Chapter Three
Cloud Droplet Formation

Effects of Ambient Pressure on Saturated Vapor Pressure (e_S)

- The saturation vapor pressure over a flat surface of pure water is given by the Clausius-Clapeyron equation,

$$e_s^*(\infty) = e_o \, \exp\left[\frac{L_v}{R_v}\left(\frac{1}{T_o} - \frac{1}{T}\right)\right] \qquad (3.1)$$

  - We have places an asterisk on e_s^* to indicate that this is the saturation vapor pressure for pure water.

  - The (∞) tells us that the surface is flat (radius of curvature is infinite).

  - Thus, $e_s^*(\infty)$ is read as the saturation vapor pressure over a flat surface of pure water.

- Equation (3.1) assumes that the pressures in the liquid is equal vapor pressure above the liquid.

  - This is only true if there is pure water vapor above the liquid.

  - If there is a mixture of dry air and vapor above the liquid, then the pressure in the liquid will be the combined pressure of the dry air and vapor, $p = p_d + e$, and so (3.1) is now suspect.

- To see if we can really use (3.1) for a mixture of dry air and vapor, such as in the real atmosphere, we need to look to the *Poynting equation*, which relates the saturation vapor pressure to the total pressure.

- We won't derive the Poynting equation. We will just state it as:

$$\left(\frac{\partial e_s}{\partial p}\right)_T = \frac{\alpha_l}{\alpha_v} \qquad (3.2)$$

where α_l is the specific volume of the liquid, and α_v is the specific volume of the vapor.

- Equation (3.2) can be integrated to obtain

$$e_s(p) = e_{so} \exp\left[\frac{\alpha_l}{R_v T}(p - e_{so})\right] \tag{3.3}$$

where e_{so} is the saturation vapor pressure without any external pressure (meaning that the total pressure is the same as the saturation vapor pressure, $p = e_{so}$).

- Equation (3.3) tells us that increasing total pressure p will increase the saturation vapor pressure. Therefore, the vapor pressure we get from the Clausius-Clapeyron equation will be too low if we have a mixture of dry air and water vapor.

- As Figure 1 illustrates, the effect of total pressure on saturation vapor pressure is very small, even at total pressures of up to 10 atmospheres.

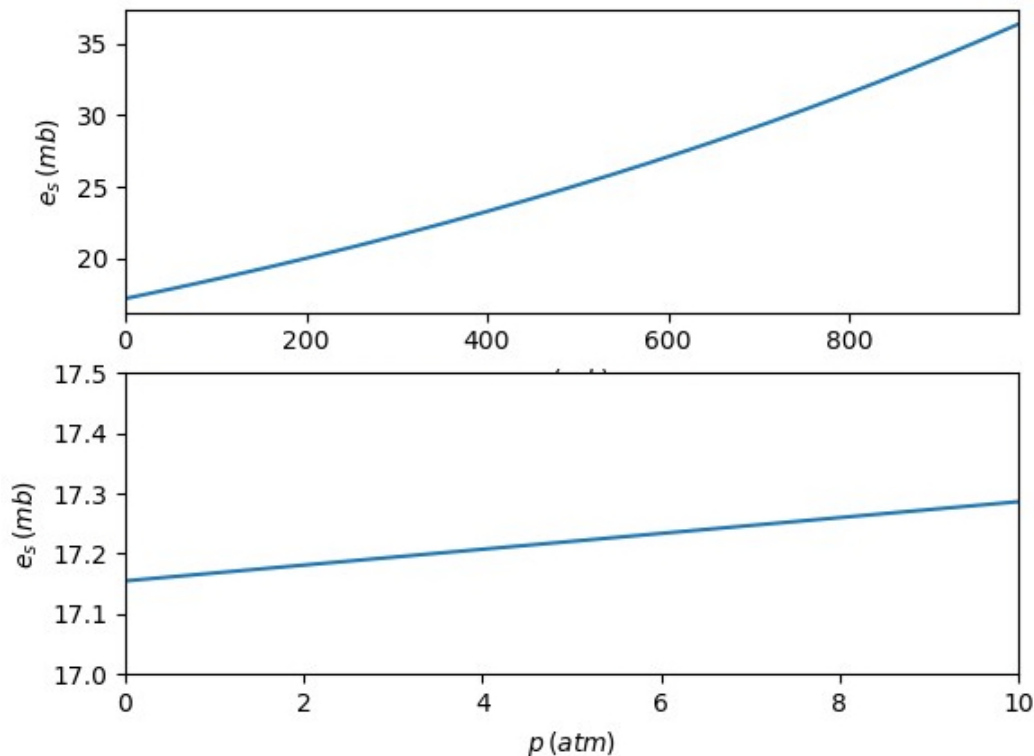- The increase in saturation vapor pressure due to ambient pressure is therefore usually ignored.

Figure 1: Saturation vapor pressure as a function of total pressure.

- The physical explanation for the increase in saturation vapor pressure with total pressure is not entirely known.

- It likely has to do with the fact that repulsive forces between molecules dominate at short distances, while attractive forces dominate at larger distance.

Curvature Effect

- Water droplets are held together by surface tension.

- Due to the squeezing of the droplet by the surface tension, the pressure inside of a water droplet is higher than the surrounding air. The pressure inside a droplet of radius r is given by the formula

$$p(r) = p_o + \frac{2\eta}{r} \tag{3.4}$$

where p_o is the pressure outside of the droplet and η is the surface tension.

- A plot of the pressure difference across the droplet interface as a function of radius is shown in Figure 2.

  - Note that very small droplets have tremendous internal pressures.

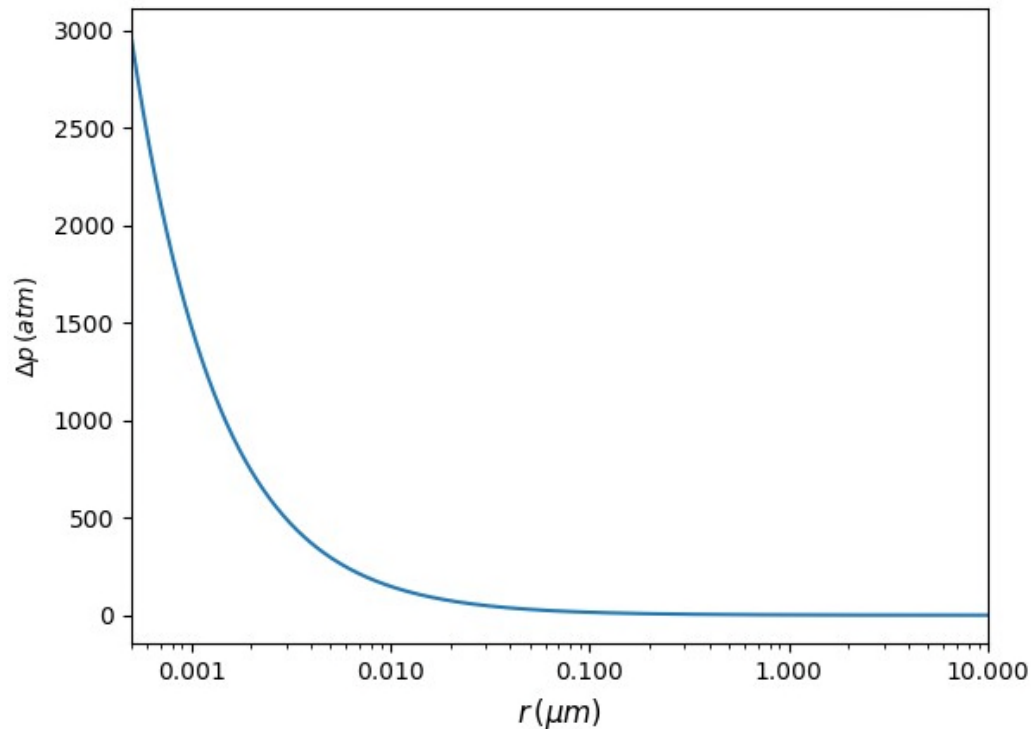 - A 1 μm droplet has an internal pressure of about 1500 atmospheres.

Figure 2: Pressure difference across droplet interface, $\Delta p = p(r) - p_o$, as a function of radius.

- Because newly formed water droplets are so small, and therefore have tremendous internal pressures, we cannot ignore the effects of pressure on saturation vapor pressure when dealing with the formation of cloud droplets.

- To find the saturation vapor pressure over a droplet we use the chain rule to write

$$\left(\frac{\partial e_s}{\partial r}\right)_T = \left(\frac{\partial e_s}{\partial p}\right)_T \left(\frac{\partial p}{\partial r}\right)_T \tag{3.5}$$

$\partial e_s / \partial p$ comes straight from the Poynting equation, (3.2) and $\partial p / \partial r$ is found by differentiating (3.4). Equation (3.5) becomes:

$$\left(\frac{\partial e_s}{\partial r}\right)_T = -\frac{\alpha_i}{\alpha_v}\frac{2\eta}{r^2} \tag{3.6}$$

- From the ideal gas law for pure water vapor we have

$$\alpha_v = \frac{R_v T}{e_s}$$

and substituting this into (3.6) and rearranging yields

$$\left(\frac{\partial \ln e_s}{\partial r}\right)_T = \frac{2\alpha_l \eta}{R_v T r^2} \tag{3.7}$$

- Integrating (3.7) with respect to r from ∞ to r results in:

$$e_s(r) = e_s(\infty)\exp\left(\frac{a}{r}\right) \tag{3.8}$$

where

$$a = \frac{2\alpha_l \eta}{R_v T} \tag{3.9}$$

- Equation (3.8) states that the saturation vapor pressure over a droplet of radius r is larger than that over a flat surface. This is called the *curvature effect*.

- *The equilibrium saturation ratio S_{eq} is defined as the saturation ratio needed for the droplet to be in equilibrium.* It is given by $S_{eq} = e_s(r)/e_s^*(\infty)$

- Figure 3 shows a plot of equilibrium saturation ratio $e_s(r)/e_s^*(\infty)$, as a function of droplet radius for a pure water droplet.

- For very small droplets the equilibrium saturation ratio is upwards of 4, or a relative humidity of 400%.

- This is why *homogenous nucleation* which is the condensation of pure water vapor doesn't occur at 100% relative humidity.
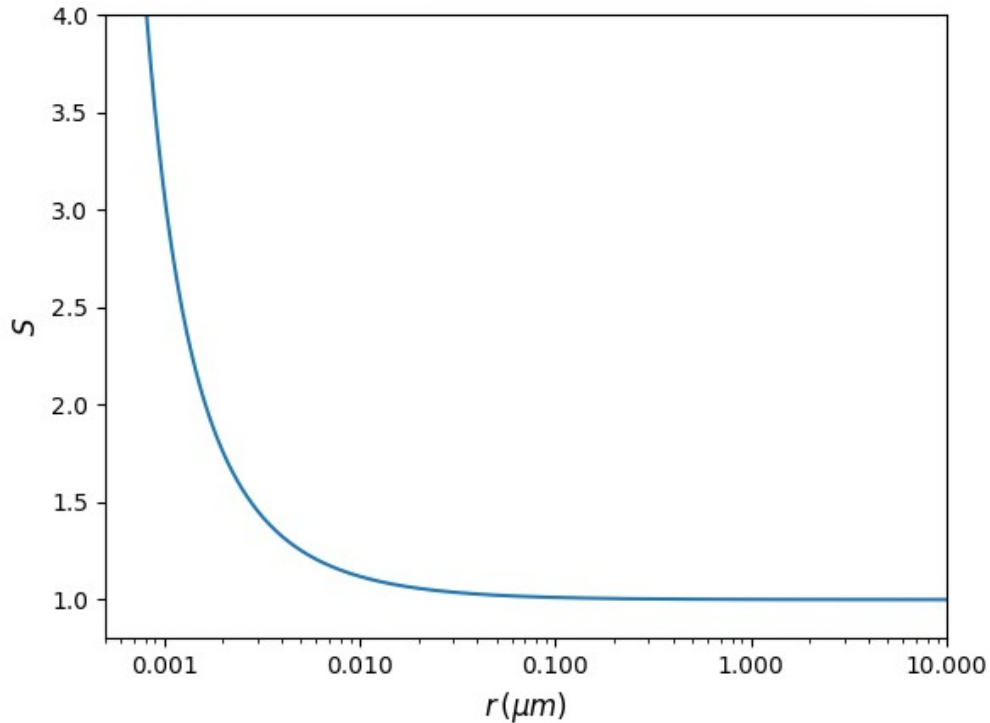

Figure 3: Equilibrium saturation ratio versus droplet radius for pure water.

Solute Effect

- The addition of an impurity, or *solute*, to liquid water lowers the saturation vapor pressure. This effect is quantified by *Raoult's Law*,

$$e_s = \chi_w e_s^*$$ (3.10)

where χ_w is the *mole fraction of water*. The mole fraction of water is defined as the number of moles of water per total number of moles of water plus solute,

$$\chi_w = \frac{n_w}{n_w + n_s}$$ (3.11)

- For dilute solutions the mole fraction of water can be approximated by

$$\chi_w \cong 1 - \frac{n_s}{n_w}$$ (3.12)

- To apply Raoult's Law to a spherical droplet of radius r we need to find the number of moles of water in the droplet. This is given by

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$$n_w = \frac{m_w}{M_w} \tag{3.13}$$

where m_w is the mass of the droplet, and M_w is the molar mass of water.
- The mass of a spherical droplet is:

$$m_w = \frac{4}{3}\pi\rho_l r^3 \tag{3.14}$$

where ρ_l is the density of liquid water.

- From (3.14) we have

$$n_w = \frac{4\pi\rho_l r^3}{3M_w} \tag{3.15}$$

- The number of moles of solute is:

$$n_s = i\,\frac{m_s}{M_s} \tag{3.16}$$

where i is the *ion factor*. The ion factor is an integer that is equal to the number of ions that the solute dissociates into when dissolved.

· The mole fraction of water in a spherical droplet is given by putting (3.15) and (3.16) into (3.12) to get

$$\chi_w = 1 - \frac{b}{r^3} \tag{3.17}$$

where

$$b = \frac{3im_s}{4\pi\rho_l}\frac{M_w}{M_s} \tag{3.18}$$

· From Raoult's Law, (3.10), the ratio of e_s / e_s^* for a droplet is

$$\frac{e_s}{e_s^*} = 1 - \frac{b}{r^3} \tag{3.19}$$

- This ratio is plotted in Figure 4 for droplets of varying radius. Note that the saturation vapor pressure of an impure droplet decreases drastically at small radii.

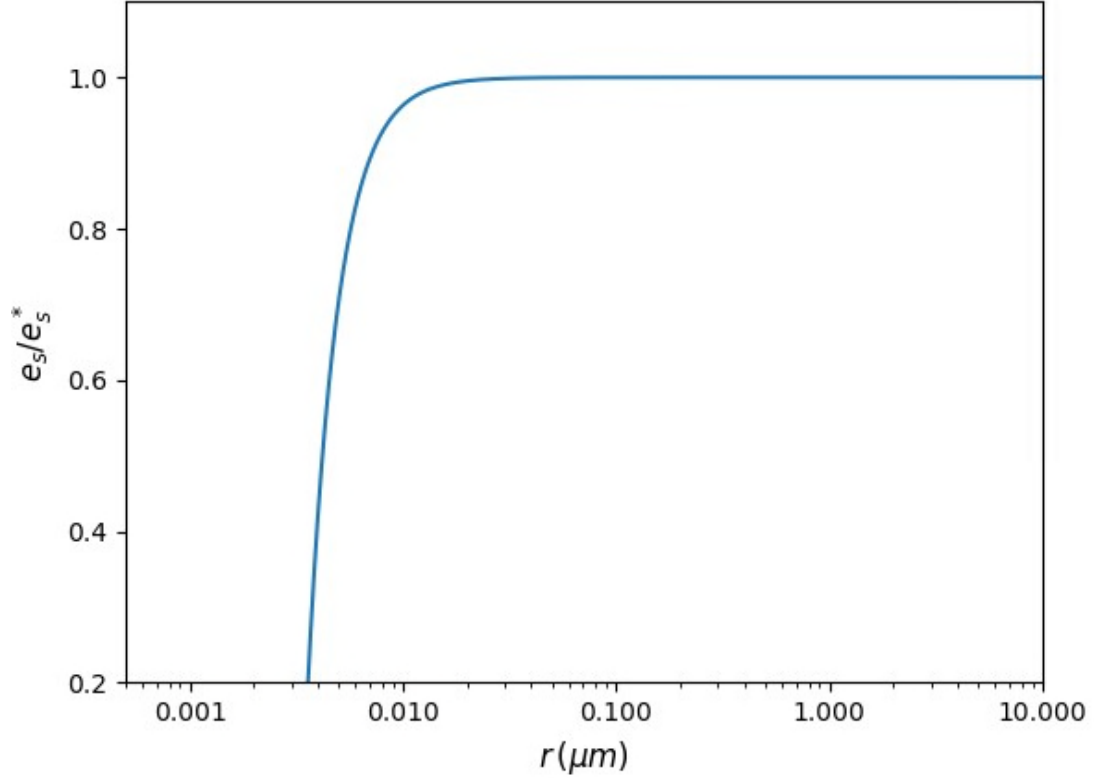- This decrease of saturation vapor pressure is known as the *solute effect*.

Figure 4: Ratio of saturation vapor pressure of impure droplet to saturation vapor pressure of pure droplet, versus droplet radius. The solute is 0.25 attograms of sodium chloride, NaCl.

Combined Curvature and Solute Effects

- The curvature effects make it more difficult to form cloud droplets, while the solute effect makes it easier.

- In real droplets both effects are present, and so we need to combine them to find the saturation vapor pressure over an impure droplet, which is given by

$$e_s(r) = e_s^*(\infty)\left(1 - \frac{b}{r^3}\right)\exp\left(\frac{a}{r}\right) \qquad (3.20)$$

- The equilibrium saturation ratio, S_{eq}, for the droplet is defined as $S_{eq} = e_s(r)/e_s^*(\infty)$ and so is:

$$S_{eq} = \left(1 - \frac{b}{r^3}\right)\exp\left(\frac{a}{r}\right) \qquad (3.21)$$

- Figure 5 shows plots of the curvature and solute effects separately, and also their combined effects.

- Note that neither effect is important once droplets are larger than 1 μm in radius. It is only very small droplets for which the curvature and solute effects must be considered.

- A plot of S_{eq} combining both the curvature and solute effects is called a *Kohler curve*. The solid line in Figure 6 is an example of a Kohler curve.
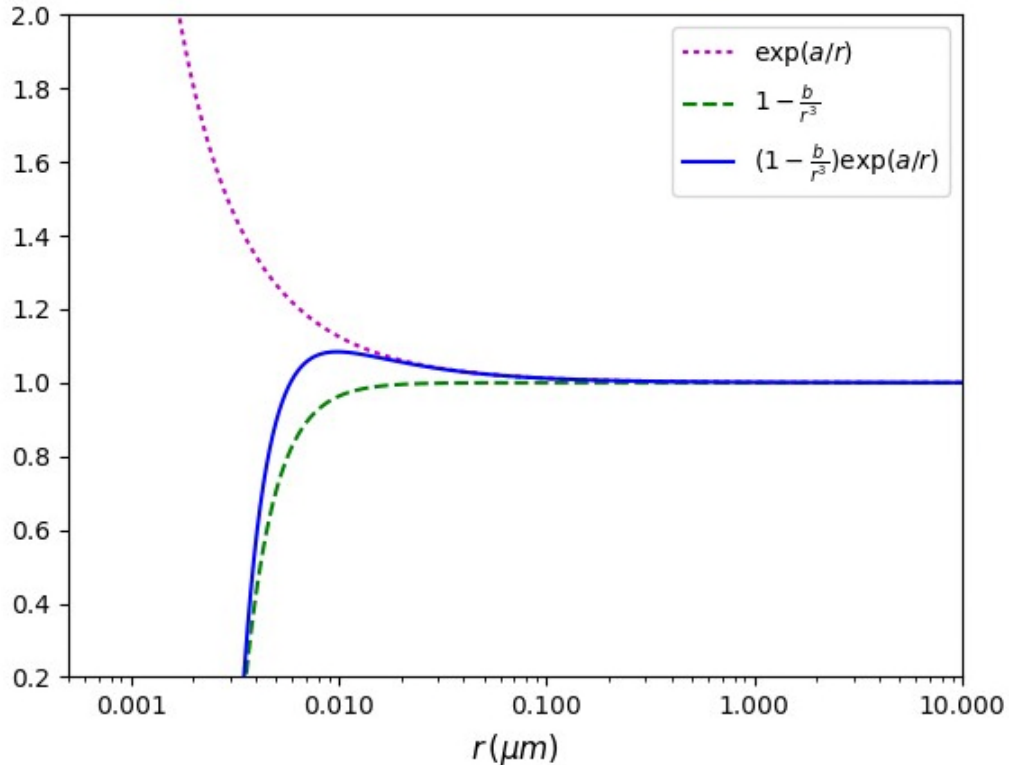

Figure 5: Plots of curvature and solute effects separately, and also combined. The plots are for a droplet containing 0.25 attograms of NaCl at a temperature of 275K.

Stability of Droplets

- We now take a more detailed look at a Kohler curve, using the one shown in Figure 6 as an example.
  - The Kohler curve becomes a maximum at the **critical radius** denoted by r^*.

  - The value of equilibrium saturation ratio at the critical radius is called the **critical saturation ratio,** and is denoted as S^*.

  - as radius gets larger the equilibrium saturation ratio goes asymptotically to unity (relative humidity of 100%), represented by the dotted line in Figure 6.
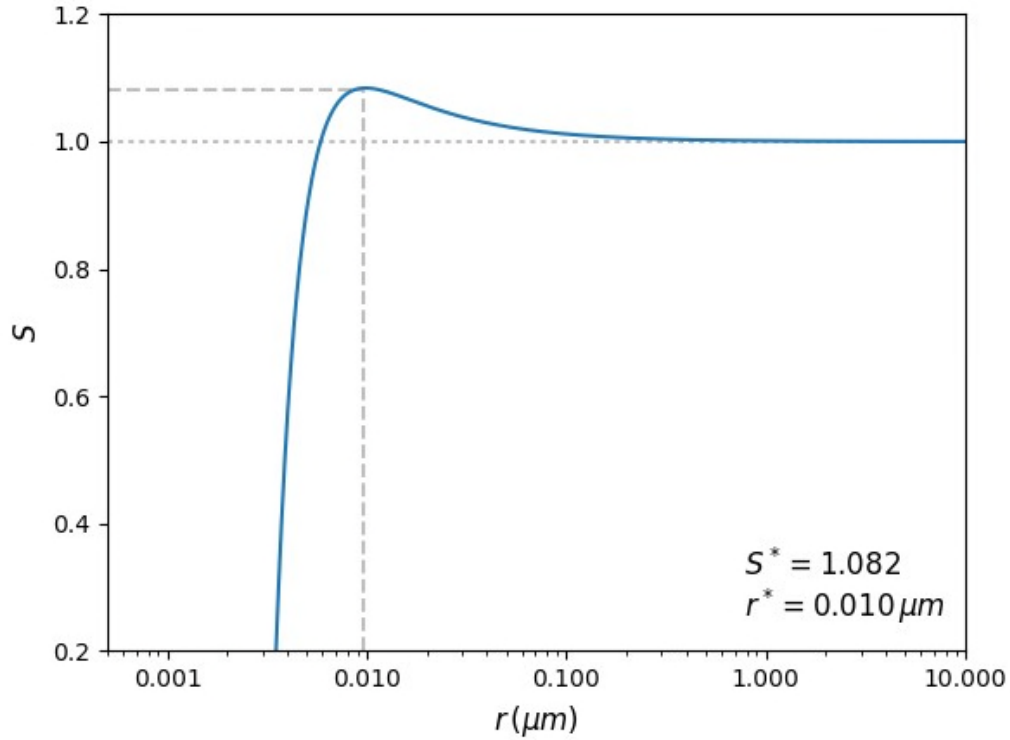
Figure 6: Kohler curve for a droplet containing 0.25 attograms of NaCl at a temperature of 275K. Dashed lines show locations of r^* and S^*. The equilibrium saturation ratio asymptotically approaches a value of one as radius increases

- The location of the critical radius, r^*, is found by setting $\partial S_{eq}/\partial r = 0$ and solving for r.

    - Because of the form of (3. 21), finding the location of r^* is not straight-forward.

    - Instead, we have to use the McLaren series expansion of $e^x = 1 + x + x^2/2! + x^3/3! + \cdots$, which for small values of x can be truncated to $e^x \cong 1 + x$.

    - Applying this approximation to the curvature term in (3.21) results in $\exp(a/r) = 1 + a/r$. Equation (3.21) then becomes

$$S_{eq} \cong 1 + \frac{a}{r} - \frac{b}{r^3} - \frac{ab}{r^4} \qquad (3.22)$$

    - The last term in (3.22) is much smaller than all the other terms, and so can be ignored. Thus, an alternative expression for the Kohler-curve is

$$S_{eq} \cong 1 + \frac{a}{r} - \frac{b}{r^3} \qquad (3.23)$$

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- Taking $\partial/\partial r$ of (3.23), setting the result equal to 0, and then solving for r yields the expression for the critical radius

$$r^* = \sqrt{\frac{3b}{a}} \qquad (3.24)$$

- Putting (3.24) back into (3.23) yields the expression for the critical saturation ratio,

$$s^* = 1 + \sqrt{\frac{4a^3}{27b}} \qquad (3.25)$$

- The significance of the critical radius is that it marks the transition from a stable equilibrium to an unstable equilibrium of the droplets.

- At radii below the critical radius $(r < r^*)$ the droplets are in stable equilibrium.

  - If a droplet increases in radius it would require an equilibrium saturation ratio that is larger than the environment $(S_{eq} > S_{env})$. The droplet will evaporate and shrink back down to its original radius.

  - If a droplet decreases in radius it would require an equilibrium saturation ratio that is less than the environment $(S_{eq} < S_{env})$. The droplet will then grow back up to its original radius.

  - Droplets at radii below the critical radius are called *haze particles*.

- At radii greater than the critical radius $(r > r^*)$, the droplets are in unstable equilibrium.

  - If a droplet grows larger it immediately finds itself in a supersaturated environment, because to the right of r^* the equilibrium saturation ratio decreases with radius. Thus, the droplet will continue to grow, and as it grows larger it requires even less of a saturation ratio.

  - Droplets whose size exceeds r^* will thus grow spontaneously.

  - Droplets whose size exceeds r^* are said to be *activated*

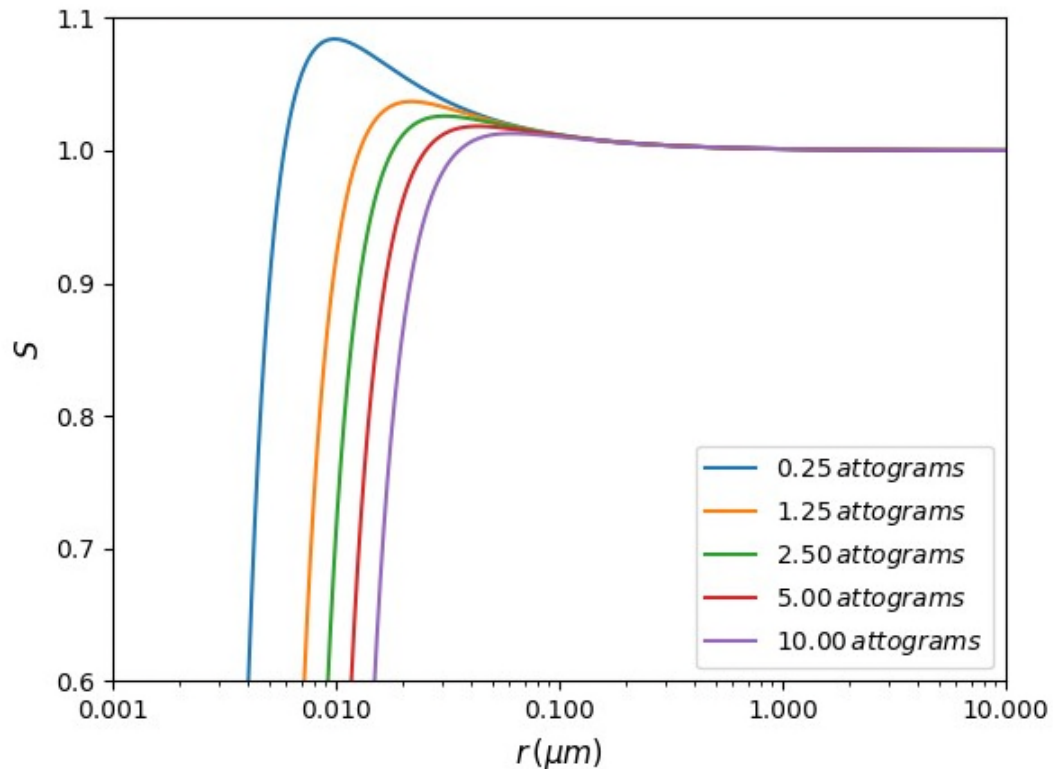- Adding more impurity to a droplet decreases S^*, and increases r^*. This is shown in Figure 7.

Figure 7: Kohler curves for varying masses of NaCl at a temperature of 275K. Note that as the mass of the solute increases the critial radius also increases, while the critical saturation ratio decreases.

Atmospheric Aerosols

- Aerosols are formed either directly by disintegration of liquids or solids (known as *primary sources*), or indirectly by condensation of gases in a process known as *gas-to-particle conversion*. Indirect sources are also known as *secondary sources*.

- Examples of primary sources are

    - wind-generated dust
    - sea spray
    - forest fires
    - combustion

- The main gases responsible for gas-to-particle conversion are

    - Sulfur dioxide (SO_2)
    - Nitrogen dioxide (NO_2)
    - Ammonia (NH_3)

- many hydrocarbons
- Aerosols are broken into three different groups based on size. These groups are

  - Aitkin nuclei particle with $r < 0.1\mu m$.
  - Large particles $0.1\mu m \leq r < 1.0\mu m$.
  - Giant particles $r \geq 1.0\mu m$

- The size distribution of aerosol populations can be specified by a distribution function $n_d(D)$, where D is the *equivalent diameter* (the diameter of a spherical particle with the same volume as the actual particle).

- In many instances the aerosol size distribution is given by the *Junge distribution*,

$$n_d(D) = cD^{-\beta} \tag{3.26}$$

Cloud Condensation Nuclei

- Homogeneous nucleation does not occur in the atmosphere, since saturation ratio rarely exceeds 1.02. Therefore, the solute effect is extremely important!

- The solute for the solute effect comes from aerosol particles in the air.

- There are two types of aerosols:

  - ➢ **Hygroscopic nuclei:** These are nuclei that are attractive to water vapor molecules, and act as collection sites for condensation

  - ➢ **Hydrophobic nuclei:** These are nuclei that are repellent to water and therefore can-not act as sites for condensation

- Not all hygroscopic nuclei are important for cloud droplet formation. Since saturation ratio rarely exceeds 1.01, only those nuclei that activate at $S < 1.02$ are available for forming cloud droplets. It is these nuclei that are known as cloud *condensation nuclei*, or *CCN*.