

# Chapter 8

## Water I. Thermodynamics

### What you need to know for this lecture

Appreciate that water can exist in three phases, liquid, solid, and gas, and understand the physical nature of these three phases in terms of the arrangement of molecules.

### Short summary

Water holds a special place in atmospheric science. The hydrological cycle of transfer of water from surface and oceanic waters, through evaporation and cloud formation and eventually rain formation has a profound effect on the thermodynamics of the atmosphere, its radiative properties and the rates of chemical reactions that remove pollutants. Understanding the conditions under which water changes phase (from ice to liquid to vapour) and the rate at which the transfer between the phases occurs is essential for understanding the properties of clouds.

Descriptions of the behaviour of water in the atmosphere abound in meteorological texts. The terms saturation, dew point, relative and specific humidity, wet bulb temperature, frost point etc are widely known but rarely well understood in terms of basic physics. Water is a pure substance that obeys the laws of thermodynamics and much about the behaviour of water in the atmosphere can be learned by thinking about it in this way.

### What you should know by the end of this lecture

1. What is meant by *evaporation*, *sublimation*, *condensation*, *melting*, and *freezing*.
2. Understand the term *equilibrium* as applied to two or more phases.
3. Understand the concept of *saturation vapour pressure* as the partial pressure of water in equilibrium with either liquid water or ice.
4. Know what is meant by a *phase line*.
5. Know how the saturation vapour pressure of liquid water and ice vary as a function of temperature.
6. Understand the meaning of the terms *saturation*, *subsaturatation* and *supersaturation*.
7. Know what is meant by *relative humidity* and how to calculate it.
8. Understand the term *supercooling* of liquid water.

## 8.1 Three phases of water

Under normal conditions water can exist in three phases—**gas (vapour), liquid, and solid (ice)**. The following formal definition of **phase** will be useful:

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*A **phase** is a state of matter that is uniform throughout, not only in chemical composition but also in physical state.*

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### 8.1.1 Phase transitions

The conversion of one phase into another is known as a **phase change** or **phase transition**. The phase changes of importance in the atmosphere are:

**Evaporation:** Conversion of liquid into vapour.

**Sublimation:** Conversion of ice into vapour.

**Condensation:** Conversion of vapour into either liquid or solid.

**Melting:** Conversion of ice into liquid.

**Freezing:** Conversion of liquid into ice.

### 8.1.2 Latent heat accompanying phase transitions

Heat added to a system leads to an increase in the internal energy of the system. So far, we have simply dealt with cases where this increase in internal energy leads to an increase in the temperature of the system. However, this is not the case where a change of phase can occur.

A change of phase is the conversion of a substance in one state of matter to another and results in the complete reordering of the molecules and any chemical bonds that were holding the molecules together. This reordering of the molecules is associated with a certain amount of energy, known as **latent heat** (literally *hidden* heat).

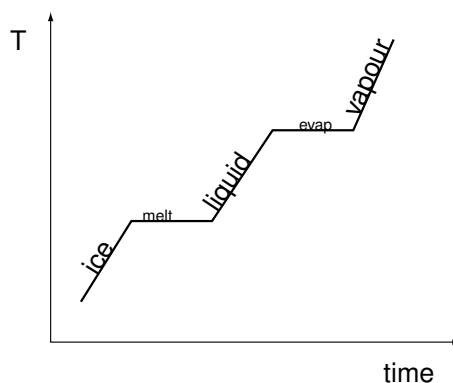


Figure 8.1: The change in temperature of a sample of water being heated from the ice phase through to the vapour phase. Phase changes are marked by the periods of constant temperature

Figure 8.1 shows the change in temperature of water as it is heated at a constant rate through the ice, liquid and vapour phases. Each phase transition is marked by a period at constant temperature where the heat supplied

is being used to effect the phase transition, rather than to increase the temperature of the system. Note that the internal energy continues to rise as heat is added ( $dU = dq$ ), but that during a phase change the internal energy is being used to reorder the molecules and break chemical bonds rather than increase the translational kinetic energy of the molecules (which is temperature).

## 8.2 The equilibrium of water vapour with pure water

Figure 8.2 shows the saturation vapour pressure of water above a *plane, pure* water surface. **Saturation vapour pressure** defines the pressure of water vapour that is required to establish **thermodynamic equilibrium** with the water surface. Thermodynamic equilibrium means three things:

1. The system of liquid and vapour phase water is at **thermal equilibrium**. That is, there are no temperature gradients that would allow heat to flow into the system.
2. The system is at **mechanical equilibrium**. That is, the pressure is constant throughout.
3. The system is at **chemical equilibrium**. Chemical equilibrium is defined in terms of a quantity known as

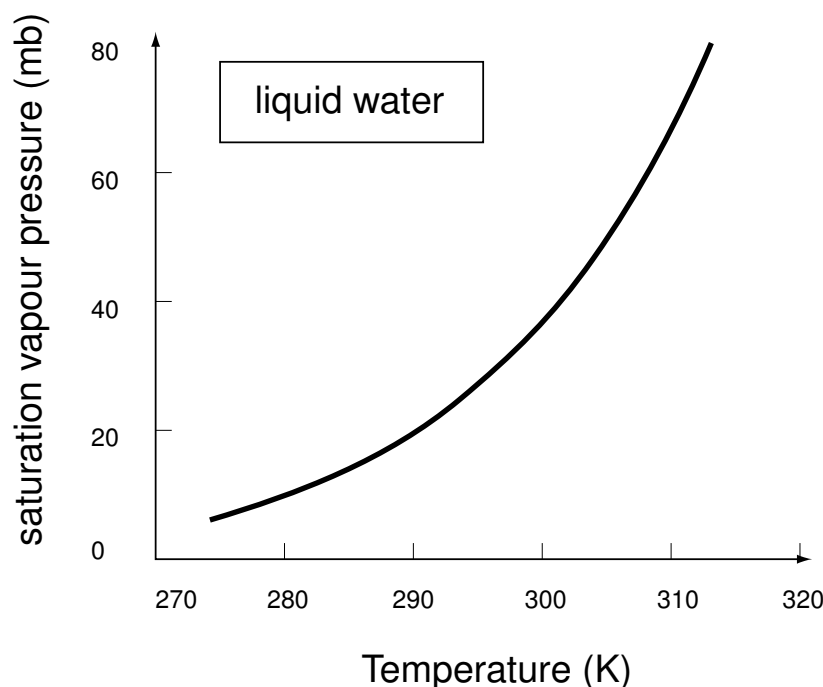


Figure 8.2: The saturation vapour pressure of pure water

*chemical potential* (which is the Gibbs free energy per mole, if you are familiar with this). However, this is beyond the scope of this course. It suffices to state here that two phases are in chemical equilibrium (also known as **phase equilibrium**) when there is **no net transfer of matter between the two phases**. In the case of equilibrium between liquid water and its vapour, this means that as many water molecules are moving from the gas phase into the liquid (condensing) as are moving from the liquid into the gas (evaporating).

There are some important points to note:

1. The words *plane* and *pure* are important in the definition of the saturation vapour pressure because the vapour pressure changes in impure (e.g., salty) water and when the water is in the form of tiny droplets rather than as a bulk liquid (see later lecture).
2. The water molecules in the gas phase may either be on their own (in which case the saturation vapour pressure simply becomes the total atmospheric pressure) or they may be mixed with air molecules (in which case the saturation vapour pressure is the partial pressure of water). There is a caveat: the saturation vapour pressure is a weak function of *total* pressure—that is, the pressure exerted on the liquid by air molecules affects the equilibrium of the liquid with water molecules. This is such a weak effect at atmospheric pressure that it is of no consequence.
3. For a given temperature there is only *one* value for the saturation vapour pressure. Thus, equilibrium between liquid and vapour phase water *fixes* the partial pressure of water in the gas phase. Consider the simple experiment in Figure 8.3 in which a chamber containing air, water vapour and liquid water is compressed at constant temperature. The *air pressure* increases, but the *partial pressure of water* remains constant. In this experiment, water molecules must therefore condense in order to maintain a fixed number density in the gas phase.

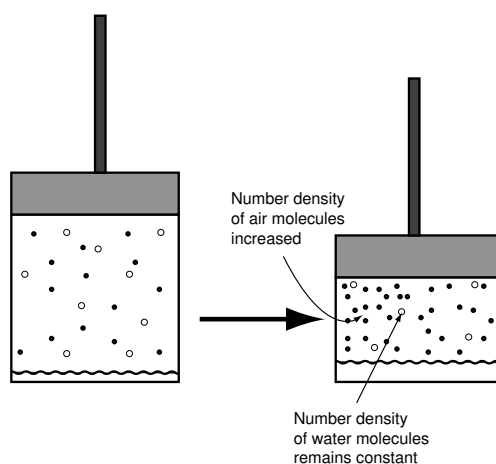


Figure 8.3: Schematic of the changes in partial pressure of air and water vapour in equilibrium with liquid water at a fixed temperature.

### 8.2.1 The Clausius-Clapeyron equation

The **Clausius Clapeyron equation** describes the conditions of pressure and temperature for two phases at equilibrium

$$\frac{dp}{dT} = \frac{l}{T\Delta v} \quad (8.1)$$

For liquid water in equilibrium with water vapour  $p$  is the saturation vapour pressure,  $l$  is the **specific latent heat of evaporation** (units:  $\text{J mol}^{-1}$ ) and  $\Delta v$  is the change in volume accompanying evaporation of one mole of liquid water.  $\Delta v$  is, for all practical purposes, the volume of one mole of water vapour since the volume of one mole of liquid water is negligible. Thus,  $\Delta v$  can be obtained from the ideal gas law

$$\Delta v = \frac{RT}{p_w},$$

where  $p_w$  is the saturation vapour pressure of liquid water. Hence,

$$\frac{d \ln p_w}{dT} = \frac{l}{RT^2} \quad (8.2)$$

This is the differential form of the Clausius-Clapeyron equation that describes the variation of saturation vapour pressure with temperature. It is enormously useful. It is applicable, with relevant values of  $l$ , to equilibrium between any condensed phase and its vapour. This includes the vapour pressure of ice, liquid water, alcohol etc.

## 8.2.2 An equation for the saturation vapour pressure

The integrated form of Equation 8.2 for the saturation vapour pressure of water over a plane, pure water surface is approximately

$$\ln(p_w/\text{mb}) = \ln 6.108 + 17.27(T/\text{K} - 273.16)/(T/\text{K} - 35.86) \quad (8.3)$$

Temperature (K)	$p_w$ (mb)	$p_w$ (Pa)
273.15	6.11	611.0
280	9.93	993.0
290	19.36	1936.0
300	36.09	3609.0
310	64.65	6465.0
320	111.65	11165.0

Table 8.1: The saturation vapour pressure of pure water

**Units of water vapour concentration.** Several units are commonly used for expressing water vapour concentrations in the atmosphere. Similar to other gases, it can be given as a *volume mixing ratio*, *number concentration* or *partial pressure*. However, meteorologists often give the concentration in grams of water per kilogram of air ( $\text{g kg}^{-1}$ ). To convert  $x \text{ g kg}^{-1}$  into something useful, like a partial pressure, do the following:  $x \text{ g water vapour} = x \text{ g}/18 \text{ g mol}^{-1}$  moles of water vapour and 1 kg of air is  $1 \text{ kg}/29 \times 10^{-3} \text{ kg mol}^{-1}$  moles of air, so the water vapour molecular mixing ratio ( $N_w/N_{\text{air}}$ ) is  $(x/18)/(1/29 \times 10^{-3})$ . The water partial pressure is therefore  $p_{\text{air}}(N_w/N_{\text{air}})$ .

The saturation vapour pressure increases exponentially, and rather steeply, with increasing temperature. For example, the increase in saturation water vapour pressure associated with increasing the temperature of water from  $0^\circ\text{C}$  to  $30^\circ\text{C}$  (approximately the change associated with moving from the Arctic to the tropical oceans) is approximately a factor of 7.

To get a feel for the importance of the change in saturation vapour pressure with temperature, consider the following common experience:

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**EXAMPLE 11** *Condensation on a window.* If a room at  $20^\circ\text{C}$  contains  $10 \text{ g kg}^{-1}$  of water vapour, calculate the temperature of a window at which condensation begins to appear ( $10 \text{ g kg}^{-1}$  water vapour is equivalent to a water partial pressure of  $1340 \text{ Pa}$ ).

We want to find the temperature at which the saturation vapour pressure in Equation 8.3 is equal to  $1340 \text{ Pa}$ . Rearranging Equation 8.3

$$T = \frac{35.86 \ln p_w - 35.86 \ln 6.108 - 17.27 \times 273.16}{\ln p_w - \ln 6.108 - 17.27}$$

gives  $T = 284.4\text{K}$ , or  $11.25^\circ\text{C}$ . This is also the temperature at which dew would form on grass during the night. This calculation therefore defines the **dew point**.

### 8.2.3 The concept of a phase line

When water vapour and liquid water coexist at equilibrium, the partial pressure of water is uniquely defined at a given temperature—it is the saturation vapour pressure. Thus, the line on Figure 8.2 can be considered as a **phase line**. As temperature is changed, the partial pressure of water will simply move up and down this line. Figure 8.4 shows the variation of the water partial pressure as air is cooled isobarically. Initially, the

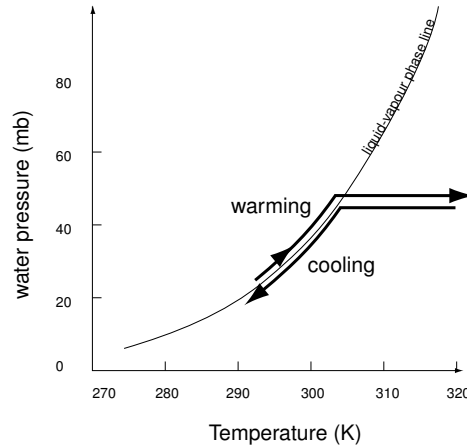


Figure 8.4: The saturation vapour pressure can be considered as a ‘phase line’. The ambient water partial pressure moves up and down this line whenever liquid water and vapour coexist. When liquid water doesn’t exist, above the dew point, the water partial pressure is constant (for constant total air pressure).

partial pressure is *lower* than the saturation vapour pressure, so only water vapour exists. At the **dew point temperature**, saturation is reached and liquid water can begin to condense. With further cooling, the water partial pressure will then move along the phase line describing equilibrium between liquid and vapour. With increasing temperature, the water partial pressure undergoes the same changes in reverse.

### 8.2.4 Subsaturation and supersaturation

At the temperature of 20 °C in Example 1 the air is said to be **subsaturated** with respect to water vapour – that is, the ambient water partial pressure is *lower* than the saturation vapour pressure. If liquid water did exist at this temperature it would evaporate. Below 11.25 °C, the air is said to be **supersaturated** with respect to water vapour - that is, the ambient water partial pressure is *higher* than the saturation vapour pressure. Under supersaturated conditions water vapour can condense. The **saturation ratio** is defined by

$$S = \frac{p}{p_w} \quad (8.4)$$

$$S > 1 \text{ for supersaturation} \quad (8.5)$$

$$S < 1 \text{ for subsaturation} \quad (8.6)$$

where  $p$  is the ambient partial pressure of water.

DEFINITION: RELATIVE HUMIDITY The percentage relative humidity is often used in meteorology. This is simply

$$\%RH = 100 \times S = 100 \times \frac{p}{p_w} \quad (8.7)$$

Experiments show that water does not appear at the temperature predicted by the equilibrium line in Figure 8.2. Unless suitable impurities are present in the vapour or on the walls of a container, water supersaturates upon cooling. This means that in the example above, water would not appear at 11.25 °C upon cooling from 20 °C, but would condense only at some lower temperature. Below the saturation temperature, the supersaturated water vapour is in a **metastable state**. The reverse process is very rare – that is, it is virtually impossible to superheat water.

Note that in the atmosphere, water vapour is rarely in thermodynamic equilibrium with liquid water, but more likely either sub- or supersaturated—that is, water is usually either evaporating or condensing: droplets are growing and shrinking in clouds, water is evaporating from puddles or condensing on walls in the bathroom etc. There are two reasons for this: firstly, the Clausius-Clapeyron equation reveals that for any given temperature, there is only *one* saturation vapour pressure. Conversely, for a given amount (partial pressure) of water vapour in the gas phase, there is only a single temperature at which this water vapour can establish equilibrium with water. The second reason is that the atmosphere is an open system and not a closed box. Water vapour and temperature are always varying, so water vapour is almost perpetually seeking, but rarely finding, equilibrium.

The rate at which water evaporates or condenses is determined by the difference between the saturation vapour pressure and the ambient water vapour partial pressure. This is dealt with in a later lecture.

### 8.3 The equilibrium of water vapour with pure ice

Figure 8.5 shows the saturation vapour pressure of water above a plane, pure ice surface. The saturation vapour pressure defines the pressure of water vapour that is required to establish thermodynamic equilibrium with the ice surface. In this state, as many molecules are leaving the ice surface as are being absorbed by it (on average). The equation describing the saturation vapour pressure over ice as a function of temperature is

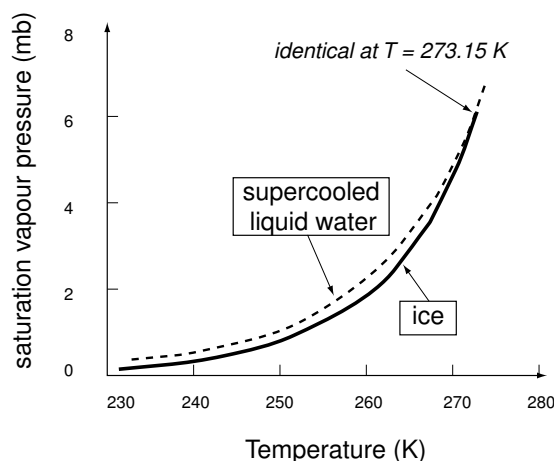


Figure 8.5: The saturation vapour pressure of pure ice (solid line) and pure liquid supercooled water (dashed line).

$$\frac{d \ln p_{\text{ice}}}{dT} = \frac{l_s}{RT^2}, \quad (8.8)$$

where  $l_s$  is the **latent heat of sublimation** (conversion of ice into vapour). An approximate integrated form of this equation is

$$\ln(p_i/\text{mb}) = \ln 6.108 + 21.87(T - 273.16)/(T - 7.66) \quad (8.9)$$

This is very similar to the equation for water vapour in equilibrium with liquid water. The small difference turns out to be one of the most important factors determining the behaviour of clouds (more on this later).

Below 273.15 K, water vapour can convert directly into ice (and vice versa) without going through the liquid phase. A common experience of this is hoar frost on the grass (resulting from conversion of water vapour to ice crystals).

## 8.4 The equilibrium of liquid water and ice

The equilibrium of liquid water and ice is not a particularly interesting or important one in the atmosphere in comparison to the equilibrium between water vapour and either ice or liquid water. The **melting temperature** at 1 Atm total pressure is 273.15 K. This is the temperature at which ice and liquid water can coexist at equilibrium, and that is the end of the story. Liquid water and ice cannot coexist in equilibrium over a wide range of temperatures as can water vapour and ice, for example. The reason for this can be seen in the Clausius-Clapeyron equation in the form

$$\frac{dT_m}{dp} = \frac{T\Delta V}{l}, \quad (8.10)$$

where  $T_m$  is the melting temperature.  $\Delta V$ , the volume change per mole accompanying the transition from ice to liquid water, is very small indeed. Ice is an anomalous solid in that its specific volume (volume per mole of water) is greater than that of water. Hence,  $dT_m/dp$  is negative; that is, the melting temperature *decreases* with increasing total pressure! The small magnitude of  $\Delta V$  ensures that the effect is small however:

$$\frac{dT_m}{dT} = -0.0076 \text{ Katm}^{-1}. \quad (8.11)$$

This implies that the melting temperature of ice decreases by 0.0075 K for every 1 atm increase in pressure. To melt ice at -10 °C would require 1100 Atm pressure to be exerted on ice. Hence it is clear why this effect is not very important in the atmosphere! Even in the upper atmosphere, where  $p$  is about 50 mb (effectively 0), the melting temperature would be 273.16 K.

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AN ASIDE: This is where the confusion often starts in understanding the phase transitions of water. Why did we use the Clausius-Clapeyron equation to derive an equation relating the *vapour pressure* of liquid water as a function of temperature, but we now use it to derive an equation relating the *total pressure* to the ice melting temperature? We can answer this temperature loosely in the following way. As mentioned before, the total pressure *does* affect the equilibrium between liquid water and its vapour, but we ignored it as being a small effect. How small? Well, we ignored the small change in  $\Delta V$  in equation 8.1 that arises due to the change in the liquid volume as a function of pressure (the compressibility of the liquid). Remember that  $\Delta V$  is the change in volume of the system accompanying evaporation of liquid water. The volume of the water vapour doesn't change with air pressure, and we ignored the change in liquid volume with external pressure, making  $\Delta V$  just a function of temperature. Things are slightly different for the equilibrium between ice and liquid water. Now, the change in



volume accompanying the phase transition is tiny, making the small alteration in  $\Delta V$  due to pressure changes much more significant. Thus, the equilibrium between ice and liquid water is controlled by mechanical pressure, while that between liquid water and its vapour is not.

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EXAMPLE 12 *An ice skater can use this property of ice to create a film of water under the skates, thus making the ice slippery. Assuming the ice surface is at  $-2^\circ\text{C}$ , a pressure of  $2.6 \times 10^7$  Pa would be required to depress the melting point to this temperature (according to Equation 8.11). Assuming a skater of mass 70 kg (hence a downward force of 700 N) the appropriate pressure could be exerted by having a contact area with the ice of  $0.25\text{ cm}^2$  ( $25\text{ mm}^2$ ), which is probably not far off the contact achieved between an ice skate and the ice surface. It is also believed that an ice surface has an inherent ‘slipperyness’ due to the change in the molecular structure close to the interface between the ice and the vapour. That’s another fascinating story.*

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## Questions for understanding

1. Define the terms dew point, frost point, supersaturation, and relative humidity. What is meant by one phase being metastable with respect to another?
2. Calculate the dew point in air containing  $5 \text{ g m}^{-3}$  water vapour at an atmospheric pressure of 1000 mb and an initial temperature of 298 K (the dew point is defined as the temperature at which air reaches saturation when cooled isobarically).
3. Explain in qualitative terms how you would expect the water content of the atmosphere to vary with altitude and latitude.
4. The tropopause is the region of the atmosphere separating the troposphere and stratosphere and occurs at about 17 km altitude or about 100 mb pressure in the tropics. Air passes through the tropical tropopause on its way into the stratosphere and gets dried to the ice saturation vapour pressure as it passes through a layer of cirrus clouds. If the temperature at the tropopause is about 190 K, calculate the mixing ratio of water vapour entering the stratosphere under these conditions.
5. Air at  $0 \text{ }^\circ\text{C}$  has a water partial pressure of 4 mb. Would a puddle of water evaporate or not under these conditions?
6. Water vapour in a sealed container is brought into equilibrium with a piece of ice at  $-2 \text{ }^\circ\text{C}$ . The container is then opened and water droplets are sprayed in. Is the water partial pressure above the water droplets supersaturated or subsaturated with respect to ice? What will eventually happen to the water droplets, assuming that they don't freeze?