Liquid-Vapor Equilibrium

Vapor Pressure

Liquids are denser than gases, therefore the collision rate among molecules is much higher in the liquid phase than in the gas phase.

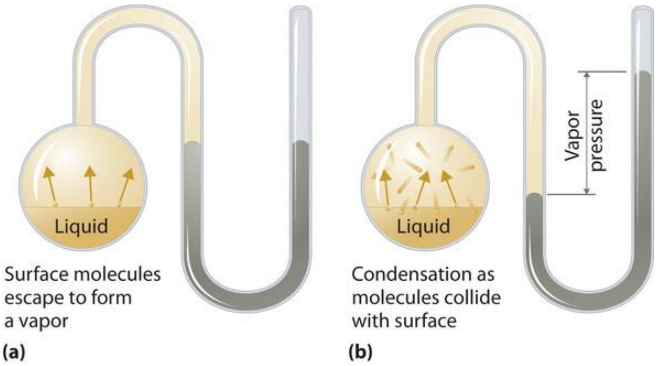
At any given temperature, a certain number of the molecules in a liquid have enough kinetic energy to escape from the surface. This process is called evaporation, or vaporization.

When a liquid evaporates, its gaseous molecules exert a vapor pressure.

As soon as some molecules leave the liquid, a vapor phase is established. The vapor pressure is measurable only when a fair amount of vapor is present. The process of evaporation does not continue indefinitely,

As the concentration of molecules in the vapor phase increases, some molecules return to the liquid phase, a process called condensation. Condensation occurs because a molecule striking the liquid surface becomes trapped by intermolecular forces in the liquid.

The rate of evaporation is constant at any given temperature, and the rate of condensation increases with increasing concentration of molecules in the vapor phase. A state of dynamic equilibrium, in which the rate of a forward process is exactly balanced by the rate of the reverse process, is reached when the rates of condensation and evaporation become equal. The vapor pressure measured under dynamic equilibrium of condensation and evaporation is called the equilibrium vapor pressure. We often use the simpler term “vapor pressure”



It is important to note that the equilibrium vapor pressure is the *maximum* vapor pressure. Vapor pressure changes with temperature, however. Plots of vapor pressure versus temperature for three different liquids are shown.

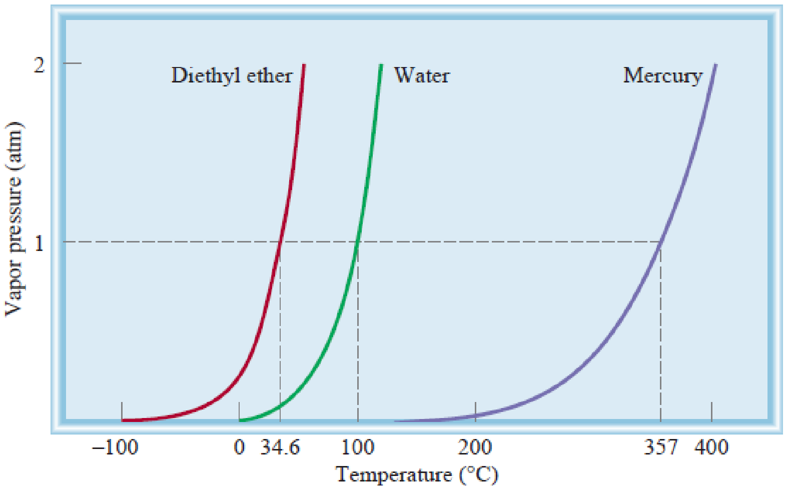


Figure. The increase in vapor pressure with temperature for three liquids. The normal boiling points of the liquids (at 1 atm) are shown on the horizontal axis.

We know that the number of molecules with higher kinetic energies is greater at the higher temperature and therefore so is the evaporation rate. For this reason, the vapor pressure of a liquid always increases with temperature.

Heat of Vaporization

A measure of how strongly molecules are held in a liquid is its molar heat of vaporization (ΔHvap). It is defined defined as the energy as kilojoules required to vaporize one mole of a liquid. The molar heat of vaporization is directly related to the strength of intermolecular forces that exist in the liquid. If the intermolecular attraction is strong, it takes a lot of energy to free the molecules from the liquid phase. Consequently, the liquid has a relatively low vapor pressure and a high molar heat of vaporization.

The quantitative relationship between the vapor pressure *P* of a liquid and the absolute temperature *T* is given by the Clausius-Clapeyron equation

$$\ln P = -\frac{\Delta H_{\text{vap}}}{RT} + C$$

$$\ln P = \left(-\frac{\Delta H_{\text{vap}}}{R}\right)\left(\frac{1}{T}\right) + C$$

LnP versus 1/T plotting is graphed by measuring the vapor pressure at different temperatures. The slope of the line described by the equation which is equal to –ΔH/R was calculated and it was found to the heat of vaporization. This value changed depend on the type of liquids by increasing temperature.

It can be used the Clausius-Clapeyron equation to calculate the vapor pressure of the liquid at a differen temperature.

$$\ln P_1 = -\frac{\Delta H_{\text{vap}}}{RT_1} + C$$

$$\ln P_2 = -\frac{\Delta H_{\text{vap}}}{RT_2} + C$$

$$\begin{aligned}\ln P_1 - \ln P_2 &= -\frac{\Delta H_{\text{vap}}}{RT_1} - \left(-\frac{\Delta H_{\text{vap}}}{RT_2}\right) \\ &= \frac{\Delta H_{\text{vap}}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\end{aligned}$$

$$\ln \frac{P_1}{P_2} = \frac{\Delta H_{\text{vap}}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$