

Estimating the enthalpy of sublimation of Iodine at standard conditions via spectrophotometry

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April 2, 2014

Abstract: *Molar energy difference and heat of sublimation of solid Iodine vapor is investigated through spectrophotometric measurements and subsequent thermo- & statistical dynamic calculations.*

Iodine vapor

Ideal gas is composed of non-interacting indistinguishable molecules. For gas we can therefore write,

$$\ln Q_s = \ln \left(\frac{q_g^N}{N!} \right) \simeq N \ln q_g - (N \ln N - N) \quad (4)$$

Introduction

This experiment concerns the acquisition of measured data by observation of absorption of optical light by Iodine vapor ($I_{2(g)}$), produced via sublimation (direct phase transition from solid to gas). We'll discuss how we can relate $I_{2(g)}$ light absorption to its vapor pressure at varying temperatures. With the vapor pressure as a function of temperature we can estimate the enthalpy of sublimation via thermodynamical and thermostatical viewpoints. For this experiment we assume $I_{2(g)}$ behaves as ideal gas and the enthalpy is independent of temperature.

in the last step we used the sterling approximation, which is a fair approximation due to N being very large in a crystal, so from equation (1), we get μ_g

$$\mu_g = -RT \left(\frac{\partial \ln Q_s}{\partial N} \right)_{T,V} = -RT \ln \frac{q_g}{N} \quad (5)$$

$I_{2(g)}$ partition function has contributions from translational, rotational, vibrational & electronic degrees of freedom, namely,

$$q_g = \underbrace{\left(\frac{2\pi mkT}{h^2} \right)^{3/2} \frac{NkT}{p}}_{\text{Translational}} \underbrace{\left(\frac{T}{\sigma \Theta_{\text{rot}}} \right)}_{\text{Rotational}} \underbrace{\frac{e^{-\Delta \epsilon_0/kT}}{1 - e^{-\Theta_{\text{vib}}}}}_{\text{Vibrational}} \quad (6)$$

The relative energy of I_2 's excited electronic states are much greater kT , so we approximate $q_{\text{el}} \approx 1$. The *rotational characteristic temperature* is given,

$$\Theta_{\text{rot}} = \frac{h^2}{8\pi^2 Ik} \quad \text{where} \quad I = \frac{m_1 m_2}{m_1 + m_2} r_0^2 \quad (7)$$

The *vibrational characteristic temperature* is,

$$\Theta_{\text{vib}} = \frac{hc}{k} \tilde{\nu}_0 \quad (8)$$

Introducing $\Delta \tilde{E} \equiv N_0 \Delta \epsilon_0$, the energy required to sublime $I_{2(s)}$ per mol and then replacing q_g from eq. (5) with the expression for it in eq. (6) yields

$$\Delta \tilde{E} - \mu_g = RT \ln \left(\left(\frac{2\pi mkT}{h^2} \right)^{3/2} \frac{kT^2 (1 - e^{-\Theta_{\text{vib}}/T})^{-1}}{\sigma \Theta_{\text{rot}} p} \right) \quad (9)$$

According to eq. (3), differentiating eq. (9) with respect to T at constant p , gives us \tilde{S}_g ,

$$\tilde{S}_g = \frac{\Delta \tilde{E} - \mu_g}{T} + \frac{7}{2}R + R \frac{\Theta_{\text{vib}}/T}{e^{\Theta_{\text{vib}}/T} - 1} \quad (10)$$

the first term of eq. (10) can be replaced with eq. (9) and Θ_{vib} with eq. (8)

Theory

Statistical Mechanics

We wish to obtain the chemical potential per mol μ for $I_{2(s)}$, μ_s and $I_{2(g)}$, μ_g . Sublimation occurs at an equilibrium where $\mu_s = \mu_g$. For a closed system at constant volume, temperature and particle number, its Helmholtz energy A can be expressed as a function of its partition function Q , $A = -kT \ln Q$, the chemical potential is then related to A by,

$$\mu = \left(\frac{\partial A}{\partial n_i} \right)_{T,V,n_{j \neq i}} = -RT \left(\frac{\partial \ln Q}{\partial N_i} \right)_{T,V,N_{j \neq i}} \quad (1)$$

Thermodynamics

From the 2nd law of thermodynamics,

$$dS = \frac{\delta Q}{T} \Rightarrow \delta Q \simeq T \Delta \tilde{S} = T(\tilde{S}_{\text{gas}} - \tilde{S}_{\text{solid}}) \quad (2)$$

where $\Delta \tilde{S}$ is the change in entropy during sublimation, meaning $\delta Q = \Delta \tilde{H}_{\text{sub}}$ the expression for the change in entropy can be written

$$\Delta S_{\text{sub}} = \tilde{S}_s - \tilde{S}_g = \left(\frac{\partial \mu_s}{\partial T} \right)_P - \left(\frac{\partial \mu_g}{\partial T} \right)_P \quad (3)$$

Iodine Crystal

$I_{2(s)}$ can be represented as an ensemble of microcanonical partition functions $q_i = \sum_j e^{-\epsilon_j^{(i)}/kT}$, where $\epsilon_j^{(i)}$ represents the energy of the i -th oscillator in the j -th quantum state of that oscillator. q_i 's geometric mean q_s have the relation

$$\ln q_s = \frac{1}{M} \sum_{i=1}^M \ln q_i \quad (11)$$

where $M = 6N - 6 \simeq 6N$, so the 3D crystals partition function,

$$\ln Q_s = M \ln q_s = \sum_{i=1}^M \ln q_i \quad (12)$$

and with equation (1), we get the chemical potential of the crystal

$$\mu_s = -6RT \ln q_s \quad (13)$$

where

$$\ln q_s = -\frac{1}{12} \sum_{j=1}^{12} \ln 1 - e^{-\Theta_j/T} \quad (14)$$

and therefore we can rewrite eq. (13) as,

$$\mu_s = \frac{RT}{2} \ln \prod_{j=1}^{12} \ln 1 - e^{-\Theta_j/T} \quad (15)$$

We obtain an expression for the change in entropy of the crystal with equations (3) and (15)

$$\tilde{S}_s = \frac{R}{2} \sum_{j=1}^{12} \left[\frac{\Theta_j/T}{e^{\Theta_j/T} - 1} - \ln \left(1 - e^{-\Theta_j/T} \right) \right], \quad (16)$$

where the values of the vibration characteristic temperatures Θ_j are calculated using phonon dispersion data, we make use of chosen means we call *representative frequencies* $\tilde{\nu}_j$ for each (of 12) vibrational mode frequency range j .

$$\Theta_j = \frac{hc}{k} \tilde{\nu}_j, \quad (17)$$

Estimation of physical quantities

The data is obtained through spectrophotometric (studying the interaction between light and matter as a function of wavelength) measurement of the absorbency of $I_{2(g)}$ for wavelengths $\lambda \in \{520, 720\}$ nm. The absorbency of the light during its path to the detector can be related by its intensity,

$$A_{I_{2(g)}} = \ln \frac{I_0}{I}, \quad (18)$$

where I and I_0 are the transmitted and incident beam intensity, respectively. Taking the difference between absorbencies of a glass vial with I_2 and an empty one, we can effectively eliminate the absorbencie of the glass.

$$A_\lambda = A_{I_{(g)}} - A_{\text{Air}} = \ln \frac{I_{\text{Air}}}{I_{I_{(g)}}}. \quad (19)$$

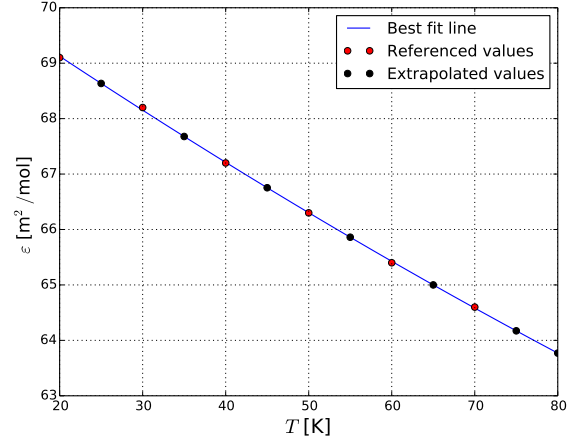


Figure 1: The molar absorption behaves linearly at sufficiently small intervals of T

Finally, A is computed taking the net absorption between absorptions at 520 nm and 700 nm,

$$A = A_{520} - A_{700}, \quad (20)$$

which is suitable for the physical considerations to be performed. Temperature T is measured at 5°C intervals, from 25 to 80°C. The absorbency measured is used in the following relation between vapor pressure p , temperature T , light path through the glass container d and the molar absorption coefficient ε of $I_{2(g)}$ at $\lambda = 520\text{nm}$. ε is obtained from a chemistry table, as can be seen from fig. 1 the data looks linear and was interpolated to estimate ε at intermediate temperatures not available in the table.

$$A = \frac{\varepsilon d}{RT} p \quad \Leftrightarrow \quad p = \frac{R}{\varepsilon d} T A \quad (21)$$

The value of p , which is easily obtained through this relation, is then used to determine $\Delta \tilde{H}_{\text{sub}}$ in the Clausius-Clapeyron equation:

$$\ln p = C - \frac{\Delta \tilde{H}_{\text{sub}}}{RT} \quad (22)$$

where C is some constant and $\Delta \tilde{H}_{\text{sub}} = \Delta H_{\text{fusion}} + \Delta H_{\text{vaporization}}$ is the enthalpy of sublimation. The nature of this equation allows the slope of $\ln p$ as a function of T^{-1} to be estimated with a 1st degree interpolation of the data points. This has the added benefit of allowing determination of the molar energy difference $\Delta \tilde{E}_{\text{sub}}$, by performing the substitution.

$$\frac{\Delta \tilde{H}_{\text{sub}}}{RT} \rightarrow \frac{\Delta \tilde{E}_{\text{sub}}}{RT} + 1,$$

meaning the two quantities, $\Delta \tilde{H}_{\text{sub}}$ and $\Delta \tilde{E}_{\text{sub}}$ are treated as being identical, as the plot retains the same slope after this substitution, the intercept being the only difference. Then, the heat of sublimation as a function of temperature can be, in contrast with the entropic considerations [equation (2)], computed using eq. (22). In the entropic considerations, the enthalpy

of sublimation is computed using equations (10) and (16) in the relation

$$\Delta\tilde{H}_{\text{sub}} = T\Delta\tilde{S} = T(\tilde{S}_g - \tilde{S}_s). \quad (23)$$

In addition, the molar energy difference can be computed by using equations (9) and (15) and imposing upon them that they be identical; From which the following relation arise:

$$\begin{aligned} \ln p - \ln \left[\frac{T^{7/2} \prod_{j=1}^{12} (1 - e^{-\Theta_j/T})^{1/2}}{1 - e^{-\Theta_{\text{vib}}/T}} \right] &= \\ &= \ln \left[\left(\frac{2\pi mk}{h^2} \right)^{3/2} \frac{k}{\sigma \Theta_{\text{rot}}} \right] - \frac{\Delta\tilde{E}_0^0}{RT}. \end{aligned} \quad (24)$$

Experimental set-up

Sublimation is an endothermic phase transitions and can be achieved for I_2 under *standard conditions* (STP) when mildly heated. We added small chunks of $I_{2(s)}$ in a glass container, and allowed sublimation to take place. A water heater controlled the temperature and a photospectrometer measured the absorbance. The spectrophotometer is of the brand Pharmacia Biotech and the model name is Ultrospec 3000. The data consists of absorbency measurements taken with a temperature gradient as elaborated in the text.

Errors in measurement

An attempt was made to seal the lid on the Iodine glass container with duct tape, but proved to be a poor insulation. When measurements were finished, the duct tape was covered in $I_{2(g)}$, clear evidence of leakage. This changes the number of particles in the system, a strict violation of our method of deriving μ from the temperature derivative of Q . Intuitively, this will directly result in less absorption of light A , and consequently underestimated vapor pressure. Additionally, as temperature rises we expect relatively more gas to escape.

We used a water based temperature regulator, the time for the samples temperature to agree with the regulators thermometer was unknown, we estimate its uncertainty to be $\Delta T = \pm 2.5$ K.

Results

Estimations of $\Delta\tilde{H}_{\text{sub}}$ with the Clausius-Clapeyron relation in eq. (22), can be seen in Fig. 2, yielding,

$$\Delta\tilde{H}_{\text{sub}} = 42.3 \text{ kJ/kg}$$

An uncertainty of $1/T$ amounting to $\Delta(1/T) = \Delta T/T^2 = 2.5 \text{ K}/T^2$, is used in the figures (2) and (3) plots, in which the best fit lines generally fit inside the error bars. We can estimate $\Delta\tilde{E}_0^0$ with eq. 24, yielding

$$\Delta\tilde{E}_0^0 = 45.0 \text{ kJ/kg}$$

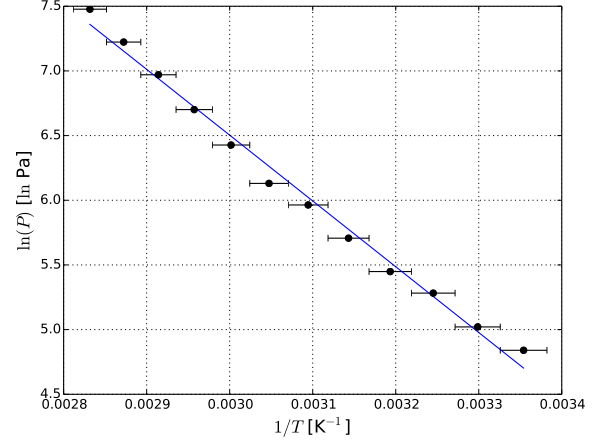


Figure 2: Plotting the data with the Clausius-Clapeyron relation, the slope is an approximation for both the enthalpy of sublimation and the molar energy difference.

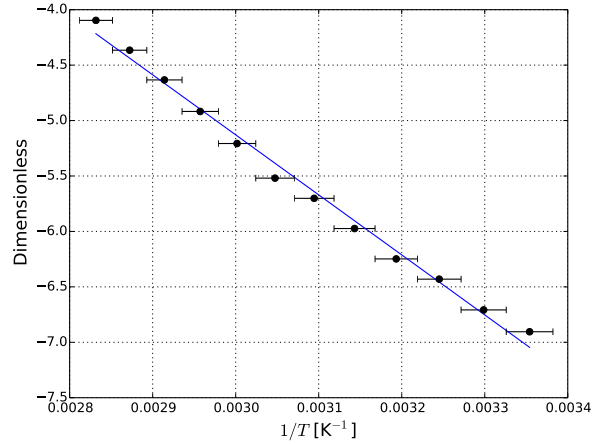


Figure 3: Computation of molar energy difference with eq. (24), using the slope of the above graph.

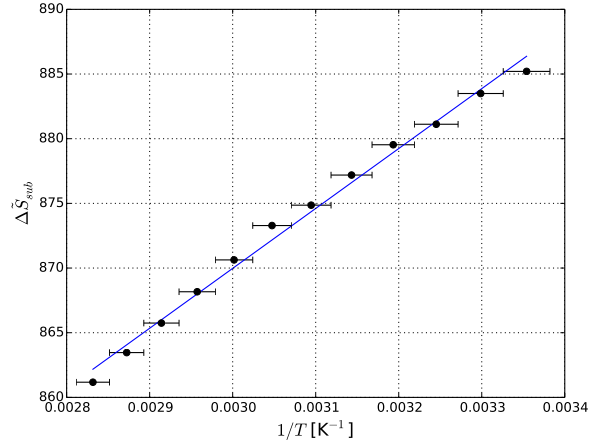


Figure 4: Computation of enthalpy of sublimation with eq. (23), using the slope of the above graph.

since $\Delta\tilde{E}_0^0$ is the energy with reference at absolute zero we know that for a given temperature, we must have $\Delta\tilde{E}_0^0 \geq \Delta\tilde{H}_{\text{sub}}$ which is in agreement with the results. For the enthalpy of sublimation, the slope of fig. 4 gives

$$\Delta\tilde{H}_{\text{sub}} = 46.32 \text{ kJ/kg.}$$

The agreement is appreciable.

References

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