The Enthalpy of Sublimation and Lattice Enthalpy of Solid Argon

Introduction

The solid state is one of the three common states of matter [1]. Like liquids, solids are condensed phases of matter, occupying a volume that is approximately independent of pressure and temperature. Unlike liquids, the particles making up a solid have fixed locations. When the positions occupied by the particles have a regular arrangement in space, the solid possesses a crystal structure [2].

Enthalpy of sublimation

Under conditions where a solid and gas are in equilibrium, the conversion of the solid into gas requires the addition of heat. This process

$$M(s) \rightarrow M(g) \tag{1}$$

is defined as sublimation. When carried out at a fixed temperature and pressure, the enthalpy change associated with this process is called the enthalpy of sublimation, ΔH_{sub}.

As is true of other first order phase transitions, the phase boundary separating the solid and gas phases is described by the Clapeyron equation [3],

$$dp/dT = \frac{\Delta H_{pt}}{T_{pt}(\Delta V_{pt})} \tag{2}$$

Since the same approximations that apply for vaporization also apply for sublimation, eq 2 can be rewritten as

$$d(\ln p)/d(1/T) = -\Delta H°_{pt}/R \tag{3}$$

the Clausius-Clapeyron equation in differential form. If the temperature and pressure are measured for a pure substance over a range of conditions for which the solid and vapor phases are in equilibrium with one another, the enthalpy of sublimation for the substance can be found from the slope of a plot of $\ln(p)$ vs $(1/T)$.

Lattice enthalpy

The lattice enthalpy (Φ) for a solid is the enthalpy change associated with the process in which a solid whose particles are initially at rest is converted into gas phase particles at large separation, so that interaction forces between gas particles are negligible [4]. For an atomic solid, such as Ar(s), the lattice enthalpy is related to the enthalpy of sublimation of the solid by the relationship

$$\Phi = \Delta H°_{sub} + {}^9/_8 R\Theta_D \tag{4}$$

where Φ is the lattice enthalpy and $\Delta H°_{sub}$ is the enthalpy of sublimation for the solid, both measured at T = 0. K. Classically, the lattice enthalpy and enthalpy of sublimation measured at absolute zero would be equal. The additional term on the right side of eq 2 is a consequence of quantum mechanics. It is a correction for the fact that even at absolute zero the particles making up the solid are not at rest. Instead, they have a zero point energy, as is the case for particles in a quadratic potential, such as the one-dimensional harmonic oscillator. Using Debye theory for vibrations in a solid, the zero point energy can be written in terms of Θ_D, the characteristic temperature of the solid [5]. Values for Θ_D are found by fitting experimental data on the heat capacity of a solid at low temperature to the form predicted from Debye theory [6]. For argon, Θ_D = 93. K [7].

A theoretical value for the lattice enthalpy of a simple solid can be calculated if the crystal structure of the solid and the interaction potential for the particles is known. A common interatomic potential used for the solids formed from noble gases such as argon is the Lennard-Jones potential [8]

$$U(r) = 4\varepsilon \left[(\sigma/r)^{12} - (\sigma/r)^{6} \right] \tag{5}$$

A generic Lennard-Jones potential is shown in Figure 1. ε is equal to the depth of the potential, and σ is the distance of separation corresponding to $U(r) = 0$. The dependence of the attractive term on $(1/r^6)$ is predicted theoretically for nonpolar particles that interact only by dispersion forces. The repulsive term is chosen to be proportional to $(1/r^{12})$ for convenience, as most of the properties of atomic solids are not strongly dependent on the exact form of the repulsive term. Values for ε and σ are determined experimentally from deviations from ideal gas behavior, gas viscosity experiments, or other gas data.
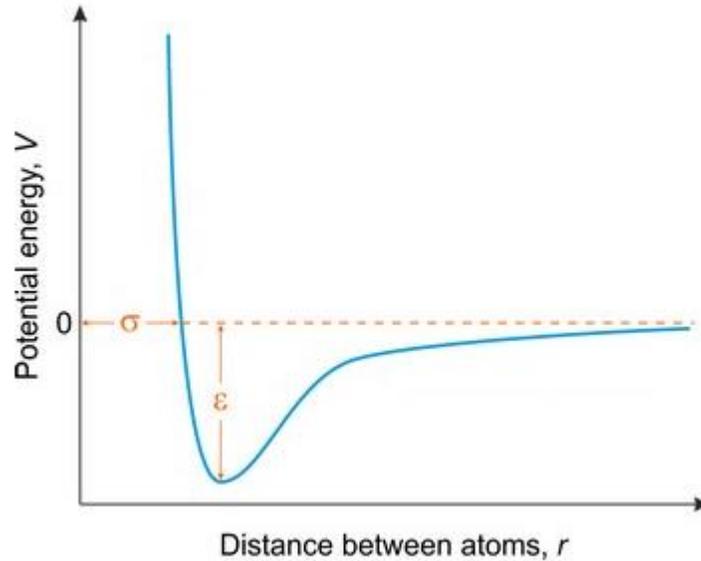

Figure 1. Lennard-Jones potential.

Argon is known from diffraction experiments to form a face centered cubic lattice in the solid state. For this crystal structure, and assuming the potential energy of interaction can be obtained as a summation of all the pairwise interaction terms, the theoretical lattice enthalpy is given by the expression [9]

$$\Phi = 2N_0\varepsilon \left\{ 14.454\,(\sigma/d)^6 - 12.132\,(\sigma/d)^{12} \right\} \tag{6}$$

where d is the distance between nearest neighbor atoms and N_0 is Avogadro's number.

Values for ε, σ, and d for argon have been obtained from a variety of experimental studies. The values used here are [7]

$$\frac{N_0\varepsilon}{R} = 119.5 \text{ K} \qquad\qquad \sigma = 0.3405 \text{ nm} \qquad\qquad d = 0.375 \text{ nm}$$

Using eq 6 and these values, a theoretical value for Φ can be calculated for the solid form of argon.

Experimental

Two complete runs should be performed, and each run should be analyzed separately. The use of two independent trials will make it easier to evaluate the consistency of the data.

In this experiment, ΔH°_{sub} for argon will be determined from measurements of the vapor pressure over a range of temperatures. Because the temperature needs to be quite low, it will be determined by measuring the vapor pressure of N_2 that is in thermal equilibrium with the argon. The temperature can then be determined from a known equation relating vapor pressure to temperature for N_2. In other words, the N_2 functions as a thermometer for the measurements on argon.

The low temperature reaction cell is a metal block containing two small chambers, as shown in Figure 2. The filling tubes for the two chambers pass through an external cap, where they are then connected to a glass manifold. The manifold also has connections to two gas cylinders (argon and nitrogen), two mercury manometers (for pressure measurements), and a vacuum pump (used to evacuate the system before filling with gas). The reaction cell has a sufficiently small diameter that it will fit within the volume of a glass Dewar, which will be used to cool the apparatus.
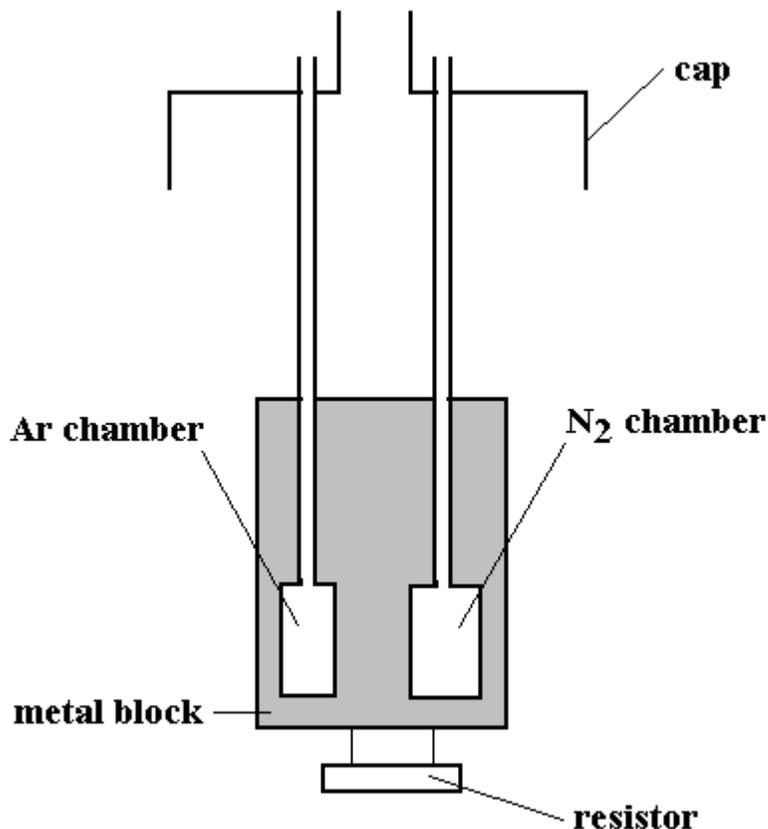
Figure 2. Reaction cell with cap.

Several surgical gloves should be cut above the finger portion of the gloves, retaining the top parts of the gloves. These will be used later as a gasket to seal the Dewar to the cap of the reaction cell. The top portions of the gloves should be slid onto the top of the Dewar. The Dewar should then be filled with liquid nitrogen.

At the beginning of the experiment the delivery pressure at the output side of the two pressure gauges connected to the gas cylinders should be adjusted to a small value, to prevent overpressuring the system. The connecting lines from the two gas cylinders are then purged by allowing gas to flow into the system and be removed by the vacuum pump. After purging, the stopcocks between the gas line and the glass manifold should be closed. All other parts of the system are then evacuated to vacuum using the vacuum pump. Following this, stopcocks on the glass manifold are closed to isolate the argon and nitrogen sides of the apparatus from one another and from the vacuum pump. At this point, each chamber in the reaction cell will be connected to its own manometer and gas cylinder.

To fill the nitrogen side of the reaction cell, the stopcock between the gas line from the nitrogen tank and the nitrogen chamber of the reaction cell should be opened <u>slowly</u>, to allow nitrogen into the system. The pressure of nitrogen can be monitored using the mercury manometer. Nitrogen should be added until the pressure in the system is approximately 1.5 atm, at which point the stopcock from the gas line should be closed. This process is then repeated on the argon side of the apparatus.

Once both sides of the reaction cell have been filled with gas, the cell should be immersed into the Dewar containing liquid nitrogen to cool the cell. This is done by placing the Dewar underneath the reaction cell on a lab jack, and then slowly raising the Dewar using the lab jack. This should be done carefully, as the reaction cell will initially be at room temperature and therefore will cause the liquid nitrogen in the Dewar to rapidly boil. Liquid nitrogen from a second Dewar should be added as needed to keep the level of liquid nitrogen in the cooling Dewar close to the top rim of the Dewar. As the system cools the pressure of nitrogen and argon in the system (indicated by the manometers) should slowly decrease. Near the end of the cooling, when the temperature of the reaction falls below 84. K (the temperature at the triple point of argon) a rapid decrease in pressure on the argon side of the system should be observed, accompanied by a brief period of rapid boiling in the liquid nitrogen Dewar, due to the heat released when argon undergoes the g $\rightarrow$ s phase transition.

After a final filling of the liquid nitrogen Dewar (and, if desired, addition of a small amount of nitrogen and argon gas to the reaction cell), the Dewar should be slowly raised until it fits under the cap above the reaction cell. At this point the reaction cell will be at a temperature of 77. K, the normal boiling point of liquid nitrogen. The glove tops used as a gasket should now carefully be attached to the cap above the cell, making a seal between the Dewar and the cap. After placing a stopper in the top vent of the cap, the connection to the vacuum pump should be opened so that it pumps on the liquid nitrogen in the Dewar. Pumping on the liquid nitrogen will cause additional cooling due to evaporation, as can be observed by the decrease in pressure in the manometer attached to the nitrogen side of the reaction cell. Pump on the Dewar for a few minutes to obtain as low a pressure as possible, and then close the connection to the vacuum pump and remove the stopper from the top vent of the cap.

At this point measurements of the pressure in the nitrogen and argon chambers can begin. Briefly pump on the argon chamber (to remove any residual air that may have leaked into the apparatus). After waiting a minute, take an initial measurement of the pressure of both chambers. Allow the liquid nitrogen in the Dewar to warm slightly (this can be done more quickly by passing electrical current through the resistor fixed below the reaction cell). After the pressure of the nitrogen chamber has increased by ~ 30 torr, stop the heating, and after waiting another minute to reestablish equilibrium, take a second pressure reading for the nitrogen and argon chambers. Continue this process until the nitrogen chamber reaches room pressure. During this process you should obtain 6 - 10 data points.

After the end of the measurements, the vacuum pump should be used to slowly remove nitrogen, and then argon, from the system. After removing the gaskets (gloves) attaching the cap to the Dewar, the Dewar can be lowered and then removed, allowing the reaction cell to warm to room temperature. Any liquid nitrogen remaining in the dewars should be placed in a safe location. ***Be very careful to keep the valves open so that the chambers continue to be evacuated by the vacuum pump during warming. Otherwise, the argon in the chamber could sublime rapidly and cause a mercury spill***. (Evacuating and then refilling the argon line before making measurements, though necessary, may introduce enough argon to exceed atmospheric pressure when all the argon sublimes, if the system is closed.) It is suggested that you notify the instructor when you are ready to warm the system.

When the apparatus has warmed to room temperature, nitrogen and argon gas from the gas cylinders can be used to flush the system and leave it at room pressure. The apparatus should be left with all stopcocks and valves on the gas cylinders closed, and with the gas from the gas cylinders vented, so that the pressure from the primary gauge of each cylinder is zero.

NOTE: EXTREME CARE SHOULD BE USED IN ALL STEPS IN THIS EXPERIMENT, AS THERE ARE HAZARDS ASSOCIATED WITH CLOSED GAS SYSTEMS, THE USE OF COMPRESSED GASES, AND WORKING AT LOW TEMPERATURES.

The primary data obtained in this experiment is the level of mercury for the high and low sides of the nitrogen and argon manometers. Since one side of these manometers is open to the room, the manometers are measuring the <u>difference</u> between room pressure and the pressure of gas in the nitrogen or argon chamber. Room pressure must

therefore be measured using the barometer in the lab. The pressure of nitrogen or argon in the chamber at each data point will then be given by the expression

$$p(N_2 \text{ or Ar chamber}) = p(\text{room}) - \Delta h \tag{7}$$

where $p(N_2 \text{ or Ar chamber})$ is the pressure of gas in the nitrogen or argon chamber, $p(\text{room})$ is room pressure (measured by the barometer), and Δh is the difference in the height of the mercury in the manometer. These are expressed in units of mm. Since 1 mmHg = 1 torr, this means Δh, expressed in mmHg, also represents the difference in torr between room pressure and the pressure in the nitrogen or argon chamber).

The experimental data should be analyzed using the Clausius-Clapeyron equation (eq 3) by plotting $\ln(p_{Ar})$ vs $1/T$, where T is the absolute temperature at the data point. The temperature is found from the pressure data obtained from measurements on the nitrogen chamber. The temperature dependence of the vapor pressure of liquid nitrogen is known, and given by the expression

$$\log_{10}(p_{N2}, \text{torr}) = 6.49594 - \frac{255.821}{(T - 6.600)} \tag{8}$$

Solving this equation for temperature gives

$$T(K) = 6.600 + \frac{255.821}{6.49594 - \log_{10}(p_{N2}, \text{torr})} \tag{9}$$

By inserting the appropriate value for pressure, the temperature at a particular data point can be found. Since both the nitrogen and argon chambers are within the same block of metal, it is a good assumption that both chambers are at the same temperature. Note that eq 9 is in terms of $\log_{10}$ and not ln. Table 1 below gives the temperature for several values of nitrogen pressure, but eq 9 should be used to find precise values for temperature for each of your data points.

Table 1. Temperature as a function of vapor pressure for N_2.

p (torr)	T (K)	p (torr)	T (K)	p (torr)	T (K)
100.0	63.500	280.0	69.785	560.0	74.860
140.0	65.412	360.0	71.535	620.0	75.675
180.0	66.926	440.0	73.004	680.0	76.431
240.0	68.757	500.0	73.975	740.0	77.138

Lab Report

Your laboratory report should include the following:

1) The details of your determination of the enthalpy of sublimation for argon, including a plot of ln(p) vs. $1/T$. You may assume that your experimental values for $\Delta H°_{sub}$ corresponds to the value at absolute zero. The error (95% confidence limits) in your value for $\Delta H°_{sub}$ should also be reported. Each of your runs should be analyzed separately. Your values for $\Delta H°_{sub}$ should be compared to one another, and also to literature values [10].

2) The calculation of the theoretical value for the lattice enthalpy (using eq 6) and the value found from your experimental value for $\Delta H°_{sub}$ (using eq 4). These values should be compared and a discussion of the agreement (or lack of agreement) between the theoretical and experimental values for Φ should be given.

3) A discussion of error in the experiment. There are several things to consider in your error discussion, including a) error in the experimental value for $\Delta H°_{sub}$ based on your plot of ln(p) vs $1/T$, b) expected error in $\Delta H°_{sub}$,

based on how precisely p and T can be measured using the experimental apparatus, c) possible systematic errors in your measurements.

References

1. Pure chemical substances typically have a single gas phase and (with the exception of He) a single liquid phase. Substances generally have several solid phases, distinguished by different crystal structures, such as elemental carbon, which has both the graphite and diamond solid phase.

2. For a discussion of the physical chemistry of solids, including crystal structures and their determination by various experimental techniques, see Chapters 20 of P. W. Atkins, J. de Paula <u>Physical Chemistry</u>, Tenth Edition, (Freeman, New York, 2014).

3. See "The determination of the enthalpy of vaporization of water" experiment for a more detailed discussion of the Clapeyron and Clausius-Clapeyron equations.

4. Some textbooks define the lattice enthalpy in the opposite sense, starting in the gas phase and ending in the solid phase. In that case, the lattice enthalpy will have the same magnitude as the definition used here, but will be opposite in sign (negative instead of positive).

5. A derivation of the expression for the zero point energy for an atomic solid using Debye theory is given in J. O. Hirschfelder, C. F. Curtiss, R. B. Bird <u>Molecular Theory of Gases and Liquids</u>, Second Edition, (Wiley, New York, 1964), pp. 1035-1044, and also in D. D. Pollock <u>Physical Properties of Materials For Engineers</u>, Second Edition, (CRC Press, Cleveland, OH, 1993), pp. 109-110.

6. Atkins and de Paula, pp. 285-286.

7. Whalley, E. and W. G. Schneider, <u>J. Chem. Phys. 23</u> (1955) 1644 - 1649.

8. Atkins and de Paula, p. 677.

9. If only interactions from the nearest neighbors to a particular atom in the lattice were taken into account, both coefficients in the bracketed term in eq 6 would be exactly equal to 12. The larger values for these coefficients is due to including all interatomic pairwise interactions, and not just those from the nearest neighbor atoms.

10. There are literature values for ΔH°_{sub}, though they are difficult to find. The following references can be found online through the FIU library website.

Ferreira, A. G. M. and L. Q. Lobo, <u>J. Chemical Thermodynamics 40</u> (2008) 1621-1626. Table 5 gives their experimental value for ΔH°_{sub} at T_t (triple point of argon), which is close to the temperature at which you have taken data. No error limits are given for their value of ΔH°_{sub}.

Beaumont, R. H., H. Chihara and J. A. Morrison, <u>Proc. Philo. Soc. (London) 78</u> (1961) 1462-1481. Table 6 gives their value for ΔH°_{sub} at T_{tr} (triple point of argon), which is again close to the temperature at which you have taken data. Note that they report their value (and uncertainty) in units of cal/mol, and so these need to be multiplied by 4.184 J/cal to convert them to standard energy units.

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