

Clausius-Clapeyron Equation

Learning Objectives

- Apply the Clausius-Clapeyron equation to estimate the vapor pressure at any temperature.
- Estimate the heat of phase transition from the vapor pressures measured at two temperatures.

The *vaporization curves* of most liquids have similar shapes with the vapor pressure steadily increasing as the temperature increases (Figure 1).

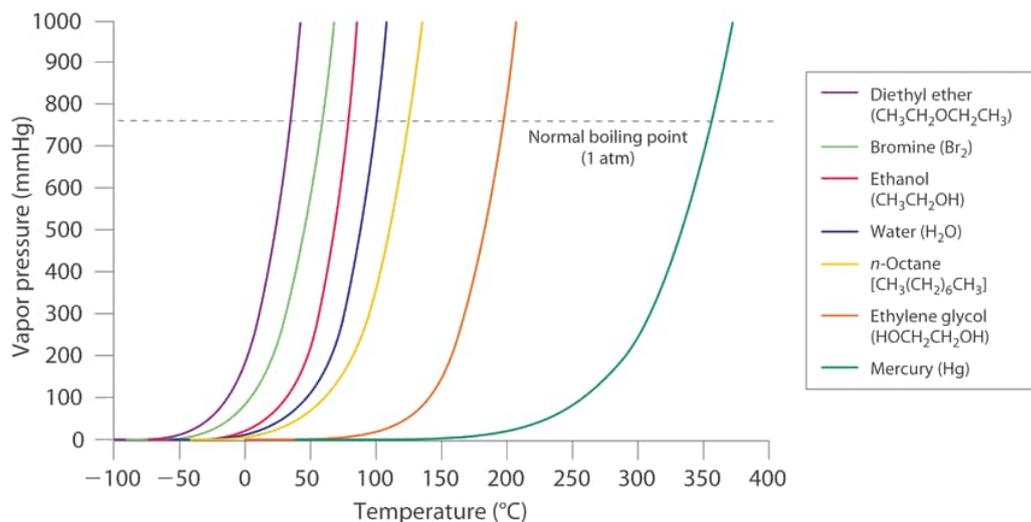


Figure 1: The Vapor Pressures of Several Liquids as a Function of Temperature. The point at which the vapor pressure curve crosses the $P = 1$ atm line (dashed) is the normal boiling point of the liquid. (CC BY-SA-NC 3.0; Anonymous)

A good approach is to find a mathematical model for the pressure increase as a function of temperature. Experiments showed that the vapor pressure P and temperature T are related,

$$P \propto \exp\left(-\frac{\Delta H_{vap}}{RT}\right) \quad (1)$$

where ΔH_{vap} is the Enthalpy (heat) of Vaporization and R is the gas constant ($8.3145 \text{ J mol}^{-1} \text{ K}^{-1}$).

A simple relationship can be found by integrating Equation 1 between two pressure-temperature endpoints:

$$\ln\left(\frac{P_1}{P_2}\right) = \frac{\Delta H_{vap}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right) \quad (2)$$

where P_1 and P_2 are the vapor pressures at two temperatures T_1 and T_2 . Equation 2 is known as the **Clausius-Clapeyron Equation** and allows us to estimate the vapor pressure at another temperature, if the vapor pressure is known at some temperature, and if the enthalpy of vaporization is known.

Alternative Formulation

The order of the temperatures in Equation 2 matters as the Clausius-Clapeyron Equation is sometimes written with a negative sign (and switched order of temperatures):

$$\ln\left(\frac{P_1}{P_2}\right) = -\frac{\Delta H_{vap}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad (3)$$

Example 1: Vapor Pressure of Water

The vapor pressure of water is 1.0 atm at 373 K, and the enthalpy of vaporization is 40.7 kJ mol^{-1} . Estimate the vapor pressure at temperature 363 and 383 K respectively.

Solution

Using the Clausius-Clapeyron equation (Equation 3), we have:

$$\begin{aligned}
 P_{363} &= 1.0 \exp \left[- \left(\frac{40,700}{8.3145} \right) \left(\frac{1}{363 \text{ K}} - \frac{1}{373 \text{ K}} \right) \right] \\
 &= 0.697 \text{ atm} \\
 P_{383} &= 1.0 \exp \left[- \left(\frac{40,700}{8.3145} \right) \left(\frac{1}{383 \text{ K}} - \frac{1}{373 \text{ K}} \right) \right] \\
 &= 1.409 \text{ atm}
 \end{aligned}$$

Note that the increase in vapor pressure from 363 K to 373 K is 0.303 atm, but the increase from 373 to 383 K is 0.409 atm. The increase in vapor pressure is not a linear process.

Discussion

We can use the Clausius-Clapeyron equation to construct the entire vaporization curve. There is a deviation from experimental value, that is because the enthalpy of vaporization varies slightly with temperature.

The Clausius-Clapeyron equation can be also applied to sublimation; the following example shows its application in estimating the heat of sublimation.

✓ Example 2: Sublimation of Ice

The vapor pressures of ice at 268 K and 273 K are 2.965 and 4.560 torr respectively. Estimate the heat of sublimation of ice.

Solution

The enthalpy of sublimation is ΔH_{sub} . Use a piece of paper and derive the Clausius-Clapeyron equation so that you can get the form:

$$\begin{aligned}
 \Delta H_{sub} &= \frac{R \ln \left(\frac{P_{273}}{P_{268}} \right)}{\frac{1}{268 \text{ K}} - \frac{1}{273 \text{ K}}} \\
 &= \frac{8.3145 \ln \left(\frac{4.560}{2.965} \right)}{\frac{1}{268 \text{ K}} - \frac{1}{273 \text{ K}}} \\
 &= 52,370 \text{ J mol}^{-1}
 \end{aligned}$$

Note that the heat of sublimation is the sum of heat of melting (6,006 J/mol at 0°C and 101 kPa) and the heat of vaporization (45,051 J/mol at 0°C).

? Exercise 2

Show that the vapor pressure of ice at 274 K is higher than that of water at the same temperature. Note the curve of vaporization is also called the curve of evaporation.

✓ Example 3: Vaporization of Ethanol

Calculate ΔH_{vap} for ethanol, given vapor pressure at 40 °C = 150 torr. The normal boiling point for ethanol is 78 °C.

Solution

Recognize that we have TWO sets of (P, T) data:

- Set 1: (150 torr at 40+273K)
- Set 2: (760 torr at 78+273K)

We then directly use these data in Equation 3

$$\ln\left(\frac{150}{760}\right) = \frac{-\Delta H_{vap}}{8.314} \left[\frac{1}{313} - \frac{1}{351} \right]$$
$$\ln 150 - \ln 760 = \frac{-\Delta H_{vap}}{8.314} \left[\frac{1}{313} - \frac{1}{351} \right]$$
$$-1.623 = \frac{-\Delta H_{vap}}{8.314} [0.0032 - 0.0028]$$

Then solving for ΔH_{vap}

$$\Delta H_{vap} = 3.90 \times 10^4 \text{ joule/mole}$$
$$= 39.0 \text{ kJ/mole}$$

📌 Advanced Note

It is important to not use the Clausius-Clapeyron equation for the solid to liquid transition. That requires the use of the more general **Clapeyron equation**

$$\frac{dP}{dT} = \frac{\Delta \bar{H}}{T \Delta \bar{V}}$$

where $\Delta \bar{H}$ and $\Delta \bar{V}$ is the molar change in enthalpy (the enthalpy of fusion in this case) and volume respectively between the two phases in the transition.

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