Statistical Thermodynamics: Sublimation of Solid Iodine

Chem 374
For March 14, 2019
Prof. Patrik Callis

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, K_{eq}** , for **I_2(s) ---> I_2(g)**, i.e., **the "vapor pressure"**, and ΔH^0, both as a function of temperature.

2. Compute **K_{eq}** using a partially completed excel **spreadsheet** which should be downloaded from the website.

3. 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 ΔG^0 and $\Delta\mu^0$ change with temperature, therefore how K_{eq} changes with temperature. This includes the "equilibrium constants" for phase changes.

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

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

$$dG = -S\,dT + V\,dP + \mu_1 dn_1 + \mu_2 dn_2$$

$$\text{where } \mu_1 = \left(\frac{\partial G}{\partial n_1}\right)_{T,P,n_2} = \overline{G}_1 \text{ is the partial molar Gibbs free energy,}$$

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

But our experiment is done at ***constant T and V***, so there is no non-pV work to worry about. It is energy instead of enthalpy that we are concerned with. The Helmholz free energy, **A**, is what determines equilibrium constant, useful work, and spontaneity at **constant volume**.

A = U – TS by ***definition***, where U in this document is energy. In terms of A, the chemical potential becomes:

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

$$dA = \; -S\,dT \qquad - \quad P\;dV \qquad + \quad \mu_1 dn_1 \qquad + \quad \mu_2 dn_2$$

$$\text{where } \mu_1 = \left(\frac{\partial A}{\partial n_1}\right)_{T,V,n_2} = \bar{A}_1 \text{ is the partial molar Helmholtz free energy for component 1}$$

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 ΔG with units of J/mol at constant temperature and pressure. $\Delta\mu$ = molar ΔA 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:

$$-RT\ln K = \Delta\bar{A}^0 = \Delta\bar{U}^0 - T\Delta\bar{S}^0$$

$$\text{Divide by -RT:} \quad \ln K = -\frac{\Delta\bar{A}^0}{RT} = -\frac{\Delta\bar{U}^0}{RT} + \frac{\Delta\bar{S}^0}{R}$$

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

$$\ln\left(\frac{K(T_2)}{K(T_1)}\right) = -\frac{\Delta_r\bar{U}^0}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

This means that in the vapor pressure experiment, the plot of lnP vs 1/T has a slope of

$-\Delta U^0/R$, not $-\Delta H^0/R$. It is easy to show that $\Delta H^0 = \Delta U^0 + RT$ from the definition

H = U + 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: ΔG^0= -RTlnK or the equivalent statement:

$$K = e^{\frac{-\Delta G^0}{RT}} = 10^{\frac{-\Delta G^0}{2.3RT}} = 10^{\frac{-\Delta G^0}{5700}}$$ at constant T=298 K and P.

At constant T and V, this becomes $K = e^{\frac{-\Delta A^0}{RT}} = 10^{\frac{-\Delta A^0}{2.3RT}} = 10^{\frac{-\Delta A^0}{5700}}$ at constant T =298.

This means if ΔA = -57000 J, K_{eq}= 1 x 10^{10} ; if ΔA = +57000 J, K_{eq}= 1 x 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*:

$$K_{2/1} = \frac{P_2}{P_1} = \frac{N_2}{N_1} = \frac{g_2}{g_1} e^{\frac{-\Delta U^0}{RT}} = 10^{\frac{-\Delta A^0}{2.3RT}} = 10^{\frac{-\Delta A^0}{5700}}$$, where N_1 and N_1 are the numbers of molecules in states 1 and 2, and g_1 and g_2 are the degeneracies of the states 1 and 2. g_1 is the number of different states with energy = U_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 = $k_B$lnW).

Boltzmann's constant k_B = 1.38x 10^{-23} J K^{-1} molecule^{-1}. When multiplied by Avogadro's Number, Boltzmann's constant becomes R = 8.3145 J K^{-1} mol^{-1}. (Thus when one sees the expression exp($-\Delta U/k_BT$), you immediately know that the units of U are J/molecule, instead of J/mol)

Therefore $\Delta S = S_2 - S_1$= Rln (g_2) - Rln (g_1) = Rln(g_2/ g_1).

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

$$K_{eq} = \frac{g_2}{g_1} e^{\frac{-\Delta U^0}{RT}} = e^{\frac{\Delta S^0}{R}} e^{\frac{-\Delta U^0}{RT}} = e^{\frac{-\Delta U^0}{RT}} e^{\frac{T\Delta S^0}{RT}} = e^{\frac{-\Delta U^0}{RT}} e^{\frac{T\Delta S^0}{RT}} = e^{\frac{-(\Delta U^0 - T\Delta S^0)}{RT}} = e^{\frac{-\Delta A^0}{RT}}$$

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**.

$Q = \sum_{states,i} e^{\frac{-U_i}{kT}}$, 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 **U_i** ***levels*** , multiplying each Boltzmann factor by the degeneracy of the energy level, we get the equivalent statement:

$$Q = \sum_{levels,i} g_i e^{\frac{-U_i}{kT}} = \sum_{levels,i} e^{\frac{TS_i}{k}} e^{\frac{-U_i}{kT}} = \sum_{levels,i} e^{\frac{-A_i}{kT}} = e^{\frac{-A}{kT}},$$

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: $q_g = q_{trans}\, q_{rot}\, q_{vib}\, q_{el}$.

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 $q_{vib} = (1 - e^{\frac{-h\nu}{kT}})^{-1}$. Because in most molecules all electronic excited states are so high above the ground state, $q_{electronic} = 1$. This is true for I_2 because the ground state of I_2 is non-degenerate.

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

Finally, instead of equation (34), which has been made completely baffling by "simplifying" it to death, you will use $\Delta A = A_{gas} - A_{solid} = -RT\ln Q_{gas} + RTQ_{solid}) +$ **ΔU^0_0(sub)** and vary the concentration (which appears in q_{trans} disguised as the volume, $V = nRT/\mathbf{p_{I2}}$) in the spreadsheet, until you **find the I_2 pressure** that makes **$\Delta A = 0$**. That will be **equilibrium**, and that **p** will be **the "vapor pressure"**

$$\Delta A = -RT\ln[(\frac{2\pi mkT}{h^2})^{3/2}\frac{kT}{p}\times\frac{kT}{\sigma hcB_0}\times(1-e^{\frac{-h\nu_{vib}}{kT}})^{-1}] + RT\ln(q_{solid}),$$

where q_{solid} is given in equations 32 and 33, and on the **spreadsheet.**

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 are to enter the data you took this year in place of that data.**

Below is from: *Experiments in Physical Chemistry*, 5th Ed., D.P. Shoemaker, C.W. Garland, and J. W. Nibler, 1998

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 $I_2(s)$–$I_2(g)$ 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 I_2 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 $\Delta\tilde{E}_0^0$ 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:

$$Q_s = \prod_i q_i \qquad \ln Q_s = \sum_i \ln q_i \tag{7}$$

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:

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

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

$$\ln Q_s = M \ln q_s = 3tN \ln q_s \tag{9}$$

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)

$$\mu_s = -3tRT \ln q_s \tag{10}$$

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

$$Q_g = \frac{q_g^N}{N!} \tag{11}$$

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

$$\ln Q_g = N \ln q_g - N \ln N + N \tag{12}$$

Using Eq. (5) again, we obtain

$$\mu_g = -RT \ln \frac{q_g}{N} \tag{13}$$

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

Gaseous I_2. The partition function q_g is very well approximated as a product of terms arising from translational, rotational, vibrational, and electronic degrees of freedom:

$$q_g = q_{\text{trans}} q_{\text{rot}} q_{\text{vib}} q_{\text{el}} \tag{14}$$

The translational partition function is given by[2]

$$q_{\text{trans}} = \left(\frac{2\pi mkT}{h^2}\right)^{3/2} V \tag{15}$$

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[3]

$$q_{\text{rot}} = \frac{kT}{\sigma hc\tilde{B}_0} = \frac{T}{\sigma\Theta_{\text{rot}}} \tag{16}$$

Here σ 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

$$\tilde{B}_0 \equiv \frac{h}{8\pi^2 Ic} \tag{17}$$

where I is the moment of inertia of the molecule

$$I = \mu r_0^2 \tag{18}$$

The reduced mass μ (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 $0.037315\ \text{cm}^{-1}$.[4] The quantity Θ_{rot} is the *rotational characteristic temperature,* given by

$$\Theta_{\text{rot}} = \frac{hc\tilde{B}_0}{k} \tag{20}$$

The factor hc/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[5]

$$q = (1 - e^{-h\nu_0/kT})^{-1} = (1 - e^{-\Theta_{\text{vib}}/T})^{-1} \tag{21}$$

where ν_0 is the molecular vibration frequency and Θ_{vib} is the *vibrational characteristic temperature,*

$$\Theta_{\text{vib}} = \frac{h\nu_0}{k} = \frac{hc\tilde{\nu}_0}{k} \tag{22}$$

For the I_2 molecule, $\tilde{\nu}_0$ has the value $213.3\ \text{cm}^{-1}$.[4]

Equation (21) as written applies to an oscillator for which the reference energy is the energy of the vibrational ground state ($v = 0$); i.e., the $v = 0$ 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 *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

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

It remains to deal with q_{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

$$q_{el} = 1 \tag{24}$$

Let us now introduce $\Delta\tilde{E}_0^0 = N_0\,\Delta\varepsilon_0$, 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

$$\mu_g = \Delta\tilde{E}_0^0 - RT\ln\left[\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\frac{kT}{p}\frac{T}{\sigma\Theta_{rot}}(1 - e^{-\Theta_{vib}/T})^{-1}\right] \tag{25}$$

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

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

where Θ_i is defined in terms of $\tilde{\nu}_i$ in the same way as Θ_{vib} is defined in terms of $\tilde{\nu}_0$ 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

$$M = 3 \times t \times N - 6 = 6N - 6 \cong 6N \tag{27}$$

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.[6,7] 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.

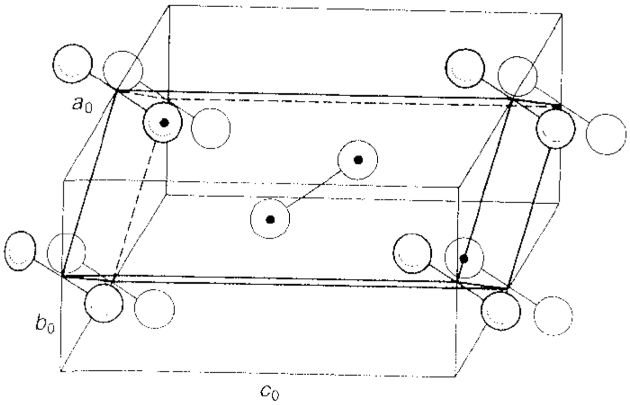

FIGURE 1
The crystal structure of $I_2(s)$.[8] The primitive unit cell, outlined in heavy lines, contains two molecules, identified by dots at the atomic centers (one half molecule each at the upper left and lower right corners, and one molecule in the body center). The light lines outline an orthorhombic non-primitive unit cell of dimensions $a_0 = 0.727$ nm, $b_0 = 0.479$ nm, $c_0 = 0.979$ nm. All molecules are in planes parallel to the **b** and **c** axes. (Not all molecules in the orthorhombic cell are shown.)

molecules.[8] 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 3×4 atoms = 12 mechanical degrees of freedom associated with each unit cell. In the gas phase, there would be three translations, two rotations, 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 $I_2(s)$ is not one of these. The librational motions for each I_2 occur about two axes (α, β) 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_α, AL_α and SL_β, AL_β vibrations, where SL denotes symmetric libration (angle displacements in phase) and AL denotes anti-symmetric 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 I_2 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 I_2 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 $12 \times (N/2) = 6N$ degrees of freedom. Thus it would seem necessary to solve a $6N \times 6N$ 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* **k**. This wave vector has a magnitude

$$k = \frac{2\pi}{\lambda} \tag{28}$$

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

$$A_j(\mathbf{r}, t) = A_{j0} \cos(2\pi \nu_j t - \mathbf{k} \cdot \mathbf{r}) \tag{29}$$

where A_j is the instantaneous amplitude of a displacement of type j ($j = 1$ to 12) in the cell at point **r**. Equation (29) describes the twelve normal modes associated with a given **k**, i.e., with a given wavelength and direction for the periodic displacements of molecules in *different cells*. All allowed **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 $k \to k_{max}$ at the Brillouin zone boundary, $\lambda \to \lambda_{min}$, a minimum wavelength for the **k** direction.

The ν versus k curves, called phonon dispersion curves,[6,7] are shown in Fig. 2 for the **a** axis direction in an I_2 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 ν_j is roughly constant for all **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.

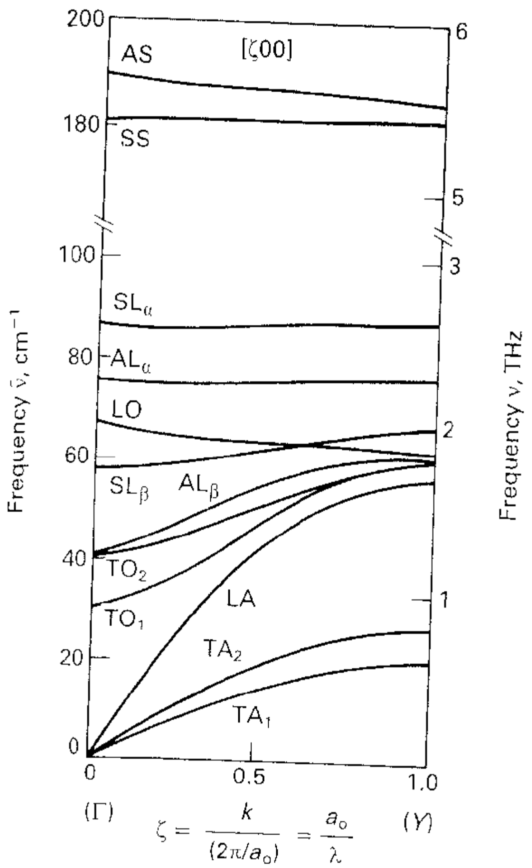

FIGURE 2
Phonon dispersion curves for $I_2(s)$ in the **a**-axis direction from the center of the BZ (Γ) to the boundary (Y) at 77 K. Adapted by permission from Smith *et al.* (Ref. 9).

acoustic frequencies range from 0 at the BZ center (point Γ) to ~1–2 THz at the BZ edge [1 terahertz(1 THz) = 10^{12} Hz = 33.3 cm^{-1}]. The notation TA means transverse (shear) acoustic, and LA means longitudinal (compression–rarefaction) acoustic.

In order to assign frequency values $\tilde{\nu}_j$ 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 Γ) 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 μ_s. 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

$$\ln q_s = \frac{1}{6N}\sum_{i=1}^{6N} \ln q_i = \frac{1}{6N}\sum_{i=1}^{12(N/2)} \ln q_i \qquad (30)$$

TABLE 1
Discrete (representative) phonon frequencies in I_2 crystals[a]

Mode no. j	Type of mode	Representative frequency $\tilde{\nu}_j$, cm^{-1}	Frequency range cm^{-1}	Point(s) in BZ[b]
1	TA_1	21.0	0–40.5	Γ, T
2	TA_2	26.5	0–53.1	Γ, T
3	LA	33.0	0–56.2	Γ, Y
4	TO_1	41.0	30.7–60.0	Γ, Y
5	TO_2	49.0	41.0–60.0	Γ, Y
6	AL_β	51.5	41.7–61.0	Γ, Y
7	SL_β	58.0	57.7–66.5	Γ, Y
8	LO	59.0	65.4–46.5	Γ, Z
9	AL_α	75.4	flat	Γ
10	SL_α	87.4	flat	Γ
11	SS	180.7	flat	Γ
12	AS	189.5	flat	Γ

[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 ν_j. Thus we can simplify Eq. (30) to

$$\ln q_s = \frac{1}{6N}\frac{N}{2}\sum_{j=1}^{12} \ln q_j = \tfrac{1}{12}\sum_{j=1}^{12} \ln q_j \tag{31}$$

where 12 is the number of degrees of freedom per unit cell. Finally, we obtain for $I_2(s)$

$$\ln q_s = -\tfrac{1}{12}\sum_{j=1}^{12} \ln(1 - e^{-\Theta_j/T}) \tag{32}$$

and

$$\begin{aligned}\mu_s = -6RT \ln q_s &= \frac{RT}{2}\sum_{j=1}^{12} \ln(1 - e^{-\Theta_j/T}) \\ &= \frac{RT}{2}\ln\left[\prod_{j=1}^{12}(1 - e^{-\Theta_j/T})\right]\end{aligned} \tag{33}$$

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

$$\ln p - \ln\left[\frac{T^{7/2}\prod_{j=1}^{12}(1 - e^{-\Theta_j/T})^{1/2}}{(1 - e^{-\Theta_{\mathrm{vib}}/T})}\right] = \ln\left[\left(\frac{2\pi mk}{h^2}\right)^{3/2}\frac{k}{\sigma\Theta_{\mathrm{rot}}}\right] - \frac{\Delta\bar{E}_0^0}{RT} \tag{34}$$

If the value of p is determined at *one* temperature, this equation can be solved for $\Delta\tilde{E}_0^0$, the value of which is needed (along with Θ_{rot} and Θ_{vib}) to determine the chemical potential of gaseous I_2. Once $\mu_s(T)$ and $\mu_g(T)$ are both known, one can calculate $\Delta\tilde{S}_{sub}$ and $\Delta\tilde{H}_{sub}$. By contrast, the Clausius–Clapeyron equation, given by

$$\ln p = \text{constant} - \frac{\Delta\tilde{H}_{sub}}{R}\frac{1}{T} \tag{35}$$

in its approximate integrated form, requires at least two values of p at different temperatures in order to obtain a value of $\Delta\tilde{H}_{sub}$.

Equation (35) has obvious similarities to Eq. (34). This correspondence can be enhanced by replacing $\Delta\tilde{H}_{sub}/RT$ with $\Delta\tilde{E}_{sub}/RT + 1$, which is equivalent since $\Delta(p\tilde{V}) \cong RT$ is an excellent approximation under the conditions of the present experiment. However, $\Delta\tilde{E}_{sub}$ 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 $\Delta\tilde{E}_0^0$ 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 $\Delta\tilde{E}_0^0$ 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 $\tilde{G}_s$ and $\tilde{G}_g$, aside from an additive constant. The entropies of the two phases can be obtained by differentiating with respect to temperature. The expressions obtained are

$$\begin{aligned}\tilde{S}_s &= -\left(\frac{\partial \tilde{G}_s}{\partial T}\right)_p = -\left(\frac{\partial \mu_s}{\partial T}\right)_p \\ &= \frac{R}{2}\sum_{j=1}^{12}\left[\frac{\Theta_j/T}{e^{\Theta_j/T}-1} - \ln(1-e^{-\Theta_j/T})\right]\end{aligned} \tag{36}$$

$$\begin{aligned}\tilde{S}_g &= -\left(\frac{\partial \tilde{G}_g}{\partial T}\right)_p = -\left(\frac{\partial \mu_g}{\partial T}\right)_p \\ &= \frac{\Delta\tilde{E}_0^0 - \mu_g}{T} + \frac{7}{2}R + R\frac{\Theta_{vib}/T}{e^{\Theta_{vib}/T}-1}\end{aligned} \tag{37}$$

The heat of sublimation at temperature T is

$$\Delta\tilde{H}_{sub} = T\,\Delta\tilde{S}_{sub} = T(\tilde{S}_g - \tilde{S}_s) \tag{38}$$