Experimental Determination of the Sublimation Pressure of Iodine

The determination of the vapor pressure of solid iodine at temperatures from 25 to 65°C in steps of about 10°C is accomplished through spectrophotometric measurements of the absorbance $A$ of the iodine vapor in equilibrium with the solid at the absorption maximum (520 nm). You should also verify that at 700 nm, where the molar absorption coefficient of iodine vapor is so small as to be negligible, the absorbance reads essentially zero. (On the short-wavelength side of the maximum there is no accessible wavelength at which the absorption is negligible; hence the baseline can be taken only from the long-wavelength side.) The absorbance is indicated directly on the spectrophotometer; at every wavelength it is related to the incident beam intensity $I_0$ and the transmitted beam intensity $I$ by the equation

$$A_\lambda = \log\left(\frac{I_0}{I}\right)$$

(34)

The test tube containing iodine in the solid and vapor states must also contain air or nitrogen at about 1 atm to provide pressure broadening of the extremely sharp and intense absorption lines of the rotational fine structure (which can be individually resolved only by special techniques of laser spectroscopy). The reason lies in the logarithmic form of Eq. (34). Within the slit width or resolution width of the kinds of spectrophotometers that may be used in this experiment, low-pressure $I_2(g)$ exhibits many very sharp lines separated by very low background absorption. The instrument effectively averages transmitted intensity $I$, not absorbance $A$, over the sharp peaks and background within the resolution width, but the logarithm of an average is not the average of the logarithm. If the extremely sharp lines are so optically "black" that varying the concentration has little effect on the amount of light transmitted in them, the absorbance is controlled mainly by the background between the lines, and the contribution of the lines to the absorbance is largely lost. Increasing the concentration of gas molecules increases the number of molecular collisions and thus decreases the time between them. This can greatly broaden the lines and lower their peak absorbances, causing them to overlap and smooth out the spectrum over the resolution width so that the absorbance readings are meaningful averages over that range. This effect is readily demonstrated experimentally by comparison of spectra taken of $I_2$ vapor with and without air present.

Figure 1, shows the absorption spectrum of $I_2$ vapor over the range of interest at the vapor pressure of iodine at 27°C, at moderate resolution and at low resolution. A low-resolution spectrum, obtained with wide slits such as those in your spectrophotometer, illustrates how the vibrational structure is averaged out, facilitating the determination of the absorbance at 520 nm.

For each temperature that you will require, there will be a thermostated water bath to hold the test tubes that contain the iodine samples. As the vapor pressure depends strongly on the temperature, keeping the samples equilibrated at the desired temperature is a primary concern in this lab. There can be some cooling of the test tubes in the fractions of a minute that it takes to bring the tube from the water bath to your spectrophotometers, so you should move the tubes and take your absorbance measurements as quickly as possible. You should record the initial (highest) value of the absorbance. To help slow the cooling of the iodine, glass beads have been placed at the bottom of the tubes to act as heat reservoirs. When you are done with your
measurement, you should replace the tubes back in their original water baths, since temperature equilibration of the system, including glass beads, can take several minutes. In your lab write up, you should estimate the magnitude of the uncertainty introduced by cooling.

**Figure 1.**
Absorbance of $I_2(g)$, in equilibrium with the solid at 26°C and in the presence of air at about 1 atm, for wavelengths ranging from 470 to 700 nm. The top curve is at moderately high resolution. The bottom curve is at relatively low resolution, about the highest suitable for this experiment.

<table>
<thead>
<tr>
<th>$t$, °C</th>
<th>$\varepsilon$, L mol$^{-1}$ cm$^{-1}$</th>
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<tbody>
<tr>
<td>20.0</td>
<td>691</td>
</tr>
<tr>
<td>30.0</td>
<td>682</td>
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<tr>
<td>70.0</td>
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</table>

**Table I. Molar absorption coefficient of iodine vapor at $\lambda = 520$ nm**
(Based on an equation derived in Ref. 13)
CALCULATIONS

For each temperature, determine the net absorbance as the difference between the absorbances at 520 and 700 nm:

\[ A = A_{520} - A_{700} \]  

(35)

The net absorbance is related to the concentration \( c \) and the pressure \( p \) of iodine vapor in the cell as follows (assuming the perfect-gas law):

\[ A = \varepsilon d c = \frac{\varepsilon d}{RT} p \]  

(36)

where \( c \) is the concentration of I\(_2\) vapor, \( p \) is the partial pressure of I\(_2\) vapor, \( d \) is the optical path length inside the inner absorption cell, and \( \varepsilon \) is the molar absorption coefficient for I\(_2\) vapor at 520 nm and temperature \( T \).

The value of the molar absorption coefficient \( \varepsilon \) at each temperature can be found from Table 1 by interpolation. Then \( p \) may be calculated with Eq. (36). In the calculations of this experiment, considerable care must be taken with units. It is desirable to obtain \( p \) in pascals for the statistical mechanical calculations; accordingly, \( \varepsilon \) should be converted into units of m\(^2\) mol\(^{-1}\), \( d \) should be in m, and \( R \) should be in units of J K\(^{-1}\) mol\(^{-1}\).

To determine \( \Delta \tilde{H}_{sub} \) from the approximate Clausius-Clapeyron equation [see the first page of the dry lab], plot \( \ln p \) against \( 1/T \) and determine the slope of the best straight-line fit to the data by graphic or least-squares methods.

The values of \( p \) and \( T \) can now be used for the statistical mechanical calculations. In order to calculate the rotational characteristic temperature \( \Theta_{rot} \) with Eq. (20), use the literature value for the rotational constant \( \tilde{B}_0 = 0.037315 \) cm\(^{-1}\) [or calculate \( \tilde{B}_0 \) from the internuclear distance in the molecule, \( r_0 = 0.2667 \) nm, with Eqs. (17) to (19)]. From the literature value of the molecular vibrational frequency in the gas phase, \( \tilde{\nu}_0 = 213.3 \) cm\(^{-1}\), calculate the vibration characteristic temperature \( \Theta_{vib} \) with Eq. (22). From the phonon frequencies given in the dry lab handout, calculate the 12 vibration characteristic temperatures \( \Theta_j \).

Calculate \( \Delta \tilde{E}_0^0 \) from Eq. (33) at each temperature using the Excel/Mathematica/Mathcad spreadsheet you developed for the dry lab. Do the values obtained for \( \Delta \tilde{E}_0^0 \) agree satisfactorily? If not, check the calculations and/or consider possible systematic errors. We can also rewrite Eq. (33) in a form that more closely matches the Clausius-Clapeyron equation:

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

(37)
Plot the LHS of Eq. (37) against \( l/T \), and determine both \( \Delta \tilde{E}_0 \) and the constant term graphically or by least squares. Does this value of \( \Delta \tilde{E}_0 \) agree with the average of the values obtained by direct application of Eq. (37)? Does the constant term agree with the theoretical value?

**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. (32) 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

\[
\tilde{S}_s = -\frac{\partial \tilde{G}_s}{\partial T} = -\left( \frac{\partial \mu}{\partial T} \right)_p = \frac{R}{2} \sum_{j=1}^{12} \left[ \Theta_j / T \ln(e^{\Theta_j/T} - 1) \right] - \ln(1 - e^{-\Theta_j/T}) \tag{38}
\]

\[
\tilde{S}_g = \frac{\partial \tilde{G}_g}{\partial T} = \left( \frac{\partial \mu}{\partial T} \right)_p = \frac{\Delta \tilde{E}_0}{T} - \frac{\mu_s}{T} + \frac{R}{2} - \frac{\Theta_vib}{e^{\Theta_vib/T} - 1} \tag{39}
\]

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

\[
\Delta \tilde{H}_{sub} = T \Delta \tilde{S}_{sub} = T(\tilde{S}_g - \tilde{S}_s) \tag{40}
\]

Calculate the molar entropies \( \tilde{S}_s \) and \( \tilde{S}_g \) of the crystalline and vapor forms of I\(_2\) at 320 K with Eqs. (38) and (39), and obtain the molar heat of sublimation \( \Delta \tilde{H}_{sub} \) with Eq. (40). Compare it with the value obtained by the Clausius-Clapeyron method and with any literature values that you can find.

**DISCUSSION**

Of the two methods of determining \( \Delta \tilde{E}_0 \) with Eqs. (33) and (37), which do you judge gives the more precise value? Which gives the more accurate value? Which provides the better test of the overall statistical mechanical approach? Compare this approach with the purely thermodynamic method using the integrated Clausius-Clapeyron equation, taking into account the approximations involved in the latter. State the average temperature corresponding to your Clapeyron value of \( \Delta H_{sub} \).
Comment on the choice of representative values of $\tilde{\nu}_j$ for the 12 vibrational modes of the crystal. How much would reasonable changes (say, 10 to 20 percent) in these values affect the results of the calculations? If possible, comment on the effect of using the Debye approximation (different crystal vibrational frequencies) for the acoustic lattice modes instead of the Einstein approximation (all the same vibrational frequency).

REFERENCES

This lab is modified for CSM use from Ch. 48 of *Experiments in Physical Chemistry, 6th edition* by D. P. Shoemaker, C. W. Garland, and J. W. Nibler (1996).

10. C. Kittel, *op. cit.*, pp. 120-121.

GENERAL READING

C. Kittel, *op. cit.*, chap. 4.