

The Kohler Equation: Why do droplets really form.

The Kelvin Equation has the form

$$e^{sat}(r) = e^{sat} \exp\left(\frac{2\sigma}{\rho_n r kT}\right)$$

To understand this in a little more depth, remember that we argued that $\Delta\mu = -\Delta w$, the amount of work per molecule it takes to do something. For the Kelvin Eq., Δw could refer to the amount of work per molecule required to stretch molecules into a curved surface with radius r , in which case

$$\Delta w = -\Delta\mu = \frac{\sigma dA}{\rho_n dV_d} = \frac{8\pi r dr}{4\pi \rho_n r^2 dr} \sigma = \frac{2\sigma}{\rho_n r}$$

where A is the droplet surface area and V is the droplet volume.

Thus we can interpret the Kelvin Eq. as being

$$e^{sat}(r) = e^{sat} \exp\left(\frac{2\sigma}{\rho_n r kT}\right) = e^{sat} \exp(-\Delta\mu/kT) = e^{sat} \exp(\Delta w/kT)$$

Somehow, we need to increase $\Delta w = -\Delta\mu$ so that a positive amount of work is required for a droplet to evaporate, such that, being lazy, the droplet is happiest to stay in the liquid phase. The way the atmosphere does this is by including aerosol matter in the droplet.

An effective way to do this is to add solute to the liquid. What this does effectively is reduce the density of water molecules at the interface between the liquid and vapor phase, since the water molecules are separated by solute ions. Consequently the density of water vapor needs to be less in order for there to be equilibrium.

Let's say we define a solution "activity" such that the activity equals the relative humidity that is required for the liquid and vapor phase to be in equilibrium. In other words, at equilibrium for pure water

$$\mu_v(T) = \mu_v^{sat}(T) + kT \ln(RH/100)$$

For a solute

$$\mu_v^{sat}(T, a_w) = \mu_v^{sat}(T, a_w = 1) + kT \ln(RH/100)$$

$$\mu_v^{sat}(T, a_w) = \mu_v^{sat}(T, a_w = 1) + kT \ln a_w$$

where, RH is the relative humidity required to maintain saturation, and a_w is bounded by 0 and 1. If $a_w < 1$ then the chemical potential at saturation is depressed compared to what it would be at equilibrium over a flat surface of pure water, so

$$\Delta\mu_{activity} = \mu_v^{sat}(T) - \mu_v(T, a_w, r \rightarrow \infty) = -kT \ln a_w$$

So, for example, a closed jar with some water in it will reach a saturation relative humidity of 100% if the water is pure, but only 80% if enough salt is added to the water to depress the water activity to $a_w = 0.8$.

Adding the curvature effect now, we can alter our expression for $\Delta\mu$ from before so that we have

$$-\Delta w = \sum \Delta\mu = \Delta\mu_{curvature} + \Delta\mu_{activity} = -\frac{2\sigma}{\rho_n r} - kT \ln a_w$$

If the activity of the solution can be lowered then the last term is positive and this increases the energy barrier between the liquid and vapor phase $\Delta\mu$, making existence of the liquid phase more stable. There is a bigger “wall” for the liquid molecules to jump over to get into the vapor phase. Our revised expression then for the vapor pressure over a solution droplet is thus

$$e^{sat}(r, a_w, T) = e^{sat}(T) \exp\left(-\left(\sum \Delta\mu\right)/kT\right)$$

$$e^{sat}(r, a_w, T) = e^{sat}(T) \exp\left(\left[\frac{2\sigma}{\rho_n r} + kT \ln a_w\right]/kT\right)$$

$$e^{sat}(r, a_w, T) = e^{sat}(T) a_w \exp\left(\frac{2\sigma}{\rho_n kTr}\right)$$

$$e^{sat}(r, a_w, T) = e^{sat}(T) a_w \exp\left(\frac{2\sigma}{\rho_l R_v Tr}\right)$$

This is known as the Kohler equation. For an “ideal” solution (usually true if very dilute)

$$a_w = \frac{n_0}{n + n_0}$$

where n_0 is the molecules of water and n molecules of solute. This is known as Raoult’s Law. For dilute solutions

$$a_w = 1 - n/n_0$$

But we must remember that salts dissociate, i.e. NaCl dissociates to Na^+ and Cl^- . We represent this using what is really a bit of a kluge, but popular nonetheless - the so called Van’t Hoff factor i .

$$n \rightarrow in$$

where, for NaCl, and NH_4HSO_4 (ammonium bisulfate) $i = 2$, and for $(\text{NH}_4)_2\text{SO}_4$ (ammonium sulfate), $i = 3$. i is essentially the number of solute ions that the molecule dissolves into. The problem with this approach is that the number i stops meaning anything physical when one starts talking about organic non-ionic species, which nonetheless are soluble.

What do we see from this?

1. The higher the concentration of the solute, the lower the equilibrium relative humidity
2. The more dissociation, the higher the solution effect.

Effectively what is happening is that, while curvature makes it easier for molecules to escape a liquid droplet, dissolving a solute makes it harder for them to escape. Effectively there are fewer liquid molecules per unit surface area for them to escape.

The Kohler curves are shown below. These show the relative humidity relative to saturation over a flat surface of pure liquid water that would be in equilibrium with a droplet of radius r containing dissolved solute. Effectively, it is $e^{sat}(r, a_w, T) / e^{sat}(T)$, an expression of how much the saturation ratio is changed by the water being curved instead of flat, and a solution instead of pure.

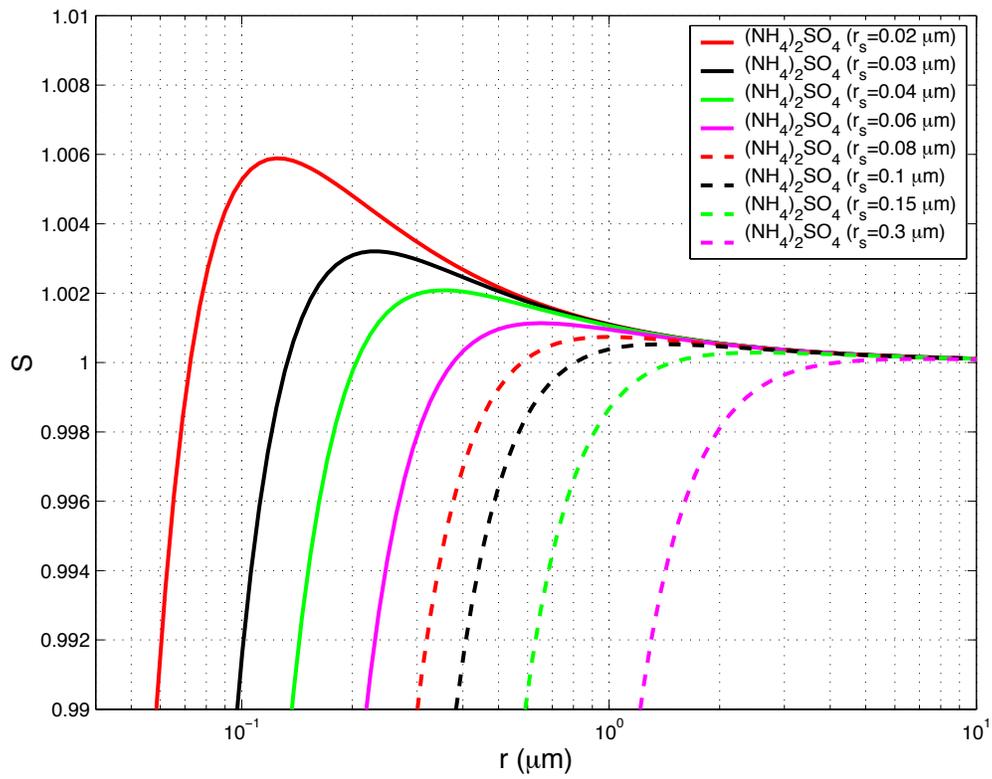


Figure 1: Kohler curves for ammonium sulfate.

The location of peak saturation ratio S^* is at r^* , the *critical radius*. Below this size the solution effect is more important than the curvature effect, and solution droplets are in a *stable* equilibrium with their environment. It is stable because, if the particle grows spontaneously, it is then too large for the ambient equilibrium saturation for the droplet, so it shrinks to its original size. Likewise, if it shrinks it grows again to its equilibrium size. These are haze particles, which are in stable equilibrium. If the haze particles get larger than r^* , then the haze particles are said to be *activated*. The curvature effect is more important than the solution effect and the particles grow spontaneously. A particle that grows spontaneously will always have an equilibrium saturation lower than the ambient saturation, so it keeps growing spontaneously by vapor diffusion. Once the droplets get big enough, the both the curvature and solution effect stop mattering much, and the droplet acts effectively like a plane surface of water.

Therefore, the function of a solute in droplet formation is to lower the amount of chemical potential energy of the water vapor (i.e. supersaturation) required to get the droplet to the size r^* where it can start to grow spontaneously of its own accord. The supersaturations required are typically less than 1%, which is quite manageable in clouds.