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1. Saturation Vapor Pressure

i. Saturation Vapor pressure e_s The saturation vapor pressure is the partial pressure of the water vapor in equilibrium with a plane surface of pure water. That means that the rate of condensation is equal to the rate of evaporation. e_s is a function of temperature alone, *it doesn't depend on the vapor content of the air*. $e_s(T)$ is highly nonlinear as it increases rapidly with increasing temperature. This explains why the amount of atmospheric water vapor will likely increase with global warming caused by increasing concentration of greenhouse gases. This pressure is defined by the integral of the Clausius Clapeyron equation. There are also approximate expressions for e_s , one of the most used is:

$$e_s(T) = 611 \exp\left(\frac{17.27T}{237.3 + T}\right) \quad (1)$$

where e_s is in Pascals and T is in Celsius.

2. Formation of Cloud Droplets

The changes from left to right in Figure 2 correspond to increasing molecular order, this means that in order for water vapor to condense into a water droplet there is a strong free energy barrier that must be overcome for droplets to form. To form a droplet by condensation of vapor, *surface tension* must be overcome by a strong gradient of vapor pressure. This means that phase transitions don't occur at $e_s(T)$, or saturation over a plane surface of water (as described above). Even if a sample of moist air is cooled adiabatically to the equilibrium saturation point for bulk water, droplets should not be expected to form. In fact, water droplets do begin

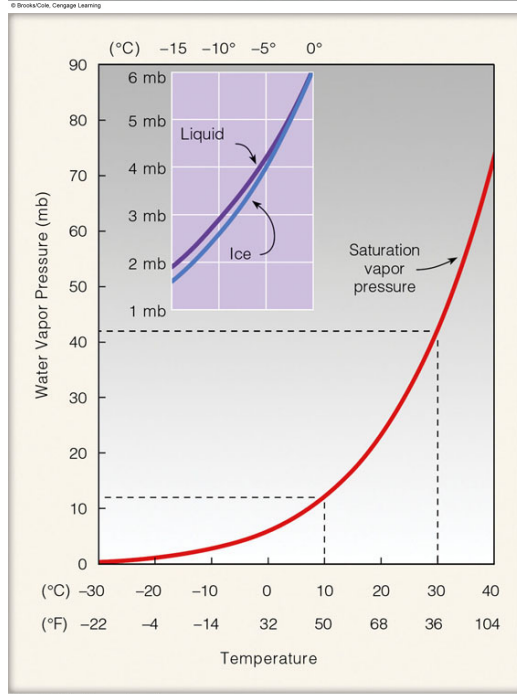
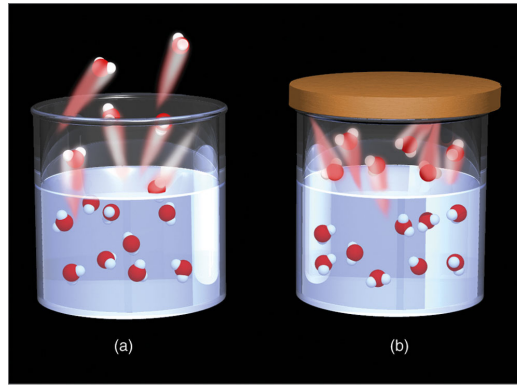


Figure 1: Saturation vapor pressure e_s over a plane surface of pure water and the difference between e_s and the saturation vapor pressure over a plane surface of ice e_{si}

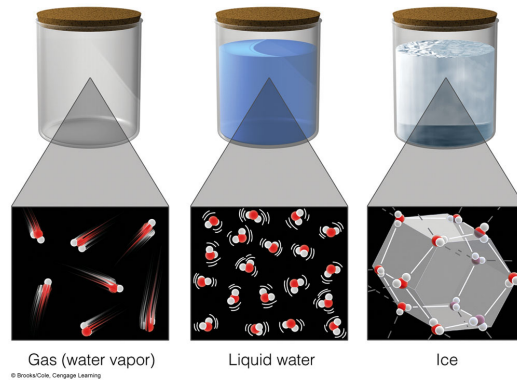


Figure 2: Saturation vapor pressure e_s over a plane surface of pure water and the difference between e_s and the saturation vapor pressure over a plane surface of ice e_{si}

to condense in pure water vapor only when the relative humidity reaches several hundred percent! However, condensation occurs in reality at relative humidities only slightly larger than 100%.

The reason why cloud droplets are observed to form in the atmosphere when ascending air just reaches equilibrium saturation is because the atmosphere contains significant concentrations of particles of micron and sub-micron size which have an affinity for water. This is called *Heterogeneous Nucleation*. There are many types of condensation nuclei in the atmosphere. Some become wetted at RH less than 100% and account for haze. Larger condensation nuclei may grow to cloud droplet size. As moist air is cooled adiabatically and RH is close to 100 the hygroscopic CCN begin to serve as centers of condensation. If ascent continues, there is supersaturation by cooling which is depleted by condensation on the nuclei. Supersaturation is when RH exceeds 100%. Air with relative humidity of 101.5% has a supersaturation of 1.5%. It is an important characteristic of the atmosphere that there are always condensation nuclei present and RH rarely exceeds 100%.

2a. Curvature Effect - Kelvin Effect

We first consider the hypothetical problem (as far as the Earth's atmosphere is concerned) of the formation of a pure water droplet by condensation from a su-

persaturated vapor without the aid of particles in the air. The first stage is a chance collision of a number of water molecules in the vapor phase to form small embryonic water droplets. As this occurs there is a change in the energy of the system (the droplet) that will be caused by two factors.

1. There is a decrease in energy because of condensation (going to a more “orderly” state).
2. There is an increase in energy because work is done in creating the surface area of the droplet. This is the work required to create an area of vapor-liquid interface (called surface energy or interfacial energy) and it has the same numerical value as surface tension.

$$\Delta E = 4\pi r^2 \sigma - \frac{4}{3}\pi r^3 R_v T \ln \frac{e}{e_s} \rho_w \quad (2)$$

The second term is the change in vapor pressure “bulk term”, it is negative because there is a decrease in the Gibbs free energy when condensation occurs, while the first term is the surface tension term.

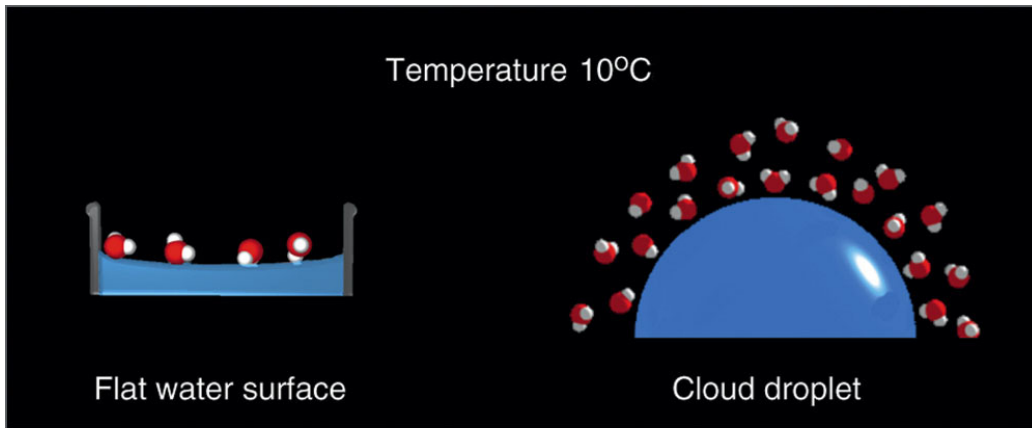
For subsaturation $e/e_s < 1$, saturation $e/e_s = 1$ and supersaturation $e/e_s > 1$. The free energy as a function of droplet radius increases monotonically for subsaturated and saturated conditions, but a system approaches thermodynamic equilibrium by reducing its free energy so droplet formation is not favored for $e/e_s \leq 1$ - a droplet formed will spontaneously evaporate. For supersaturated conditions, there is a maximum energy at r_c and then the energy decreases and condensation is more efficient than evaporation.

$r < r_c$ droplet evaporates back to initial state.

$r > r_c$ droplet grows spontaneously through condensation of vapor and is said to be activated.

The critical radius for a given temperature is:

Above r_c the droplet grows spontaneously through condensation. r_c describes an unstable equilibrium - any perturbation will take the droplet away from this state. However, the requirements for supersaturation are very high (much higher than those observed). An embryonic droplet as large as $0.01 \mu m$ still requires a supersaturation of 12% to be sustained. Yet, supersaturations exceeding 1% are rarely observed. *Cloud formation cannot be explained by homogeneous nucleation.*



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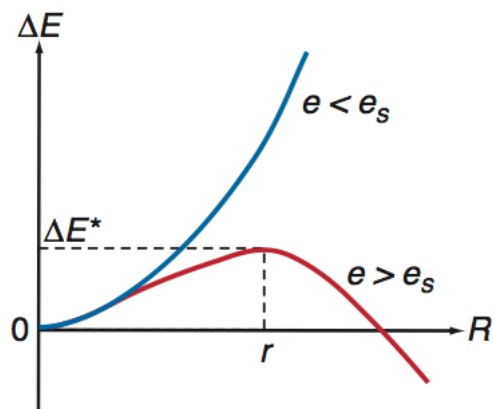


Fig. 6.1 Increase ΔE in the energy of a system due to the formation of a water droplet of radius R from water vapor with pressure e ; e_s is the saturation vapor pressure with respect to a plane surface of water at the temperature of the system.

2b. Solution effect- Raoult's Law

Water condenses onto existing particles of atmospheric aerosol termed *cloud condensation nuclei CCN*. These particles support condensation at supersaturation values well below those required for homogeneous nucleation - primarily because of their size.

Hygroscopic particles, like sodium chloride and ammonium sulfate are even more effective. In the presence of moisture $NaCl$ and $(NH_4)_2SO_4$ absorb vapor and readily dissolve. The resulting solution has a saturation vapor pressure below that of pure water - because e_s is proportional to the absolute concentration of water molecules on the surface of the droplet. Consequently, a droplet containing dissolved salt favors condensation more than would a pure water droplet of the same size.

Saturation pressure over solution Droplets. Over a plane water surface, the reduction in vapor pressure due to the presence of non-volatile solute is:

$$\frac{e'}{e_s(\infty)} = \frac{n_w}{n_w + n_d} = \left(1 + \frac{n_d}{n_w}\right)^{-1} \quad (3)$$

e' is the equilibrium vapor pressure over a solution with n_w molecules of water and n_d molecules of solute. For $n_d \ll n_w$:

We can express $n_w = m_w/M_w$ (total mass over molecular weight), and $m_w = (\frac{4}{3}\pi r^3 \rho_w - m_d)$ and (m_d is the mass of the solute). In the case of the solute, what really matters is not the number of molecules of solute but the number of molecules formed in the solution (dissociation). While a similar expression may be obtained for n_d , except when the solute dissociates into ions, $n_d = im_d/M_d$ where i is the number of ions per molecule $i = 2$ for $NaCl$.

This is called *Heterogeneous Nucleation*.

i. Combining the Solution and Curvature effect: Köhler Curves The equation that describes the equilibrium supersaturations for solutions containing specified amounts of solute can be approximated as:

$$\boxed{\frac{e'(r)}{e_s(\infty)} = 1 + \frac{a}{r} - \frac{b}{r^3}} \quad (4)$$

Where the first term is the curvature term and the second term is the solution

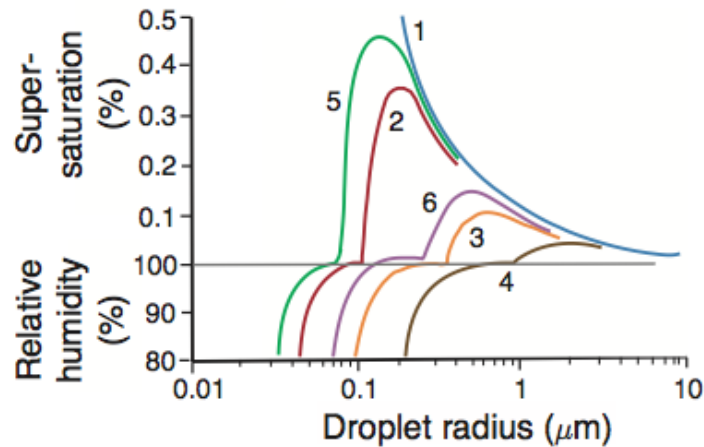


Fig. 6.3 Variations of the relative humidity and supersaturation adjacent to droplets of (1) pure water (blue) and adjacent to solution droplets containing the following fixed masses of salt: (2) 10^{-19} kg of NaCl, (3) 10^{-18} kg of NaCl, (4) 10^{-17} kg of NaCl, (5) 10^{-19} kg of $(\text{NH}_4)_2\text{SO}_4$, and (6) 10^{-18} kg of $(\text{NH}_4)_2\text{SO}_4$. Note the discontinuity in the ordinate at 100% relative humidity. [Adapted from H. R. Pruppacher, "The role of natural and anthropogenic pollutants in cloud and precipitation formation," in S. I. Rasool, ed., *Chemistry of the Lower Atmosphere*, Plenum Press, New York, 1973, Fig. 5, p. 16, copyright 1973, with kind permission of Springer Science and Business Media.]

term. Using this expression we can obtain *Köhler Curves*.

For a fixed r , $e'(r)/e_s(\infty)$ decreases with increasing solute and eventually become negative ($RH < 100\%$).

At $r < r_t$ a droplet is in stable equilibrium - perturbed droplet is restored to original state. - *haze*

At $r > r_t$ a droplet is in unstable equilibrium - perturbed droplet is restored to original state.- *can enlarge into cloud drops*

If we plot the variation of the relative humidity adjacent to a solution droplet as a function of its radius, we obtain what is referred to as a *Köhler Curves*. Several such curves are shown in the figure. Below a certain droplet radius, the relative humidity adjacent to a solution droplet is less than that which is in equilibrium with a plane surface of pure water at the same temperature (100%). As the droplet increases in size, the solution becomes weaker, the Kelvin curvature effect becomes the dominant influence, and eventually the relative humidity of the air adjacent to the droplet becomes essentially the same as the adjacent to a pure water droplet of the same size.

If we analyze solution droplets containing 10^{-19} kg of NaCl. If it were placed in air with a supersaturation 0.4%, condensation would occur on this particle to form a solution droplet, and the droplet would grow along the red curve. As it does so, the supersaturation adjacent to the droplet is less than the ambient supersaturation. Consequently, the droplet will grow over the peak in its Kohler curve and down the right-hand side of this curve to form a fog or cloud droplet. A droplet that has passed over the peak in its Kohler curve and continues to grow is said to be *activated*.

Now consider a particle of $(NH_4)_2SO_4$ with mass 10^{-19} kg that is placed in the same ambient supersaturation of 0.4%. In this case, condensation will occur on the particle and it will grow as a solution droplet along its Kohler curve until it reaches point A. At point A the supersaturation adjacent to the droplet is equal to the ambient supersaturation. If the droplet at A should grow slightly, the supersaturation adjacent to it would increase above the ambient supersaturation, and therefore the drop would evaporate back to point A. If the drop at A should evaporate slightly, the supersaturation adjacent to it would decrease below the ambient supersaturation and the droplet would grow by condensation back to A. Hence the droplet at A is in stable equilibrium with the ambient supersaturation. Droplets in this state are said to be *unactivated or haze droplets*. Haze droplets in the atmo-

sphere can considerably reduce visibility by scattering light.

Continental aerosols are the dominant source of CCNs - sea salt is not common in cloud droplets. Cumulus clouds have droplet number densities of order 10^2cm^{-3} over maritime regions and 10^3cm^{-3} for continental regions. This implies smaller size of the droplets in continental regions because the liquid water content doesn't differ much.