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).

\[ P \propto \exp \left(- \frac{\Delta H_{\text{vap}}}{RT} \right) \label{1} \]

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

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

\[ \ln \left( \frac{P_1}{P_2} \right) = \frac{\Delta H_{\text{vap}}}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \label{2} \]

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

Example \( \PageIndex{1} \): 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 \ref{2B}), we have:

\[
\begin{align}
P_{363} &= 1.0 \exp \left[- \left( \dfrac{40,700}{8.3145} \right) \left( \dfrac{1}{363\;K} - \dfrac{1}{373\;K} \right) \right] \\
&= 0.697\;\text{atm} \\
\end{align}
\]

\[
\begin{align}
P_{383} &= 1.0 \exp \left[- \left( \dfrac{40,700}{8.3145} \right) \left( \dfrac{1}{383\;K} - \dfrac{1}{373\;K} \right) \right] \\
&= 1.409\;\text{atm} \\
\end{align}
\]

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 \(\PageIndex{2}\): 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 \(\Delta H_{\text{sub}}\). Use a piece of paper and derive the Clausius-Clapeyron equation so that you can get the form:

\[
\begin{align}
\Delta H_{\text{sub}} &= \dfrac{ R \ln \left( \dfrac{P_{273}}{P_{268}} \right)}{\dfrac{1}{268\;K} - \dfrac{1}{273\;K}} \\
&= \dfrac{8.3145 \ln \left( \dfrac{4.560}{2.965} \right)}{ \dfrac{1}{268\;K} - \dfrac{1}{273\;K} } \\
&= 52,370\;\text{J/mol}\nonumber \\
\end{align}
\]

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 \(\PageIndex{2}\)

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 \(\PageIndex{3}\): Vaporization of Ethanol

Calculate \(\Delta H_{\text{vap}}\) 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: \((150 \text{ torr at } 40+273K)\)
- Set 2: \((760 \text{ torr at } 78+273K)\)

We then directly use these data in Equation \ref{2B}

\[
\begin{align*}
\ln \left( \frac{150}{760} \right) &= \frac{-\Delta H_{\text{vap}}}{8.314} \left[ \frac{1}{313} - \frac{1}{351} \right] \\
\ln 150 - \ln 760 &= \frac{-\Delta H_{\text{vap}}}{8.314} \left[ \frac{1}{313} - \frac{1}{351} \right] \\
-1.623 &= \frac{-\Delta H_{\text{vap}}}{8.314} \left[ 0.0032 - 0.0028 \right] \\
\Delta H_{\text{vap}} &= 3.90 \times 10^4 \text{ joule/mole} \\
&= 39.0 \text{ kJ/mole}
\end{align*}
\]

Then solving for \((\Delta H_{\text{vap}})\)

\[
\begin{align*}
\Delta H_{\text{vap}} &= 3.90 \times 10^4 \text{ joule/mole} \\
&= 39.0 \text{ kJ/mole}
\end{align*}
\]

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.

Contributors and Attributions

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