

Determination of the Heat of Vaporization

In a liquid at equilibrium, molecules have a distribution of energies defined by the Boltzmann distribution. When a molecule at the surface of the liquid has sufficiently more energy than the average energy it evaporates. In principle, when a molecule with high kinetic energy leaves the liquid phase, the average kinetic energy of the liquid would drop. However, temperature remains constant during a phase transition. Therefore, the liquid must absorb heat from the surroundings to replace the lost kinetic energy when vaporization occurs. The heat of vaporization ($\Delta_{\text{vap}}H$) is the quantity of heat absorbed by the liquid required to vaporize a sample while maintaining a constant temperature. In this lab the heat of vaporization is measured using two different methods. In the first method, the vapor pressure of the liquid is measured as a function of temperature. In the second method, a known volume of the sample is evaporated and the amount of heat transferred from the surroundings to the sample is measured.

When a liquid is in equilibrium with its vapor phase, the rate of the molecules leaving the liquid is equal to the rate of the molecules entering the liquid. The partial pressure of the molecules in the vapor phase at this equilibrium defines the vapor pressure of the substance at a given temperature. Figure 1 shows a typical liquid-vapor phase boundary, which can be found by measuring the vapor pressure as a function of temperature. The phase boundary represents pressure-temperature points at which the liquid and vapor phases exist in equilibrium. As the temperature is increased the vapor pressure increases until a certain critical temperature is reached. At the critical temperature (T_c) the surface between the two phases disappears and a single homogeneous phase is formed which is called a supercritical fluid.

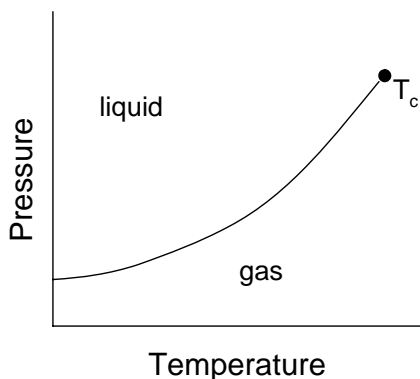


Figure 1 – Liquid-vapor phase boundary.

When a liquid is heated in an open container the vapor pressure increases until it becomes equal to the external pressure. When this occurs vaporization can occur throughout the liquid rather than just on the surface of the liquid. The temperature at which the vapor pressure of the liquid is equal to the external pressure is the boiling point. The slope of the phase boundary is given by the Clapeyron equation.

$$dP/dT = \Delta_{\text{vap}}S / \Delta_{\text{vap}}V \quad (1)$$

Here P is pressure, T is temperature, $\Delta_{\text{vap}}S$ is the change in entropy accompanying the phase change ($S_l - S_g$) and $\Delta_{\text{vap}}V$ is the change in molar volume accompanying the phase change ($V_{m,l} - V_{m,g}$). When the vapor and liquid are in equilibrium the chemical potential of the molecules in the vapor phase is equal to the chemical potential of the molecules in the liquid phase ($\mu_l = \mu_g$) and as a result the change in Gibbs free energy accompanying the phase transition is zero, $\Delta_{\text{vap}}G = 0$. Equation 1 can be rewritten as:

$$dP/dT = \Delta_{\text{vap}}H / T \Delta_{\text{vap}}V \quad (2)$$

Here $\Delta_{\text{vap}}H$ is the change in enthalpy accompanying the phase change ($H_l - H_g$) or the heat of vaporization. The heat of vaporization is a measure of the attractive forces between molecules in a liquid. This attractive force must be overcome for a molecule to leave the liquid and enter into the gas phase.

In order to transform the Clapeyron equation into a more useful form, a few assumptions are made:

- 1) The temperature is not near the critical temperature
- 2) The density of the vapor is low
- 3) The molar volume of the liquid is much less than the molar volume of the vapor, $V_{m,l} \ll V_{m,g}$, therefore $\Delta_{\text{vap}}V \approx V_{m,g}$.
- 4) The vapor behaves ideally, and as a result $V_{m,g} = RT/P$.
- 5) The heat of vaporization is approximately independent of temperature.

$$dP/dT = \Delta_{\text{vap}}HP/RT^2 \quad (3)$$

Here R is the gas constant. Equation 3 can be rewritten to give a linear relationship between pressure and temperature by using $d \ln P = dp/p$ and $d(1/T) = -dT/T^2$. Integration of equation 3 gives:

$$\ln P = -(\Delta_{\text{vap}}H/RT) + C \quad (4)$$

This is known as the Clausius-Clapeyron equation. Here C is a constant of integration.

A plot of $\ln P$ versus $1/T$ give a linear relationship from which $\Delta_{\text{vap}}H$ can be found.

Experimental

Part 1. – Indirect Method for Determination of the Heat of Vaporization

The system for making vapor pressure measurements is shown in Figure 1. Refer to this figure while reading the procedure description below.

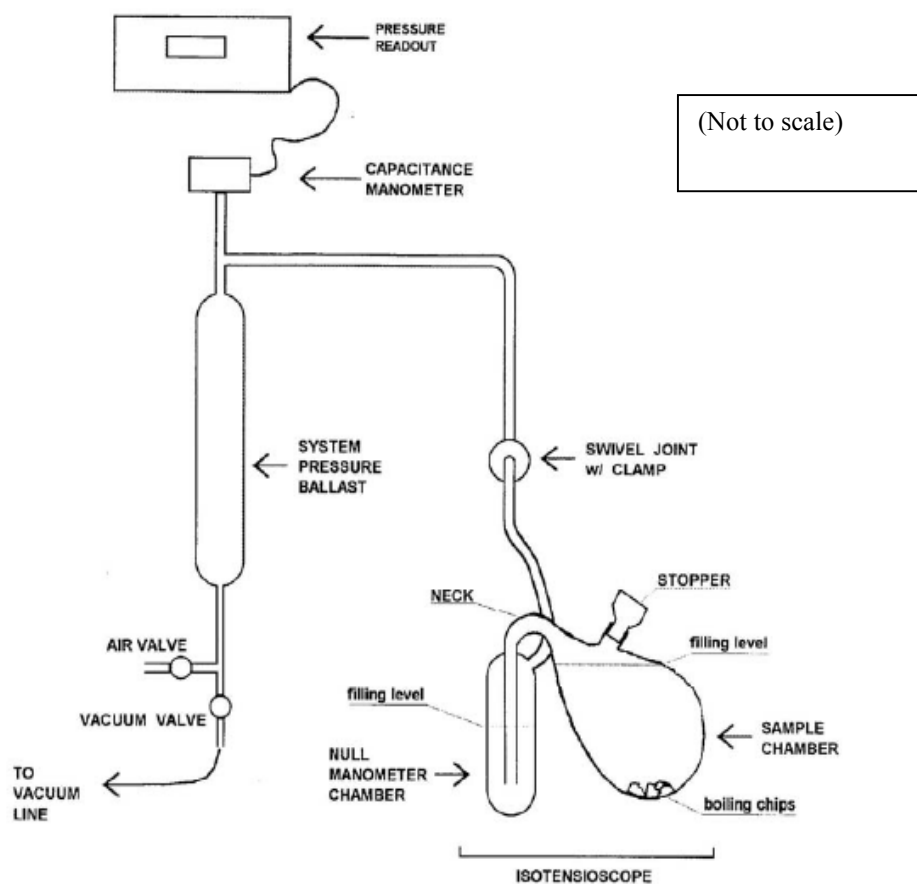


Figure 1 Vapor Pressure Apparatus

In this part the vapor pressure is measured as a function of temperature using a special sample holder called an isotensioscope. The isotensioscope is connected to a

capacitance manometer and a pressure ballast chamber, which is connected through valves to a vacuum line and air source (room air) to adjust the pressure in the isotensioscope. The left half of the isotensioscope uses some of the sample in a null (balancing) manometer to isolate the air in the pressure ballast from the sample vapor being measured. The entire isotensioscope is immersed in a water bath to control the temperature.

NOTE ON NEEDLE VALVES - Needle valves do NOT need to be closed hard to shut off flow.

NOTE ON VACUUM SYSTEM - Always check with any other group using the same vacuum line before evacuating your system. If they are using the vacuum line to make a small pressure adjustment in their system, the sudden change of pressure in the vacuum line when you start to evacuate your apparatus can ruin their experiment run.

A. System Check and Set-up

1. Attach the empty isotensioscope to the swivel joint, insert the stopper, close the air bleed valve, open the vacuum valve and evacuate the system. When the pressure is below 100 torr, close the vacuum valve and watch the manometer. The reading should not change more than 2-3 torr in 5 minutes.
2. Open the air valve slowly and let air fill the system; close the air valve.
3. Remove the stopper and fill the right side (sample chamber) of the isotensioscope as full as possible with the sample liquid; reinsert stopper.
4. Open the vacuum valve and slowly reduce the pressure until the sample starts boiling steadily. Close the valve; the sample should continue boiling.
5. Rotate the isotensioscope at the swivel joint to allow some sample to run into the null manometer chamber (left side) until it is about half full. Rotate back to normal position. The sample should still be boiling as evidenced by bubbles coming from the central tube in the null manometer chamber.

6. If the bubbling is violent, raise the system pressure slightly by opening the air valve slightly, then closing it when the rate of bubbling is reduced. Allow the gentle bubbling to continue for about 5 minutes to flush out any air remaining above the sample.
7. Raise the water bath and stirrer to immerse the isotensioscope. The water level must be above the neck between the chambers. Continually adjust the system pressure (using air or vacuum as required) to maintain light bubbling in the null chamber as the sample comes to thermal equilibrium with the bath.
(This step can be combined with Step 6 above).
8. Turn on the stirring part of the stirring hotplate and adjust the speed to a slow rotation (1/2 to 1 rev/sec). Stirring motors tend to speed up as they warm up, so carefully monitor the stirring. If the speed is too fast the stirring bar may "jump" and break the isotensioscope or the thermocouple tube.

B. Temperature-Vapor Pressure Measurements

Temperature measurements are made using a thermocouple in a glass tube connected to an electronic linearizing and compensating circuit (the thermocouple module). This is connected to a portable digital multimeter (DMM). Make sure that the hand-lettered numbers on the thermocouple plug, thermocouple module and DMM are all the same; they have been calibrated as a unit. With the switch on the thermocouple module in the OFF position, set the DMM to the millivolt DC range. It should read more than 100. (This is the battery check for the thermocouple module.) Now set the thermocouple module to the °C position. The DMM will now read temperature in degrees Celsius. Note: the DMM has a battery saving feature that will blank the display after about 1/2 hour. To recall the display simply switch the DMM to the DC volts range then back to the millivolt range.

When the level of the liquid in the inner tube of the null chamber is the same as that in the outer part, the pressure of the air in the system (ballast chamber) is the same as the pressure of the sample vapor in the sample chamber. The system pressure is measured with the capacitance manometer. The pressure in the system is adjusted using the air and vacuum valves.

The temperature of the water bath is raised using the heating part of the stirring hotplate. Start with a setting of 1-2. Take data readings at 2-3 degree increments to the maximum system pressure (atmospheric pressure). If you wish, you can lower your starting temperature (and vapor pressure) by adding some ice to the bath.

As you proceed, you will need to increase the heat setting to achieve higher temperatures. As you raise the temperature of the sample the vapor pressure increases and bubbles will emerge from the inner tube of the null chamber. This is acceptable; the system pressure can be raised to rebalance the levels. If you lower the sample temperature, the vapor pressure decreases and liquid will be pulled from the null chamber and eventually air from the system back into the sample chamber. This should not be allowed to happen. Therefore if you lower the temperature you must constantly use the vacuum valve to keep the levels in the null chamber roughly balanced. It is a good idea to keep the levels balanced at all times when raising the temperature and vapor pressure as this will minimize evaporation of the liquid in the null manometer.

Part 2- Direct Determination of the Heat of Vaporization

Vaporization is an endothermic process. When a sample is vaporized, energy is transferred from the surroundings to the sample. In this case the surroundings consist of an ice water bath contained in an insulated thermos. When a sample is vaporized, heat is removed from the ice water bath and as a result more ice is formed. Heat is a quantity, which can only be defined in terms of experimental measurements. In this experiment, the quantity of heat is defined in terms of the volume change in an ice calorimeter, since the density of ice is less than water. Thus, if heat is abstracted from an ice-water mixture, some of the liquid will freeze, and the volume of the mixture will increase. The change in volume from water to ice is 0.0906 mL/g at 0°C. Measuring the change in volume and knowing the heat of fusion for ice at 0°C (79.71 cal/g) allows one to calculate the $\Delta_{\text{vap}}H$ of a sample.

The ice calorimeter cell is shown in Fig. 2a, and the assembled calorimeter is shown in Fig. 2b. The calorimeter is made from a commercial vacuum bottle in which the cap has been modified to hold a 1 mL measuring (graduated) pipette and sample cell.

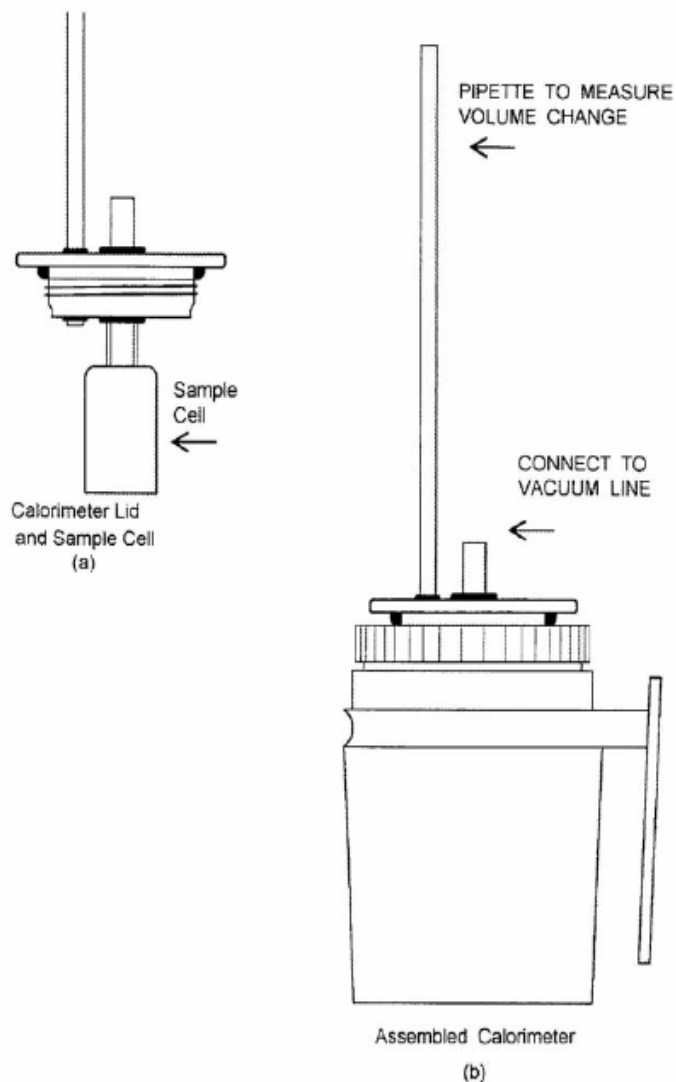


Figure 2. Ice calorimeter.

Fill the calorimeter dewar with a loose, slushy ice-water mixture so that the cell attached to the lid will enter the mixture easily. Make sure the interior of the cell is clean and dry. Evacuate the cell to dry it if necessary. Stopper the cell to avoid spilling water into it.

Place the calorimeter cell into the dewar and screw the stopper down until water rises in the pipette. Be careful not to get small chips of ice between the plastic top and the lip of the dewar as this prevents achieving a good seal. It is important not to leave air bubbles under the stopper in this process.

Add enough sample (typically 2 to 5 mL) to the cell using a volumetric transfer pipette to give a volume change in the water-ice mixture of 0.3 to 0.6 mL when the sample is vaporized. The cell is attached to a vacuum line through a stopcock. A trap is included in the vacuum line to condense the evaporated gases. Arrange the hose and cell so that they will not be disturbed during the measurements. This is important since the plastic stopper is flexible enough to cause serious volume changes if there is any change in the forces on the top.

Adjust the volume reading on the pipette to approx. 0.3 mL. The level may be raised or lowered by adding or removing some water with a syringe and teflon tube inserted into the top end of the pipette. Read and record the volume every a minute for about five minutes. Then open the stopcock to the vacuum system to vaporize the liquid. Continue to read and record the volume every minute until it has been again falling linearly with time for about five minutes. Plot the volume as a function of time on graph paper, and determine the volume change on vaporization. This is the vertical ΔV between the initial and final straight lines.

Repeat the experiment using the same amount of sample until you have at least three consistent values for the volume change. Between runs, you will need to open the calorimeter and remove the film of ice that forms on the outside of the sample cell.

CALCULATIONS

1) From the data from Part 1 (Indirect Method for Determination of the Heat of Vaporization) plot $\ln P$ vs. $1/T$. Find the heat of vaporization of your sample and the error.

2) From the data in Part 2 (Direct Determination of the Heat of Vaporization) plot the volume vs. time and determine the amount of ice that was formed from the vaporization of your sample. Calculate the heat of vaporization for your sample and an error value.

Heat of fusion of ice at $0^\circ\text{C} = 79.71 \text{ cal/g}$

Volume change for ice \rightarrow water at $0^\circ\text{C} = -0.0906 \text{ mL/g}$

Discussion

- Compare the $\Delta_{\text{vap}}H$ values from both methods with each other and with the literature value. Discuss any differences. Which method is more accurate?
- Discuss the possible sources of error.
- For Part 1, estimate experimental errors in P and T. How will these errors affect the error in $\Delta_{\text{vap}}H$? What approximations are used in the derivation of the Clausius-Clapeyron equation? Are these approximations justified in this experiment?
- For Part 2, errors may result from air bubbles inside the calorimeter and the possibility that vaporization cools the material enough that the vapor leaves the calorimeter at a temperature lower than 0°C . Another possible source of error is that the thermos is not perfectly insulated. Discuss how these errors, along with any other sources of error, would affect your final result.

References

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2. *Handbook of Chemistry*, N.A. Lange, ed., McGraw-Hill Book Co.
3. *Experiments in Physical Chemistry*, Shoemaker, D. P., Garland, C. W., Steinfeld, J. I., and J. W. Nibler, 4th Edition, 1981, pp. 197-205.