Statistical Thermodynamics: Sublimation of Solid Iodine

Chem 374
For March 23, 2017
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**Purpose:**

1. To review basic fundamentals ideas of Statistical Mechanics as applied to a pure solid and pure diatomic gas. Apply common equations for translational, rotational, and vibrational partition functions to compute the equilibrium constant for $I_2(s) \rightarrow I_2(g)$, i.e., the “vapor pressure”, and $\Delta H^0$, both as a function of temperature.

2. Compare the calculations with what you measured earlier in the semester.

**Introduction:**

Here we give some notes to clarify the several pages of Statistical-Mechanical background and application to the vapor pressure of $I_2$ solid reproduced below from a textbook.

**a. chemical potential**

The Van’t Hoff Equation tells how $\Delta G^0$ and $\Delta \mu^0$ change with temperature, therefore how K changes with temperature. This includes the “equilibrium constants” for phase changes.

$\mu^0$ is called the chemical potential. At **constant $T$ and $P$**, it is defined as:

$$
\frac{dG}{dT} = \left( \frac{\partial G}{\partial T} \right)_{P,n_1,n_2} dT + \left( \frac{\partial G}{\partial P} \right)_{T,n_1,n_2} dP + \left( \frac{\partial G}{\partial n_1} \right)_{T,P,n_2} dn_1 + \left( \frac{\partial G}{\partial n_2} \right)_{T,P,n_1} dn_2
$$

$$
dG = -SdT + VdP - \mu_1dn_1 + \mu_2dn_2
$$

where $\mu_1 = \left( \frac{\partial G}{\partial n_1} \right)_{T,P,n_2}$ is the partial molar Gibbs free energy,

but is most commonly called the "chemical potential" of component 1.

But our experiment is done at **constant $T$ and $V$**. Now there is no non-$pV$ work to worry about. It is energy instead of enthalpy that we are concerned with. The Helmholtz free energy, $A$, is what determines equilibrium constant, useful work, and spontaneity at **constant volume**.
A = E – TS by definition, where E in this document is energy. In terms of A, the chemical potential becomes:

\[
dA = \left( \frac{\partial A}{\partial T} \right)_{V,n_1,n_2} dT + \left( \frac{\partial A}{\partial V} \right)_{T,n_1,n_2} dV + \left( \frac{\partial G}{\partial n_1} \right)_{T,V,n_2} dn_1 + \left( \frac{\partial G}{\partial n_2} \right)_{T,V,n_1} dn_2
\]

\[
dA = -S dT - P dV + \mu_1 dn_1 + \mu_2 dn_2
\]

where \( \mu_i = \left( \frac{\partial A}{\partial n_i} \right)_{T,V,n_2} \) is \( \bar{A}_i \) the partial molar Helmholtz free energy for component \( i \).

This is the chemical potential when \( V \) is constant.

Partial molar quantities are necessary to talk about properties of mixtures in which the composition changes. We used a mixture of 2 substances for illustration, but the same equations apply to any number of components.

For a pure substance, like pure \( I_2 \) \( \Delta \mu = \) molar \( \Delta G \) with units of J/mol at constant temperature and pressure. \( \Delta \mu = \) molar \( \Delta A \) at constant temperature and volume.

When 2 or more phases are in equilibrium, the chemical potential is the same in each phase for every component. This is another way of saying the obvious: \( \Delta G = 0 \) for transferring any component between any two phases at constant \( T \) and \( P \).

No matter what the conditions, when 2 or more phases are in equilibrium, the chemical potential is the same in each phase for every component. \( \Delta A = 0 \) for transferring any component between any two phases at constant \( T \) and \( V \).

By the way, the Van’t Hoff Equation for the constant \( V \) case is:

\[
-RT \ln K = \Delta \bar{A}^0 = \Delta \bar{E}^0 - T \Delta \bar{S}^0
\]

Divide by -RT:

\[
\ln K = -\frac{\Delta \bar{A}^0}{RT} = -\frac{\Delta \bar{E}^0}{RT} + \frac{\Delta \bar{S}^0}{R}
\]

Subtract for two different values of \( T \), assuming constant \( \Delta \bar{H}^0 \) and \( \Delta \bar{S}^0 \)

\[
\ln \left( \frac{K(T_2)}{K(T_1)} \right) = -\frac{\Delta \bar{E}^0}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)
\]

This means that in the vapor pressure experiment, the plot of \( \ln P \) vs \( 1/T \) has a slope of \(-\Delta \bar{E}^0/R\), not \(-\Delta \bar{H}^0/R\). It is easy to show that \( \Delta \bar{H}^0 = \Delta \bar{E}^0 + RT \) from the definition \( H = E + PV \).
b. Statistical Thermodynamics

Statistical mechanics was invented by Boltzmann. It is conceptually quite simple, but is unfortunately presented in textbooks in such a way as to appear frightening and impossible to learn.

You already know the basic idea: \( \Delta G^0 = -RT \ln K \) or the equivalent statement:

\[
K = e^{-\frac{\Delta G^0}{RT}} = 10^{\frac{-\Delta G^0}{2.303RT}} = 10^{\frac{-\Delta G^0}{5700}} \text{ at constant } T=298 \text{ K and } P.
\]

At constant \( T \) and \( V \), this becomes \( K = e^{-\frac{\Delta A^0}{RT}} = 10^{\frac{-\Delta A^0}{2.303RT}} = 10^{\frac{-\Delta A^0}{5700}} \) at constant \( T=298 \).

This means if \( \Delta A = -57000 \text{ J} \), \( K = 1 \times 10^{10} \); if \( \Delta A = +57000 \text{ J} \), \( K = 1 \times 10^{-10} \)

The above expression for \( K \) is the well-known Boltzmann distribution, which we have been constantly applying this semester in lecture and lab. This is best memorized as the simple ratio of probabilities to be in energy levels 1 and 2 at equilibrium:

\[
K_{2/1} = \frac{P_2}{P_1} = \frac{N_2}{N_1} = \frac{g_2 \ e^{-\frac{\Delta E}{RT}}}{g_1} = 10^{\frac{-\Delta A^0}{2.303RT}} = 10^{\frac{-\Delta A^0}{5700}}, \text{ where } N_1 \text{ and } N_1 \text{ are the numbers of molecules in states 1 and 2, and } g_1 \text{ and } g_2 \text{ are the degeneracies of the states 1 and 2. } g_1 \text{ is the number of different states with energy } E_1.
\]

The degeneracy is what Boltzmann called the number of available states in his remarkable molecular statement of entropy: \( S = k_B \ln(g) \). (usually written as \( S = k_B \ln W \)).

Boltzmann’s constant \( k_B = 1.38 \times 10^{-23} \text{ J K}^{-1} \text{ molecule}^{-1} \). When multiplied by Avogadro’s Number, Boltzmann’s constant becomes \( R = 8.3145 \text{ J K}^{-1} \text{ mol}^{-1} \). (Thus when one sees the expression \( \exp(-\Delta E/k_B T) \), you immediately know that the units of \( E \) are J/molecule, instead of J/mol)

Therefore \( \Delta S = S_2 - S_1 = R \ln (g_2) - R \ln (g_1) = R \ln (g_2 / g_1) \).

And, \( \frac{g_2}{g_1} = e^{\frac{\Delta S}{R}} \) giving:

\[
K = \frac{g_2 \ e^{-\frac{\Delta G^0}{RT}}}{g_1} = e^{\frac{\Delta S}{R}} \ e^{-\frac{\Delta G^0}{RT}} = e^{\frac{\Delta S}{R}} \ e^{\frac{\Delta A^0}{RT}} = e^{\frac{\Delta S}{R}} \ e^{\frac{T \Delta S}{RT}} = e^{\frac{-(\Delta G^0-T \Delta A^0)}{RT}} = e^{\frac{-\Delta A^0}{RT}}
\]
c. Partition functions

At the outset, let’s be clear that this terrible thing (partition function) as used here is nothing more than the number of available states in a constant temperature system.

\[ Q = \sum_{\text{states}, i} e^{-\frac{E_i}{kT}}, \]

a weighted sum of states weighted by Boltzmann factors, which is what is meant by available. As the state energy increases, it is less available at a given temperature. (The most evident display of this is atmospheric pressure as a function of altitude!)

Now, if we sum over E levels, multiplying each Boltzmann factor by the degeneracy of the energy level, we get the equivalent statement:

\[ Q = \sum_{\text{levels}, i} g_i e^{-\frac{E_i}{kT}} = \sum_{\text{levels}, i} e^{\frac{T_S}{kT} - \frac{E_i}{kT}} = \sum_{\text{levels}, i} e^{\frac{T_S}{kT}} = e^{\frac{T_S}{kT}}, \]

or \[ \ln Q = -\frac{A}{kT}, \] or \[ A = -kT \ln Q \]

This is coincidently closely related to the Q in \( \Delta G = \Delta G^0 + RT \ln Q. \)

d. Molecular partition functions

In the gaseous state, a molecule’s translational, rotational, vibrational, and electronic degrees of freedom behave independently. The total number of available states, \( q_g \), is just the product of the individual partition functions for the various degrees of freedom: \( q_g = q_{\text{trans}} q_{\text{rot}} q_{\text{vib}} q_{\text{el}}. \)

Each of these is the sum over all quantum states, each weighted by its degeneracy and Boltzmann factor. These are well approximated by simple integrals for translational and rotational, because the energy levels are quite close together. For vibrational and electronic we must sum. Vibrations are assumed to be harmonic oscillators, for which the sum of Boltzmann factors is a simple power series that can easily be shown to be \( q_{\text{vib}} = \left(1 - e^{\frac{-\hbar \nu}{kT}}\right)^{-1}. \) Because in most molecules all electronic excited states are so high above the ground state, \( q_{\text{electronic}} = 1. \) This is true for I\(_2\) because the ground state of I\(_2\) is non-degenerate.

e. Vapor Pressure = \( K_{eq} = \exp(-\Delta A^0/RT) \)

Finally, instead of equation (34), which has been made completely baffling by “simplifying” it to death, we will use \( \Delta A = A_{\text{gas}} - A_{\text{solid}} = -RT \ln Q_{\text{gas}} + RTQ_{\text{solid}} \) and vary the concentration (which appears in \( q_{\text{trans}} \) disguised as the volume = nRT/pressure) in the attached spreadsheet, until we find the pressure that makes \( \Delta A = 0. \) That will be equilibrium, and that will be the “vapor pressure”
\[ \Delta A = -RT \ln[(\frac{2 \sqrt{\pi} mkT}{h^2})^{3/2} \frac{kT}{p} \times \frac{kT}{\omega hCB_0} \times (1 - e^{-\frac{-h\nu_{\text{ vib}}}{kT}})^{-1}] + RT \ln(q_{\text{solid}}), \]

where \( q_{\text{solid}} \) is given in equations 32 and 33, and on the spread sheet.

A few more helpful details will be mentioned during our lab meeting, during which we will work on setting up your spread sheet.

The spreadsheet is complete except for the formulas for the gas partition functions, which have all been set =1. You should make a start on filling in these formulas before coming to class if possible.

The table of experimental values is from a previous year. You should enter the data you took this year in place of that data.

**EXPERIMENT 48**

**STATISTICAL THERMODYNAMICS OF IODINE SUBLIMATION**

This experiment is in some respects similar to two other experiments concerning enthalpy changes attending phase transformations, namely Exps. 13 and 47. However, it differs from them in that the experimental data, which are vapor pressures of solid iodine at several temperatures, are obtained from optical absorption measurements. As in the other experiments mentioned, the enthalpy change (here the heat of sublimation of solid iodine) can be calculated with the Clausius–Clapeyron equation, which requires the values of vapor pressures at two or more temperatures.

The system I₂(s)–I₂(g) also provides an opportunity for the application of statistical mechanics to derive thermodynamic information from spectroscopic data. For the gas phase, the vibrational frequency of the I₂ molecule, needed in formulating the vibrational partition function, can be obtained from the absorption spectrum in the visible region (see Exp. 42); the rotational partition function in the gas phase will be calculated from the known internuclear distance in the iodine molecule. For the crystalline phase, published phonon dispersion curves, obtained by inelastic neutron scattering spectroscopy, will be used to determine the vibrational frequencies. With the above information and statistical mechanical theory, the molar energy difference $\Delta E_0^\circ$ between the vibrational ground states of crystalline and gaseous iodine can be determined from a measurement of vapor pressure at one temperature. From the fully defined partition functions for both crystalline and gaseous iodine, the entropy
partition functions of the individual oscillators:

\[ Q_i = \prod_i q_i \quad \ln Q_s = \sum_i \ln q_i \quad \tag{7} \]

Since many of these oscillators differ from each other in the values of their frequencies, energy levels, and partition functions, it is convenient to define a new quantity \( q_s \), which is the geometric mean of all of the \( q_i \) for the crystal:

\[ q_s = \left[ \prod_{i=1}^M q_i \right]^{1/M} \quad \ln q_s = \frac{1}{M} \sum_{i=1}^M \ln q_i \quad \tag{8} \]

where \( M \) is the number of oscillators. Then, for the crystal,

\[ \ln Q_s = M \ln q_s = 3tN \ln q_s \quad \tag{9} \]

where \( t \) is the number of atoms in a molecule. Since \( \ln q_s \) can be shown to be independent of \( N \), we find from Eq. (5)

\[ \mu_s = -3tRT \ln q_s \quad \tag{10} \]

For a one-component ideal gas, the microcanonical partition function for an individual molecule is \( q_g \). Therefore, under all ordinary conditions, we may write for a gas

\[ Q_g = \frac{q_g^N}{N!} \quad \tag{11} \]

where the division by \( N! \) takes into account the fact that the individual molecules are indistinguishable. With the aid of the Sterling approximation for \( \ln(N!) \) we obtain

\[ \ln Q_g = N \ln q_g - N \ln N + N \quad \tag{12} \]

Using Eq. (5) again, we obtain

\[ \mu_g = -RT \ln \frac{q_g}{N} \quad \tag{13} \]

We will now develop expressions for the microcanonical partition functions \( q_s \) and \( q_g \) to substitute into Eqs. (10) and (13).

**Gaseous 1.** The partition function \( q_g \) is very well approximated as a product of terms arising from translational, rotational, vibrational, and electronic degrees of freedom:

\[ q_g = q_{\text{trans}} q_{\text{rot}} q_{\text{vib}} q_{\text{el}} \quad \tag{14} \]

The translational partition function is given by \(^2\)

\[ q_{\text{trans}} = \left( \frac{2\pi m k T}{h^2} \right)^{3/2} V \quad \tag{15} \]
where \( m \) is the molecular mass, \( k \) is the Boltzmann constant, \( T \) is the absolute temperature, \( h \) is Planck's constant, and \( V \) is the volume within which the molecule is constrained to move.

For a molecule as massive as \( I_2 \), the rotational energy levels are very closely spaced and the partition function has the simple form

\[
q_{\text{rot}} = \frac{kT}{\hbar c \tilde{B}_0} = \frac{T}{\sigma \Theta_{\text{rot}}} \tag{16}
\]

Here \( \sigma \) is the symmetry number of the molecule, \( c \) is the velocity of light, and \( \tilde{B}_0 \) is the rotational constant (conventionally expressed in units of cm\(^{-1} \) with \( c \) expressed in cm s\(^{-1} \) units) defined by

\[
\tilde{B}_0 = \frac{\hbar}{8 \pi^2 \xi c} \tag{17}
\]

where \( \xi \) is the moment of inertia of the molecule

\[
\xi = \mu r_0^2 \tag{18}
\]

The reduced mass \( \mu \) (not to be confused with chemical potential) is defined by

\[
\mu = \frac{m_1 m_2}{m_1 + m_2} \tag{19}
\]

where \( m_1 \) and \( m_2 \) are the respective atomic masses. In \( I_2 \) the interatomic distance \( r_0 \) is 0.2667 nm, and the rotational constant \( \tilde{B}_0 \) is 0.037315 cm\(^{-1} \).\(^4\) The quantity \( \Theta_{\text{rot}} \) is the rotational characteristic temperature, given by

\[
\Theta_{\text{rot}} = \frac{\hbar c \tilde{B}_0}{k} \tag{20}
\]

The factor \( \hbar c/k \) has the value 1.43877 cm K. Since the \( I_2 \) molecule is end-for-end symmetric, \( \sigma = 2 \).

For the vibrational partition function the molecule is regarded as a quantum-mechanical harmonic oscillator, for which

\[
q = (1 - e^{-\hbar \nu_0/kt})^{-1} = (1 - e^{-\Theta_{\text{vib}}/T})^{-1} \tag{21}
\]

where \( \nu_0 \) is the molecular vibration frequency and \( \Theta_{\text{vib}} \) is the vibrational characteristic temperature,

\[
\Theta_{\text{vib}} = \frac{\hbar \nu_0}{k} = \frac{\hbar \tilde{\nu}_0}{k} \tag{22}
\]

For the \( I_2 \) molecule, \( \tilde{\nu}_0 \) has the value 213.3 cm\(^{-1} \).\(^4\)

Equation (21) as written applies to an oscillator for which the reference energy is the energy of the vibrational ground state (\( \nu = 0 \)); i.e., the \( \nu = 0 \) state in a gas molecule has been assigned zero energy. For the present situation, in which \( I_2 \) molecules in the vapor phase are in equilibrium with crystalline iodine, it is more convenient to take the reference energy to be that of an \( I_2 \)
molecule in the crystal when the \textit{crystal} is in its ground vibrational state.† Accordingly, the energy of the vibrational ground state of an I$_2$ molecule in the ideal gas phase is taken to be $\Delta \varepsilon_0$, which is the energy required to remove a molecule from the crystal at absolute zero temperature. Thus, we should write for the I$_2$ molecule in the gas phase

$$ q_{\text{vib}} = (1 - e^{-\Theta_{\text{vib}}/T})^{-1} e^{-\Delta \varepsilon_0/kT} \quad (23) $$

It remains to deal with $q_{\text{el}}$. The excited electronic states of I$_2$ are separated from the ground electronic state by an energy difference that is very large compared to $kT$. Therefore

$$ q_{\text{el}} = 1 \quad (24) $$

Let us now introduce $\Delta \tilde{E}_0 = N_0 \Delta \varepsilon_0$, the energy needed to sublime 1 mol of crystalline I$_2$ into the ideal gas phase at the absolute zero, and replace $V$ by its ideal-gas equivalent $NkT/p$. We can then combine Eqs. (13) to (16), (23), and (24) to obtain

$$ \mu_n = \Delta \tilde{E}_0 - RT \ln \left[ \left( \frac{2 \pi m kT}{\hbar^2} \right)^{3/2} \frac{kT}{p} \frac{p}{\sigma \Theta_{\text{rot}}} (1 - e^{-\Theta_{\text{vib}}/T})^{-1} \right] \quad (25) $$

\textbf{Crystalline I$_2$.} The partition function for the crystalline state of I$_2$ consists solely of a vibrational part; the crystal does not undergo any significant translation or rotation, and the electronic partition function is unity for the crystal as it is for the gas.

The geometric mean partition function for the crystal can be expressed as

$$ q_n = \left[ \prod_{i=1}^{M} (1 - e^{-\Theta_i/T})^{-1} \right]^{1/M} \quad (26) $$

where $\Theta_i$ is defined in terms of $\tilde{v}_i$ in the same way as $\Theta_{\text{vib}}$ is defined in terms of $\tilde{v}_0$ in Eq. (22). Since the number of iodine atoms is $2N$ for a crystal containing $N$ molecules of I$_2$, and since each atom contributes three degrees of freedom, the number of modes of vibration for the crystal is

$$ M = 3 \times 2 \times N - 6 = 6N - 6 = 6N \quad (27) $$

The subtracted number 6 represents the 3 translational and 3 rotational degrees of freedom of the crystal as a whole and will henceforth be ignored.

We now present a brief discussion of the vibrations occurring in a crystal. The crystal can be thought of as a gigantic molecule with a huge number of normal modes, and the student may find it useful to review the discussion of normal modes for small molecules given in Exps. 36, 37, and 39. In the case of the I$_2$ crystal, each primitive (smallest) unit cell contains two

† It should be noted that the location of the energy zero is arbitrary; a different, but equally reasonable, choice is made in Exp. 47. All that matters is a consistent choice for the two phases in equilibrium—here gaseous and crystalline I$_2$. 

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molecules. Figure 1 shows that these two molecules are distinguished easily because their spatial orientations are different. As a consequence of this crystal structure, there are $3 \times 4$ atoms = 12 mechanical degrees of freedom associated with each unit cell. In the gas phase, there would be three translations, two rotational, and one vibration for each of the two $I_2$ molecules. In the crystal, however, only vibrations occur: six lattice modes, four librational modes, and two internal vibration (bond-stretching) modes.

Let us consider first the center-of-mass motions for each of the two $I_2$ molecules in a unit cell. These types of motion account for six degrees of freedom and give rise to two kinds of lattice vibration. When both $I_2$ molecules in a given cell move in phase with each other (say, for example, both are displaced in the $+x$ direction at the same time), there are three so-called acoustic vibrations. When the two $I_2$ molecules in a given cell move out of phase (say one is displaced in the $+x$ direction while the other is displaced in the $-x$ direction), there are three optic vibrations.†

The four librations (torsional oscillations or rocking motions) arise because the crystal-field potential prevents the $I_2$ molecule from rotating as it would in the gas phase. There are some special crystals, called plastic crystals, in which symmetrical molecules that interact weakly can still undergo hindered rotation in the solid phase, but $I_2(x)$ is not one of these. The librational motions for each $I_2$ occur about two axes ($\alpha$, $\beta$) perpendicular to the $I-I$ bond direction. The librations of the two $I_2$ molecules in the same unit cell are coupled—giving rise to $SL_\alpha$, $AL_\alpha$, and $SL_\beta$, $AL_\beta$ vibrations, where $SL$ denotes symmetric libration (angle displacements in phase) and $AL$ denotes antisymmetric libration (angle displacements out of phase).

Finally, there are two $I-I$ bond-stretching vibrations that are essentially the same as the gas-phase stretching mode. As expected, these vibrations are

† The name optic mode comes from the behavior of ionic crystals such as $Na^+Cl^-$. When $Na^+$ and $Cl^-$ in a given cell move out of phase with each other, there is an oscillating electric dipole. Optical absorption will occur for light having frequency equal to that of the optic lattice mode.
coupled to produce a SS (symmetric stretch) in-phase vibration and an AS (antisymmetric stretch) out-of-phase vibration. In the latter case, one I₂ bond is stretching while the other is being compressed. As a result of interactions in the crystalline phase,⁸ ⁹ these SS and AS vibrations have lower frequencies than the gas-phase vibration at 213.3 cm⁻¹.

Now we must consider the fact that the motions of the I₂ molecules in any given unit cell are coupled to those of the molecules in other unit cells. An entire crystal of N/2 unit cells has 12 × (N/2) = 6N degrees of freedom. Thus it would seem necessary to solve a 6N × 6N secular determinant to obtain the normal-mode frequencies. However, symmetry and the periodicity of the lattice can be used to greatly simplify the problem,⁶ ⁷ and we can talk about 12 vibrational modes associated with each of N/2 discrete values of a wave vector \( \mathbf{k} \). This wave vector has a magnitude

\[
k = \frac{2\pi}{\lambda}
\]

and a direction that specifies the propagation direction of a traveling wave (i.e., of the “crests and troughs” of the periodic displacements). The vibrational wave motion in the crystal can be represented by traveling-wave equations of the general form

\[
A_j(\mathbf{r}, t) = A_{j0} \cos(2\pi v_j t - \mathbf{k} \cdot \mathbf{r})
\]

where \( A_j \) is the instantaneous amplitude of a displacement of type \( j \) \((j = 1 \text{ to } 12)\) in the cell at point \( \mathbf{r} \). Equation (29) describes the twelve normal modes associated with a given \( \mathbf{k} \), i.e., with a given wavelength and direction for the periodic displacements of molecules in different cells. All allowed \( \mathbf{k} \) values lie inside a Brillouin zone (BZ), a region bounded by a polyhedron in reciprocal space that is centered around \( k_x, k_y, k_z = 0, 0, 0 \).⁶ ⁷ As \( k \to 0 \), adjacent cell displacements approach being in phase, and \( \lambda \to \infty \); when \( k \to k_{\text{max}} \) at the Brillouin zone boundary, \( \lambda \to \lambda_{\text{min}} \), a minimum wavelength for the \( \mathbf{k} \) direction.

The \( v \) versus \( k \) curves, called phonon dispersion curves,⁶ ⁷ are shown in Fig. 2 for the \( a \) axis direction in an I₂ crystal. These and similar dispersion curves in other directions were obtained by Smith et al.⁹ using the technique of inelastic neutron scattering.¹⁰ ¹² The frequencies of internal stretching and libration are not affected greatly by the coupling between unit cells; i.e., each \( v_j \) is roughly constant for all \( \mathbf{k} \) values for these modes. In contrast, the center-of-mass motion is strongly affected, especially for the acoustic branches \( TA_1 \), \( TA_2 \), and \( LA \). These lattice vibrations are three-dimensional analogs of the one-dimensional vibrations of a violin string or the air in an organ pipe and the two-dimensional vibrations of a drum head. In the continuum (long-wave) limit, they represent three-dimensional vibrations in a bowl of Jello. Such

† The BZ is the locus of all points in reciprocal space that are closer to 0, 0, 0 than to any other reciprocal lattice point; its volume is equal to that of the primitive unit cell in the reciprocal lattice. See Exp. 46 for a discussion of the reciprocal lattice.
acoustic frequencies range from 0 at the \( BZ \) center (point \( \Gamma \)) to \( \sim 1-2 \) THz at the \( BZ \) edge \([1 \text{ terahertz} (1 \text{ THz}) = 10^{12} \text{ Hz} = 33.3 \text{ cm}^{-1}\]). The notation \( TA \) means transverse (shear) acoustic, and \( LA \) means longitudinal (compression–rarefaction) acoustic.

In order to assign frequency values \( \tilde{\nu}_i \) to each of the 12 branches, we average the available values\(^9\) over the Brillouin zone. The resulting values are given in Table 1, where limiting values at the zone center (point \( \Gamma \)) and zone edge (points \( Y, T, \) or \( Z \)) are also given. The choice of a single frequency for each mode corresponds to a version of the Einstein model for a solid.\(^{1,6}\) This is quite reasonable for all branches except the three acoustic branches. For those three modes, the Debye model\(^{1,6}\) would provide a better approximation. However, the simpler Einstein approximation for \( TA_1, TA_2, \) and \( LA \) is adequate for the present purposes.

We can now formulate the desired expressions for \( q_s \) and \( \mu_z \). Using Eqs. (8) to (10), together with the fact that \( t = 2 \) for \( I_2 \) and each unit cell contains two \( I_2 \) molecules, we find

\[
\ln q_s = \frac{1}{6N} \sum_{i=1}^{6N} \ln q_i = \frac{1}{6N} \sum_{i=1}^{12(N/2)} \ln q_i
\]  

\( (30) \)
TABLE 1
Discrete (representative) phonon frequencies in I₂ crystals

<table>
<thead>
<tr>
<th>Mode no.</th>
<th>Type of mode</th>
<th>Representative frequency $\nu_j$, cm$^{-1}$</th>
<th>Frequency range</th>
<th>Point(s) in BZ$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>TA₁</td>
<td>21.0</td>
<td>0–40.5</td>
<td>Γ, T</td>
</tr>
<tr>
<td>2</td>
<td>TA₂</td>
<td>26.5</td>
<td>0–53.1</td>
<td>Γ, T</td>
</tr>
<tr>
<td>3</td>
<td>LA</td>
<td>33.0</td>
<td>0–56.2</td>
<td>Γ, Y</td>
</tr>
<tr>
<td>4</td>
<td>TO₁</td>
<td>41.0</td>
<td>30.7–60.0</td>
<td>Γ, Y</td>
</tr>
<tr>
<td>5</td>
<td>TO₂</td>
<td>49.0</td>
<td>41.0–60.0</td>
<td>Γ, Y</td>
</tr>
<tr>
<td>6</td>
<td>AL₀</td>
<td>51.5</td>
<td>41.7–61.0</td>
<td>Γ, Y</td>
</tr>
<tr>
<td>7</td>
<td>SL₀</td>
<td>58.0</td>
<td>57.7–66.5</td>
<td>Γ, Y</td>
</tr>
<tr>
<td>8</td>
<td>LO</td>
<td>59.0</td>
<td>65.4–46.5</td>
<td>Γ, Z</td>
</tr>
<tr>
<td>9</td>
<td>ALᵺ</td>
<td>75.4</td>
<td>flat</td>
<td>Γ</td>
</tr>
<tr>
<td>10</td>
<td>SLᵺ</td>
<td>87.4</td>
<td>flat</td>
<td>Γ</td>
</tr>
<tr>
<td>11</td>
<td>SS</td>
<td>180.7</td>
<td>flat</td>
<td>Γ</td>
</tr>
<tr>
<td>12</td>
<td>AS</td>
<td>189.5</td>
<td>flat</td>
<td>Γ</td>
</tr>
</tbody>
</table>

$^a$ Estimated from Ref. 9.

$^b$ Points T and Z are not shown in Fig. 2; they are elsewhere on the surface of the BZ. See Ref. 9.

The number of discrete k values is $N/2$, the number of primitive unit cells in the crystal. Each of these is assumed to yield the same set of 12 branch frequencies $\nu_j$. Thus we can simplify Eq. (30) to

$$\ln q_s = \frac{1}{6N} \sum_{j=1}^{12} \ln q_j = \frac{1}{12} \sum_{j=1}^{12} \ln q_j$$

(31)

where 12 is the number of degrees of freedom per unit cell. Finally, we obtain for I₂(s)

$$\ln q_s = -\frac{1}{12} \sum_{j=1}^{12} \ln(1 - e^{-\Theta/T})$$

(32)

and

$$\mu_r = -6RT \ln q_s = \frac{RT}{2} \sum_{j=1}^{12} \ln(1 - e^{-\Theta/T})$$

$$= \frac{RT}{2} \ln \left[ \prod_{j=1}^{12} (1 - e^{-\Theta/T}) \right]$$

(33)

**Equilibrium between crystal and gas.** On substituting the expressions of Eqs. (25) and (33) into Eq. (2) and doing some rearranging and simplifying, we obtain

$$\ln \rho = \ln \left[ \frac{T^{7/2} \prod_{j=1}^{12} (1 - e^{-\Theta/T})^{1/2}}{(1 - e^{-\Theta_{cr}/T})} \right] = \ln \left[ \frac{(2\pi m k)}{h^2} \right]^{3/2} \frac{k}{\sigma \Theta_{cr}} \frac{\Delta E_0}{RT}$$

(34)
If the value of \( p \) is determined at one temperature, this equation can be solved for \( \Delta E_0^s \), the value of which is needed (along with \( \Theta_{\text{rot}} \) and \( \Theta_{\text{vib}} \)) to determine the chemical potential of gaseous \( I_2 \). Once \( \mu_s(T) \) and \( \mu_g(T) \) are both known, one can calculate \( \Delta S_{\text{sub}} \) and \( \Delta H_{\text{sub}} \). By contrast, the Clausius–Clapeyron equation, given by

\[
\ln p = \text{constant} - \frac{\Delta H_{\text{sub}}}{R} \frac{1}{T}
\]  

(35)

in its approximate integrated form, requires at least two values of \( p \) at different temperatures in order to obtain a value of \( \Delta H_{\text{sub}} \).

Equation (35) has obvious similarities to Eq. (34). This correspondence can be enhanced by replacing \( \Delta H_{\text{sub}}/RT \) with \( \Delta E_0^s/RT + 1 \), which is equivalent since \( \Delta(pV) = RT \) is an excellent approximation under the conditions of the present experiment. However, \( \Delta E_0^s \) is temperature dependent and refers to the energy of sublimation at the temperature of the experiment rather than at absolute zero. This temperature dependence is reflected in the statistical treatment by the variation with \( T \) of the second term on the left-hand side (LHS) of Eq. (34).

If \( p \) values have been measured at several temperatures, the LHS of Eq. (34) can be plotted against \( 1/T \), and the value for \( \Delta E_0^s \) can be determined from the slope of a straight line fitted graphically or by least squares. In addition, the intercept can be compared with the predicted value of the constant term on the RHS of Eq. (34). Alternatively, it is possible to calculate a \( \Delta E_0^s \) value from each \( p, T \) data point and see how well these values agree.

**Entropy and enthalpy of sublimation.** Since we have a system of only one component, the chemical potentials for \( I_2 \) in crystalline and gaseous forms, given in Eqs. (33) and (25) respectively, are equivalent to the molar Gibbs free energies \( G_c \) and \( G_g \). Aside from an additive constant, the entropies of the two phases can be obtained by differentiating with respect to temperature. The expressions obtained are

\[
S_c = -\left( \frac{\partial G_c}{\partial T} \right)_p = -\left( \frac{\partial \mu_c}{\partial T} \right)_p
\]

\[
= R \sum_{j=1}^{12} \left[ \frac{\Theta_j/T}{e^{\Theta_j/T} - 1} - \ln(1 - e^{-\Theta_j/T}) \right]
\]  

(36)

\[
S_g = -\left( \frac{\partial G_g}{\partial T} \right)_p = -\left( \frac{\partial \mu_g}{\partial T} \right)_p
\]

\[
= \frac{\Delta E_0^s - \mu_g}{T} + \frac{7}{2} R + R e^{\Theta_{\text{vib}}/T} \frac{\Theta_{\text{vib}}/T}{e^{\Theta_{\text{vib}}/T} - 1}
\]  

(37)

The heat of sublimation at temperature \( T \) is

\[
\Delta H_{\text{sub}} = T \Delta S_{\text{sub}} = T (S_g - S_c)
\]  

(38)