Liquid-vapor equilibrium (some considerations)

1. The Clausius-Clapeyron equation

The so-called Clausius-Clapeyron equation relates the equilibrium vapor pressure of a pure substance, p, with temperature, T. For a system composed of a liquid and its vapor at equilibrium $G_{\rm m}(l) = G_{\rm m}(g)$. Since $dG_{\rm m} = -S_{\rm m} \cdot dT + V_m \cdot dp$, equating $dG_{\rm m}(l) = dG_{\rm m}(g)$ yields the Clausius-Clapeyron equation, with no approximations, for a vaporization process in material equilibrium (no mass exchange between system and surroundings):

$$\frac{dp}{dT} = \frac{\Delta_{l}^{g} H_{m}}{T \cdot \Delta_{l}^{g} V_{m}}$$
(1)

Now, let us make some simplifying approximations. Since $V_m(g) >> V_m(l)$ we can assume that $\Delta_l^g V_m \cong V_m(g)$, and considering ideal gas behavior we can use the relation $V_m(g) = R \cdot T / p$. Simple algebraic rearrangements yield the approximate form of the Clausius-Clapeyron equation:

$$\frac{d\ln p}{dT} = \frac{\Delta_{\rm l}^{\rm g} H_{\rm m}}{R \cdot T^2} \tag{2}$$

If considering $\Delta_l^g H_m$ independent of *T*, the indefinite integral of equation (2) gives:

$$\ln p = -\frac{\Delta_{\rm l}^{\rm g} H_{\rm m}}{R} \cdot \frac{1}{T} + C \tag{3}$$

where *C* is an integration constant. For relatively small temperature intervals (≈ 20 K) and temperatures not very near the critical temperature, *T*_c, equation (3) is accurate enough and the graphical representation of $\ln p = f(1/T)$ should yield a straight line with slope $\Delta_l^g H_m/R$ and intercept *C*.

2. Standard molar quantities of vaporization; temperature and pressure corrections

Logarithms are dimensionless quantities and thermodynamics must be consistent with that. In fact, the correct representation of the logarithmic term in equation (3) is $\ln (p/p^*)$, where p^* is a reference pressure, which can be any chosen pressure (e.g. $p^* = 1$ Pa, $p^* = 760$ mmHg, etc.). If $p^* = 10^5$ Pa then $p^* = p^0$, the standard state pressure. Remember that the units of pressure of p and p^* inside the logarithm must be same. Equation (3) then reads:

$$\ln(p/p^*) = -\frac{\Delta_l^g H_m}{R} \cdot \frac{1}{T} + C \tag{4}$$

Multiplying both sides of the equation by $-R \cdot T$ and knowing that $\Delta_l^g G_m = -R \cdot T \cdot \ln(p/p *) = \Delta_l^g H_m - T \cdot \Delta_l^g S_m$, gives:

$$C = \frac{\Delta_l^g S_m(T, p*)}{R}$$
(5)

The slope of the linear representation of equation (4) gives $\Delta_{I}^{g}H_{m}(\langle T \rangle, \langle p \rangle)/R$, from where $\Delta_{I}^{g}H_{m}(\langle T \rangle, \langle p \rangle)$ can be easily calculated. The value of ΔH thus derived refers to the average temperature, $\langle T \rangle$, and average pressure, $\langle p \rangle$ of the experimental interval used in the ln p = f(1/T) representation. $\Delta_{I}^{g}S_{m}(\langle T \rangle, \langle p \rangle)$ can be derived using equation (6):

$$\Delta_{l}^{g} S_{m}(< T >,) = \frac{\Delta_{l}^{g} H_{m}(< T >,)}{< T >}$$
(6)

since for all the (*T*, *p*) pairs of points along the liquid-gas curve in the phase diagram liquid and gas are in thermodynamic equilibrium, and hence $\Delta_1^g G_m = 0$. Note that while the ΔS calculated by equation (6) refers to $\langle p \rangle$, that calculated by equation (5) refers to p^* . Both ways are valid for calculating ΔS , however, always keep in mind to which pressure they refer.

Normally, it is of interest to refer the molar quantities of vaporization to $p = p^0 = 10^5$ Pa and T = 298.15 K, or another set of (p, T) conditions. In this way, some corrections must be applied in order to derive the standard molar enthalpies, $\Delta_l^g H_m^0(298.15\text{K})$ and entropies, $\Delta_l^g S_m^0(298.15\text{K})$, of vaporization, at T = 298.15 K, from $\Delta_l^g H_m(< T >,)$ and $\Delta_l^g S_m(< T >,)$, respectively. The value of $\Delta_l^g H_m^0(298.15\text{K})$ is obtained according to the following thermodynamic cycle, considering 1 mol of compound that vaporizes:



where $\Delta H(1)$ and $\Delta H(2)$ correspond to the change in enthalpy due to a pressure and a temperature change. For most compounds, the changes in *H* due to a pressure change are negligible when compared to the value of $\Delta_1^{g} H_m^0$ (298.15K). Moreover, $\Delta H(1)$ and $\Delta H(2)$ nearly cancel each other in the cycle shown in the figure and so it is usual to neglect the contribution of pressure for the enthalpy correction.

The change in *H* with *T* at constant *p* can be calculated remembering that at constant pressure $dH = \partial q_p = C_p \cdot dT$, where C_p is the heat capacity at constant pressure. After rearrangement, considering that the process takes place at $p = p^0 = 10^5$ Pa, this yields for $\Delta H(1)$ and $\Delta H(2)$, on a molar basis:

$$\left(\frac{\partial\Delta H(1)}{\partial T}\right)_{p} = C_{p,\mathrm{m}}^{0}(\mathbf{l}) \tag{7}$$

$$\left(\frac{\partial\Delta H(2)}{\partial T}\right)_p = C_{p,\mathrm{m}}^0(\mathrm{g}) \tag{8}$$

For most substances, the values of $C_{p,m}^0(l)$ and of $C_{p,m}^0(g)$ are in the 10² order of magnitude and these corrections are often significant. $\Delta_l^g H_m^0(298.15K)$ is then calculated as follows:

$$\Delta_{l}^{g} H_{m}^{0}(298.15K) = \Delta H(1) + \Delta_{l}^{g} H_{m}(\langle T \rangle, \langle p \rangle) - \Delta H(2)$$

$$= \int_{298.15K}^{\langle T \rangle} C_{p,m}^{0}(l) \cdot dT + \Delta_{l}^{g} H_{m}(\langle T \rangle, \langle p \rangle) - \int_{298.15K}^{\langle T \rangle} C_{p,m}^{0}(g) \cdot dT$$

$$= \Delta_{l}^{g} H_{m}(\langle T \rangle, \langle p \rangle) - \int_{298.15K}^{\langle T \rangle} \Delta_{l}^{g} C_{p,m}^{0} \cdot dT$$
(9)

where the relation $\Delta_1^g C_{p,m}^0 = C_{p,m}^0(g) - C_{p,m}^0(l)$ was used. In many situations the function that describes the dependence of $C_{p,m}^0(l)$ and of $C_{p,m}^0(g)$ with *T* is not known, and the value of $\Delta_1^g C_{p,m}^0$ must be estimated. A normal way to do this is to consider $\Delta_1^g C_{p,m}^0$ independent of *T* in equation (9), put it outside the integral and assume that a mean and constant value of $\Delta_1^g C_{p,m}^0(\bar{T})$ holds for the considered temperature interval, where $\bar{T} = (\langle T \rangle + 298.15)/2$. Since $C_{p,m}^0(l)$ is generally higher than $C_{p,m}^0(g)$, $\Delta_1^g C_{p,m}^0 < 0$ and $\Delta_1^g H_m^0$ will decrease with increasing temperature.

For the derivation of $\Delta_l^g S_m^0(298.15K)$ a thermodynamic cycle similar to the one presented before for ΔH is used, considering 1 mol of compound that vaporizes:



where $\Delta S(1)$ and $\Delta S(2)$ correspond to the change in entropy due to a pressure and a temperature change, and can be equated by using the equation:

$$dS = \frac{c_p}{T} \cdot dT - \frac{V}{T} \cdot dp \tag{10}$$

Integrating, this yields for $\Delta S(1)$ and $\Delta S(2)$, on a molar basis:

$$\Delta S(1) = \int_{298.15\text{K}}^{} \frac{c_{p,\text{m}}(l)}{T} \cdot dT - \int_{10^5\text{Pa}}^{} \frac{V_m(l)}{T} \cdot dp$$
(11)

$$\Delta S(2) = \int_{298.15\text{K}}^{} \frac{c_{p,\text{m}}(g)}{T} \cdot dT - \int_{10^5\text{Pa}}^{} \frac{V_{\text{m}}(g)}{T} \cdot dp$$
(12)

Since $V_{\rm m}$ for liquids has only a small variation with p the second term of equation (11) can be neglected. Assuming ideal gas behavior, and that the final pressure is $p = p^0 = 10^5$ Pa, $\Delta_1^{\rm g} S_m^0$ (298.15*K*) can then be calculated by the equation:

$$\Delta_{l}^{g} S_{m}^{0}(298.15K) = \Delta S(1) + \Delta_{l}^{g} S_{m}(\langle T \rangle, \langle p \rangle) - \Delta S(2)$$

$$= \Delta_{l}^{g} S_{m}(\langle T \rangle, \langle p \rangle) - \int_{298.15K}^{\langle T \rangle} \frac{\Delta_{l}^{g} C_{p,m}^{0}}{T} \cdot dT + R \cdot \ln\left(\frac{\langle p \rangle}{10^{5}}\right)$$
(13)

For the term containing $\Delta_l^g C_{p,m}^0$ the same treatment described for $\Delta_l^g H_m^0(298.15K)$ can be employed for derivation of $\Delta_l^g S_m^0(298.15K)$.

The standard molar Gibbs energy of vaporization, at T = 298.15 K, $\Delta_l^g G_m^0(298.15$ K), can then be calculated by equation (14) and the vapor pressure at T = 298.15 K by equation (15):

$$\Delta_{\rm l}^{\rm g} G_{\rm m}^{\rm 0}(298.15K) = \Delta_{\rm l}^{\rm g} H_{\rm m}^{\rm 0}(298.15K) - 298.15 \cdot \Delta_{\rm l}^{\rm g} S_{\rm m}^{\rm 0}(298.15K)$$
(14)

$$p = p^0 \cdot \exp\left(\frac{-\Delta_l^g G_m^0}{R \cdot 298.15}\right) \tag{15}$$

where $p^0 = 10^5$ Pa, and the relation $\Delta_l^g G_m^0(T) = -R \cdot T \cdot \ln(p/p^0)$ was used.