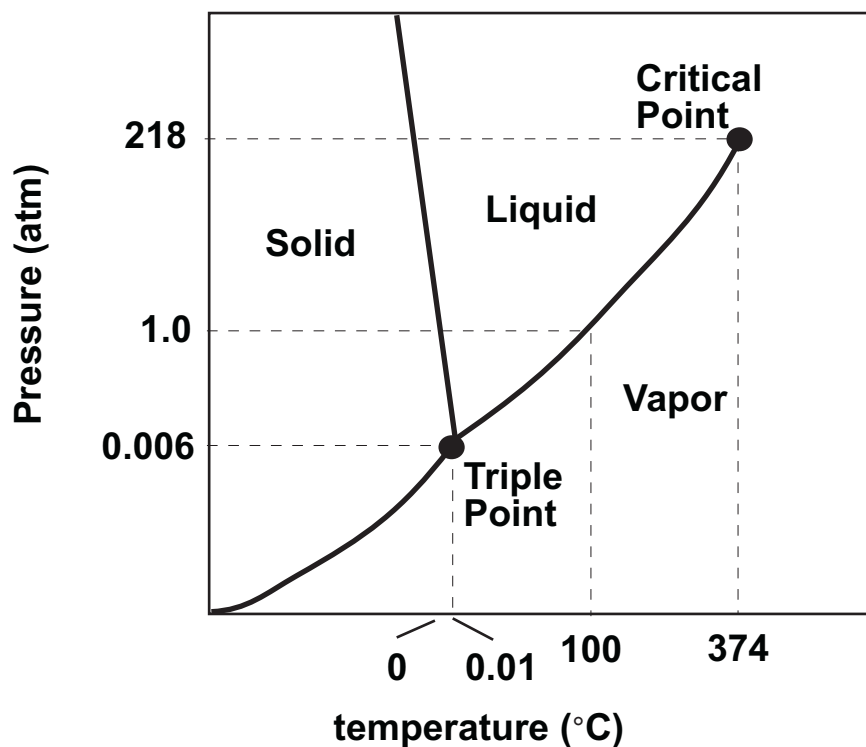


Phase Diagrams

Phase Diagram for H₂O



In General

On the lines, the two phases are in equilibrium

Solid-liquid equilibrium line

Solid-vapor equilibrium line

Vapor-liquid equilibrium line

Fusion: from liquid to solid

Melting: from solid to liquid

Sublimation: from solid to vapor

Deposition: from vapor to solid

Evaporation: from liquid to vapor

Condensation: from vapor to liquid

At the triple point, all three phases are in equilibrium

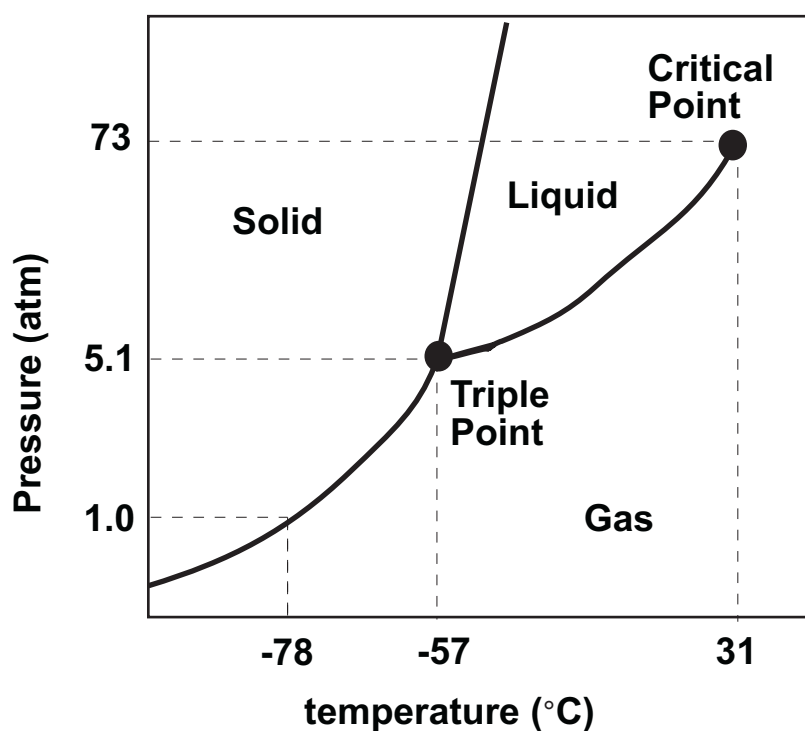
Specific to water

The slope of the solid-liquid equilibrium line is negative. This means that the liquid phase is denser than the solid phase. Hydrogen bonding packs the liquid more tightly than the solid. The result of this is that:

Ice Floats

Water melts as pressure is applied (ice skating)

Phase Diagram for CO₂

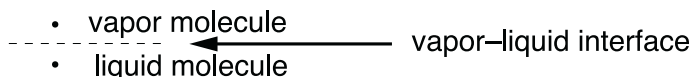


Specific to carbon dioxide

The slope of the solid-liquid equilibrium line is positive. This means that the solid phase is denser than the liquid phase. Solid carbon dioxide sinks in liquid carbon dioxide--unlike water, it will freeze from the bottom up.

Equilibrium: Physical Equilibrium: Student Review Notes**Vapor Liquid Equilibrium**

Vapor-liquid equilibrium looks at the interface between the liquid and vapor phase. This is an example of a system in physical equilibrium. It's very important that you understand **equilibrium as a dynamic process**. It does not mean that things stop. In this case, equilibrium means that at a given temperature an equal number of molecules at the vapor-liquid interface will both condense and evaporate--that is the equilibrium condition. This means that liquids exert a pressure or vapor pressure, P^{sat} that is a function of temperature above the liquid interface.



For pure liquids, you can typically look up the vapor pressure at a given temperature. You'll see this in gas problems that read something like "the total pressure of a container in which a gas is collected over water is 775 mm Hg. At the temperature of the container, the P^{sat} of water is 22 mm Hg." What you are supposed to realize is that the vapor pressure from the liquid water contributes to the overall pressure in the container and in this case, the pressure of the gas would be 753 mm Hg.

Raoult's Law: Vapor Pressure of a component in a mixture

For solutions that are mixtures, you cannot assume that the vapor pressure of each volatile component will be the value it would have as a pure species. Raoult's Law is a simple way of calculating a vapor pressure for each volatile component in a liquid mixture.

$$P_A = X_A P^{\text{sat}}$$

This just says that the vapor pressure of species A, P_A , is equal to the mole fraction of species A, X_A , times the vapor pressure of pure A at the specified temperature. Basically it is a direct proportionality with mole fraction. For a two component mixture of volatile liquids, the vapor pressure would be the sum of the vapor pressures of each component:

$$P_{\text{total}} = P_A + P_B = X_A P^{\text{sat}} + X_B P^{\text{sat}} = X_A P^{\text{sat}} + (1 - X_A) P^{\text{sat}}$$

Raoult's Law is an idealization of how solutions behave in the real world--it's simply based on the number of positions at the vapor-liquid interface available to each component in a mixture. There are two types of deviations from ideal behavior with which you should be familiar (familiar enough to explain them in an essay).

Positive Deviations:

Indicates that the attractive forces between unlike molecules of the solution are weaker than they would be for a pure solution of any component of the mixture. As a result, it is easier for molecules to jump into the vapor phase than it would be for a pure solution of each component (the nearest neighbors are not interacting as strongly as would be the case for pure solutions). As a result of this, the solution exhibits a higher vapor pressure than predicted by Raoult's Law.

Negative Deviations:

Indicates that the attractive forces between unlike molecules of the solution are stronger than they would be for a pure solution of any component of the mixture. As a result, it is harder for molecules to jump into the vapor phase than it would be for a pure solution of each component (the nearest neighbors are interacting more strongly than would be the case for pure solutions). As a result of this, the solution exhibits a lower vapor pressure than predicted by Raoult's Law.

