}\), and the zero point energy, using Clusius value of the Debye \( \theta \) is 140 cal mole\(^{-1}\). The heat of vaporization at 0°C is therefore 2589 cal mole\(^{-1}\), and adding the zero point energy this becomes 2729 cal mole\(^{-1}\). A standard error of about 50 cal mole\(^{-1}\) is probably a reasonably good rough estimate.

3. Xenon

The heat of vaporization at the normal boiling point 165.1°C has been measured by Clusius and Riccoboni as 3020 ± 3 cal mole\(^{-1}\). The \( \int_{0}^{165.1} C_P \, dT \) is from the data of Clusius and Riccoboni; 1566 cal mole\(^{-1}\). The heat of expansion at 165.1°C from 760 mm to zero pressure is calculated from Eq. (13) as 38 cal mole\(^{-1}\). The \( \int_{0}^{165.1} \rho C_P(\rho) \, dT \) is 801 cal mole\(^{-1}\). The heat of sublimation at 0°C is therefore 3828 cal mole\(^{-1}\). The zero point energy using the Clusius value of \( \theta \) is 123 cal mole\(^{-1}\), so the heat of sublimation at 0°C, including the zero point energy, is 3946 cal mole\(^{-1}\).

---


\(^{30}\) Mathias, Crommelin, and Meihuizen, Ann. Physik 8, 467 (1937).