Raindrops and snowflakes are among the smallest meteorological entities observable without special equipment. Yet from the perspective of cloud microphysics, the particles commonly encountered in precipitation are quite remarkable precisely because of their large sizes. To form raindrops, cloud particles have to increase in mass a million times or more, and these same cloud particles are nucleated by aerosol as small as 0.01 μm. To account for growth through such a wide range of sizes in time periods as short as 10 min or so for some convective clouds, it is necessary to consider a number of physical processes. Scientific investigations of these processes is the domain of cloud microphysics studies, which is the main subject of this chapter.

We begin with a discussion of the nucleation of cloud droplets from water vapor and the particles in the air that are involved in this nucleation (Section 6.1). We then consider the microstructures of warm clouds (Sections 6.2 and 6.3) and the mechanisms by which cloud droplets grow to form raindrops (Section 6.4). In Section 6.5 we turn to ice particles in clouds and describe the various ways in which ice particles form and grow into solid precipitation particles.

The artificial modification of clouds and attempts to deliberately modify precipitation are discussed briefly in Section 6.6.

Cloud microphysical processes are thought to be responsible for the electrification of thunderstorms. This subject is discussed in Section 6.7, together with lightning and thunder.

The final section of this chapter is concerned with chemical processes within and around clouds, which play important roles in atmospheric chemistry, including the formation of acid rain.

6.1 Nucleation of Water Vapor Condensation

Clouds form when air becomes supersaturated with respect to liquid water (or in some cases with respect to ice). The most common means by which supersaturation is produced in the atmosphere is through the ascent of air parcels, which results in the expansion of the air and adiabatic cooling (see Sections 3.4 and 3.5). Under these conditions, water vapor condenses onto some of the particles in the air to form a cloud of small water droplets or ice particles. This section

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1 If the water vapor pressure in the air is \( e \), the supersaturation (in percent) with respect to liquid water is \( \left( \frac{e}{e_s} - 1 \right) \times 100 \), where \( e_s \) is the saturation vapor pressure over a plane surface of liquid water at the temperature of the air. A supersaturation with respect to ice may be defined in an analogous way. When the term supersaturation is used without qualification, it refers to supersaturation with respect to liquid water.

2 The first person to suggest that clouds form by the adiabatic cooling of moist air appears to have been the scientist and poet Erasmus Darwin in 1788.

3 Erasmus Darwin (1731–1802) English freethinker and radical. Anticipated the theory of evolution, expounded by his famous grandson, by suggesting that species modify themselves by adapting to their environment.

4 It was widely accepted well into the second half of the 19th century that clouds are composed of numerous small bubbles of water! How else can clouds float? Although John Dalton had suggested in 1793 that clouds may consist of water drops that are continually descending relative to the air, it was not until 1850 that James Espy clearly recognized the role of upward-moving air currents in suspending cloud particles.

5 James Pollard Espy (1785–1860) Born in Pennsylvania. Studied law; became a classics teacher at the Franklin Institute. Impressed by the meteorological writings of John Dalton, he gave up teaching to devote his time to meteorology. First to recognize the importance of latent heat release in sustaining cloud and storm circulations. Espy made the first estimates of the dry and saturated adiabatic lapse rates based on experimental data.
is concerned with the formation of water droplets from the condensation of water vapor.

### 6.1.1 Theory

We consider first the hypothetical problem (as far as the Earth’s atmosphere is concerned) of the formation of a pure water droplet by condensation from a supersaturated vapor without the aid of particles in the air (i.e., in perfectly clean air). In this process, which is referred to as *homogeneous nucleation* of condensation, the first stage is the chance collisions of a number of water molecules in the vapor phase to form small embryonic water droplets that are large enough to remain intact.

Let us suppose that a small embryonic water droplet of volume $V$ and surface area $A$ forms from pure supersaturated water vapor at constant temperature and pressure. If $\mu_v$ and $\mu_l$ are the Gibbs free energies per molecule in the liquid and the vapor phases, respectively, and $n$ is the number of water molecules per unit volume of liquid, the decrease in the Gibbs free energy of the system due to the condensation is $nV(\mu_v - \mu_l)$. Work is done in creating the surface area of the droplet. This work may be written as $A\sigma$, where $\sigma$ is the work required to create a unit area of vapor–liquid interface (called the *interfacial energy* between the vapor and the liquid, or the *surface energy* of the liquid). The student is invited to show in Exercise 6.9 that the surface energy of a liquid has the same numerical value as its *surface tension*. Let us write

$$\Delta E = A\sigma - nV(\mu_v - \mu_l) \quad (6.1)$$

then $\Delta E$ is the net increase in the energy of the system due to the formation of the droplet. It can be shown that

$$\mu_v - \mu_l = kT \ln \frac{e}{e_s} \quad (6.2)$$

where $e$ and $T$ are the vapor pressure and temperature of the system and $e_s$ is the saturation vapor pressure over a plane surface of water at temperature $T$. Therefore,

$$\Delta E = A\sigma - nVkT \ln \frac{e}{e_s} \quad (6.3)$$

For a droplet of radius $R$, (6.3) becomes

$$\Delta E = 4\pi R^2 \sigma - \frac{4}{3} \pi R^3 nkT \ln \frac{e}{e_s} \quad (6.4)$$

Under subsaturated conditions, $e < e_s$. In this case, $\ln (e/e_s)$ is negative and $\Delta E$ is always positive and increases with increasing $R$ (blue curve in Fig. 6.1). In other words, the larger the embryonic droplet that forms in a subsaturated vapor, the greater the increase in the energy, $\Delta E$, of the system. Because a system approaches an equilibrium state by reducing its energy, the formation of droplets is clearly not favored under subsaturated conditions. Even so, due to random collisions of water molecules, very small embryonic droplets continually form (and evaporate) in a subsaturated vapor, but they do not grow large enough to become visible as a cloud of droplets.

Under supersaturated conditions, $e > e_s$, and $\ln (e/e_s)$ is positive. In this case, $\Delta E$ in (6.4) can be either positive or negative depending on the value of $R$. The variation of $\Delta E$ with $R$ for $e > e_s$ is

![Fig. 6.1 Increase $\Delta E$ 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.](image-url)
also shown in Fig. 6.1 (red curve), where it can be seen that \( \Delta E \) initially increases with increasing \( R \), reaches a maximum value at \( R = r \), and then decreases with increasing \( R \). Hence, under supersaturated conditions, embryonic droplets with \( R < r \) tend to evaporate, since by so doing they decrease \( \Delta E \). However, droplets that manage to grow by chance collisions to a radius that just exceeds \( r \) will continue to grow spontaneously by condensation from the vapor phase, since this will produce a decrease in \( \Delta E \). At \( R = r \), a droplet can grow or evaporate infinitesimally without any change in \( \Delta E \). We can obtain an expression for \( r \) in terms of \( e \) by setting \( d(\Delta E)/dR = 0 \) at \( R = r \). Hence, from (6.4),

\[
r = \frac{2\sigma}{nkT \ln \frac{e}{e_s}} \tag{6.5}
\]

Equation (6.5) is referred to as Kelvin’s equation, after Lord Kelvin who first derived it.

We can use (6.5) in two ways. It can be used to calculate the radius \( r \) of a droplet that is in (unstable) equilibrium with a given water vapor pressure \( e \). Alternatively, it can be used to determine the saturation vapor pressure \( e \) over a droplet of specified radius \( r \). It should be noted that the relative humidity at which a droplet of radius \( r \) is in (unstable) equilibrium is \( 100e/e_s \), where \( e/e_s \) is by inverting (6.5). The variation of this relative humidity with droplet radius is shown in Fig. 6.2. It can be seen from Fig. 6.2 that a pure water droplet of radius 0.01 \( \mu \text{m} \) requires a relative humidity of \( \sim 112\% \) (i.e., a supersaturation of \( \sim 12\% \)) to be in (unstable) equilibrium with its environment, while a droplet of radius 1 \( \mu \text{m} \) requires a relative humidity of only 100.12\% (i.e., a supersaturation of 0.12\%).

**Exercise 6.1** (a) Show that the height of the critical energy barrier \( \Delta E^* \) in Fig. 6.1 is given by

\[
\Delta E^* = \frac{16\pi \sigma^3}{3(nkT \ln \frac{e}{e_s})^2}
\]

(b) Determine the fractional changes in \( \Delta E^* \) and \( r \) if the surface tension, \( \sigma \), is decreased by 10\% by adding sodium laurel sulfate (a common ingredient in soap) to pure water. Neglect the effect of the sodium laurel sulfate on \( n \) and \( e \). (c) What effect would the addition of the sodium laurel sulfate have on the homogeneous nucleation of droplets?

**Solution:** (a) With reference to Fig. 6.1, \( \Delta E = \Delta E^* \) when \( R = r \). Therefore, from (6.4),

\[
\Delta E^* = 4\pi r^2 \sigma - \frac{4}{3} \pi r^3 nkT \ln \frac{e}{e_s}
\]

Using (6.5)

\[
\Delta E^* = 4\pi r^2 \sigma - \frac{4}{3} \pi r^2 (2\sigma)
\]

or

\[
\Delta E^* = 4\pi r^2 \sigma
\]

Substituting for \( r \) from (6.5) into this last expression

\[
\Delta E^* = \frac{16\pi \sigma^3}{3(nkT \ln \frac{e}{e_s})^2}
\]

(b) Differentiating the last equation with respect to \( \sigma \)

\[
\frac{d(\Delta E^*)}{d\sigma} = \frac{16\pi \sigma^2}{(nkT \ln \frac{e}{e_s})^2}
\]

---

Fig. 6.2 The relative humidity and supersaturation (both with respect to a plane surface of water) at which pure water droplets are in (unstable) equilibrium at 5 °C.

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9 The equilibrium is unstable in the sense that if the droplet begins to grow by condensation it will continue to do so, and if the droplet begins to evaporate it will continue to evaporate (compare with Fig. B3.4b).
or

\[
\frac{d(\Delta E^*)}{\Delta E^*} = \frac{3}{\sigma} \frac{d\sigma}{\sigma}
\]

If the surface tension of the droplet is decreased by 10%, i.e., if \(d\sigma/\sigma = -0.1\), then \(d(\Delta E^*)/\Delta E^* = -0.3\) and the critical energy barrier \(\Delta E^*\) will be decreased by 30%. From (6.5), \(dr/r = d\sigma/\sigma\). Therefore, if \(\sigma\) is decreased by 10%, \(r\) will also be decreased by 10%.

(c) As shown in Fig. 6.1, \(r\) is the critical radius that an embryonic droplet must attain, due to the chance collision of water molecules, if it is to continue to grow spontaneously by condensation. Therefore, for a specified supersaturation of the ambient air, if \(r\) is decreased (which it is by the addition of the sodium laurel sulfate), the homogeneous nucleation of droplets will be achieved more readily.

Because the supersaturations that develop in natural clouds due to the adiabatic ascent of air rarely exceed a few percent (see Section 6.4.1), it follows from the preceding discussion that even if embryonic droplets of pure water as large as 0.01 \(\mu m\) in radius formed by the chance collision of water molecules, they would be well below the critical radius required for survival in air that is just a few percent supersaturated. Consequently, droplets do not form in natural clouds by the homogeneous nucleation of pure water. Instead they form on atmospheric aerosol by what is known as heterogeneous nucleation.

As we have seen in Section 5.4.5, the atmosphere contains many particles that range in size from submicrometer to several tens of micrometers. Those particles that are wettable can serve as centers upon which water vapor condenses. Moreover, droplets can form and grow on these particles at much lower supersaturations than those required for homogeneous nucleation. For example, if sufficient water condenses onto a completely wettable particle 0.3 \(\mu m\) in radius to form a thin film of water over the surface of the particle, we see from Fig. 6.2 that the water film will be in (unstable) equilibrium with air that has a supersaturation of 0.4%. If the supersaturation were slightly greater than 0.4%, water would condense onto the film of water and the droplet would increase in size.

Some of the particles in air are soluble in water. Consequently, they dissolve, wholly or in part, when water condenses onto them, so that a solution (rather than a pure water) droplet is formed. Let us now consider the behavior of such a droplet.

The saturation vapor pressure of water adjacent to a solution droplet (i.e., a water droplet containing some dissolved material, such as sodium chloride or ammonium sulfate) is less than that adjacent to a pure water droplet of the same size. The fractional reduction in the water vapor pressure is given by Raoult's law

\[
\frac{e'}{e} = f
\]

where \(e'\) is the saturation vapor pressure of water adjacent to a solution droplet containing a mole fraction \(f\) of pure water and \(e\) is the saturation vapor pressure of water adjacent to a pure water droplet of the same size and at the same temperature. The mole fraction of pure water is defined as the number of moles of pure water in the solution divided by the total number of moles (pure water plus dissolved material) in the solution.

Consider a solution droplet of radius \(r\) that contains a mass \(m\) (in kg) of a dissolved material of molecular

\[\text{mass}
\]

---

10 That aerosol plays a role in the condensation of water was first clearly demonstrated by Coulier in 1875. His results were rediscovered independently by Aitken in 1881 (see Section 5.4.5).


12 Cloud physicists use the terms homogeneous and heterogeneous differently than chemists. In chemistry, a homogeneous system is one in which all the species are in the same phase (solid, liquid or gas), whereas a heterogeneous system is one in which species are present in more than one phase. In cloud physics, a homogeneous system is one involving just one species (in one or more phases), whereas a heterogeneous system is one in which there is more than one species. In this chapter these two terms are used in the cloud physicist’s sense.

13 A surface is said to be perfectly wettable (hydrophilic) if it allows water to spread out on it as a horizontal film (detergents are used for this purpose). A surface is completely unwettable (hydrophobic) if water forms spherical droplets on its surface (cars are waxed to make them hydrophobic).

14 François Marie Raoult (1830–1901) Leading French experimental physical chemist of the 19th century. Professor of chemistry at Grenoble. His labors were met with ample, though tardy recognition (Commander of de la Legion of d’ Honnour; Davy medallist of the Royal Society, etc.).
weight $M_s$. If each molecule of the material dissociates into $i$ ions in water, the effective number of moles of the material in the droplet is $i(1000 \, m)/M_s$. If the density of the solution is $\rho'$ and the molecular weight of water $M_w$, the number of moles of pure water in the droplet is $1000(\frac{4}{3}\pi \rho' - m)/M_w$. Therefore, the mole fraction of water in the droplet is

$$f = \frac{\left(\frac{4}{3}\pi \rho' - m\right)/M_w}{\left(\frac{4}{3}\pi \rho' - m\right)/M_w + \frac{i m M_w}{M_s (\frac{4}{3}\pi \rho' - m)}} \quad (6.7)$$

Combining (6.5)–(6.7) (but replacing $\sigma$ and $n$ by $\sigma'$ and $n'$ to indicate the surface energy and number concentration of water molecules, respectively, for the solution) we obtain the following expression for the saturation vapor pressure $e'$ adjacent to a solution droplet of radius $r$

$$e' \approx \frac{s}{e_s} = \frac{\exp\left[\frac{2\sigma'}{n'kTr}\right]}{\left[1 + \frac{im M_w}{M_s (\frac{4}{3}\pi \rho' - m)}\right]} \quad (6.8)$$

Equation (6.8) may be used to calculate the saturation vapor pressure $e'$ (or relative humidity $100e'/e_s$, or supersaturation $\left(\frac{e'}{e_s} - 1\right)100$) adjacent to a solution droplet with a specified radius $r$. If we plot the variation of the relative humidity (or supersaturation) adjacent to a solution droplet as a function of its radius, we obtain what is referred to as a Köhler curve. Several such curves, derived from (6.8), are shown in Fig. 6.3. 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 (i.e., 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 that adjacent to a pure water droplet of the same size.

To illustrate further the interpretation of the Köhler curves, we reproduce in Fig. 6.4 the Köhler curves for solution droplets containing $10^{-19}$ kg of NaCl (the red curve from Fig. 6.3) and $10^{-19}$ kg of (NH₄)₂SO₄ (the green curve from Fig. 6.3). Suppose that a particle of NaCl with mass $10^{-19}$ kg were placed in air with a water supersaturation of 0.4% (indicated by the dashed line in Fig. 6.4). Condensation would occur on this particle to form a solution droplet, and the droplet would grow along the red curve in Fig. 6.4. As it does so, the supersaturation adjacent to the surface of this solution droplet will initially increase, but even at the peak in its Köhler curve the supersaturation adjacent to the droplet is less than the ambient supersaturation. Consequently, the droplet will grow over the peak in

### Footnotes

15 Hilding Köhler (1888–1982) Swedish meteorologist. Former Chair of the Meteorology Department and Director of the Meteorological Observatory, University of Uppsala.
its Köhler 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 Köhler curve and continues to grow is said to be activated.

Now consider a particle of (NH₄)₂SO₄ 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 Köhler curve (the green curve in Fig. 6.4) 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 droplet would evaporate back to point A. If the droplet 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 in Fig. 6.4. Hence, in this case, the solution droplet at A is in stable equilibrium with the ambient supersaturation. If the ambient supersaturation were to change a little, the location of A in Fig. 6.4 would shift and the equilibrium size of the droplet would change accordingly. Droplets in this state are said to be unactivated or haze droplets. Haze droplets in the atmosphere can considerably reduce visibility by scattering light.

### 6.1.2 Cloud Condensation Nuclei

Section 5.4 discussed atmospheric aerosol. A small subset of the atmospheric aerosol serves as particles upon which water vapor condenses to form droplets that are activated and grow by condensation to form cloud droplets at the supersaturations achieved in clouds (~0.1–1%). These particles are called cloud condensation nuclei (CCN). It follows from the discussion in Section 6.1.1 that the larger the size of a particle, the more readily it is wetted by water, and the greater its solubility, the lower will be the supersaturation at which the particle can serve as a CCN. For example, to serve as a CCN at 1% supersaturation, completely wettable but water-insoluble particles need to be at least \(~0.1\) \(\mu\)m in radius, whereas soluble particles can serve as CCN at 1% supersaturation even if they are as small as \(~0.01\) \(\mu\)m in radius. Most CCN consist of a mixture of soluble and insoluble components (called mixed nuclei).

The concentrations of CCN active at various supersaturations can be measured with a thermal diffusion chamber. This device consists of a flat chamber in which the upper and lower horizontal plates are kept wet and maintained at different temperatures, with the lower plate being several degrees colder than the upper plate. By varying the temperature difference between the plates, it is possible to produce maximum supersaturations in the chamber that range from a few tenths of 1% to a few percent (see Exercise 6.14), which are similar to the supersaturations that activate droplets in clouds. Small water droplets form on those particles that act as CCN at the peak supersaturation in the chamber. The concentration of these droplets can be determined by photographing a known volume of the cloud and counting the number of droplets visible in the photograph or by measuring the intensity of light scattered from the droplets. By repeating the aforementioned procedure with different temperature gradients in the chamber, the concentrations of CCN in the air at several supersaturations (called the CCN supersaturation spectrum) can be determined.

Worldwide measurements of CCN concentrations have not revealed any systematic latitudinal or seasonal variations. However, near the Earth’s surface, continental air masses generally contain larger concentrations of CCN than marine air masses (Fig. 6.5). For example, the concentration of CCN in the continental air mass over the Azores, depicted in Fig. 6.5,
is about \(\sim 300 \text{ cm}^{-3}\) at 1% supersaturation, in the marine air mass over Florida it is \(\sim 100 \text{ cm}^{-3}\), and in clean Arctic air it is only \(\sim 30 \text{ cm}^{-3}\). The ratio of CCN (at 1% supersaturation) to the total number of particles in the air (CN) is \(\sim 0.2–0.6\) in marine air; in continental air this ratio is generally less than \(\sim 0.01\) but can rise to \(\sim 0.1\). The very low ratio of CCN to CN in continental air is attributable to the large number of very small particles, which are not activated at low supersaturations. Concentrations of CCN over land decline by about a factor of five between the planetary boundary layer and the free troposphere. Over the same height interval, concentrations of CCN over the ocean remain fairly constant or may even increase with height, reaching a maximum concentration just above the mean cloud height. Ground-based measurements indicate that there is a diurnal variation in CCN concentrations, with a minimum at about 6 a.m. and a maximum at about 6 p.m.

The observations just described provide clues as to the origins of CCN. First of all it appears that the land acts as a source of CCN because the concentrations of CCN are higher over land and decrease with altitude. Some of the soil particles and dusts that enter the atmosphere probably serve as CCN, but they do not appear to be a dominant source. The rate of production of CCN from burning vegetable matter is on the order of \(10^{12}–10^{15}\) per kg of material consumed. Thus, forest fires are a source of CCN. About 80% of the particles emitted by idling diesel engines are CCN at 1% supersaturation. About 70% of the particles emitted by the 1991 Kuwait oil fires were CCN at 1% supersaturation. Although sea-salt particles enter the air over the oceans by the mechanisms discussed in Section 5.4.1, they do not appear to be a dominant source of CCN, even over the oceans.

There appears to be a widespread and probably a fairly uniform source of CCN over both the oceans and the land, the nature of which has not been definitely established. A likely candidate is gas-to-particle conversion, which can produce particles up to a few tenths of a micrometer in diameter that can act as CCN if they are soluble or wettable. Gas-to-particle conversion mechanisms that require solar radiation might be responsible for the observed peak in CCN concentrations at \(\sim 6\) p.m. Many CCN consist of sulfates. Over the oceans, organic sulfur from the ocean [in the form of the gases dimethyl sulfide (DMS) and methane sulfonic acid (MSA)] provides a source of CCN, with the DMS and MSA being converted to sulfate in the atmosphere. Evaporating clouds also release sulfate particles (see Section 6.8.9).

### 6.2 Microstructures of Warm Clouds

Clouds that lie completely below the 0°C isotherm, referred to as warm clouds, contain only water droplets. Therefore, in describing the microstructure of warm clouds, we are interested in the amount of liquid water per unit volume of air (called the liquid water content (LWC), usually expressed in grams per cubic meter\(^{16}\)), the total number of water droplets per unit volume of air (called the cloud droplet concentration, usually expressed as a number per cubic centimeter), and the size distribution of cloud droplets (called the droplet size spectrum, usually displayed as a histogram of the number of droplets per cubic centimeter in various droplet size intervals). These three parameters are not independent; for example, if the droplet spectrum is known, the droplet concentration and LWC can be derived.

In principle, the most direct way of determining the microstructure of a warm cloud is to collect all the droplets in a measured volume of the cloud and then to size and count them under a microscope. In the early days of cloud measurements, oil-coated slides were exposed from an aircraft to cloudy air along a measured path length. Droplets that collided with a slide, and became completely immersed in the oil, were preserved for subsequent analysis. An alternative method was to obtain replicas of the droplets by coating a slide with magnesium oxide powder (obtained by burning a magnesium ribbon near the slide). When water droplets collide with these slides they leave clear imprints, the sizes of which can be related to the actual sizes of the droplets. Direct impaction methods, of the type described earlier, bias against smaller droplets, which tend to follow the streamlines around the slide and thereby avoid

\(^{16}\) Bearing in mind that the density of air is approximately \(1 \text{ kg m}^{-3}\), a LWC of \(1 \text{ g m}^{-3}\) expressed as a mixing ratio is approximately the same as \(1 \text{ g kg}^{-3}\).