Skills to Develop

• 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. The vapor pressure steadily increase as the temperature increases. 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,

\[ P \propto e^{- \Delta H_{\text{vap}} / RT} \label{1} \]

where

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

If \( P_1 \) and \( P_2 \) are the vapor pressures at two temperatures \( T_1 \) and \( T_2 \), then a simple relationship can be found:

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

This 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

Note the order of the temperatures in Equation \( \ref{2} \) matters as the Clausius-Clapeyron Equation is often written with a negative sign (and switched order of temperatures):

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

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 \( \ref{2} \)), we have:

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

\[
\begin{align*}
P_{\text{383}} &= 1.0 \exp \left[- \frac{40,700}{8.3145} \left( \frac{1}{383} - \frac{1}{373} \right) \right] \\
&= 1.409 \text{ atm}
\end{align*}
\]
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 \( \PageIndex{2} \): Heat of 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:

\[
\Delta H_{\text{sub}} = \frac{R \ln \left( \frac{P_{273}}{P_{268}} \right)}{\frac{1}{268 \ K} - \frac{1}{273 \ K}}
\]

\[
\Delta H_{\text{sub}} = \frac{8.3145 \ln \left( \frac{4.560}{2.965} \right)}{\frac{1}{268 \ K} - \frac{1}{273 \ K}}
\]

\[
\Delta H_{\text{sub}} = 52,370 \ J \ mol^{-1}
\]

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 \( \PageIndex{3} \): Heat of 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 torr at 40+273K)
- Set 2: (760 torr at 78+273K)

\[
\ln P = \frac{-\Delta H_{\text{vap}}}{RT} + c
\]
Substituting into the above equation twice produces:

\[
\ln 150 = \dfrac{-\Delta H_{\text{vap}}}{(8.314)\times (313)} + c
\]

and

\[
\ln 760 = \dfrac{-\Delta H_{\text{vap}}}{(8.314)\times (351)} + c
\]

Subtract these two equations, to produce:

\[
\begin{align}
\ln 150 - \ln 760 &= \dfrac{-\Delta H_{\text{vap}}}{8.314} \left[ \dfrac{1}{313} - \dfrac{1}{351} \right] \\
-1.623 &= \dfrac{-\Delta H_{\text{vap}}}{8.314} \left[ 0.0032 - 0.0028 \right]
\end{align}
\]

Solving for \( \Delta H_{\text{vap}} \):

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

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

\[
\dfrac{dP}{dT} = \dfrac{\Delta \bar{H}}{T \Delta \bar{V}}\label{14.8}
\]

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

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