CLAUSIUS-CLAPERYON EQUATION

I. Review

The exact Clapeyron equation, $dp/dT = \Delta S/\Delta V$, 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
$d \ln p/d(1/T) \simeq -\Delta\bar{H}/R$

C. Effect of hydrostatic pressure on vapor pressure

A. Clapeyron Equation for Condensed Phases

$X(a) = X(b)$ in equilibrium at p_o, T_o; $\Delta G = 0$

$$\left(\frac{dp}{dT}\right)_{coex} = \frac{\Delta S}{\Delta V} = \frac{\Delta H}{T\Delta V} \tag{1}$$

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

By choosing b to be the high-temperature phase, ΔH is always positive and the slope of the coexistence line depends on the sign of ΔV. 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

$$\Delta p \sim (\Delta H/T\Delta V)\Delta T \tag{2}$$

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

$$\frac{d\ln p}{d(1/T)} = -\frac{\Delta\overline{H}/\Delta Z}{R} \quad \text{(exact)} \qquad (3)$$

where $\Delta Z = Z_g - Z_l = p\Delta\overline{V}/RT$ 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 $\Delta\overline{H}$ from the slope of ln p vs. 1/T:

1. assume $\overline{V}_l \ll \overline{V}_g$
2. assume ideal gas $\overline{V}_g = RT/p$

Therefore, $\Delta Z \simeq Z_g \simeq 1$ and

$$\frac{d\ln p}{d(1/T)} \simeq -\frac{\Delta\overline{H}}{R} \text{(approx.)} \qquad (4)$$

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 ΔH is independent of T,

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

$$\ln\frac{p_2}{p_1} \sim \frac{\Delta H}{R}\left(\frac{T_2 - T_1}{T_1T_2}\right) \qquad (5)$$

Trouton's Rule

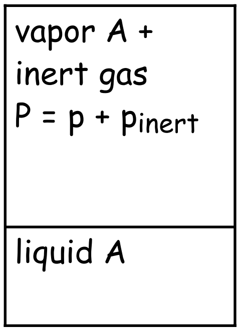
$$\Delta\overline{S}_{vap} = \Delta\overline{H}_{vap}/T_b \simeq 88 \text{ J K}^{-1}\text{ mol}^{-1} \qquad (6)$$

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_{liq}, or 3 $\text{cm}^3\text{mole}^{-1}$). From statistical mechanics (5.62),

$$\Delta\overline{S}_{vap} = R\ln(V_{gas}/V_{free,\,liquid}) = R\ln(10^4) = 75 \text{ J K}^{-1}\text{ mol}^{-1},$$

close to the empirical value !

C. Effect of inert gas pressure on the vapor pressure p of liquid A



At constant temperature T:

p_o is vapor pressure of A in the absence of inert gas

$P = p + p_{inert}$ is total pressure if inert gas present at partial pressure p_{inert}

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

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

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

$$d \ln p = \frac{\bar{V}_l}{RT}\, dP \qquad (7b)$$

and integrate to obtain

$$\ln \frac{p}{p_o} \simeq \frac{\bar{V}_l}{RT}(P - p_o) \qquad \therefore\ p > p_o \qquad (8)$$

This effect is small in practice. For example, $p_o = 0.27$ Torr for Hg at 100°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 6.11×10^{-3} bar and 273.16K and its normal boiling point is 1.013 bar (= 1 atm) and 373.15K. The latent heat of vaporization ΔH_{vap} varies with temperature, ranging from 45,050 J mol^{-1} at ~273K to 40,660 J mol^{-1} at ~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°C, 30°C, 80°C, 90°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) $\Delta\bar{V}_{vap} = \bar{V}_{gas} - \bar{V}_{liq} \simeq \bar{V}_{gas}$ and (b) $\bar{V}_g \simeq RT/p$. 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) $\Delta\bar{H}_{vap}$ independent of T over a short range of T.

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

Which we can <u>compare with actual measured values below:</u>

T_2 = 20°C = 293.15K

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

$$= 1.353$$

$p = 3.871\,(6.11\times 10^{-3}) = 0.0237$ bar at 20°C <u>0.0233 bar</u>

T_2 = 30°C = 303.15K

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

$$= 1.963$$

$p = 7.122\,(6.11\times 10^{-3}) = 0.0435$ bar at 30°C <u>0.0424 bar</u>

T_2 = 80°C = 353.15K Now use ΔH_{vap} at 100°C!

$$\ln\frac{p_2}{1\,bar} = -\frac{40660}{8.314}\left(\frac{1}{T_2} - \frac{1}{373.15}\right)$$

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

$= -0.742$ or $p = 0.476$ bar at 80°C <u>0.4733 bar</u>

T_2 = 90°C = 363.15K

$$\ln p = -4890.5\,(2.754\times 10^{-3} - 2.680\times 10^{-3})$$

= −0.360 or p = 0.697 bar at 90°C <u>0.701 bar</u>

<u>Note</u>: If one assumed $\Delta\bar{H}_{vap} = a + bT$, then $a = 57{,}041.5$ J and $b = -43.90$ J K^{-1}. Integrating the approximate Clapeyron equation for this choice of $\Delta\bar{H}$ yields

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

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

which is a better integrated form.