

D. The Clausius-Clapeyron Equation

Adapted from

<http://www.me.tulane.edu/Faculty/Sailor/courses/Me371/Latent%20Heat.pdf>

One of the characteristics of reversible phase transition in a one-component system (pure substance), is the absorption or release of energy (in the form of heat) during the process. In the case of vaporization of a pure liquid, the amount of energy (heat) required to vaporize a unit mass of saturated liquid, at a given temperature and pressure, is called latent heat or enthalpy of vaporization. Application of the First Law of Thermodynamics to this type of phase change shows that the latent heat is equal to the difference in enthalpy between the final (vapor) and the initial (saturated liquid) phases at the same pressure and temperature, i.e.,

$$h_{fg} = h_g - h_f \quad (1)$$

where h_{fg} is the latent heat of vaporization for water. The condition for both phases of a pure substance to be in a state of unconstrained equilibrium at the same temperature and pressure is that their Gibbs' functions are equal.

$$g_f(p, T) = g_g(p, T) \quad \text{and hence} \quad dg_f = dg_g \quad (2)$$

The Gibbs' function is, in general, defined as $g = h - Ts$. Differentiating this we obtain:

$$dg = dh - Tds - s dT \quad (3)$$

The combination of the First and Second Laws of Thermodynamics for a reversible process yields

$$Tds = dh - v dp \quad (4)$$

Substituting the earlier expressions into equation (4) we can write

$$dg = v dp - s dT \quad (5)$$

which is applicable for each phase individually. Given the condition expressed by equation. 2, the above can be expressed as:

$$dp (v_g - v_f) = dT (s_g - s_f) \quad (6)$$

It is known that

$$s_g - s_f = (h_g - h_f) / T \quad (7)$$

and, therefore equation 6 becomes

$$\frac{dp}{dT} = \frac{h_g - h_f}{T(v_g - v_f)} = \frac{h_{fg}}{T v_{fg}} \quad (8)$$

This equation is called the *Clausius-Clapeyron Equation*, and it provides relationship between the slope of the saturation line, dp/dT , and the changes in the specific volume and enthalpy associated with the phase change at a fixed pressure and temperature.

Assuming that h_{fg} is constant over the range of temperatures measured, the specific volume for steam is much greater than that for liquid water ($v_g \gg v_f$), and the vapor can be treated as a perfect gas ($v_g = RT/p$), the Clausius-Clapeyron equation can be put into the form

$$h_{fg} = \frac{RT^2}{p} \left(\frac{dp}{dT} \right) \quad (9)$$

Here, R is the gas constant for water vapor. Integrating:

$$p = p_0 e^{\frac{h_{fg}}{R} \left(\frac{1}{T_0} - \frac{1}{T} \right)} = 4.58 e^{\left(\frac{19.0738}{273.15+t^{\circ}\text{C}} \right)} \text{ mmHg} \quad (10)$$

p = saturation pressure of water vapor in mmHg @ t °C

$T_0 = 273.15$ °K

$p_0 = 4.58$ mmHg @ T_0 ;

$h_{fg} = M_{\text{vapor}} C_{\text{vapor}} = 18.016 \text{ (g / mol)} * 2.4045 * 10^3 \text{ (joules / g)} = 43319 \text{ joules/mol}$;

$R = 8.3143 \text{ joules / mol / }^{\circ}\text{K}$

$h_{fg} / R = 5210$ °K

That equation is nearly valid for water vapor from 0°C to 100°C.

Note: Annex D is included to show how Clausius-Clapeyron equation may be obtained from the first and second law of thermodynamics. In the present paper the Tetens formula has been used instead.