

Classical Thermodynamics I: Sublimation of Solid Iodine

Chem 374

For February 22, 2018

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Purpose:

1. To measure the vapor pressure of solid iodine at different temperatures using the absorbance of the vapor. In the process, become more familiar with the concepts of partial pressure and vapor pressure.

2. To use the famous and widely exploited Van't Hoff Equation to recover the enthalpy and entropy of sublimation of solid iodine.

Introduction:

The Van't Hoff Equation tells how ΔG^0 and $\Delta\mu^0$ (the chemical potential change, which for a pure substance is simply the molar Gibbs energy change) change with temperature, and therefore how the equilibrium constant, K , changes with temperature. This includes the "equilibrium constants" for phase changes:

Consider the reaction $I_2(s) \rightleftharpoons I_2(g)$.

$$K_{eq} = \left(\frac{P_{I_2(g)}}{X_{I_2(s)}} \right)_{eq}$$

assuming ideal behavior, where $(P_{I_2(g)})_{eq} = [I_2(g)]RT$ from the ideal gas law is the partial pressure at equilibrium. $X_{I_2(s)}$ is the mole fraction of I_2 in the solid, in case it is not pure. We will assume this is pure and = 1. In that case, $K_{eq} = (P_{I_2(g)})_{eq}$, which is known as the *vapor pressure of $I_2(s)$* .

Temperature dependence of any K_{eq} is well approximated by the Van't Hoff Equation, which provides a means of obtaining ΔH^0 and ΔS^0 as follows (providing these are constant):

Note: The superscript 0 means all reactants and products are in their standard states. This has nothing to do with temperature; it means the following:

gases: ideal and at partial pressure = 1 bar = molar concentration x RT with $R = 0.083145 \text{ Lbar mol}^{-1} \text{ K}^{-1}$

liquids and solids: mole fraction = 1, i.e., pure

solutes: typically 1 M and ideal.

Note that highly concentrated solutions one may use either the liquid or solute standard state, which changes the units and values used in K and the corresponding ΔG^0 , ΔH^0 and ΔS^0 values.

In the equations below, the bar over the standard properties indicates **per mole**. All values are functions of T , but we are assuming ΔH^0 and ΔS^0 are independent of temperature.

$$-RT \ln K = \Delta \bar{G}^0 = \Delta \bar{H}^0 - T\Delta \bar{S}^0$$

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

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

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

This means that a plot of $\ln K$ vs. T^{-1} has a slope of $-\Delta H^0/R$ and an intercept of $\Delta S^0/R$. Some special cases are:

Activity of solvent required to reach a certain melting point

$$\ln\left(\frac{a}{1}\right)_{eq} = -\frac{\Delta\bar{H}_{fus}^0}{R}\left(\frac{1}{T_{fus}} - \frac{1}{273}\right) \quad (\text{Not relevant for this experiment})$$

Vapor Pressure as a function of T :

$$\ln\left(\frac{P_{vap,T_2}}{P_{vap,T_1}}\right)_{eq} = -\frac{\Delta\bar{H}_{vap}^0}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

In the latter case, the equation goes by the name Clausius-Clapeyron Equation, but it is just a special case of the Van't Hoff Eq.

You should be able to relate this behavior qualitatively to the part of LeChatelier's Principle relating the shift of equilibrium as temperature is changed.

Procedure

Follow the procedure on pages 4-6 of this document, which were excerpted from Ch. 48 of the book, "Experiments in Physical Chemistry, 6th edition" by D. P. Shoemaker, C. W. Garland, and J. W. Nibler (1996) and directly copied from:

http://inside.mines.edu/fs_home/dwu/classes/CH353/labs/iodine/Wet%20Lab%201/WetLab1.pdf

!!!!DO NOT DO the parts starting with "CALCULATIONS TO BE COMPLETED AFTER THE DRY LAB:" on the 6th page of this document.

We will do the statistical mechanics part of this experiment report **later in the semester**.

Instead please do the following calculations and discussion.

Calculations (1. -4.)

1. Determine ΔH^0 and ΔS^0 as indicated above.
2. Determine an estimate of the precision of your results and discuss what factors beyond your control could affect the accuracy of your results.
3. Compare your results with published values. Cite your references. Your score on this part will depend on how many temperatures for which you can find the data, and for how authoritative the source is. For example, work found at the National Institute for Standards and Technology(NIST) website for work using several temperatures similar to yours would be the highest, and that for one temperature quoted by a participant in typical "What is the answer..." type of forum would not be worth much.

Finding good published values is not as simple as you might think. Consider the following from Wikipedia under "Standard Conditions for Temperature and Pressure" –which is not to be confused with [Standard state](#). Standard state is defined above.

In chemistry, **standard condition for temperature and pressure** (informally abbreviated as **STP**) are standard sets of conditions for experimental measurements, to allow comparisons to be made between different sets of data. The most used standards are those of the International Union of Pure and Applied Chemistry (IUPAC) and the National Institute of Standards and Technology (NIST), although these are not universally accepted standards. Other organizations have established a variety of alternative definitions for their standard reference conditions. The current version of IUPAC's standard is a temperature of 0 °C (273.15 K, 32 °F) and an absolute pressure of 100 kPa (14.504 psi, 0.986 atm),^[1] while NIST's version is a temperature of 20 °C (293.15 K, 68 °F) and an absolute pressure of 101.325 kPa (14.696 psi, 1 atm). International Standard Metric Conditions for natural gas and similar fluids ^[2] is 288.15 Kelvin and 101.325 kPa.”

The following is one way to get some information:

- a. Go to the NIST website: <http://webbook.nist.gov/chemistry/>
- b. Under Search Options, click on **name**.
- c. type the word **iodine** in the search box, and check the gas phase, or phase transition box
- d. Clicking on **Phase change data** gives you a formula and a plot of vapor pressure vs. T

Finding values for ΔH^0 and ΔS^0 at different temperatures is not so easy. It will be acceptable for this report to use values tabulated at 298.15 K, which may be found in the appendix of almost all physical chemistry text books.

4. The values of ΔH^0 and ΔS^0 of sublimation for I_2 might seem surprising to you compared to those of liquid water at room temperature. Comment on these differences and speculate on the origin of these differences. Later when we consider the statistical mechanics of iodine solid and gas, the reason for these differences will become clearer.

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

$$A_\lambda = \log\left(\frac{I_0}{I}\right)_\lambda \quad (34)$$

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.

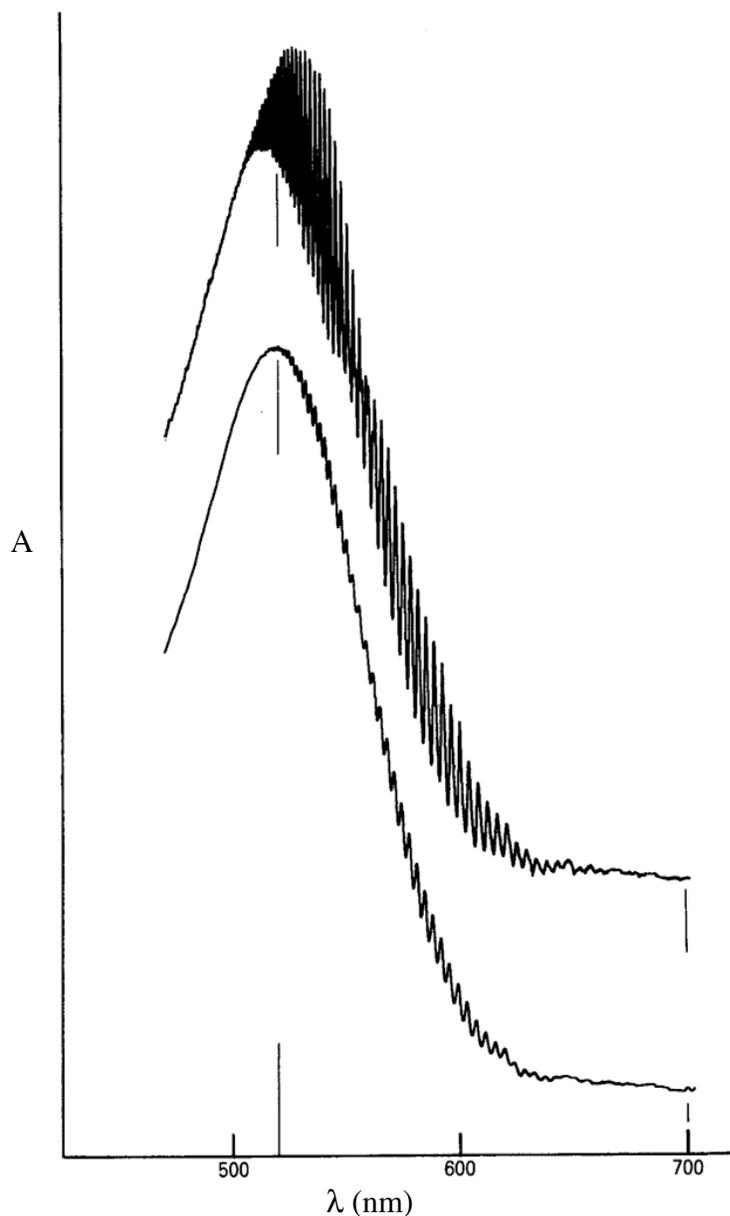


Figure 1.

Absorbance of $I_2(g)$, in equilibrium with the solid at $26^\circ C$ 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.

$t, ^\circ C$	$\epsilon, L \text{ mol}^{-1} \text{ cm}^{-1}$
20.0	691
30.0	682
40.0	672
50.0	663
60.0	654
70.0	646

Table I. Molar absorption coefficient of iodine vapor at $\lambda = 520 \text{ nm}$

(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:

$$A = A_{520} - A_{700} \quad (35)$$

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):

$$A = \epsilon dc = \frac{\epsilon d}{RT} p \quad (36)$$

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 (for typical test tubes, this is about 1 cm), and ϵ is the molar absorption coefficient for I_2 vapor at 520 nm and temperature T .

The value of the molar absorption coefficient ϵ 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, ϵ should be converted into units of $\text{m}^2 \text{mol}^{-1}$, d should be in m, and R should be in units of $\text{J K}^{-1} \text{mol}^{-1}$.

To determine $\Delta\tilde{H}_{sub}$ from the approximate Clausius-Clapeyron equation

$$\ln p = \text{constant} - \frac{\Delta\tilde{H}_{sub}}{RT}$$

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.

CALCULATIONS TO BE COMPLETED AFTER THE DRY LAB: Not for Feb. 22, 2018

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

$$\ln p - \ln \left[\frac{T^{7/2} \prod_{j=1}^{12} (1 - e^{-\Theta_j/T})^{1/2}}{(1 - e^{-\Theta_{vib}/T})} \right] = \ln \left[\left(\frac{2\pi mk}{h^2} \right)^{3/2} \frac{k}{\sigma \Theta_{rot}} \right] - \frac{\Delta \tilde{E}_0^0}{RT} \quad (37)$$

Plot the LHS of Eq. (37) against $1/T$, and determine both $\Delta \tilde{E}_0^0$ and the constant term graphically or by least squares. Does this value of $\Delta \tilde{E}_0^0$ 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

$$\begin{aligned} \tilde{S}_s &= - \left(\frac{\partial \tilde{G}_s}{\partial T} \right)_p = - \left(\frac{\partial \mu_s}{\partial T} \right)_p \\ &= \frac{R}{2} \sum_{j=1}^{12} \left[\frac{\Theta_j/T}{e^{\Theta_j/T} - 1} - \ln(1 - e^{-\Theta_j/T}) \right] \end{aligned} \quad (38)$$

$$\begin{aligned} \tilde{S}_g &= - \left(\frac{\partial \tilde{G}_g}{\partial T} \right)_p = - \left(\frac{\partial \mu_g}{\partial T} \right)_p \\ &= \frac{\Delta \tilde{E}_0^0 - \mu_g}{T} + \frac{7}{2} R + R \frac{\Theta_{vib}/T}{e^{\Theta_{vib}/T} - 1} \end{aligned} \quad (39)$$

The heat of sublimation at temperature T is

$$\Delta \tilde{H}_{sub} = T \Delta \tilde{S}_{sub} = T(\tilde{S}_g - \tilde{S}_s) \quad (40)$$

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 $\Delta \tilde{E}_0^0$ 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 ΔH_{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

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GENERAL READING

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