Clausius-Clapeyron Equation

Let's revisit solid-gas & liquid-gas equilibria. We can make an approximation:

\[ V_{\text{gas}} \gg V_{\text{solid}}, V_{\text{liquid}} \]
\[ \Delta V_{\text{subl}}, \Delta V_{\text{vap}} \approx V_{\text{gas}} \]

We can ignore the molar volume of the condensed phase compared to the gas.

Taking the Clapeyron equation (exact), e.g. for solid-gas eq. and using the approximation above:

\[ \frac{dp}{dT} = \frac{\Delta S_{\text{subl}}}{\Delta V_{\text{subl}}} = \frac{\Delta H_{\text{subl}}}{T \Delta V_{\text{subl}}} \approx \frac{\Delta H_{\text{subl}}}{T V_{\text{gas}}} \]

Assuming an ideal gas, \( V_{\text{gas}} = \frac{RT}{p} \)

\[ \Rightarrow \frac{dp}{dT} = \frac{p \Delta H_{\text{subl}}}{RT^2} \quad \frac{dp}{dT} = \frac{dp}{p} \frac{d\ln p}{dT} = \frac{\Delta H_{\text{subl}}}{RT^2} \]

This is the Clausius-Clapeyron Equation

for liq-gas, replace \( \Delta H_{\text{sub}} \) with \( \Delta H_{\text{vap}} \)

i.e.

\[ \frac{dp}{dT} = \frac{p \Delta H_{\text{vap}}}{RT^2} \quad \frac{dp}{dT} = \frac{d\ln p}{dT} = \frac{\Delta H_{\text{vap}}}{RT^2} \]

The Clausius-Clapeyron equation relates the temperature dependence of the vapor pressure of a liquid or a solid to \( \Delta H_{\text{vap}} \) or \( \Delta H_{\text{sub}} \) (respectively).
We can make another approximation: Assuming $\Delta H_{\text{subl}}$ independent of $T$, 
\[
\int_{p_1}^{p_2} \frac{dp}{p} = \frac{\Delta H_{\text{subl}}}{R} \int_{T_1}^{T_2} \frac{1}{T^2} dT
\]
\[
\ln \frac{p_2}{p_1} = -\frac{\Delta H_{\text{subl}}}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) = \frac{\Delta H_{\text{subl}}}{R} \left( \frac{T_2 - T_1}{T_1 T_2} \right)
\]

This is the Integrated Clausius-Clapeyron Equation (for liq-gas, replace $\Delta H_{\text{subl}}$ with $\Delta H_{\text{vap}}$)

i.e. $\ln \frac{p_2}{p_1} = -\frac{\Delta H_{\text{vap}}}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) = \frac{\Delta H_{\text{vap}}}{R} \left( \frac{T_2 - T_1}{T_1 T_2} \right)$

In practice this is how you determine vapor pressure over a liquid or solid as a function of $T$.

Clausius-Clapeyron problems have the two following forms:

1. You know $(T_1, p_1)$ and $(T_2, p_2)$ for s-g or l-g coexistence and want to know $\Delta H_{\text{subl}}$ or $\Delta H_{\text{vap}}$
2. You know $(T_1, p_1)$ and $\Delta H_{\text{subl}}$ or $\Delta H_{\text{vap}}$ for s-g or l-g coexistence and want to know $(T_2, p_2)$ (coexistence).

This allows you, for example, to calculate that the boiling point in Denver is 97°C.
Effect of inert gas pressure on vapor pressure over a liquid or solid

\[ \text{Total pressure } p = p_A + p_{\text{Inert}} \]

\[ p_o = \text{equil. vapor pressure of pure } A \text{ at temperature } T \]

\[ p_{A} = \text{equil. partial pressure of } A \text{ in presence of inert gas} \]

What is \( p_A(p) \)?

At equilibrium, \( \mu_A(g,T,p_A) = \mu_A(\ell,T,p) \)

Differentiate both sides w.r.t. \( p \)

\[ d\mu = d\bar{\mu} = -5dT + Vdp \Rightarrow \left( \frac{\partial \mu}{\partial p} \right)_T = V \]

\[ \left( \frac{\partial \mu_A(g,T,p_A)}{\partial p} \right)_T = \left( \frac{\partial \mu_A(\ell,T,p)}{\partial p} \right)_T \]

\[ V_g \left( \frac{\partial p_A}{\partial p} \right)_T = V_i \Rightarrow \left( \frac{\partial p_A}{\partial p} \right)_T = \frac{V_i}{V_g} > 0 \]

Presence of inert gas increases \( p_A \). \( V_i \ll V_g \) (away from critical point) so the effect is small.

If \( A \) is ideal gas

\[ V_g = \frac{RT}{p_A} \Rightarrow \frac{RT}{p_A} dp_A = V_i dp \]

\[ RT \int_{p_0}^{p_A} \frac{dp_A}{p_A} = V_i \int_{p_0}^{p} dp \quad RT \ln \frac{p_A}{p_0} = V_i(p - p_0) \]

For example, for mercury (Hg)

\( p_{\text{Hg}} = 0.2700 \text{ torr at } 100^\circ\text{C} \) (pure Hg)

\( p_{\text{Hg}} = 0.2701 \text{ torr at } 1 \text{ bar total pressure} \)

\( p_{\text{Hg}} = 0.2830 \text{ torr at } 100 \text{ bar total pressure} \)
Sample Problem:

A new molecule (a drug), renol, has been synthesized and its phase diagram needs exploring. Near its triple point it is found that the vapor pressure over the liquid ($p_l$) and over the solid ($p_s$) are given by

\[ \ln p_l = -\frac{3,010 \text{ K}}{T} + 13.2 \quad \ln p_s = -\frac{3,820 \text{ K}}{T} + 16.1 \]

(a) Calculate the triple point temperature $T_{tp}$ and pressure $p_{tp}$.

Set \( \ln p_s = \ln p_l \Rightarrow -\frac{3,010 \text{ K}}{T} + 13.2 = -\frac{3,820 \text{ K}}{T} + 16.1 \)

Solve for $T$ \( \Rightarrow T_{tp} = 279 \text{ K} \)
\( \Rightarrow p_{tp} = 11.1 \text{ bar} \)

(b) Is renol a solid, a gas, or a liquid at (1 bar, 298 K)?

Phase diagram shows it’s a gas.

Must be since slopes of $(s,g)$ and $(l,g)$ coexistence curves are always positive.

(c) What is $\Delta H_{\text{subl}}$? (approximate)

Use Clausius-Clapeyron equation:

\[ \frac{d \ln p_s}{dT} = \frac{3,820 \text{ K}}{T^2} = \frac{\Delta H_{\text{subl}}}{RT^2} \]

\[ \Delta H_{\text{subl}} = \left(8.314 \text{ J/K-mol}\right)(3,820 \text{ K}) = 31,760 \text{ J} = 31.8 \text{ kJ} \]
Another example:

RDX (1,3,5-trinitro-1,3,5-triazacyclohexane) is widely used in military applications, including high explosives and rocket and gun propellants. It is also a common ingredient of commercial and military plastic explosives, including C-4 and Semtex, and is often employed for illicit or criminal purposes. It is a white solid with a melting point in the pure state of 204 °C (481 K).

Designing reliable detectors for the presence of RDX requires having an accurate knowledge of its vapor pressure as a function of temperature. Literature data have been reviewed in a recent DOT/TSA report, “Vapor Pressure Data Base for Explosives and Related compounds,” by J. C. Wormhoudt (Oct. 2003).

Vapor pressure data for RDX are shown in the diagram. The vapor pressure data are well described by the Clausius-Clapeyron equation to within ±95% confidence limits. Note that the vapor pressure of RDX at 300 K (at which, for example, an explosives detector at an airport security screening station would have to operate is only $10^{-11}$ bar. Note also that since all reported data are for temperatures less than 450 K the process represented by these data is actually sublimation rather than evaporation from the liquid phase.
$p \sim 10^{-8}$ Torr
$\sim 10^{-11}$ bar
(10 parts per trillion!)

- RDX Data Points
- Clausius-Clapeyron Fit to All Data
- 95% Confidence Limits
- 95% Prediction Limits

400K
300K = 3.3