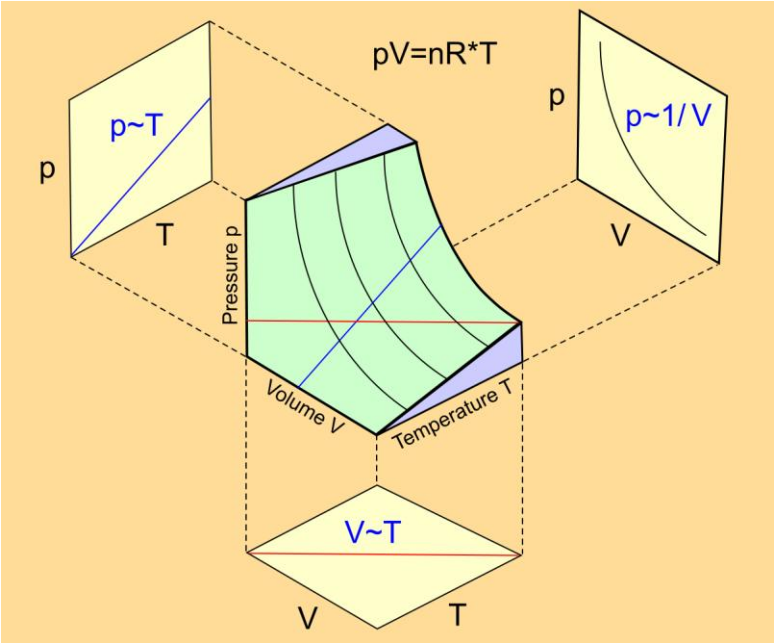
Lapse Rate. Prof. Ruiz (Doc), UNC-Asheville (1978-2021), DoctorPhys on YouTube.
Prerequisites: Chemistry, Physics I, II. Calculus I, II, III. Thermodynamics.

Chapter M. The Clapeyron Equation. The ideal gas law $pV = nR*T$ is a very good approximation for real gases in many scenarios. Note that any two of the variables p, V, and T for a fixed number of moles determine the value of the third variable. So we can write $p = p(T,V)$, $V = V(T,p)$, or $T = T(p,V)$, and even $f(p,V,T) = 0$ Such an equation describing the state of the system is often referred to an *equation of state*.

The ideal gas law applies to only a limited region of the entire range of ice, liquid water, and gas. When it comes to ice and liquid water we do not have a nice equation similar to the ideal gas law for describing the substance.

Before considering water, here is the 3D plot for the ideal gas law. Note the surface that appears. We call this 3D representation a *p-V-T diagram* or *p-V-T surface diagram*. The right figure also includes three projections unto three distinct planes. In each of the three planes, one of the state variables pressure, temperature, or volume, is constant.

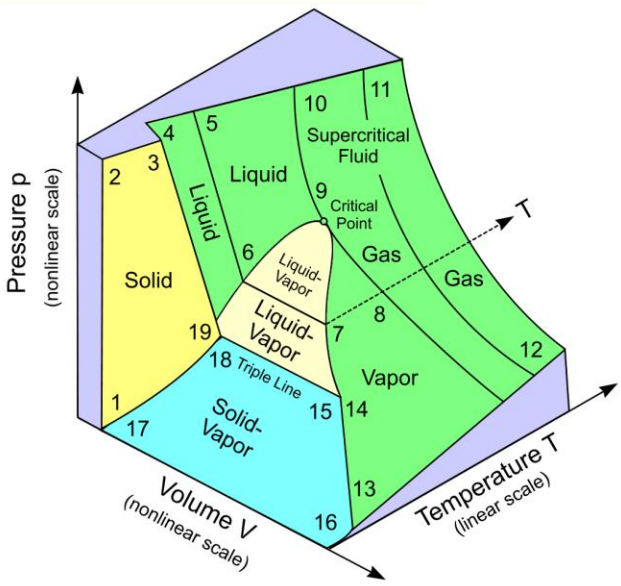


Remember the three gas laws that we introduced earlier and then combined them into the ideal gas law? These three laws are represented in the three projected planes above. Each plane is a slice of the 3D diagram where one of the three variables is constant. Compare these projections with the table below.

Boyle's Law	Charles's Law	Gay-Lussac's Law
		
Robert Boyle 1627-1691	Jacques Charles 1746-1823	Joseph Gay-Lussac 1778-1850
$p \sim \frac{1}{V}$ at constant T	$V \sim T$ at constant p	$p \sim T$ at constant V

Since we do not have explicit equations of state in formula form for all states of H_2O, we use a graphical representation constructed from experiments. The result is our p-V-T surface, which serves as our equation of state. You pick two of the three variables from p, T, V and the third one is determined.

All the information is on the surface. The space below or behind the surface does not have any meaning. The diagram is a powerful way to represent observational data. We will consider 1 kg of H_2O so that the volume axis is also the specific volume (but I will keep V for now instead of our usual α notation). The p-axis and V-axis are logarithmic. Remember that a log axis cannot start with exactly zero because every time you take a step along the axis you multiply by a number such as 10 rather than add. Our volume axis starts at something like 10^{-4} m for 1 kg of H_2O. Always remember that all the information is on the surface. Let's take a tour.



1-2. We begin at 1, low p and T. The volume is finite. We squeeze the ice in a container with imaginary walls, keeping T constant, and move towards 2, high pressure. The volume of ice decreases very slightly because ice is close to being incompressible. If we were to start at 17 and then proceed to 16, we expand our confining walls around the ice. We have sublimation (a change of the solid phase directly to the gas phase), vapor forming more and more. Think of the line between 1 and 17 as the beginning of the solid-vapor region with 100% ice at the solid yellow wall (saturated ice). At the other end (between 15 and 14) we are at the right edge of the blue region. We have 100% vapor (saturated vapor). Technically vapor is gas. But we like to use "vapor" instead of "gas" for regions where "gas" boundaries meet the other phases of liquid or solid. It is best to remember it this way: "vapor" is gas below the temperature at the critical point, which temperature we can call T_c.

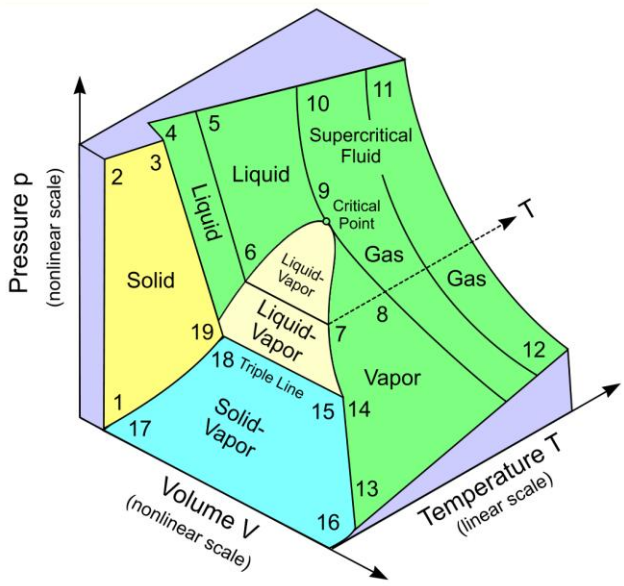
2-3. We increase the temperature by heating the ice. It expands a very little as the ordered arrangements of the water molecules (crystalline lattice) increases in size a small amount.

3-4. When we arrive at the edge to the right of 3, the ice starts melting. Since liquid water takes up less volume than ice, the volume decreases and we move to the back green wall. On the edge just to the right of 3 we have saturated ice. We are at the melting temperature, the pressure stays the same, and melting begins. We have a phase change. As we approach the green wall more and more water forms as the ice melts. When we hit the green wall we have liquid saturation (all liquid water and no longer any ice). The melting is complete.

4-5. As we heat the liquid at high pressure we move to 5, but a strange thing happens with water that is not seen in our p-V-T surface unless we could zoom in a lot. Water decreases slightly in volume from T = 0 °C to 4° C since in this temperature range small ice-like remnants are present and they

break apart allowing greater compaction. The volume decreases. By 4 °C, the vast majority of the ice-like remnants have broken down, and expansion takes over. However, the volume increase is very gentle since liquid expansion is nearly insensitive to temperature. When up you compare traveling 4-to-5 (water) with 1-to-19 (ice), the water's slight volume increase per unit temperature increase is greater than ice's (1-19). The reason is that it is easier to change the disordered water molecules in water than the ordered lattice structure of the ice. But both are nearly insensitive to temperature, regarding volume changes. If we keep going to 10 we reach the supercritical fluid region once we pass the temperature of the critical point marked in the diagram. Here, H_2O behaves neither as a liquid nor as a gas. It has properties of both. It can enter pores like a gas and dissolve things like a liquid, but it is neither. The transition to supercritical fluid is gradual and becomes noticeable near 0.9 T_c. By 1.05 T_c we are clearly in the supercritical fluid region.

5-6. We lower the pressure at constant T and the liquid expands a little. When we reach the intersection of lines just below 6 we are at the left edge of the liquid-vapor line just below 6-7, where at the edge near 6 we have saturated liquid (100% liquid, no vapor).



6-7. Along this path the pressure and temperature remain constant. More vapor is forming and the volume increases as vapor takes up much more space than liquid. When we get to 7 we have saturated vapor (100% vapor, no liquid). This line from 6 to 7 is a phase change. Consider it boiling for that particular temperature and pressure. Going backwards from 7 to 6 is liquefaction. All of the steps along the journey are equilibrium states. The nonequilibrium counterparts to boiling and liquefaction are evaporation and condensation. These processes do not follow paths on the surface of our p-V-T diagram. However, when meteorologists idealize thermodynamic paths, e.g., consider a saturated vapor cloud slowly rising in the atmosphere, the system is at equilibrium always and those states will follow some kind of path on the p-V-T surface, of course different from the 6-7 line since the temperature drops with a rising parcel. Such an ideal infinitesimally slow process where no energy is lost to friction or uncontrolled heat transfer is said to be reversible. Think reversible as meaning we can turn around and take the thermodynamic path in reverse super slowly.

7-8. The terrain from 7 to 8 involves increasing T and decreasing p (a downward terrain for pressure). We leave the light yellow dome region and move into vapor territory. We are heading to the temperature of the critical point (T_c).

8-9. We increase p at T_c with decreasing V as we head to the critical point. The gas starts to lose its gas properties as we near the critical point and when we get there, the gas and supercritical fluid state become indistinguishable. Note that coming to this point from the liquid-vapor region along the

constant volume line directly under the critical point, liquid and vapor also lose their distinction and become one with the indistinguishable gas and supercritical fluid at the critical point.

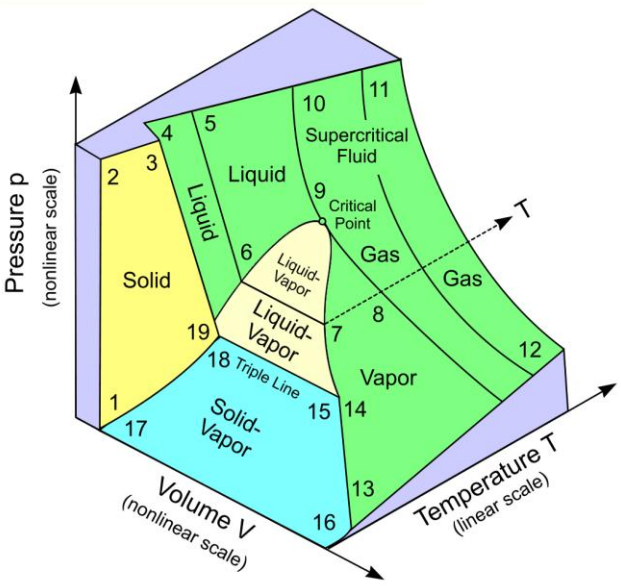
9-10. Pressure increases and volume decreases. If we consider the label 10 to represent a point to the right of the T_c line, say 1.05 T_c, it is clearly in the supercritical fluid region.

10-11. We move to higher temperatures in the supercritical-fluid region, expanding.

11-12. We lower pressure and eventually enter the gas region, where the ideal gas law can be applied. The transition from supercritical fluid to gas is gradual along our path.

12-13. Coming down from 12 to 13 temperature and pressure drop in a region where pV = nR*T applies. But since the pressure scale is nonlinear, p is decreasing more drastically. Volume needs to increase to offset the drastic drop in pressure so that the equation is balanced.

13-14. When we move up the line to the left of 13-14, we are on the saturated vapor boundary of the solid-vapor region. As T and p increase there is a competition. Increasing T causes expansion and increasing p causes compression. Pressure wins since vapor (and gas) respond more to pressure changes than temperature. It is easier to push the vapor volume down than it is to expand it by heating it. At the point where the yellow, green, and blue regions meet near 14 we are at the right edge of the triple line with vapor saturation.



15-16. Traveling down the line to the right of 15-16 is the reverse of the path to the left of 13-14.

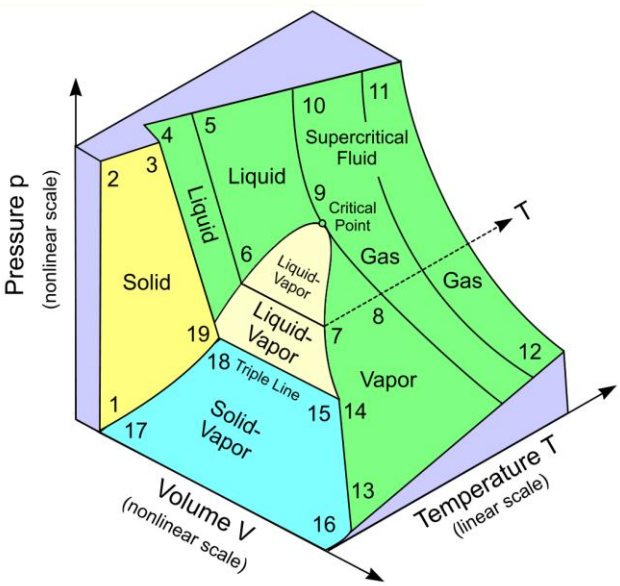
16-17. Decreasing the volume of the solid-vapor mixture encourages deposition of the vapor to solid.

17-18. Increasing T at the solid-saturated side causes a slight increase in volume.

We should address the path 19-6-9 moving up the left side of the yellow dome. Here, the temperature and pressure increase. Increasing pressure wants to push the liquid to a smaller volume, while increasing temperature encourages expansion. Temperature wins since the liquid is so incompressible that the tendency towards smaller volume is less than the expansion due to the increase in temperature. As temperature and pressure increase going up the 6-9 path the temperature wins by a larger margin. When you get to 9 liquid and vapor are indistinguishable. Coming down the other side, i.e., the 9-7-14 path a similar competition occurs. Decreasing pressure encourages the vapor to expand and decreasing temperature causes a competing contraction. But now we are vapor saturated

and vapor responds dramatically to pressure and less so to temperature changes. Therefore, the vapor expands and the volume expands.

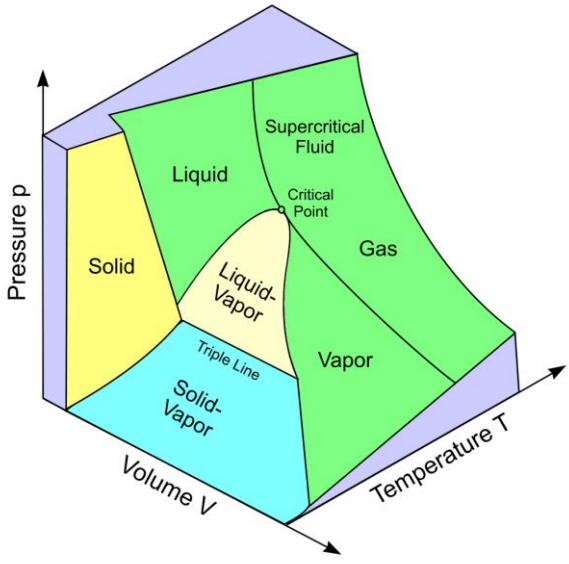
Finally, consider the line above 18 to 15 and the line above 6 to 7. Heat transfer occurs in each causing phase changes. Traditionally, this heat transfer has been referred to as "latent heat" because there is no temperature change, in contrast to "sensible" heat that we can sense with a thermometer.



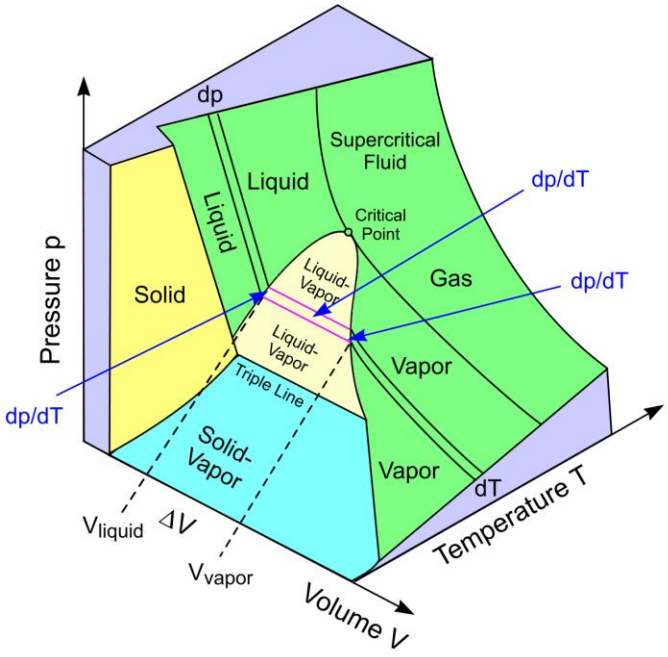
Along the line above 6-7 and paths parallel to it in the dome region, the temperature and pressure remain the same. We have a phase change from liquid to vapor. But as you increase the temperature and pressure the liquid and vapor phases start to resemble each other more and more. Therefore, less latent heat is needed. If we use a money analogy, it costs less and less to go from liquid-saturation (left side) to vapor saturation (right side). At the critical point the liquid and vapor phases are identical and we are there with no needed latent heat. No money is spent. It is free and a done deal.

The triple line is tricky. At the green wall we start off with liquid saturation. As we move to the right along the triple line we have a liquid-ice (liquid-solid) section of the 18-to-15 line. Remember that ice takes up more volume than water. Eventually we reach ice saturation at the 19 (18) corner, then an ice-vapor line segment, and finally vapor saturation a the far right 14 (15) end.

Below is the p-V-T surface diagram for water with less labels.



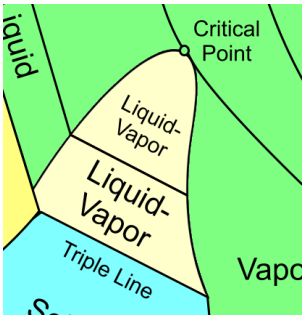
I am going to give one of the several derivations of the Clapeyron equation that one can find in texts. It is my favorite. We will be calculating dp/dT (see the figure below).



Left Figure: p-V-T Surface Diagram for Water.

Let's take another look at the p-V-T surface diagram for the phases of water and do a quick review. Even though we do not have a nice equation to describe the state of water over all its phases, we have our empirically constructed surface diagram. We might say our diagram is for $\mathrm{H_2O}$ since water usually means the liquid phase, and the other two phases are ice and gas. For temperatures less than the temperature of the critical point we refer to the gas as vapor.

Along the triple line, solid, liquid, and vapor coexist, but two at any given point except at the ends, as we have discussed. The triple line has an exact temperature of 0.01 °C by definition as an exact reference. The triple line is often referred to as a triple point as it looks like a point when viewed in a p-T two-dimensional projected plane or looking down the volume axis. At temperatures beyond the critical point (374 °C) and pressures below the critical pressure, we have a gas. Note the similarity of this region to our earlier ideal-gas diagram. The ideal gas behavior at high temperatures in the above figure exists where you see the label gas and vapor. An important region for application to the atmosphere is the liquid-vapor region - the yellow dome-like region.



The left boundary of the central pastel yellow section indicates 100% liquid and 0% vapor. The line across the yellow region represents mixtures of liquid and vapor at a given pressure and temperature. We will need our equations

$$(20)\ \boxed{g = u - sT + p\alpha} \quad \text{and} \quad (21)\ \boxed{dg = -sdT + \alpha dp}.$$

Along the line drawn that crosses across the liquid-vapor region in the p-V-T figure we have $dg = -sdT + \alpha dp = 0$. Verify from the above full p-V-T figure that both the temperature and pressure are indeed constant along this line for the phase change.

The initial Gibbs function is that for the water, while the final Gibbs function is that for the vapor. The Gibbs function is $g = u - sT + p\alpha$ and it remains constant during the phase change since we have already noted that $dg = 0$ along the phase-change line. Let the Gibbs function for the liquid water be

$$g_l = u_l - s_l T + p\alpha_l ,$$

where we do not need subscripts for the constant T and p since these are the same for both the liquid water and vapor. For the vapor phase

$$g_v = u_v - s_v T + p\alpha_v .$$

Setting the liquid and vapor result equal to each other since the Gibbs function is a constant,

$$g_l = g_v \quad \text{leads to} \quad u_l - s_l T + p\alpha_l = u_v - s_v T + p\alpha_v .$$

Bring the $s_v T$ from the right side to the left side.

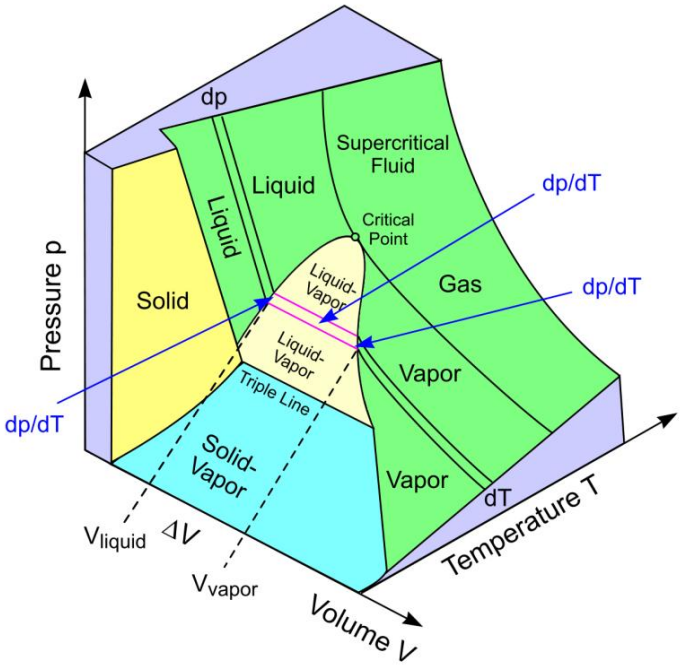
$$u_l - s_l T + p\alpha_l = u_v - s_v T + p\alpha_v \quad \Rightarrow \quad u_l + s_v T - s_l T + p\alpha_l = u_v + p\alpha_v$$

Rearranging,

$$u_l + s_v T - s_l T + p\alpha_l = u_v + p\alpha_v \quad \Rightarrow \quad (s_v - s_l)T + u_l + p\alpha_l = u_v + p\alpha_v .$$

$$(s_v - s_l)T = u_v - u_l + p\alpha_v - p\alpha_l \quad \Rightarrow \quad (s_v - s_l)T = (u_v - u_l) + p(\alpha_v - \alpha_l)$$

We will show that right-hand side is also the difference in the enthalpies using (13) $\boxed{h = u + p\alpha}$.



$$(s_v - s_l)T = (u_v - u_l) + p(\alpha_v - \alpha_l) \quad \Rightarrow$$
$$(s_v - s_l)T = (u_v + p\alpha_v) - (u_l + p\alpha_l) \quad \Rightarrow$$
$$(s_v - s_l)T = h_v - h_l$$

Summary:

$$(s_v - s_l)T = (u_v - u_l) + p(\alpha_v - \alpha_l)$$
$$(s_v - s_l)T = h_v - h_l$$

From (18) $\boxed{l_v = h_v - h_l}$ we finally obtain

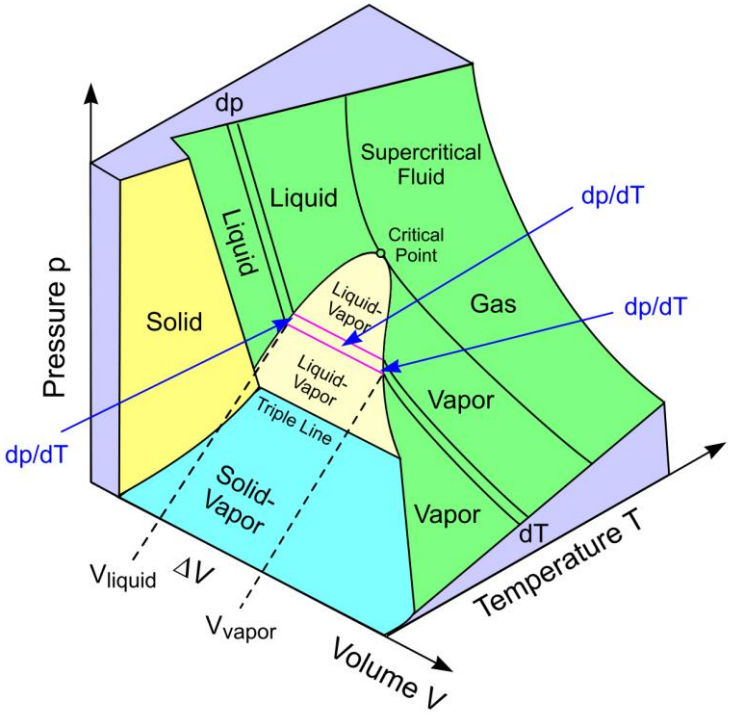
$$\boxed{l_v = (s_v - s_l)T} \quad \text{and}$$
$$l_v = (u_v - u_l) + p(\alpha_v - \alpha_l) .$$

It was nice to start with the Gibbs function and see how all the variables fit together as it is very instructive and we will use what

we learned shortly. But watch this. From (17) $ds = \frac{\delta q}{T}$ we can write $\delta q = Tds$, which we often use to combine the first and second laws as $du = Tds - pd\alpha$.

$$\delta q = Tds \quad \Rightarrow \quad q = T\Delta s \quad \Rightarrow \quad l_v \equiv q_{l\to v} = T\left(\Delta s\right)_{l\to v} = T\left(s_v - s_l\right) \quad \Rightarrow \quad \boxed{l_v = (s_v - s_l)T}$$

The heat $l_v = (u_v - u_l) + p(\alpha_v - \alpha_l)$ supplied so that the water changes phase goes into internal energy and the work the vapor does by expanding. Now we want to move an infinitesimal amount off our original liquid-vapor line to a parallel similar line in order find the slope dp/dT along the right border of the light yellow region, which is the same slope for all points along the lower purple line. Later we will project our result onto the p-T plane by looking down the volume axis from the temperature axis.



At the far right border, we have saturation. The moist air has its maximum vapor at the given temperature and pressure. The right border, as well as the dome region, is tilted sloping upward, indicating both increasing temperature and pressure. The Gibbs function will change accordingly. Therefore, we start with

$$dg = -sdT + \alpha dp\,.$$

Before, we had set the Gibbs function for the liquid water equal to the Gibbs function of the vapor. Now, we do the same for their differentials

$$dg_l = -s_l dT + \alpha_l dp \quad \text{and} \quad dg_v = -s_v dT + \alpha_v dp$$

as they both undergo the infinitesimal increases dT and dp. The result is

$$-s_l dT + \alpha_l dp = -s_v dT + \alpha_v dp\,.$$

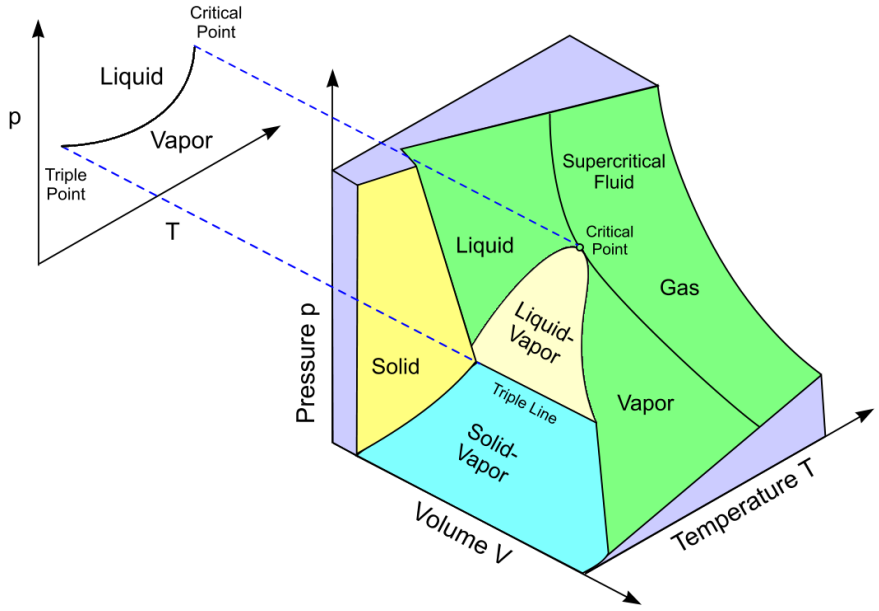
Rearranging terms, $s_v dT - s_l dT = \alpha_v dp - \alpha_l dp$, and $(s_v - s_l)dT = (v_v - v_l)dp$. Then,

$$\frac{dp}{dT} = \frac{s_v - s_l}{\alpha_v - \alpha_l}.$$

Now recall $l_v = (s_v - s_l)T$ which we said we would be needing. We will use it as $s_v - s_l = \frac{l_v}{T}$.

$$\frac{dp}{dT} = \frac{s_v - s_l}{\alpha_v - \alpha_l} \quad \Rightarrow \quad \frac{dp}{dT} = (s_v - s_l)\frac{1}{\alpha_v - \alpha_l} \quad \Rightarrow \quad \frac{dp}{dT} = \frac{l_v}{T}\frac{1}{\alpha_v - \alpha_l} \quad \Rightarrow \quad \frac{dp}{dT} = \frac{l_v}{T}\frac{1}{\Delta\alpha}$$

We have the Clapeyron equation. (23) $\boxed{\frac{dp}{dT} = \frac{l_v}{T\Delta\alpha}}$



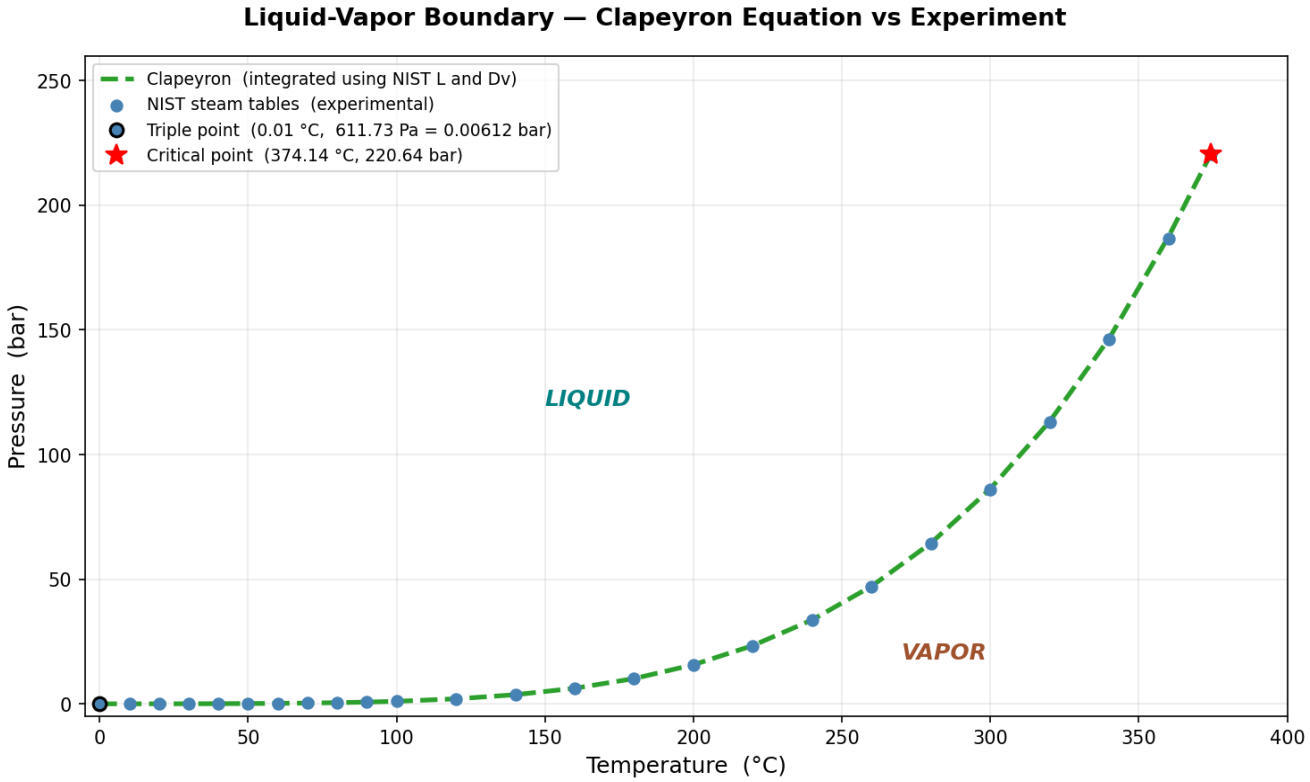
From the above slope function, we can sketch a plot of the function $p = p(T)$ projected unto the p-T plane.

As the temperature T increases, the specific enthalpy of vaporization l_v decreases, reaching zero at the critical point. But the dominant factor is the change in specific volume $\Delta\alpha$. That change is large at the triple line and decreases to zero at we approach the critical temperature. The large change at the triple line results in little slope. As we approach the critical temperature the smaller and smaller $\Delta\alpha$ is observed as steeper and steep slopes. What about at the critical temperature? Think of the liquid-vapor dome as slanted towards rising pressures and rising temperatures.

The derivative $\frac{dp}{dT}$ is the same for each point on each corresponding boiling line. When we stand on the critical point as a terrain, the slope of the land is somewhat steep, but some finite value. The derivative $\frac{dp}{dT} = \frac{l_v}{T\Delta\alpha}$ which is indeterminate at T_c since $l_v = 0$ and $\Delta\alpha = 0$ there. However, from standing on the critical point we know the terrain does not slope directly upwards as it would have to in order to realize infinite slope. Mathematically speaking, you can use L'Hospital's rule to show that the slope is finite.

Note that for our projection of $p = p(T)$ unto the p-T plane we went with a linear p-axis. Strictly speaking the p-axis of our 3D is a log axis. But for this region of pressure and temperature, the practice is to use linear axes. See the concave-convex discussion at the end of this chapter.

Below is a plot of the pressure $p = p(T)$ extracted from the Clapeyron equation $\frac{dp}{dT} = \frac{l_v}{T\Delta\alpha}$. Integration was performed on $\frac{dp}{dT} = \frac{l_v}{T\Delta\alpha}$ using experimental values for l_v, T, and $\Delta\alpha$ from the National Institute of Standards and Technology. Note the excellent agreement between theory (the green dashed plot) and experiment (the blue dots).



The plot starts with the triple-point temperature $T = 0.01°C$ and ends at the critical-point temperature $T = 374°C$. Extending the curve backwards at $T = 0.01°C$ the horizontal line has ice above it and gas below.

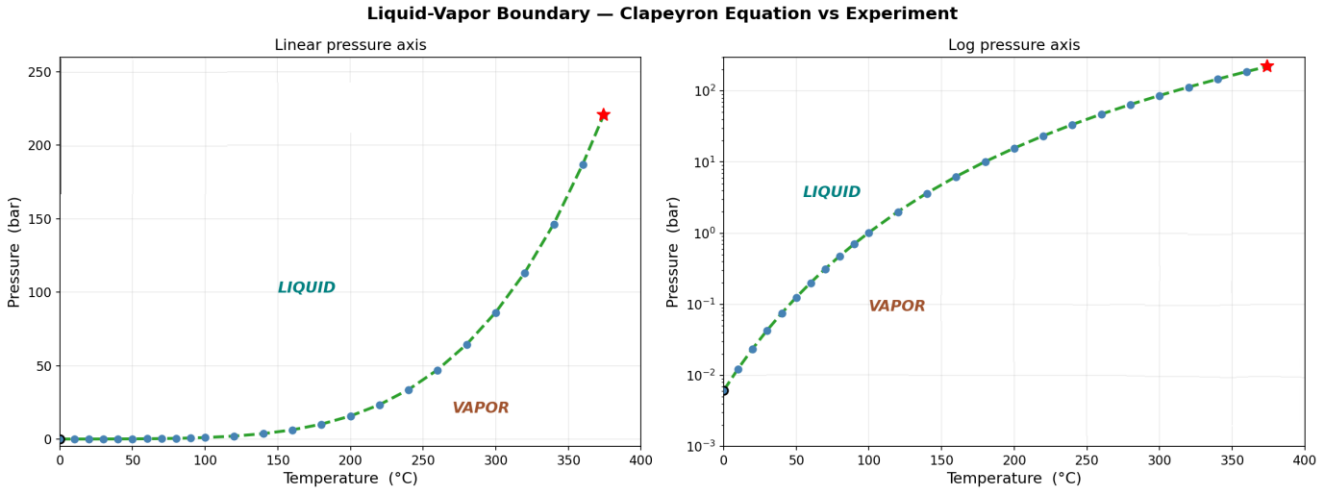
The pressure starts out with a very low 0.00612 bar at the triple point and rises to 220 bar at the critical point. Below are some pressure units. One atmosphere of pressure, historically defined as an average of atmospheric pressure at sea level. Today, the definition is exactly as

$1\ \text{atm} \equiv 101{,}325\ \text{Pa}$, where Pa stands for pascals.

Relating to bar, we have $1\text{ bar} = 100{,}000\text{ Pa} = \dfrac{100{,}000}{101{,}325}\text{ atm} = 0.987\text{ atm}$.

Think of 1 bar as being a tad less than 1 atm.

Convex-Concave Discussion



While the linear plot is concave, the log plot is convex. The reason lies with transforming from linear pressure to log pressure. Here is a simple example to illustrate this effect. Consider a simple quadratic $y = x^2$. This simple function has the similar gross characteristic as increasing in a concave fashion. The change in the slope for a concave curve is positive since the slope keeps increasing. We verify this feature for our quadratic function.

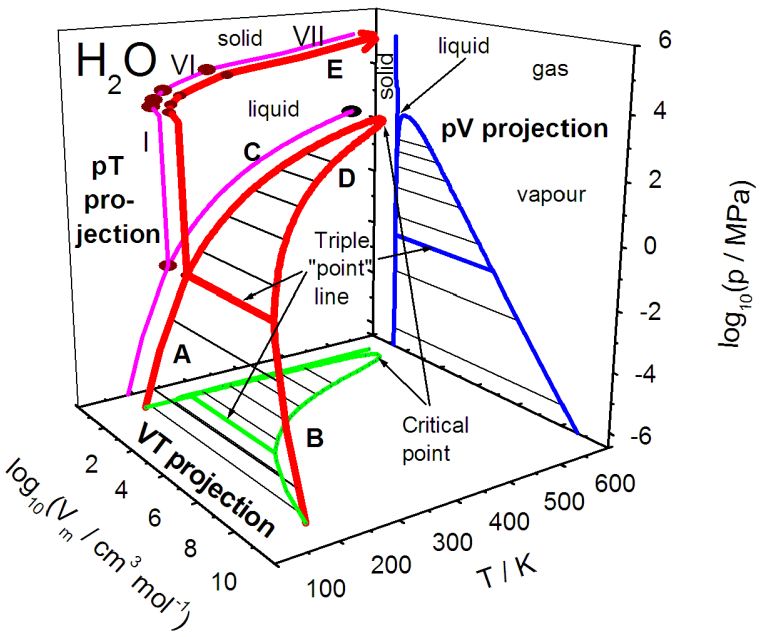
$$\frac{d^2y}{dx^2} = \frac{d}{dx}\left[\frac{d}{dx}(x^2)\right] = \frac{d}{dx}[2x] = 2 > 0$$

Slope increasing means the concave shape.

Now we consider the natural log of the function $y = x^2$. Call it u.

$$\frac{d^2u}{dx^2} = \frac{d}{dx}\left[\frac{d}{dx}(\ln x^2)\right] = \frac{d}{dx}\left[\frac{d}{dx}(2\ln x)\right] = \frac{d}{dx}\frac{2}{x} = -\frac{2}{x^2} < 0$$

Here we have decreasing slope, i.e., a convex shape.



At the left is a 3D version published by Prof. Leslie Glasser. The convex projection in the p-T plane appears due to the log scales along the volume and pressure axes. Note that this excellent figure of Prof. Glasser has projections in all three planes!

Figure from L. Glasser, 2002. "Equations of State and Phase Diagrams." *Journal of Chemical Education* **79** (7): 874-876.

There is a later publication that allows you to rotate the main part of the figure. Use the following link.

https://biomodel.uah.es/Jmol/plots/phase-diagrams/

Reference. "Interactive 3D phase diagrams using Jmol." A. Herráez, R.M. Hanson and L. Glasser (2009) *Journal of Chemical Education* **86**: 566.

Textbooks simplify the p-T plot using scales that are neither strictly log or linear. See the figure below. We call such a graph a schematic. The schematic illustrates the main chemistry.