CLAUSSIUS–CLAPERYON EQUATION

I. Review

The exact Clapeyron equation, \( \frac{dp}{dT} = \frac{\Delta S}{\Delta V} \), was obtained for two-phase equilibrium in a one-component system.

II. Lecture topics

*A. Clapeyron Equation for solid-liquid and solid-solid equilibria

*B. Approximate Clausius-Clapeyron Equation for liquid-gas and solid-gas
\[ \frac{d\ln p}{d(1/T)} \approx -\frac{\Delta H}{R} \]

C. Effect of hydrostatic pressure on vapor pressure

A. Clapeyron Equation for Condensed Phases

\[ X(a) = X(b) \text{ in equilibrium at } p_0, T_0; \quad \Delta G = 0 \]

\[ \left(\frac{dp}{dT}\right)_{coex} = \frac{\Delta S}{\Delta V} = \frac{\Delta H}{T\Delta V} \]

\[ \Delta H = T\Delta S = H_b - H_a, \quad \Delta V = V_b - V_a \]

By choosing \( b \) to be the high-temperature phase, \( \Delta H \) is always positive and the slope of the coexistence line depends on the sign of \( \Delta V \). For melting, most \( \Delta V = V_{liq} - V_{sol} > 0 \) but in a few cases (\( H_2O, Ga, Ge, Si, Bi \)) \( \Delta V < 0 \). In many cases of solid-solid or solid-liquid, the coexistence line is approximately linear

\[ \Delta p \sim (\Delta H / T\Delta V) \Delta T \]

B. Vaporization and Sublimation

For \( X(l) = X(g) \) [or \( X(s) = X(g) \)], one always has \( \Delta H > 0 \) and \( \Delta V > 0 \), and the coexistence line is curved. We can rewrite the exact Clapeyron equation in the form
\[
\frac{\text{dln} p}{\text{d}(1/T)} = -\frac{\Delta H / \Delta Z}{R} \quad \text{(exact)} \quad (3)
\]

where \( \Delta Z = Z_g - Z_l = p \Delta V / RT \) is the difference in compressibility factors for gas and liquid. Empirically one finds that a plot of \( \ln p \) vs. \( 1/T \) is close to linear. In a range of low pressures and temperatures (far from the critical point), one can obtain \( \Delta H \) from the slope of \( \ln p \) vs. \( 1/T \):

1. assume \( \bar{V}_l \ll \bar{V}_g \)
2. assume ideal gas \( \bar{V}_g = RT/p \)

\[
\frac{\text{d ln } p}{\text{d}(1/T)} \sim -\frac{\Delta H}{R} \quad \text{(approx.)} \quad (4)
\]

This is the famous **CLAUSIUS-CLAPEYRON** equation, and it is a very good approximation far from \( T_c \).

If we go one step further and

3. assume \( \Delta H \) is independent of \( T \),

it is possible to integrate Eq. (4) to obtain

\[
\ln \frac{p_2}{p_1} \sim \frac{\Delta H}{R} \left( \frac{T_2 - T_1}{T_1 T_2} \right) \quad (5)
\]

**Trouton's Rule**

\[
\Delta \tilde{S}_{\text{vap}} = \Delta \tilde{H}_{\text{vap}} / T_b \sim 88 \ J \ K^{-1} \ mol^{-1} \quad (6)
\]

is an empirical rule that works roughly (to within ±10%) for a wide range of normal liquids. \( T_b \) is the boiling point of the liquid at \( p = 1 \) atm. Trouton's rule can be rationalized on the basis of the ratio of the "free volumes" of the gas (ca. 30,000 \( \text{cm}^3 \text{mole}^{-1} \)) and the liquid (ca. 10% of \( V_{\text{liq}} \), or 3 \( \text{cm}^3 \text{mole}^{-1} \)). From statistical mechanics (5.62),

\[
\Delta \tilde{S}_{\text{vap}} = R \ln \left( \frac{V_{\text{gas}}}{V_{\text{free, liquid}}} \right) = R \ln (10^4) = 75 \ J \ K^{-1} \ mol^{-1},
\]

close to the empirical value!
C. Effect of inert gas pressure on the vapor pressure $p$ of liquid $A$

Vapor $A$ + inert gas

\[ P = p + p_{\text{inert}} \]

Liquid $A$

At constant temperature $T$:

- $p_0$ is vapor pressure of $A$ in the absence of inert gas
- $P = p + p_{\text{inert}}$ is total pressure if inert gas present at partial pressure $p_{\text{inert}}$

At equilibrium $\mu_A(g,T,p) = \mu_A(l,T,P)$ and

\[
\left[ \frac{\partial \mu_A(g)}{\partial p} \right]_T = \left[ \frac{\partial \mu_A(l)}{\partial P} \right]_T \Rightarrow \frac{RT}{P} \left( \frac{\partial p}{\partial P} \right) = \bar{V}_1, \tag{7a}
\]

where the gas phase is treated as a mixture of ideal gases. One can rewrite Eq. (7a) as

\[
d \ln p = \frac{\bar{V}_1}{RT} dP \tag{7b}
\]

and integrate to obtain

\[
\ln \frac{p}{p_0} = \frac{\bar{V}_1}{RT} (P - p_0) \quad \therefore \quad p > p_0 \tag{8}
\]

This effect is small in practice. For example, $p_0 = 0.27$ Torr for Hg at $100^\circ C$. The vapor pressure is $p = 0.2701$ Torr when $P = 1$ bar and $p = 0.283$ Torr when $P = 100$ bar.

D. Sample Problem

Liquid water has a triple point at $6.11 \times 10^{-3}$ bar and $273.16K$ and its normal boiling point is $1.013$ bar ($= 1$ atm) and $373.15K$. The latent heat of vaporization $\Delta H_{\text{vap}}$ varies with temperature, ranging from $45,050 \text{ J mol}^{-1}$ at $\sim 273K$ to $40,660 \text{ J mol}^{-1}$ at $\sim 373K$. The vapor and liquid densities (and therefore molar volumes) are not available. Predict the vapor pressure $p$ in bar of liquid water at $T = 20^\circ C$, $30^\circ C$, $80^\circ C$, $90^\circ C$.

The approximate Clausius-Clapeyron equation can be used, but you should give the physical assumptions on which it is based.
Answer: \((d\ln p/dT) \sim \Delta H_{vap}/RT^2\) is based on

(a) \(\Delta \tilde{V}_{vap} = \tilde{V}_{gas} - \tilde{V}_{liq} \approx \tilde{V}_{gas}\) and (b) \(\tilde{V}_g \approx RT/p\). Furthermore, we will use the integrated form

\[
\ln \frac{p_2}{p_1} = -\frac{\Delta H_{vap}}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)
\]

based on (c) \(\Delta H_{vap}\) independent of \(T\) over a short range of \(T\).

\[
\ln \frac{p_2}{6.11 \times 10^{-3}} = -\frac{45050}{8.314} \left( \frac{1}{T_2} - \frac{1}{273.16} \right)
\]

Which we can compare with actual measured values below:

\(T_2 = 20°C = 293.15K\)

\[
\ln(p/6.11 \times 10^{-3}) = -5418.6 (3.411 \times 10^{-3} - 3.661 \times 10^{-3})
\]

\[
= 1.353
\]

\[
p = 3.871 (6.11 \times 10^{-3}) = 0.0237 \text{ bar at } 20°C \quad 0.0233 \text{ bar}
\]

\(T_2 = 30°C = 303.15K\)

\[
\ln(p/6.11 \times 10^{-3}) = -5418.6 (3.299 \times 10^{-3} - 3.661 \times 10^{-3})
\]

\[
= 1.963
\]

\[
p = 7.122 (6.11 \times 10^{-3}) = 0.0435 \text{ bar at } 30°C \quad 0.0424 \text{ bar}
\]

\(T_2 = 80°C = 353.15K\) \quad Now use \(\Delta H_{vap}\) at 100°C!

\[
\ln \frac{p_2}{1\text{ bar}} = -\frac{40660}{8.314} \left( \frac{1}{T_2} - \frac{1}{373.15} \right)
\]

\[
\ln p = -4890.5 (2.832 \times 10^{-3} - 2.680 \times 10^{-3})
\]

\[
= -0.742 \quad \text{or} \quad p = 0.476 \text{ bar at } 80°C \quad 0.4733 \text{ bar}
\]

\(T_2 = 90°C = 363.15K\)

\[
\ln p = -4890.5 (2.754 \times 10^{-3} - 2.680 \times 10^{-3})
\]
Note: If one assumed $\Delta H_{\text{vap}} = a + bT$, then $a = 57,041.5 \text{ J}$ and $b = -43.90 \text{ J K}^{-1}$.

Integrating the approximate Clapeyron equation for this choice of $\Delta H$ yields

$$\int_{p_1}^{p_2} d\ln p \approx \frac{1}{R} \int_{T_1}^{T_2} \left( \frac{a + bT}{T_2} \right) dT$$

$$\ln\left(\frac{p_2}{p_1}\right) = -\frac{a}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) + \frac{b}{R} \ln \frac{T_2}{T_1},$$

which is a better integrated form.