

1. The Clausius-Clapeyron Equation

We will utilize the Carnot cycle to derive an important relationship, known as the *Clausius-Clapeyron Equation or the first latent heat equation*. This equation describes how saturated vapor pressure above a liquid changes with temperature and also how the melting point of a solid changes with pressure.

Let the working substance in the cylinder of a Carnot ideal heat engine be a liquid in equilibrium with its saturated vapor and let the initial state of the substance be T and e_s ,

Leg1-2 Let the cylinder be placed on a source of heat at temperature T and let the substance expand isothermally until a unit mass of the liquid evaporates. In this transformation the pressure remains constant at e_s , and the substance passes from state 1 to 2. If the specific volumes of liquid and vapor at temperature T are α_l and α_v , respectively, the increase in the volume of the system in passing from 1 to 2 is $(\alpha_v - \alpha_l)$. Also the heat absorbed from the source is L_v where L_v is the latent heat of vaporization.

Leg2-3 The cylinder is now placed on a nonconducting stand and a small adiabatic expansion is carried out from 2 to 3 in which the temperature falls from T to $T - dT$ and the pressure from $e_s - de_s$.

Leg3-4 The cylinder is placed on the heat sink at temperature $T - dT$ and an isothermal and isobaric compression is carried out from state 3 to 4 during which vapor is condensed.

Leg4-1 We finalize by an adiabatic compression from $e_s - de_s$ and $T - dT$ to e_s and T .

All the transformations are reversible, so

We can define the efficiency as in the Carnot Cycle

$$\eta = \frac{w}{q_h} = \frac{q_h - q_c}{q_h} = \frac{T_h - T_c}{T_h} \quad (1)$$

And in this specific case of an infinitesimal cycle

We can define the efficiency as in the Carnot Cycle

$$\frac{dw}{q_h} = \frac{dT}{T} \quad (2)$$

The work done in the cycle is equal to the area enclosed on a $p - V$ diagram. Therefore

$$dw = (\alpha_v - \alpha_l)de_s \quad (3)$$

Also, $q_h = l_v$, therefore,

$$\frac{l_v}{T} = \frac{(\alpha_v - \alpha_l)de_s}{dT} \quad (4)$$

Which can be re-written as

$$\boxed{\frac{de_s}{dT} = \frac{l_v}{T(\alpha_v - \alpha_l)}} \quad (5)$$

Which is the *Clausius-Clapeyron Equation*

1a. Proof of Clausius-Clapeyron using Gibbs Function or Gibbs Free Energy

For any two phases (1 and 2) in equilibrium

$$g_1 = g_2 \quad (6)$$

$$(7)$$

Proof: In equilibrium T and P of both phases are equal. There is no NET transfer of mass, $dg_1 = 0$ and $dg_2 = 0$.

Now, if there is a change of temperature from T by dT and the corresponding change in pressure from P by dP and liquid is vaporizing. The Gibbs free energy of the vapor will change by the same amount as that of the liquid.

$$dg_1 = dg_2 \quad (8)$$

$$(9)$$

applying the fundamental relations:

$$-(s_2 - s_1)dT + (\alpha_2 - \alpha_1)dp = 0 \quad (10)$$

or

$$\frac{dp}{dT} = \frac{\Delta s}{\Delta \alpha} \quad (11)$$

Since

$$ds = \frac{l}{T} \quad (12)$$

Then

$$\boxed{\frac{dp}{dT} = \frac{l}{T\Delta\alpha}} \quad (13)$$

Where l is the latent heat appropriate to the phases present. This is the *Clausius-Clapeyron equation* and related the equilibrium vapor pressure to the temperature of the heterogeneous system. It constitutes an equation of state for the heterogeneous system when two phases are present. It is a more generalized form of the equation.

l_v latent heat of vaporization (liquid-gas) = $2.5 \times 10^6 \text{ Jkg}^{-1}$ at 0°C

l_f latent heat of fusion (solid-liquid) = $3.34 \times 10^5 \text{ Jkg}^{-1}$ at 0°C

l_s latent heat of sublimation (solid-vapor) = $2.83 \times 10^6 \text{ Jkg}^{-1}$ at 0°C

$$l_s = l_f + l_v$$

However, the latent heat is a property of the system and depends on the thermodynamic state (generally expressed as a function of temperature)

i. Water-Ice l is the latent heat of fusion. It is more convenient to express the equation as:

$$\frac{dT}{dp} = \frac{T\Delta\alpha}{l} \quad (14)$$

Because the change in volume during fusion is negligible, the equation of state becomes:

$$\frac{dT}{dp} \approx 0 \quad (15)$$

So the surface of water and ice in a T-p diagram is vertical.

ii. Water-Vapor or Ice-Vapor The change of volume is approximately equal to that of the vapor produced:

$$\Delta\alpha \approx \frac{R_v T}{p} \quad (16)$$

$$\frac{dp}{dT} = \frac{lp}{T^2 R_v} \quad (17)$$

which can also be expressed as:

$$\left(\frac{d \ln p}{dT} \right)_{\text{vaporization or sublimation}} = \frac{l}{R_v T^2} \quad (18)$$

for l constant

$$\ln \frac{p_2}{p_1} = \frac{l}{R_v} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (19)$$

Using the respective l_v for vaporization and l_s for sublimation yields (p_w, p_i in mb).

$$\ln \frac{e_{s2}}{e_{s1}} = \frac{l_v}{R_v} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (20)$$

$$\ln \frac{e_{si2}}{e_{si1}} = \frac{l_s}{R_v} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (21)$$

For a better approximation we can use an equation to express the change in latent heat with temperature. (HW)

These equations describe the surfaces that correspond to vapor being in chemical equilibrium with a condensed phase and to the system pressure equaling the equilibrium vapor pressure.

We can apply these equations to vapor in equilibrium with liquid water below $0^\circ C$, that is to supercooled water. Figure 1 shows saturation vapor pressures above supercooled water and ice down to $-30^\circ C$. The two curves intersect at $0^\circ C$ and diverge at lower temperatures. The vapor pressure for sub cooled water always being greater than that for ice at the same temperature. This is consistent with our interpretation of saturation vapor pressure as a measure of evaporation rate. We expect water in the less tightly bound liquid state to evaporate more rapidly than ice at the same temperature. Note the maximum difference between the two

pressures at -12.5°C (Figure 2 and Figure 3).

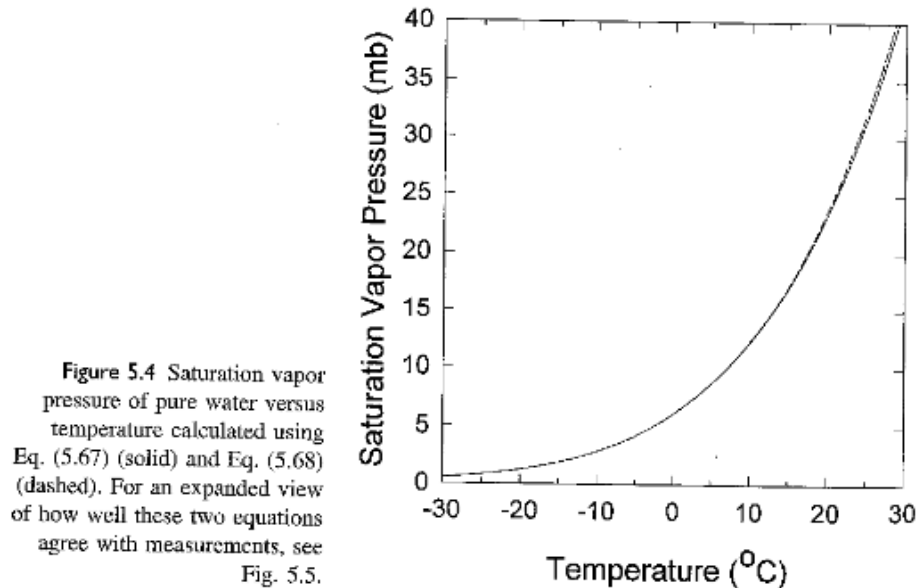


Figure 1: From Bohren and Albrecht

”This difference has profound consequences. Cloud droplets freeze at temperatures below 0°C when they have the help of ice nuclei to initiate freezing. Nature has many cloud condensation nuclei, but very few ice nuclei, consequently clouds of supercooled water droplets are the rule rather than the exception. The cloud may be mostly sub cooled water droplets, but if one droplet happens to form on an ice nucleus it would have an advantage over its neighbors. Evaporation proceeds more slowly from an ice crystal than from a water droplet at the same temperature, and hence an ice crystal in an environment of mostly sub cooled water droplets grows at the expense of its neighbors shrinking (Figure 4). As the ice grain grows, it falls faster than its smaller neighbors, therefore colliding with them. They freeze upon contact (riming) making the ice grain even larger. As it consumes sub cooled water droplets on its descent, it falls ever faster with an ever larger cross-sectional area, both of which serve to increase its ability to grow even larger. Thus the rich (ice grains) get richer and the poor (sub cooled water droplets) get poorer. This is the Bergeron Process. ” From Bohren and Albrecht.

Figure 5.6 Saturation vapor pressure of ice and subcooled water (pure water existing as liquid at a temperature below the nominal freezing point).

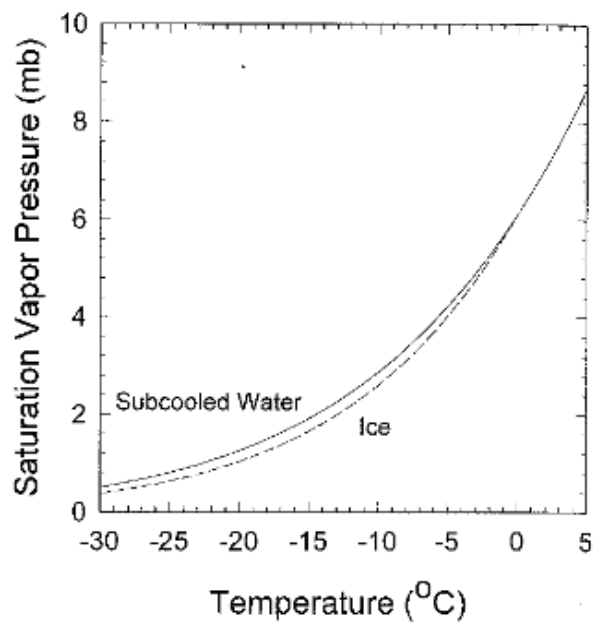


Figure 2: From Bohren and Albrecht

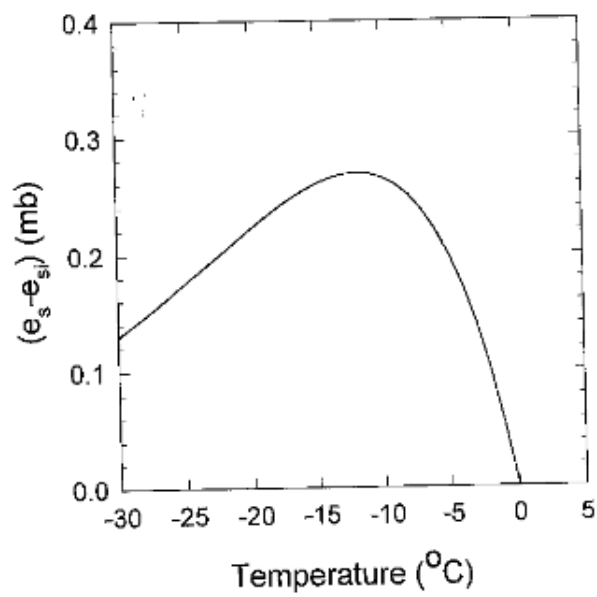
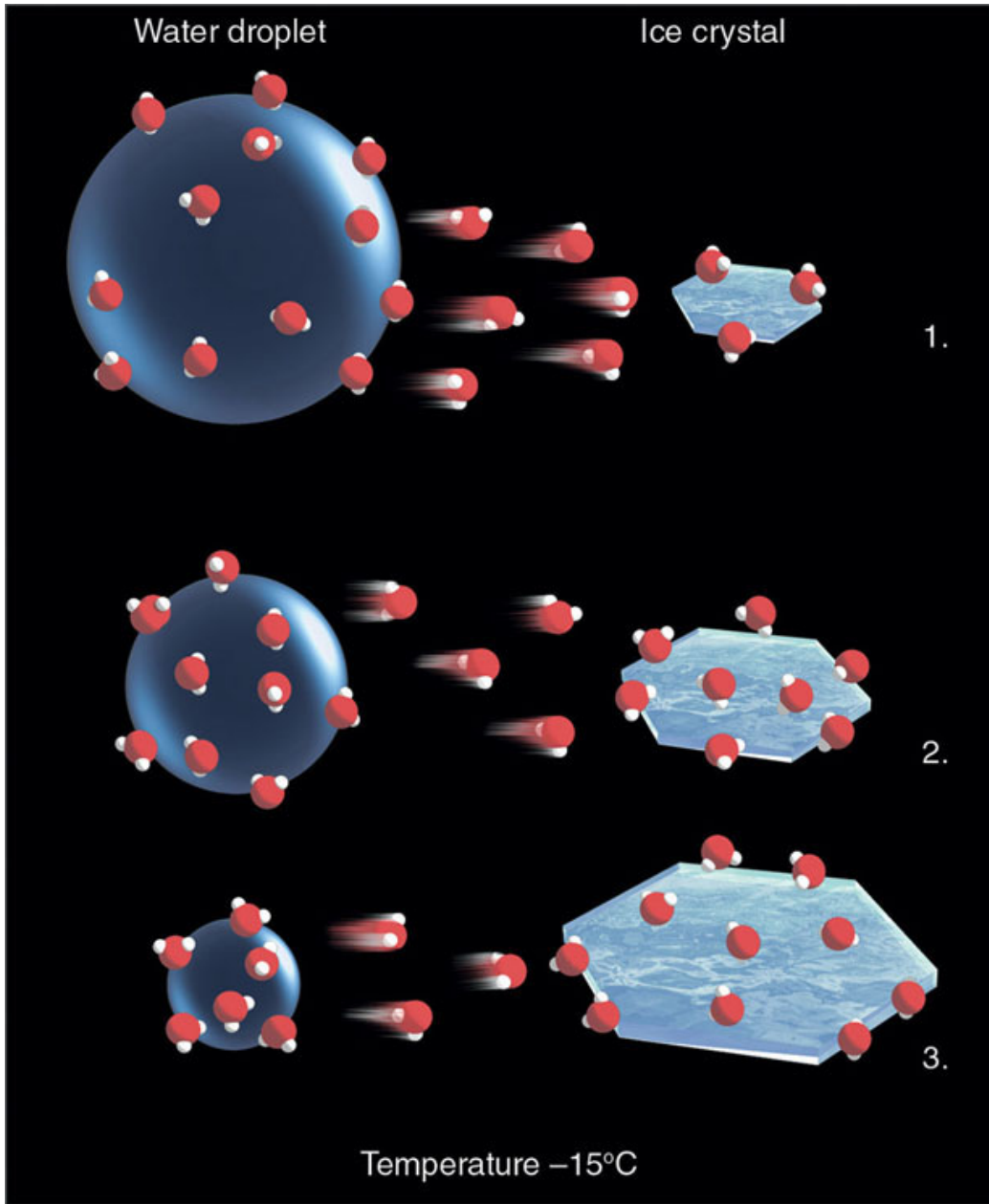


Figure 5.7 Difference between the saturation vapor pressure of subcooled water e_s and that of ice e_{ii} . Note the maximum at about -12°C .

Figure 3: From Bohren and Albrecht



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Figure 4: Bergeron Process From Ahrens

We can also look at the p - α diagram. At temperatures below the critical point ($374\text{ }^{\circ}\text{C}$ for water) a change in specific volume associated with isothermal compression before condensation is described to a good approximation by the ideal gas law. At higher temperatures and pressures, however, the ideal gas law is inadequate. Above these there are no phase boundaries and we have a supercritical fluid. Above the critical temperature a liquid cannot be formed by an increase in pressure.

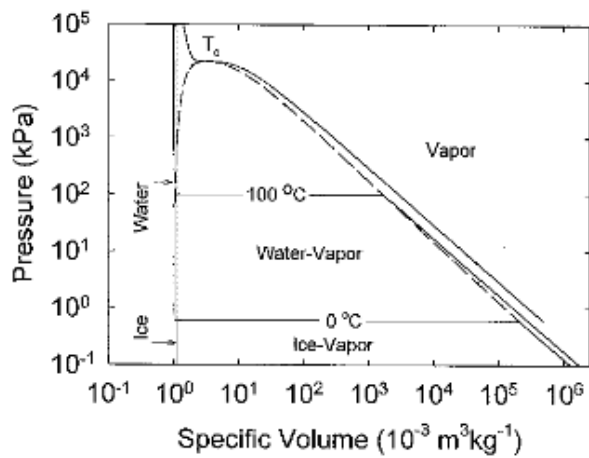


Figure 5.11 Equilibrium pressure and specific volume states of water in all three phases. The dashed envelope is the set of all states for which the transition from vapor to liquid or vice versa occurs. On a logarithmic scale isotherms for a wide range of temperatures, from the triple point to the critical point, are closely packed together. At pressures greater than the triple-point pressure, the ice-phase line is indicated by a dotted line.

Figure 5: From Bohren and Albrecht

Consider isobaric heat rejection of a mass of water vapor (well below the critical point). Temperature and volume both decrease, reflecting the two degrees of freedom possessed by a homogeneous system. Eventually, the process encounters the boundary separating homogeneous states, wherein only vapor is present, from heterogeneous states, wherein water and vapor coexist at equilibrium. At this state, the slope of the process changes discontinuously because the temperature of the system can no longer decrease. Instead, isobaric heat rejection results in condensation of vapor, which is attended by a sharp reduction in volume at constant temperature. This behavior continues until the vapor has been converted entirely into water, at which point the system is again homogeneous and the slope of the process changes discontinuously a second time. Beyond that state heat rejection

results in a decrease of both temperature and volume, defecting the two degrees of freedom again possessed by the system.

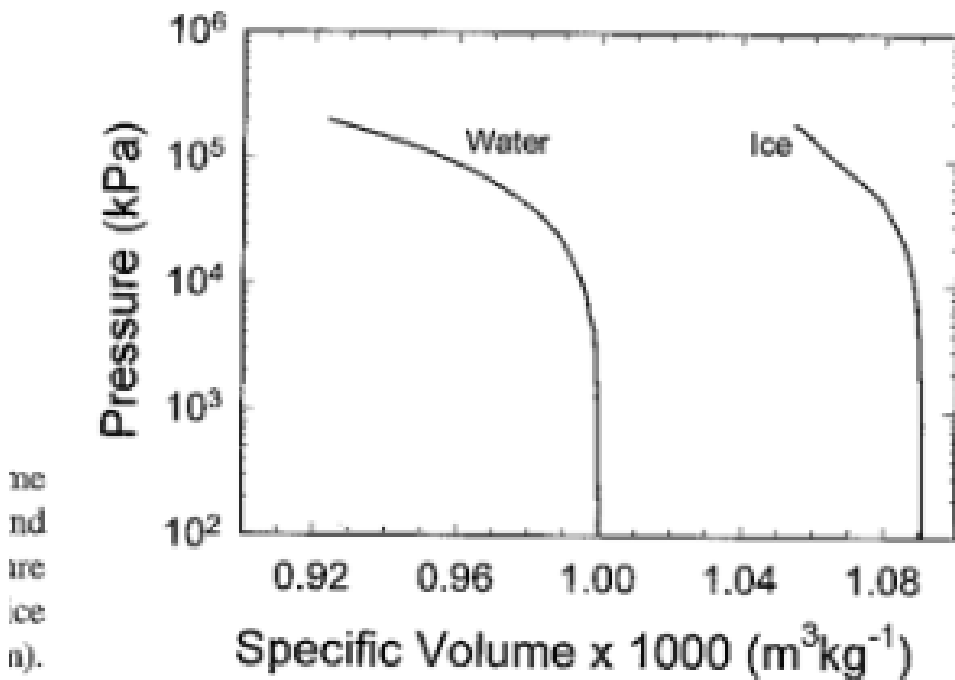


Figure 6: From Bohren and Albrecht

There exists a single state at which all three phases coexist in equilibrium. The triple point for water is $p_T = 6.11\text{mb}$, $T_T = 273.15\text{K}$, $\alpha_{T_v} = 2.06 \times 10^5\text{m}^3/\text{kg}$, $\alpha_{T_w} = 1 \times 10^{-3}\text{m}^3/\text{kg}$ and $\alpha_{T_i} = 1.09 \times 10^{-3}\text{m}^3/\text{kg}$. Another interesting aspect is that the specific volume of ice is larger than the specific volume of water. This means that ice expands upon freezing, while other substances (carbon dioxide) contract upon freezing. The triple point (273.16 K) is the temperature at which pure ice, water vapor and pure liquid water are in equilibrium (at a pressure of 6.11mb, the ice