Köhler theory describes saturation (S_{Kohler}) over a curved solution droplet. Since atmospheric droplets are curved, and since they form on aerosol particles that contain salt (the cloud condensation nuclei or CCN), these affects need to be accounted for. Köhler theory does that.

Assignment –

Consider two aerosol particles. They have different dry radii and both are composed of sodium chloride. The temperature is 278.15 K.

1) Creat the graphs shown below and make sure that you plot the graphs <u>exactly</u> as shown. Turn in the IDL code that generates the Köhler curves for the two particle dry radii. I <u>do not</u> want to see declarations of the defined system variables, the loop that makes the solution droplet radius, or the graphic plotting code.

2) With pencil and paper (no IDL), evaluate the haze particle radii (there are two, one for the $r_d = 0.02$ µm and one for the $r_d = 0.06$ µm) at $S_{Kohler} = 0.99$. An approximation is to assume the curvature term is small relative to the solute term. Use that approximation to evaluate the haze particle radii. Provide a few sentences about how you did this. Don't forget to mention the approximation.

3) For $r_d = 0.02$ µm, and using IDL Newton, evaluate the haze particle radius at $S_{Kohler} = 0.99$. For this calculation no approximation is needed. Turn in your user-defined function and the code that calls the user-defined function though Newton. Are you using a "common block" to communicate the "state" information to the user-defined function? This can be accomplished in less than 20 lines of IDL code.
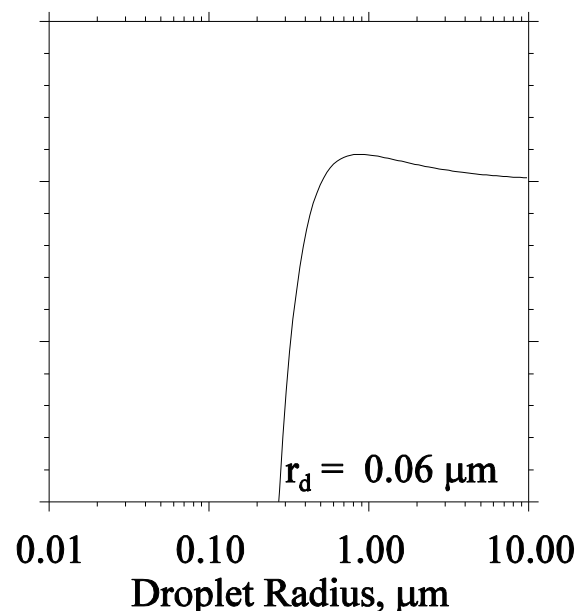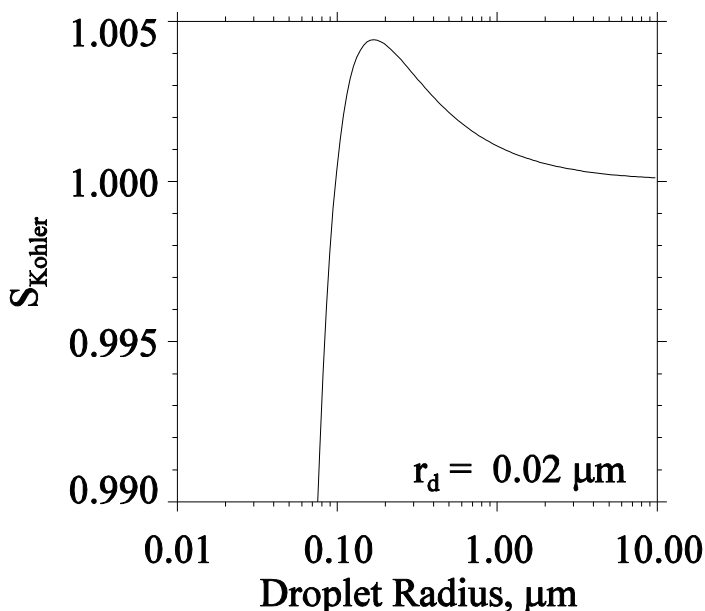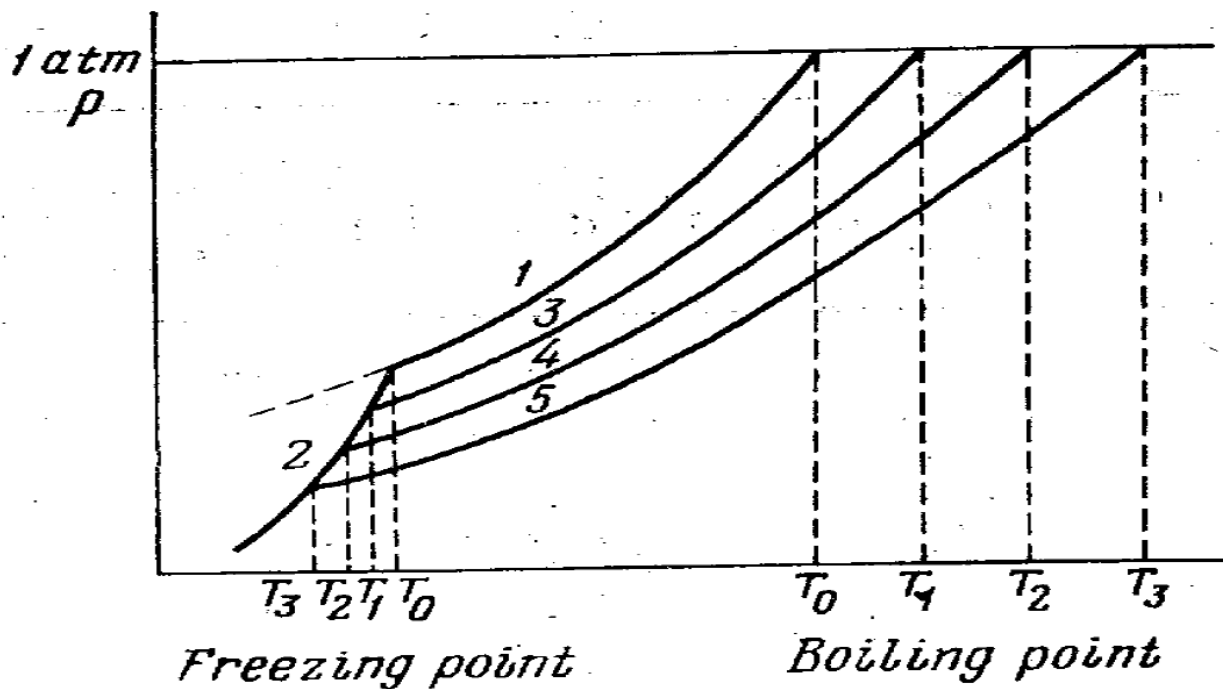
Fig. 7.12. Schematic representation of the dependence of vapour pressure on temperature:

1—pure liquid solvent; *2*—pure solid solvent; *3*, *4*, and *5*—solvent above solutions with increasing concentration of the non-volatile substance; curves *1*, *3*, *4*, and *5* diverge in moving to the right since $(p_0 - p)/p_0 = $ const and the difference $p_0 - p$ increases with increasing p_0.
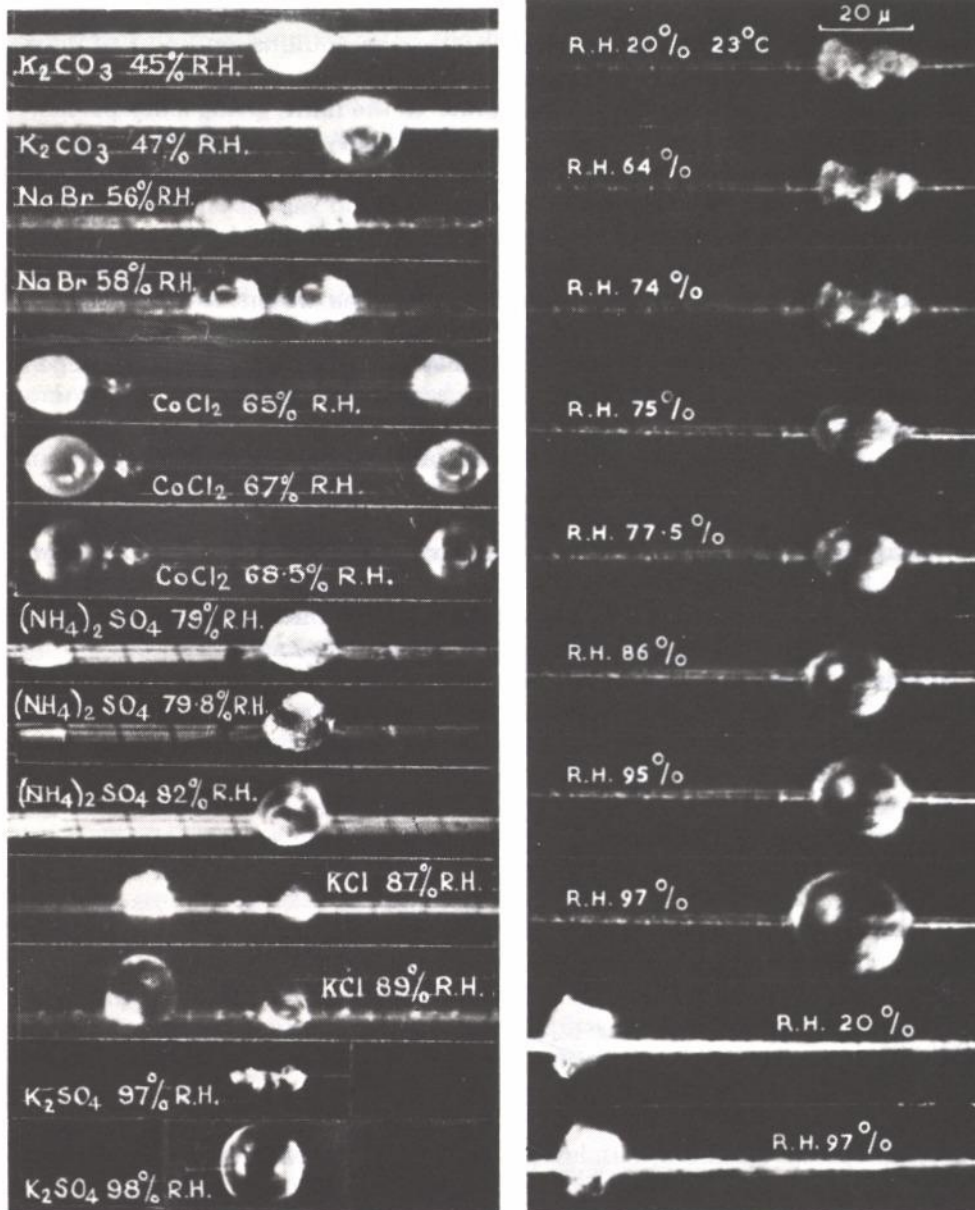
Fig. 4.2. Phase transitions for laboratory aerosol particles.

Fig. 4.3. Phase transition for a natural atmospheric particle. (The upper particle was identified from its phase transition behaviour as a giant sea-salt particle, the lower particle was an insoluble mineral particle).

Derivation of the Köhler Equation

Consider a solution containing water and dissolved salt. At this point we are considering a bulk solution; i.e., something you can create in your kitchen by adding salt to a volume of liquid water. The solution has two components; we will use the subscript "1" to indicate the solvent (water) and the subscript "2" to indicate the salt.

Water activity (a_1) is defined as the ratio of the vapor pressure over the solution divided by the vapor pressure over pure water (i.e., $a_1 = e_s' / e_s$). According to Raoult's Law, water activity can be expressed in terms of the mole amounts of water and salt (n_1 and n_2, respectively), and the vant Hoff factor (i).

$$a_1 = \frac{n_1}{n_1 + i \cdot n_2} \tag{1}$$

Equation (1) arranges to Equation (2)

$$a_1 = \frac{1}{1 + i \cdot \frac{n_2}{n_1}} \tag{2}$$

Now consider an aerosol particle that is spherical and composed of pure sodium chloride. If the particle is exposed to water vapor close to saturation, with $S < 1$, the particle deliquesces and becomes a solution droplet. Assume that all the salt is dissolved and the water and salt contribute to the volume of the solution droplet as if they were separate components. The mole amount of water within the solution droplet is

$$n_1 = \frac{4\pi}{3} \cdot \frac{\rho_\ell}{M_1} \cdot \left(r^3 - r_d^3 \right) \tag{3}$$

Here r_d is the radius of the dry salt particle, M_1 is molecular weight of water, and r is the radius of the solution droplet. The mole amount of salt in the solution droplet is

$$n_2 = \frac{4\pi}{3} \cdot \frac{\rho_2}{M_2} \cdot r_d^3 \tag{4}$$

Combining (2), (3) and (4), the water activity can be described in terms of the vant Hoff factor, the two radii, and pure-component properties

$$a_1 = \frac{1}{1 + i \cdot \frac{\rho_2 \cdot M_1}{\rho_\ell \cdot M_2} \cdot \frac{r_d^3}{\left(r^3 - r_d^3 \right)}} \tag{5}$$

Assuming the second term in the denominator of Equation 5 is small relative one, and making a Taylor series expansion, Equation (5) simplifies to Equation (6)

$$a_1 = 1 - i \cdot \frac{\rho_2 \cdot M_1}{\rho_\ell \cdot M_2} \cdot \frac{r_d^3}{\left(r^3 - r_d^3 \right)} \tag{6}$$

Saturation over a solution droplet (S_{Kohler}) can be approximated as the product of water activity and the Kelvin effect. For the latter we assume that the vapor-liquid surface energy (σ) is not altered by the presence of dissolved salt. With these assumptions, S_{Kohler} becomes

$$S_{Kohler} = \left(1 - i \cdot \frac{\rho_2 \cdot M_1}{\rho_\ell \cdot M_2} \cdot \frac{r_d^3}{\left(r^3 - r_d^3 \right)} \right) \cdot \exp\left(\frac{2\sigma}{\rho_\ell R_v T r} \right) \tag{7}$$

For most applications relevant to atmospheric science, the Kelvin term can be linearized. In that limit the saturation over a curved solution droplet is

$$S_{Kohler} = \left(1.-i\cdot\frac{\rho_2\cdot M_1}{\rho_\ell\cdot M_2}\cdot\frac{r_d^3}{\left(r^3-r_d^3\right)}\right)\cdot\left(1+\frac{2\sigma}{\rho_\ell R_v Tr}\right) \tag{8}$$

After multiplying out the two terms on the right side of Equation (8), and examining the result, we see that one of the four terms is small in comparison to the other three. Neglecting that smallest term, the right side of Equation (8) becomes

$$S_{Kohler} = 1.-i\cdot\frac{\rho_2\cdot M_1}{\rho_\ell\cdot M_2}\cdot\frac{r_d^3}{\left(r^3-r_d^3\right)}+\frac{2\sigma}{\rho_\ell R_v Tr} \tag{9}$$

Also, in Equation 9, we neglect r_d^3 relative to the r^3

$$S_{Kohler} = 1.+\frac{2\sigma}{\rho_\ell R_v Tr}-i\cdot\frac{\rho_2\cdot M_1}{\rho_\ell\cdot M_2}\cdot\frac{r_d^3}{r^3} \tag{10}$$

Finally, we define two parameters $a = 2\cdot\sigma/(\rho_\ell\cdot R_v\cdot T)$ and $b = i\cdot\rho_2\cdot M_1\cdot r_d^3/(\rho_\ell\cdot M_2)$ and we see that the latter is proportional to the amount of salt (cf. Equation 4). With these definitions the Köhler Equation becomes

$$S_{Kohler}(r) = 1.+\frac{a}{r}-\frac{b}{r^3} \tag{11}$$

The Köhler Equation describes saturation over a curved solution droplet. Solution droplets are classified as "haze particle" or as "cloud droplet" by comparing saturation at the maximum of the Köhler curve to the ambient saturation (S).

$S < S_{Kohler,max}$
Haze Particle
"Unactivated"

$S > S_{Kohler,max}$
Cloud Droplet
"Activated"

Note: In an upcoming lecture, we will see that S is time-dependent. The time-dependent theory we develop has S increasing to a maximum, with S slightly greater than one, a few tens of meters above the lifted condensation level.

We note that there are three terms on the rhs of the Köhler Equation (Equation 11). The second is the curvature term, this enhances saturation for the same reason it enhances saturation over a curved surface of pure water (Kelvin effect). The third is the solute term. This lowers the saturation for the same reason that the presence of solute lowers the vapor pressure over a flat solution.