LATENT HEATS OF PURE SUBSTANCES

When a pure substance is liquefied from the solid state or vaporized from the liquid at constant pressure, no change in temperature occurs; these heat effects are called the latent heat of fusion and the latent heat of vaporization.

\[
\Delta H = T \Delta V \frac{dP_{\text{Sat}}}{dT} \quad \text{............1}
\]

Where \(\Delta H\) = latent heat.
\(\Delta V\) = volume change accompanying the phase change.
\(P_{\text{Sat}}\) = vapor pressure.

For pure liquid \((dP_{\text{Sat}} / dT)\) is slope vapor pressure vs. temperature, \(\Delta V\) is the difference between molar volumes of saturated vapor and saturated liquid, and \(\Delta H\) is the latent heat of vaporization. Thus value of \(\Delta H\) calculated from vapor pressure and volumetric data.

There is a method for studies heat effect accompanying a phase change, these methods developed for below purposes:

- Prediction of the heat of vaporization at the normal boiling point,
- Estimation of the heat of vaporization at any temperature from the known value at a single temperature.

Riedel proposed below equation for predicate heat of vaporization at normal boiling point

\[
\frac{\Delta H_n}{T_n} = \frac{1.092(\ln P_C - 1.013)}{0.930 - T_{r_n}} \quad \text{............2}
\]

\(T_n\) = normal boiling point.
\(\Delta H_n\) = molar latent heat of vaporization at \(T_n\).
\(P_C\) = critical pressure, bar.
\(T_{r_n}\) = reduced temperature at \(T_n\).

Unit of \((\Delta H_n / T_n)\) depend on \(R\) that we choose it

\[
\frac{\Delta H_n}{T_n} = \frac{1.092(\ln P_C - 1.013)}{0.930 - T_{r_n}} = R \left[ \frac{1.092(\ln 220.5 - 1.013)}{0.930 - 0.577} \right] = 13.52R
\]

thus for \(R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}\),
and at normal boiling point for water as 100 °C
\(\Delta H_n = (13.52)(8.314)(373.15) = 41,940 \text{ J mol}^{-1}\)
Estimates of the latent heat of vaporization of a pure liquid at any temperature from the known value at a single temperature may be based on a known experimental value or on a value estimated by Eq. (2). The method proposed by Watson

\[ \frac{\Delta H_2}{\Delta H_1} = \left( \frac{1-T_{r2}}{1-T_{r1}} \right)^{0.38} \] ........3

**TWO-PHASE SYSTEMS**

The molar or specific volume for saturated liquids is different from that for saturated vapor at same T and P and this is true as well for U, H, and S except is the molar Gibbs energy. So for pure substance

\[ dG^{\alpha\beta} = 0 \]

\[ G^\alpha = G^\beta \]

Where \( G^\alpha \) and \( G^\beta \) are molar Gibbs energies for individual phases

\[ V^\alpha dP^{Sat} - S^\alpha dT = V^\beta dP^{Sat} - S^\beta dT \]

\[ \frac{dP^{Sat}}{dT} = \frac{S^\beta - S^\alpha}{V^\beta - V^\alpha} = \frac{\Delta S^{\alpha\beta}}{\Delta V^{\alpha\beta}} \] ........4

Where \( \Delta S^{\alpha\beta} \) and \( \Delta V^{\alpha\beta} \) are entropy and volume changes which occur when a unit amount of pure chemical species it transferred from \( \alpha \) phase to \( \beta \) phase at constant temperature and pressure.

\[ dH^{\alpha\beta} = TdS^{\alpha\beta} + VdP^{\alpha\beta} \]

Integration lead to \( \Delta H^{\alpha\beta} = T\Delta S^{\alpha\beta} \)

\[ \therefore \Delta S^{\alpha\beta} = \frac{\Delta H^{\alpha\beta}}{T} \]

\[ \frac{dP^{Sat}}{dT} = \frac{\Delta S^{\alpha\beta}}{\Delta V^{\alpha\beta}} = \frac{\Delta H^{\alpha\beta}}{T\Delta V^{\alpha\beta}} \]

\[ \frac{dP^{Sat}}{dT} = \frac{\Delta H^{\alpha\beta}}{T\Delta V^{\alpha\beta}} \] ........5

Equation (5) is called Clapeyron equation
For case which transition from liquid phase \(l\) to vapor phase \(v\), \(\Delta H^{\alpha\beta}\) represent latent heat of vaporization \(\Delta H^v\)

\[
\frac{dP_{Sat}}{dT} = \frac{\Delta H^v}{TV_{lg}^1}
\]

In case of vapor which assumed as an ideal gas \(v^g \gg v^l\)

\[
v_{lg}^1 = v^g = \frac{RT}{P_{sat}}
\]

\[
\therefore \frac{dP_{Sat}}{dT} = \frac{\Delta H^v}{RT^2 / P_{sat}}
\]

\[
\frac{dP_{Sat}}{T} = \frac{P_{Sat}}{RT^2} \Delta H^v \text{.........................6}
\]

Equation (6) called Clausius /Clapeyron, by rearrange and integrate it

\[
\int \frac{dP_{Sat}}{P_{Sat}} = \frac{\Delta H^v}{R} \int \frac{dT}{T^2}
\]

\[
\ln P_{Sat} = -\frac{\Delta H^v}{RT} + C.
\]

\[
\Delta H^v = -R \frac{d \ln P_{Sat}}{d(1/T)} \text{.....7}
\]

Equation (7) represents a relation between saturated pressure and temperature at the range from triple point to critical point and this represent a straight line equation which A and B are constant (see the figure)

This equation gives a rough approximation of vapor-pressure relation

The Antoine equation, which is more satisfactory for general use

\[
\ln P_{Sat} = A - \frac{B}{T + C}
\]

Where A, B and C are constants.
The accurate representation of vapor-pressure data over a wide temperature range requires an equation of greater complexity

\[ \ln P^{Sat} = A - \frac{B}{T} + D \ln T + F T^6 \]

Where A, B, D, and F are constants.

**Two-Phase Liquid / Vapor Systems**

When a system consists of saturated-liquid and saturated-vapor phases coexisting in equilibrium, the total value of any extensive property of the two-phase system is the sum of the total properties of the phases. Written for the volume, this relation is:

\[ nV = n^lV^l + n^vV^v \]

*total number of moles* \( n = n^l + n^v \)

\[ V = x^lV^l + x^vV^v \]

\[ V = (1 - x^v)V^l + x^vV^v \]

The mass or molar fraction of the system that is vapor \( x^v \) is called the quality. Analogous equations can be written for the other extensive thermodynamic properties. All of these relations are represented by the generic equation:

\[ M = (1 - x^v)M^l + x^vM^v \]

Where \( M \) represents \( V, U, H, S, \) etc.