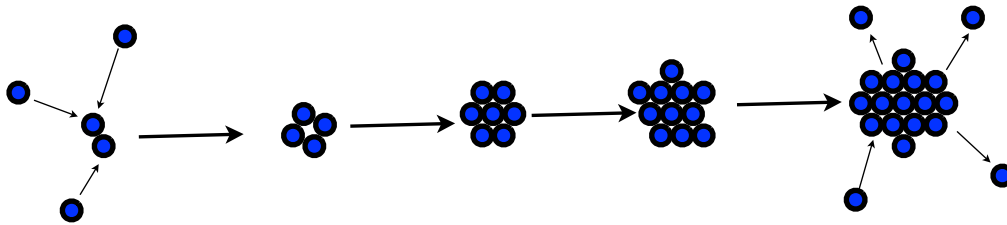


## 10. Cloud Condensation Nuclei

Observations of relative humidity around cloud bases, where new cloud droplets are created, suggest that the relative humidity there barely exceeds 100%. It means that the droplets there are already bigger than at least  $0.01\ \mu\text{m}$ . Where do they come from?

In order for a droplet to form, the water molecules should coalesce through the random collisions forming clusters of water molecules progressively bigger and bigger as depicted in the figure below. During this *nucleation* process, the influx of new molecules joining the cluster should exceed the outflux of molecules that are breaking off. As discussed above, the equilibrium relative humidity for tiny droplets that consist of just a few hundred molecules can be very large (several hundred percent), which is never observed in clouds. The statistical thermodynamics and laboratory experiments suggest that for the atmospheric conditions, it would take relative humidity of at least 300-400% to form the cloud droplets purely by chance. Thus, it can be concluded that the *homogeneous nucleation* of droplets, that is formation of droplets without the aid of other particles, cannot explain formation of cloud droplets in clouds.



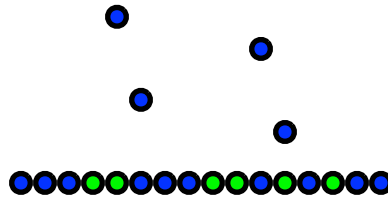
In the atmosphere, cloud droplets form with the aid of particles called *cloud condensation nuclei*, or CCN. There are two basic types of CCN by the mode of action: soluble and insoluble.

Insoluble CCN are particles that have affinity for water or *hygroscopic*, that is, they attract water molecules to their surface. The examples are particles of smoke, soot, black carbon, tiny particles of clay, among others. For atmospheric conditions that are close to saturation over liquid water, the insoluble CCN can provide the surface for water molecules to attach, so eventually, water may form a thin film around the insoluble CCN. The resultant droplet may be relatively large, say,  $0.1\ \mu\text{m}$ , to diminish the curvature effects on saturation vapor pressure, so that even small excess of relative humidity over 100% may be sufficient for the droplet to keep growing and become a cloud droplet.

The soluble CCN consist of water-soluble particles of sea salt, sulfates, and some organic matter. The soluble CCN first act similar to insoluble, but as long as the film of water is formed on the CCN surface, it will start dissolving, which actually reduces

the saturation vapor pressure and causes the resultant droplet attract even more molecules of water and grow even faster until all the CCN material is dissolved.

Why can the presence of solute in water reduce saturation vapor pressure? It is because the ions of dissolved material reduce the effective area of the surface that is covered by the water molecules as depicted by the sketch below with the ions shown as green circles.



As the result of blocking some of the surface by the ions, the flux of water molecules evaporating from the surface is deminished; therefore, to be in equilibrium, the flux of condensing water molecules should also decrease, which means the reduction of the saturation vapor pressure.

Let us now quantify this solute effect. Let's consider a droplet with radius  $r$  which contains ions of dissolved CCN particle of mass  $m_s$ . From the qualitative consideration above, it follows that, to the first order, the ratio of saturation vapor pressures over solute  $e'_s$  and saturation pressure over pure water  $e_s$  should be equal to the ratio of surface area of the solute occupied by the water molecules to the total surface area. As the water molecules' and ions' sizes are about the same (a few Angstrom units or  $10^{-10}$  m), this ratio is equal to the ratio of number of water molecules to the total number of molecules and ions at the surface, which is the same as the ratio of number of water molecules in the solute to the total number of molecules and ions in a given volume. The latter should be approximately equal to the total number of water molecules of pure water occupying the same volume, which we denote  $n_{H_2O}$ . Given the number of ions in the same volume  $n_s$ , we can write

$$\frac{e'_s(r)}{e_s(r)} = \frac{n_{H_2O} - n_s}{n_{H_2O}} = 1 - \frac{n_s}{n_{H_2O}} \tag{10.1}$$

that is the vapor pressure over solute is reduced relative to the pressure over pure water by the molecular fraction of the soluble substance in the solute, which is called a Raoult's Law. The number of water molecules in a droplet of pure water is equal to the number of moles of water in that droplet times the Avagadro's number  $N_A$ . The number of moles is equal to mass of the droplet  $m_{H_2O} = (4/3)\pi r^3 \rho_L$  ( $\rho_L$  is the liquid-water density) divided by the molar mass of water  $M_{H_2O} = (0.016 \text{ kg/mole})$ , that is

$$n_{H_2O} = \frac{4\pi r^3 \rho_L N_A}{3M_{H_2O}}$$

The number of ion is equal to the mass of dry CCN particle  $m_s$  divided by the molar mass  $M_s$  of the water-soluble substance in CCN times the Avagadro's number times the dissociation factor  $i$ , which is the number of ions produced from one molecule of the substance (for example, for sodium chloride NaCl, dissolves into two ions, Na+ and Cl-, that is  $i=2$ ):

$$n_s = \frac{im_s N_A}{M_s}$$

Substituting both expressions into (10.1), we get

$$\frac{e'_s(r)}{e_s(r)} = 1 - \frac{b}{r^3} \quad (10.2)$$

where

$$b = \frac{3iM_{H_2O}}{4\pi\rho_L M_s} m_s \quad (10.3)$$

Note that the saturation vapor pressures in (10.2) are over curved droplet surface. Combining with the Kelvin equation (9.6), we get

$$e'_s(r) = e_s(r) \left(1 - \frac{b}{r^3}\right) = e_s(\infty) \left(1 - \frac{b}{r^3}\right) e^{a/r}$$

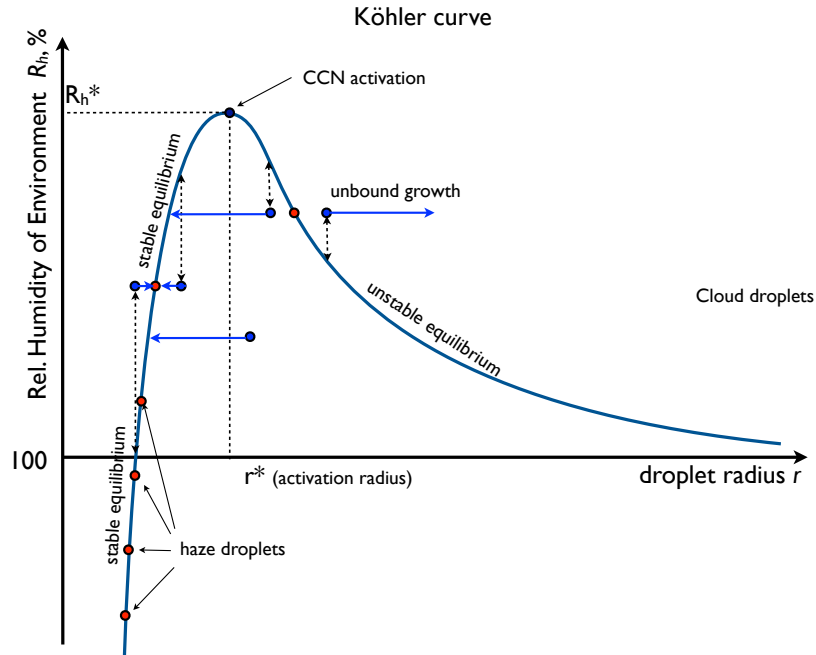
Assuming that our droplet has radius much large than  $a \approx 0.001 \mu\text{m}$ , that is  $r \gg a$ , and hence,  $a/r \ll 1$ , the exponent can be approximated by  $e^{a/r} \approx 1 + a/r$ , so that the above equation can be rewritten as

$$\frac{e'_s(r)}{e_s(\infty)} = \left(1 + \frac{a}{r}\right) \left(1 - \frac{b}{r^3}\right)$$

After multiplying the expressions in the parentheses and ignoring the  $ab/r^4$  as much smaller than either  $a/r$  or  $b/r^3$ , we finally arrive at the following Köhler equation:

$$\frac{e'_s(r)}{e_s(\infty)} = 1 + \frac{a}{r} - \frac{b}{r^3} \quad (10.4)$$

Thus, the saturation vapor pressure over a droplet formed on dissolved CCN is increased by the surface curvature effect, but decreased by the solute effect. Note that while the coefficient  $a$  depends only on physical constants and temperature, the coefficient  $b$  depends on mass  $m_s$  of dry CCN particle and its chemical composition.

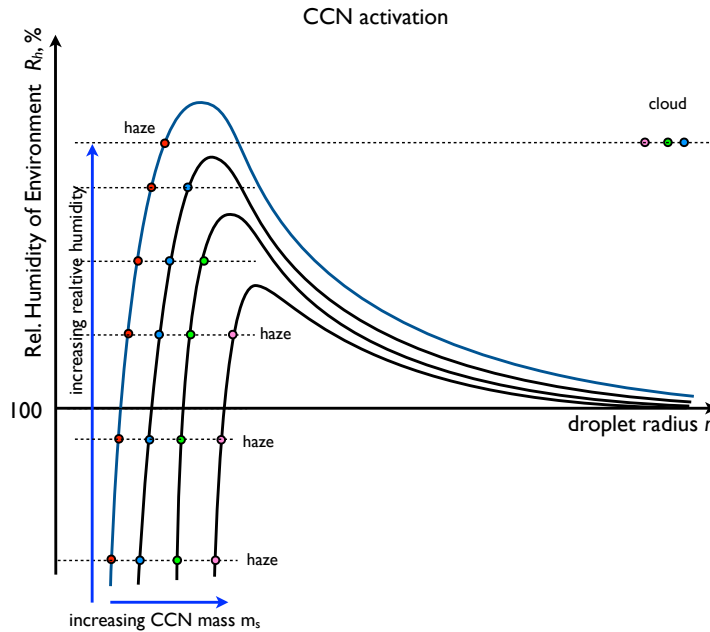


The dependence of the equilibrium relative humidity on the droplet radius, a so-called Köhler curve, is shown in the figure above. Unlike the case of pure water, the equilibrium relative humidity reaches a maximum value  $R_h^*$  at some corresponding radius  $r^*$ , called *CCN activation* relative humidity and activation radius. For droplets with smaller radius, the equilibrium  $R_h$  is decreasing with decreasing radius, and even becomes smaller than 100% for very small droplets. As it is easily seen from the figure, the equilibrium sizes larger than  $r^*$  are unstable, similar to the case of pure water droplets. However, for the droplets smaller than  $r^*$ , the equilibrium is stable. Moreover, for a given relative humidity smaller than  $R_h^*$ , the stable part of the Köhler curve serves as an attractor for the droplets smaller than the equilibrium sizes that are larger than  $r^*$ . All droplets slightly larger than the unstable equilibrium size could grow unbound to become cloud droplets. The droplets sitting on the stable-equilibrium part of the Köhler curve are called *haze droplets*. One can see that the haze can exist even when relative humidity is below 100%. Haze is often observed when it is relatively humid but not cloudy when there are a lot of sulfate particles as the result of pollution.

It is easy to find the maximum value of  $R_h^*$  and a corresponding  $r^*$  by taking the derivative of (10.4) and making it equal to zero. The result is the following:

$$R_h^* = 1 + \sqrt{\frac{4a^3}{27b}} \qquad r^* = \sqrt{\frac{3b}{a}} \qquad (10.5)$$

Note that  $R_h^*$  is always larger than 100%. The coefficient  $b$  is proportional to the dry-CCN mass  $m_s$ , that is  $b \sim m_s$ , so the excess of activation relative humidity over 100%, or super-saturation,  $R_h^* - 1 \sim 1/\sqrt{m_s}$ , decreases, while activation radius  $r^* \sim \sqrt{m_s}$  increases with increasing dry-CCN mass.



Let's consider the activation process as illustrated by the figure above. Let's assume that we have a population of CCN with identical chemical composition (say, sea salt), but different sizes, and, hence, different masses. Let's also assume that initial relative humidity is not far below than 100%, so we have a population of stable haze droplets of different sizes as shown in the figure by dots with different colors. Note that different sizes are entirely due to the differences in size of dry CCN from which these haze droplets grew. So, for each CCN size, there is a corresponding value of  $b$ , and, hence, a separate Köhler curve. Let's now gradually raise the relative humidity, for instance, as the result of cooling of adiabatically rising air. As long as the relative humidity remains below the activation value  $R_h^*$  for a given curve, the corresponding haze droplet remains on the stable-equilibrium part of the curve. When the  $R_h$  exceeds the  $R_h^*$  for a given curve, the corresponding haze droplet would activate and start growing unbound and become a cloud droplet. As relative humidity increases, more and more haze droplets activate and become cloud droplets. As cloud droplets grow, they consume water vapor, thus having the tendency to reduce relative humidity. Eventually, the rate of generation of  $R_h$  due to adiabatic cooling becomes exactly compensated by the reduction rate of  $R_h$  due to the sink of vapor condensing on cloud droplets, and  $R_h$  reaches its maximum value in the updraft. As cloud droplets continue to consume the vapor (as  $R_h$  is still  $>100\%$ ), the  $R_h$  may start

gradually decreasing. As the result, the haze droplets with  $R_h^*$  higher than the maximum  $R_h$  will not activate and, hence, will remain tiny haze droplets inside the growing cloud. At the same time, all CCN with corresponding  $R_h^*$  smaller than the maximum  $R_h$  will become cloud droplets.