

# Liquid-vapor equilibrium: $\Delta H$ and $\Delta S$ for vaporization

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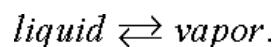
**Goal:** Vapor pressure data is presented for two liquids over a given temperature range and the heat of vaporization and entropy change for vaporization are determined.

**Prerequisites:** An introductory knowledge of thermodynamic relationships that apply to phase equilibrium systems.

**Resources you will need:** This exercise should be carried out within a software environment that is capable of data manipulation and which can generate a best-fit line for an x-y data set. You will also be graphing the data along with the fitted function.

## Background:

One of the simplest equilibrium systems to consider is a pure liquid in contact with its vapor



A liquid-vapor equilibrium can be established by pouring a liquid inside of a small flask and applying a vacuum to degas the liquid and to evacuate the air-space above the liquid, whereupon the flask is sealed.

After sealing the vessel, liquid will continue to vaporize and the pressure of the vapor will correspondingly rise. But as the vapor pressure increases, the opposite process can occur. Namely, gas molecules can condense and re-enter the liquid phase. These two competing processes, vaporization and condensation, each occur at their respective rates. And when these rates become equal, the system will exist in a dynamic equilibrium and the vapor pressure will have a constant value.

What governs whether the equilibrium lies more toward the liquid phase or the gas phase in a particular system? Temperature is certainly expected to have an impact. As temperature rises, the increased kinetic motion of molecules tends to overcome intermolecular attractions and a greater fraction of the molecules will reside in the vapor phase. Consequently, the vapor pressure of the system is expected to rise with increasing temperature.

Thermodynamics provides a framework for describing how vapor pressure depends on temperature. As a starting point, we consider the Clapeyron equation which applies to any type of phase equilibrium

$$\frac{dp}{dT} = \frac{\Delta H_m}{T \Delta V_m}, \quad (1)$$

where  $p$  is the pressure and  $T$  the absolute temperature of a two phase system, and  $\Delta H_m$  and  $\Delta V_m$  are the molar enthalpy change and molar volume change associated with the phase transition in question. The Clapeyron equation is an exact thermodynamic relationship and its derivation is given in most physical chemistry texts. Written in the form of equation (1), the Clapeyron equation tells us that the slope of a vapor pressure versus temperature plot (or more specifically, a tangent line drawn at some point on this plot) is related to  $\Delta H_m$  and  $\Delta V_m$  for vaporization.

Assuming that the volume occupied by one mole of liquid is negligible in comparison to the volume occupied by one mole of vapor, the volume change that accompanies vaporization can be written as

$$\Delta V_m = V_{m,gas} - V_{m,liquid} \approx V_{m,gas}. \quad (2)$$

If we further assume that the volume of one mole of vapor behaves as an ideal gas then

$$V_{m, \text{gas}} = \frac{RT}{p}, \quad (3)$$

and equation (1) becomes

$$\frac{dp}{dT} = \frac{p\Delta H_{\text{vap}}}{RT^2}. \quad (4)$$

Assuming the molar enthalpy of vaporization is constant with respect to temperature, equation (4) can be rearranged and integrated,

$$\int \frac{dp}{p} = \left( \frac{\Delta H_{\text{vap}}}{R} \right) \int \frac{dT}{T^2}, \quad (5)$$

yielding the following expression for how the vapor pressure depends upon temperature

$$\ln p = - \left( \frac{\Delta H_{\text{vap}}}{R} \right) \frac{1}{T} + C, \quad (6)$$

where  $C$  is a constant. According to equation (6), a plot of  $\ln p$  versus  $1/T$  should be linear and the slope is related to the heat of vaporization.

An expression that is similar to equation (6) can be obtained by setting the right-hand-side of the expressions

$$\Delta G = -RT \ln K \quad (7)$$

and

$$\Delta G = \Delta H - T\Delta S \quad (8)$$

equal to one another and rearranging into the form

$$\ln K = - \left( \frac{\Delta H}{R} \right) \frac{1}{T} + \frac{\Delta S}{R}. \quad (9)$$

In a liquid-vapor equilibrium system, the equilibrium constant can be written as

$$K = a_{\text{vap}} \approx \frac{p}{p^\theta}, \quad (10)$$

where  $a_{\text{vap}}$  is the activity of the vapor,  $p$  is the vapor pressure, and  $p^\theta$  is standard pressure (760 mmHg). Substitution into equation (9) gives us

$$\ln \left( \frac{p}{p^\theta} \right) = - \left( \frac{\Delta H_{\text{vap}}}{R} \right) \frac{1}{T} + \frac{\Delta S_{\text{vap}}}{R}. \quad (11)$$

Just as we saw earlier, the slope of a logarithmic plot of vapor pressure versus  $1/T$  is related to the heat of vaporization. But equation (11) implies that the y-intercept of this plot is related to the entropy change for

vaporization.

In the exercise below, you will analyze vapor pressure data for two liquids, fluorobenzene and benzenethiol, in order to determine  $\Delta H_{vap}$  and  $\Delta S_{vap}$  for each.

### Experimental Data:

Click on the following links and save each data set on your computer. Each file consists of two columns of numbers: the values in the first column are temperatures in degrees Celsius and the second column contains the corresponding vapor pressures of the liquid in units of millimeters of mercury (mmHg).

[Vapor pressure of fluorobenzene from 39 to 120 °C](#)

[Vapor pressure of benzenethiol from 114 to 212 °C](#)

The data were obtained from D.W. Scott, et. al, *Journal of the American Chemical Society*, **78**, 5457 (1956) and D.W. Scott, et. al, *Journal of the American Chemical Society*, **78**, 5463 (1956). The authors used a technique called 'comparative ebulliometry' which involves balancing the vapor pressure of the unknown liquid at each temperature against the vapor pressure of a known liquid (water was used as the known) inside of a closed vessel.

### Exercise:

1. Inspect the vapor pressures that are listed in each data set and report the normal boiling point of each liquid. Compare these boiling points to appropriate literature values (calculate the percent differences).
2. Import each data set into an appropriate quantitative analysis software environment and manipulate the data into a form so that you can plot each as  $\ln(p/p^{\theta})$  versus  $1/T$ . In each case, calculate a best-fit line and plot it along with the original data. Is the plot entirely linear (can you detect any curvature in the data)?
3. Using the parameters from your best-fit lines, calculate  $\Delta H_{vap}$  and  $\Delta S_{vap}$  for each liquid (report your answers with appropriate units). Compare your answers with literature values (calculate the percent differences).
4. Trouton's rule states that  $\Delta S_{vap} \approx 88 \text{ J K}^{-1} \text{ mol}^{-1}$  for a wide range of liquids (as long as the molecules are not strongly associated in the liquid phase). How well do the  $\Delta S_{vap}$  values calculated in step (3) agree with the Trouton rule prediction? Based on your comparison, what might you deduce about the arrangement of fluorobenzene or benzenethiol molecules in the liquid phase (are the molecules structurally packed in a more highly ordered or less ordered fashion than would normally be expected for a liquid)?

Suggestions for improving this web site are welcome. You are also encouraged to submit your own data-driven exercise to this web archive. All inquiries should be directed to the curator: Tandy Grubbs, Department of Chemistry, Unit 8271, Stetson University, DeLand, FL 32720.

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