

## 12.3: PT Phase Diagrams

Let's now discuss the pressure–temperature diagram of a typical substance, as reported in Figure 12.3.1. Each of the lines reported in the diagram represents an equilibrium between two phases, and therefore it represents a condition that reduces the number of degrees of freedom to one. The lines can be determined using the Clapeyron equation, Equation 12.1.8. The interpretation of each line is as follows:

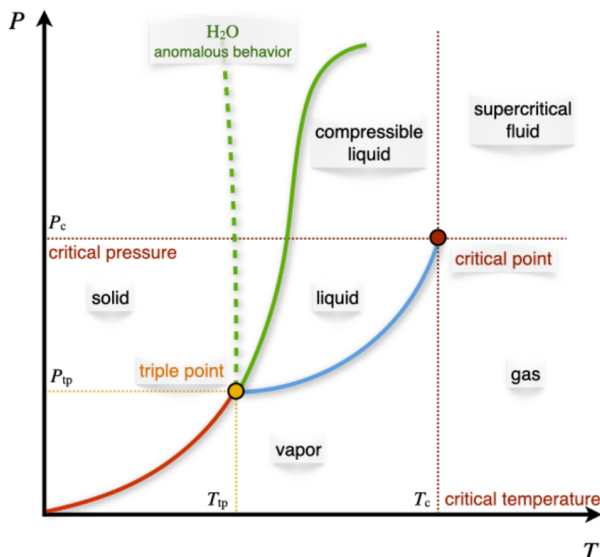


Figure 12.3.1: The Pressure–Temperature Phase Diagram.

### Liquid ⇌ Gas equilibrium

For this equilibrium we can use Trouton's rule, Equation 7.1.5, and write:

$$\Delta_{\text{vap}}S = S_g - S_l \cong 88 \frac{\text{kJ}}{\text{mol}} > 0 \quad \text{always}, \quad (12.3.1)$$

where the entropy of vaporization is always positive, even for cases where the Trouton's rule is violated. The difference in molar volumes is easily obtained, since the volume of the gas is always much greater than the volume of the liquid:

$$\bar{V}_g - \bar{V}_l \cong \bar{V}_g = 22.4 \frac{\text{L}}{\text{mol}} > 0 \quad \text{always}. \quad (12.3.2)$$

Replacing these values in the Clapeyron equation, we obtain:

$$\frac{dP}{dT} = \frac{88}{22.4} \left( \frac{0.0831}{8.31} \right) = 0.004 \text{ bar} > 0 \quad \text{always}, \quad (12.3.3)$$

which is always positive, regardless of violations to the Trouton's rule. Notice how small this value is, meaning that the liquid–gas equilibrium curve is mostly flat as  $T \rightarrow 0$ .

### Solid ⇌ Gas equilibrium

If we look at the signs of each quantity, this case is similar to the previous one:

$$\begin{aligned} \Delta_{\text{subl}}S &> 0 \quad \text{always} \\ \Delta_{\text{subl}}\bar{V} &> 0 \quad \text{always} \\ \frac{dP}{dT} &> 0 \quad \text{always}. \end{aligned} \quad (12.3.4)$$

However, the Trouton's rule is not valid for the solid–gas equilibrium, and  $\frac{dP}{dT}$  will be larger than for the previous case.

## Solid $\rightleftharpoons$ Liquid equilibrium

The final curve is for the solid-liquid equilibrium, for which we have:

$$\Delta_{\text{fus}} S = \frac{\Delta_{\text{fusion}} H}{T_m} > 0 \quad \text{always,} \quad (12.3.5)$$

since fusion is always an exothermic process, ( $\Delta_{\text{fus}} H > 0$ ). On the other side:

$$\Delta_{\text{fusion}} \bar{V} = \bar{V}_l - \bar{V}_s > 0 \quad \text{generally.}$$

In other words, the difference of the molar volume of the liquid and that of the solid is positive for most substances, but it might be negative (for example for  $\text{H}_2\text{O}$ ). As such:

$$\frac{dP}{dT} > 0 \quad \text{generally.} \quad (12.3.6)$$

For  $\text{H}_2\text{O}$  and a few other substances,  $\frac{dP}{dT} < 0$ , an anomalous behavior that has crucial consequences for the existence of life on earth.<sup>1</sup> For this importance, this behavior is also depicted in Figure 12.3.1 using a dashed green line.

Since the differences in molar volumes between the solid and the liquid phases are usually small (changes are generally of the order of  $10^{-3}$  L),  $\frac{dP}{dT}$  is always much larger than for the previous two cases. The resulting lines for the solid-liquid equilibria are still almost vertical, regardless of the signs of their angular coefficients.

## The triple point and the critical point

The only point in the  $PT$  diagram where all the three phases coexist is called the triple point. The number of degrees of freedom at the triple point for every 1-component diagram is  $f = 1 - 3 + 2 = 0$ . The fact that the triple point has zero degrees of freedom means that its coordinates,  $T_{\text{tp}}$ ,  $P_{\text{tp}}$ ,  $\bar{V}_{\text{tp}}$ , are uniquely determined for each chemical substance. For this reason, the value of the triple point of water was fixed by definition—rather than measured—until 2019. This definition was necessary to establish the base unit of the thermodynamic temperature scale in the SI (the Kelvin).<sup>2</sup>

In addition to the triple point where the solid, liquid, and gas phases meet, a triple point may involve more than one condensed phase. Triple points are common for substances with multiple solid phases (polymorphs), involving either two solid phases and a liquid one or three solid phases. Helium is a special case that presents a triple point involving two different fluid phases, called the lambda point. Since the number of degrees of freedom cannot be negative, the Gibbs phase rule for a 1-component diagram sets the limit to how many phases can coexist to just three. Therefore, quadruple points (or higher coexistence points) are not possible for pure substances, even for polymorphs.<sup>3</sup>

Another point with a fixed position in the  $PT$  diagram is the critical point,  $T_c$ ,  $P_c$ ,  $\bar{V}_c$ . We have already given the definition of the critical temperature in [Definition: Critical Temperature](#). This point represents the end of the liquid-gas equilibrium curve. This point is also semantically important to define different regions of the phase diagram, as in Figure 12.3.1. A gas whose pressure and temperature are below the critical point is called a *vapor*. A gas whose temperature is above the critical one and the pressure is below its critical one is called a *supercritical fluid*. Finally, a liquid whose pressure is above the critical point is called a *compressible liquid*.<sup>4</sup>

1. As is well explained by [Wikipedia](#): “The unusual density curve and lower density of ice than of water is vital to life—if water were most dense at the freezing point, then in winter the very cold water at the surface of lakes and other water bodies would sink, lakes could freeze from the bottom up, and all life in them would be killed. Furthermore, given that water is a good thermal insulator (due to its heat capacity), some frozen lakes might not completely thaw in summer.[34] The layer of ice that floats on top insulates the water below. Water at about 4 °C (39 °F) also sinks to the bottom, thus keeping the temperature of the water at the bottom constant.”
2. For more information on the 2019 redefinition of the SI units, see [this Wikipedia page](#).
3. Notice that quadruple points are possible for 2-component diagrams.
4. Notice that the temperature of a liquid must be below the critical point, otherwise it is no longer a liquid but rather a supercritical fluid.

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