

10.11: Vapor-Liquid Equilibrium

When a liquid such as water or alcohol is exposed to air in an open container, the liquid evaporates. This happens because the distribution of speeds (and hence kinetic energies) among molecules in a liquid is similar to that illustrated for gases, shown again below.

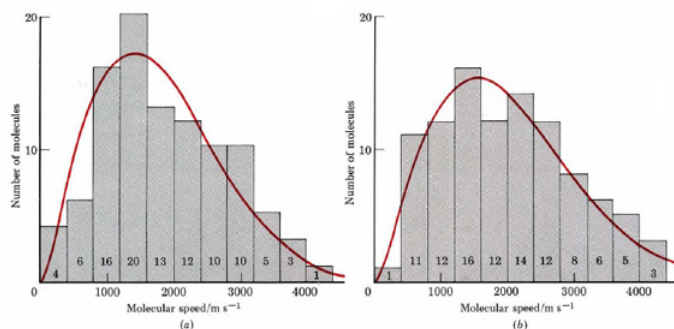


Figure 10.11.1 The distribution of molecular speeds in a sample of 100 H_2 molecules at (a) 300 K and (b) 373 K. The colored line on each graph is the theoretical distribution given by the Maxwell-Boltzmann law.

At any given instant a small fraction of the molecules in the liquid phase will be moving quite fast. If one of these is close to the surface and is traveling upward, it can escape the attraction of its fellow molecules entirely and pass into the gas phase. As the higher energy molecules depart, the average energy of the molecules in the liquid decreases and the temperature of the liquid falls. Heat energy will be absorbed from the surroundings, an effect which you can feel if you let water or alcohol evaporate from your skin. Absorption of heat maintains the average molecular speed in the liquid, so that, given enough time, all the liquid can evaporate. The heat absorbed during the entire process corresponds to the enthalpy of vaporization.

If the liquid is placed in a closed, rather than an open, container, we no longer find that it evaporates completely. Once a certain partial pressure of gas has been built up by the evaporation of liquid, no more change occurs, and the amount of liquid remains constant. The partial pressure attained in this way is called the vapor pressure of the liquid. It is different for different liquids and increases with temperature for a given liquid. So long as some liquid is present, the vapor pressure is always the same, regardless of the size of the container or the quantity of liquid.

For example, we find that any size sample of water held at 25°C will produce a vapor pressure of 23.8 mmHg (3.168 kPa) in any closed container, provided only that all the water does not evaporate. On the macroscopic level, once the vapor pressure has been attained in a closed container, evaporation appears to stop, as seen in the water bottle below.



Figure 10.11.1 On the right is the macroscopic view of the molecular interpretation of vapor pressure. The vapor pressure remains constant (and looks constant in the macroscopic image) because every molecule which escapes (like A) is immediately replaced by another molecule reentering from the vapor (like B). Any given molecule spends some of its time in the vapor and some in the liquid.

On the microscopic level, though, molecules are still escaping from the liquid surface into the vapor above, as shown in the accompanying figure. The amount of vapor remains the same only because molecules are reentering the liquid just as fast as they are escaping from it. The molecules of the vapor behave like any other gas: they bounce around colliding with each other and the walls of the container. However, one of these “walls” is the surface of the liquid. In most cases a molecule colliding with the liquid surface will enter the body of the liquid, not have enough energy to escape, and be recaptured.

When the liquid is first introduced into the container, there are very few molecules of vapor and the rate of recapture will be quite low, but as more and more molecules evaporate, the chances of a recapture will become proportionately larger. Eventually the vapor pressure will be attained, and the rate of recapture will exactly balance the rate of escape. There will then be no net evaporation of liquid or condensation of gas.

Once the vapor-liquid system has attained this state, it will appear on the macroscopic level not to be undergoing any change in its properties. The amount, the volume, the pressure, the temperature, the density, etc., of both liquid and gas will all remain constant with time. When this happens to a system, it is said to be in an **equilibrium state** or to have attained **equilibrium**.

Later, we will encounter many other quite different examples of equilibrium, but they all have one property in common. The lack of change on the macroscopic level is always the result of two opposing microscopic processes whose rates are equal. The effect of each process is to nullify the effect of the other. Since both microscopic processes are still in motion, such a situation is often referred to as **dynamic equilibrium**.

The magnitude of the vapor pressure of a liquid depends mainly on two factors: the strength of the forces holding the molecules together and the temperature. It is easy to see that if the intermolecular forces are weak, the vapor pressure will be high. Weak intermolecular forces will permit molecules to escape relatively easily from the liquid. The rate at which molecules escape will thus be high. Quite a large concentration of molecules will have to build up in the gas phase before the rate of reentry can balance the escape rate. Consequently the vapor pressure will be large.

By contrast, strong intermolecular forces result in a low escape rate, and only a small concentration of molecules in the vapor is needed to balance it. The vapor pressure of a liquid is quite a sensitive indicator of small differences in intermolecular forces. In the case of the alkanes, for example, we find that the vapor pressure of normal pentane at 25°C is 512.3 mmHg (68.3 kPa) while that of normal hexane is 150.0 mmHg (20.0 kPa) and that of normal heptane only 45.7 mmHg (6.1 kPa), despite the fact that the intermolecular forces for the three substances differ by less than 10 percent. The following video compares the vapor pressures of pentane, hexane, and heptane, by injecting each into a column of mercury. If you look closely, you can see the small amount of each liquid on top of the mercury. This serves to demonstrate the described difference in vapor pressure: stronger intermolecular forces result in lower vapor pressure.

The other major factor governing the magnitude of the vapor pressure of a liquid is temperature. At a low temperature only a minute fraction of the molecules have enough energy to escape from the liquid. As the temperature is raised, this fraction increases very rapidly and the vapor pressure increases with it, which makes sense given our previous discussion on [temperature and gases](#). Moreover, the higher the temperature, the more rapid the rate of increase of the energetic fraction of molecules. The result is a variation of vapor pressure with temperature like that shown for four liquid alkanes. Note from this figure how the vapor-pressure increase for a 10°C increase in temperature is larger at higher temperatures.

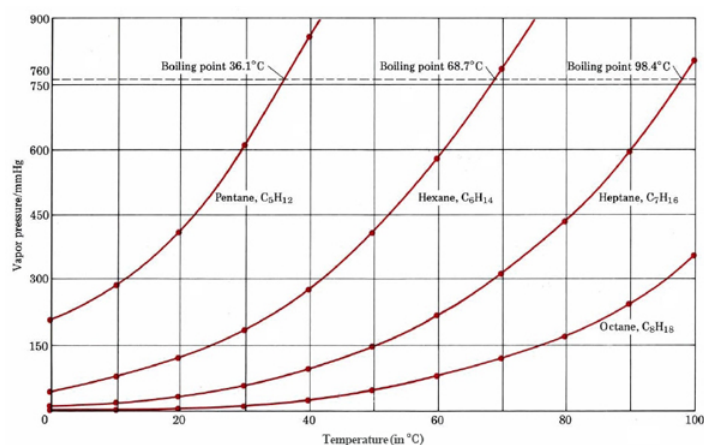
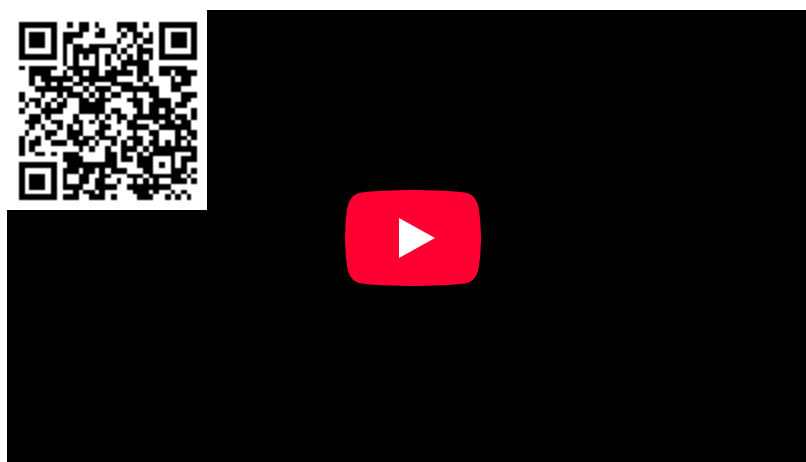


Figure 10.11.3 The vapor pressure of four liquid alkanes.

The following video also showcases the effect of heat on vapor pressure. The subject is one of the novelty "drinking bird" devices. These birds operate due to vapor pressure. There are two distinct spaces above the liquid, one in the base of the bird, and one in the head of the bird which is connected to the liquid by a long glass tube. By heating the head of the bird, the temperature of the vapor there increases, thus the vapor pressure increases, and it pushes the liquid back down into the base. When the base is heated, the gas in the base increases in vapor pressure compared to the head, and thus pushes liquid back up the neck of the bird.



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