Phase Diagram of Water

The phase diagram of water is fairly complicated, particularly at high pressures, but we are not going to pay attention to all the different kinds of ice that can exist!

A general phase diagram for a liquid-gas-solid system

The lines represent conditions where 2 phases co-exist, referred to as a phase boundary. Where two lines intersect we have a triple-point. A critical point is a point where a phase boundary disappears. At temperatures above the critical point the liquid and vapor phases are indistinguishable, we call this a supercritical fluid, or more simply a gas. The dotted line shows the behavior of water, which is anomalous (ie. it expands upon freezing).

A phase region on a phase diagram represents the equilibrium state of the material under the stated conditions. Materials can, however, exist in non-equilibrium states and we will try to produce one by the end of the lecture.

Melting Ice with Salt

We know that if we add salt to ice it will melt it. Does it do this by raising or lowering the temperature?

Melting Ice with Pressure
In fact the salt lowers the melting point of the ice and thus also its temperature (I'll explain why when we discuss entropy). We'll use this fact to try to cool some bottles of water below their freezing point.

We can see from the phase diagram of water that increased pressure also leads to a decreased melting point. Does this explain why the ice under an iceskate blade is slippery?

**Pressure Melting: ice skates**

We can do a simple calculation to estimate the pressure exerted by the blades of a skate.

If the area is small the pressure is large. In the case of the blades, the surface in contact with the ice is tiny because the width of the blade is less than 0.5 mm.

![Iceskate Blade](image)

\[ P = \frac{F}{A} = \frac{mg}{lw} \]

For an 80 Kg person, assuming a blade of 30 cm length and 0.5 mm wide, the pressure on each foot will be \( \sim 27 \text{ atm} \). Not so large, especially considering that the slope \( P \) Vs \( T \) for melting ice has such a large slope. This means that this pressure will change the melting temperature by less than 1 \( \text{C} \)!

In fact the reason that iceskates work is because there is always layer of water on the surface of ice (as long as the temperature is above -35\( ^\circ \text{C} \)), and there is quite an interesting story behind it.

**PV Diagram**
Evaporation

Within a liquid there will be a distribution of velocities for the molecules and the most energetic ones can leave the liquid and join the vapor phase, which is evaporation. The reverse process can also happen where lower energy molecules in the vapor phase join the liquid through condensation. In a closed system at equilibrium these processes occur at the same rate. The amount of vapor in the air under this condition is the saturated vapor pressure, which will depend on the temperature and the overall pressure.

Boiling

Boiling occurs when the saturated vapor pressure equals the external pressure. Normally we boil water by increasing the
temperature…but it can also be done by decreasing the pressure. See here for the vapor pressure of water.

If we do it this way will the temperature of the water increase or decrease?

**Partial Pressure and Humidity**

Air can contain a varying amount of water, with the total pressure of the air being due to many different kinds of molecule. The partial pressure of a particular gas is the pressure due to a particular kind of gas molecule.

We define humidity in terms of the partial pressure of \( \text{H}_2\text{O} \) compared to the saturated vapor pressure of \( \text{H}_2\text{O} \).

\[
\text{Humidity} = \frac{\text{partial pressure of H}_2\text{O}}{\text{saturated vapor pressure of H}_2\text{O}} \times 100\%.
\]

**Van der Waals Equation of State**

Some corrections can be made to the ideal gas law which help to make it a better representation of a real gas. These corrections were developed by Johannes Diderik Van Der Waals.

The first correction is to consider the molecules as having a finite volume, this reduces the volume in which molecules can move around without collisions. We reduced the amount of volume by a parameter \( b \) which represents the amount of unavailable volume in a mole of gas.

\[
P V = n R T \rightarrow P (V - nb) = n R T
\]

or \( P \left( \frac{V}{n} - b \right) = RT \)

The second correction is to consider attractive forces between molecules. These reduce the pressure by a factor which is proportional to the square of the density. It is proportional to the square of the density because we consider both the number of molecules subject to the force, and the number of molecules exerting the force.

\[
P = \frac{RT}{V - b} - a \left( \frac{n}{V} \right)^2
\]

\[
P = \frac{RT}{V - b} - \frac{a}{(\frac{V}{n})^2}
\]

or \( P + \frac{a}{(\frac{V}{n})^2} \left( \frac{V}{n} - b \right) = RT \)

The values of \( a \) and \( b \) are empirical parameters which depend on the gas and can be found here.

**Form of the Van Der Waals equation**
The Van Der Waals equation works pretty well under certain conditions. We should be careful that below the critical point it predicts oscillations that are not observed. Maxwell suggested replacing this path with a straight line so that areas below and above the line are equal, which is described here.

**Mean Free Path**

Another parameter that depends on the size of the molecules in the gas is the mean free path, the average distance a molecule moves without a collision.

To determine this we should consider the distance a molecule traveling at the mean speed of the gas moves in a time interval $\Delta t$, $\bar{v}\Delta t$ divided by the number of collisions in that time.

The number of collisions that would occur if the other molecules in the gas were stationary is $\frac{N}{V} \pi (2r)^2 \bar{v} \Delta t$

$$l_m = \frac{\bar{v} \Delta t}{(N/V)\pi(2r)^2 \bar{v} \Delta t} = \frac{1}{4\pi r^2 (N/V)}$$

However, as the other molecules are not stationary the number of collisions will be due to the relative velocity $\frac{N}{V} \pi (2r)^2 \bar{v} \Delta t \rightarrow \frac{N}{V} \pi (2r)^2 v_{rel} \Delta t$

It can be shown that $v_{rel} = \sqrt{2}\bar{v}$, so

$$l_m = \frac{\bar{v} \Delta t}{(N/V)\pi \sqrt{2}(2r)^2 \bar{v} \Delta t} = \frac{1}{4\pi \sqrt{2}r^2 (N/V)}$$