

## CHAPTER SIX

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# Water and its transformations

The fundamental equations derived in the previous chapter can only be applied to closed systems (i.e. to systems that do not exchange mass) that are homogeneous (i.e. they involve just one phase). In such cases we do not need to specify how thermodynamic functions depend on the composition of the system. Only two independent variables ( $T$  and  $p$ , or  $p$  and  $V$ , or  $p$  and  $T$ ) need to be known. Since the total mass ( $m$ ) remains constant, if we know the values of the extensive variables per unit mass we can extend the equations to any mass by multiplying by  $m$  or by  $n$  (the number of moles).

A heterogeneous system involves more than a single phase. In this case we are concerned with the conditions of internal equilibrium between the phases. Even if the heterogeneous system is assumed to be (as a whole) a closed system the phases constitute homogeneous but open “subsystems” which can exchange mass between them. In this case the fundamental equations must be modified to include extra terms to account for the mass exchanges. These extra terms involve a function  $\mu$  called the chemical potential,  $\mu = \mu(T, p)$ . We will not go into the details of defining  $\mu$ ; we will only accept that in the case of open systems something else must be included to account for the heterogeneity of the system. In this book we are concerned with a heterogeneous system that involves dry air ( $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{CO}_2$ ,  $\text{Ar}$ ) and water, with the water existing in vapor and possibly one of the condensed phases (water or ice). Then one component of the system is the dry air (which is assumed to remain always unchanged and in a gaseous state) and the other component is the water substance which can exist in two phases. Thus dry air is a closed system whereas the two phases are two open systems. The system composed of dry air, water vapor, liquid water, and ice is also of interest but it is quite unstable and as a result it cannot exist in equilibrium.

## 6.1 Thermodynamic properties of water

In this chapter we will put aside dry air and we will concentrate on the one-component heterogeneous system “water” comprised of vapor and one of the condensed phases. Water vapor, like dry air, can be treated to a good approximation as an ideal gas. Accordingly, water vapor obeys the equation of state and if it existed only by itself its states would be determined by two independent variables. When, however, water vapor coexists with liquid water or ice things become a little complicated (or less complicated depending on the point of view). In this case, the mixture does not constitute an ideal gas and the equations applicable to ideal gases do not apply. One phase requires two independent variables ( $p$  and  $T$ ) and the other phase two more ( $p'$  and  $T'$ ). Then, equilibrium between the phases will require that  $p = p'$  and  $T = T'$ . However, since the mass of each open subsystem does not remain constant another criterion for equilibrium must be considered. This criterion is given by  $\mu = \mu'$  and expresses equilibrium in the terms responsible for the mass exchange. Accordingly, for equilibrium between the two phases the following three constraints must be satisfied:

$$p = p'$$

$$T = T'$$

$$\mu = \mu'.$$

The first two equations reduce the number of independent variables to two (say  $p$  and  $T$ ). Then, the third equation  $\mu = \mu(p, T) = \mu'(p', T') = \mu'(p, T)$  reduces the number of independent variables by one more. Since  $\mu(p, T) = \mu'(p, T)$  it follows that  $p = f(T)$ . Thus, if we fix the temperature at which the phases exist in equilibrium the value of pressure also becomes fixed. This defines curves along which equilibrium between two phases can exist. We conclude that in the case of a one-component system involving two phases in equilibrium the number of independent variables (otherwise known as degrees of freedom) is one, not four.

Let us now consider the case of a one-component system involving all its phases (vapor, liquid, solid). Following the same arguments as above the following constraints must be satisfied for equilibrium

$$p = p' = p''$$

$$T = T' = T''$$

$$\mu = \mu' = \mu''.$$

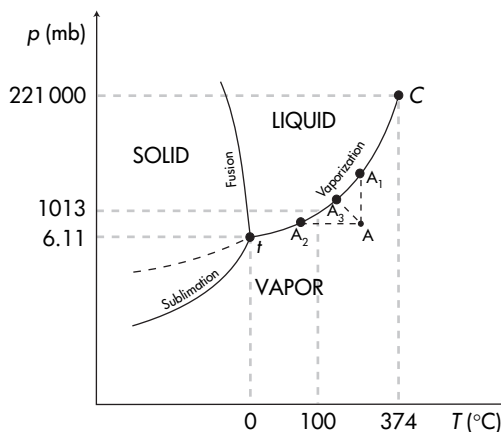
Then the first two equations reduce the number of independent variables from six to two. The first equality of the third equation reduces them by one more and the second equality by yet one more.

Thus, we remain with zero independent variables, meaning that all values are fixed, which implies that coexistence of all phases at equilibrium requires just a point, called the triple point, in the  $p, V, T$  state space. It follows that the greater the number of phases the fewer the degrees of freedom. The following formula suggested by Gibbs generalizes the above as it gives the number of independent state variables,  $N$ , for a heterogeneous system involving  $C$  different and non-reactive components in a total of  $P$  phases:

$$N = C + 2 - P. \quad (6.1)$$

Figure 6.1 shows the triple point for water as well as the curves  $p = f(T)$  representing the phase transition equilibria. We call the three equilibria vaporization (gas  $\leftrightarrow$  liquid), fusion (liquid  $\leftrightarrow$  ice), and sublimation (gas  $\leftrightarrow$  solid). Along the curves for vaporization and sublimation, vapor is in equilibrium with water and ice, respectively. As such these curves provide the equilibrium vapor pressure for water and ice. Vapor in equilibrium with a condensed phase is often called *saturated* and the corresponding equilibrium vapor pressure is called *saturation vapor pressure*. There is no real distinction between the two terms. Note that the extension of the vaporization curve to temperatures below the triple point corresponds to supercooled water, with vapor pressure over supercooled water being greater than that over ice. This is a metastable equilibrium where supercooled water and water vapor coexist. Here the system of supercooled water and water vapor may be stable with respect to small changes in temperature and pressure but introduction of ice in the system makes it unstable and as a result water freezes. The triple point corresponds to  $p_t = 6.11$  mb and  $T = 273$  K (more accurately 273.16 K). Because of the different densities of liquid water, ice, and water vapor, the specific volumes for liquid

**Figure 6.1**  
Phase-transition equilibria  
for water.



water,  $a_w$ , ice,  $a_i$ , and water vapor,  $a_v$ , at the triple point are:

$$a_w = 1.000 \times 10^{-3} \text{ m}^3 \text{ kg}^{-1}$$

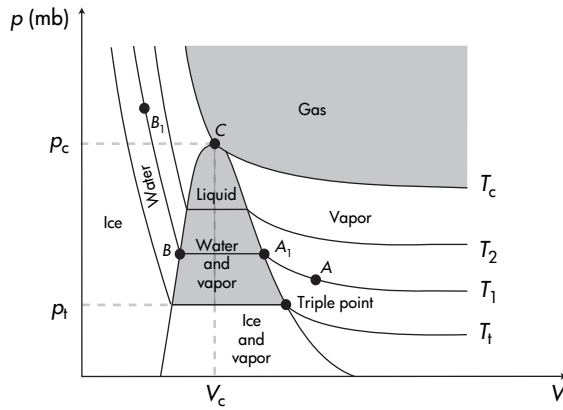
$$a_i = 1.091 \times 10^{-3} \text{ m}^3 \text{ kg}^{-1}$$

$$a_v = 206 \text{ m}^3 \text{ kg}^{-1}.$$

An interesting feature of Figure 6.1 is that the vaporization curve ends at point  $C$  where the temperature ( $T_C$ ) is  $374^\circ\text{C}$  and the pressure ( $p_C$ ) is approximately  $2.21 \times 10^5$  mb. Beyond this critical point there is no line to separate liquid from vapor. Otherwise stated, beyond point  $C$  there is no discontinuity between the liquid and the gaseous phase. This indicates that beyond point  $C$  we cannot differentiate between the liquid and the vapor phase. In order to understand the significance of critical point  $C$  let us consider point  $A$  representing the temperature and the pressure of a sample of water vapor below critical point  $C$ . If we decrease the volume while keeping the temperature constant the pressure increases until it becomes equal to the pressure at point  $A_1$  where it will condense. Similarly, if we keep the pressure constant and cool the gas until its temperature becomes equal to the temperature corresponding to point  $A_2$ , the gas will condense. Obviously the gas will condense if we perform any intermediate process described by line  $AA_3$ . Thus, there are three ways by which the gas can become liquid. We either have to cool it at constant pressure or compress it at constant temperature or simultaneously compress it and cool it. All three ways require crossing the equilibrium line. The fact that there is an end to the vaporization curve means that above  $T_C$  we cannot liquefy a gas by compressing it at a constant temperature and that above  $p_C$  we cannot liquefy a gas by cooling it at a constant pressure. Because in our atmosphere temperature and pressure are well below the critical point, water vapor can condense. For the other gases in the atmosphere ( $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{Ar}$ ) the critical temperatures are very low ( $-147^\circ\text{C}$ ,  $-119^\circ\text{C}$ ,  $-122^\circ\text{C}$ , respectively) and so they do not condense.

Let us now consider phase changes along isotherms in the ( $p, V$ ) domain. Such a domain (shown in Figure 6.2) is called an Amagat–Andrews diagram. We start with a sample of water vapor at a state corresponding to point  $A$  in Figure 6.1 (i.e. at a temperature  $T_1$  and pressure  $p_1$  greater than the triple point temperature  $T_t$  and pressure  $p_t$ ). If we compress the vapor isothermally the pressure increases until we reach point  $A_1$ . At this point liquid water and water vapor coexist in equilibrium. This means that some water vapor has condensed to form liquid water and that liquid and vapor are in equilibrium. Now what will happen if we further compress the vapor? Since we are on the equilibrium curve the pressure of the vapor depends

**Figure 6.2**  
An Amagat–Andrews  
diagram.



only on temperature. As such, since the transformation is isothermal, as long as liquid and vapor coexist a further decrease in volume cannot change the pressure. Do not get confused here. The ideal gas law *does not* apply to the mixture. Thus, if we keep on compressing the vapor we will observe that more vapor condenses to form liquid water (with liquid and vapor being always in equilibrium) until we reach point  $B$  where all vapor is condensed. This part will be represented in the  $(p, V)$  diagram by the horizontal (constant  $p$ ) stretch  $A_1B$ . A further (small) compression causes the liquid water's pressure to increase rapidly (owing to the low compressibility of liquids). This part is indicated by the segment  $BB_1$ . The complete isotherm is depicted in Figure 6.2 by the line  $AA_1BB_1$ . For higher temperatures we observe that the horizontal stretch of the isotherms decreases until it reduces to a point. This is the point  $C$  corresponding to the critical state  $T_c, p_c, V_c$ . The isotherms above the critical temperature are monotonic decreasing functions with no discontinuity. They go over into equilateral hyperbolas which is how ideal gases behave. For temperatures below  $T_1$  the horizontal stretch of the isotherms increases. A solid line in Figure 6.2 connects the beginning and end points of the horizontal stretches. This line together with the critical isotherm and the isotherm corresponding to the triple point temperature ( $T_t$ ) partition the diagram into six regions: vapor, gas, liquid water, ice, liquid water plus vapor, and ice plus vapor. Here the distinction between gas and vapor reflects only the fact that above  $T_c$  no two-phase discontinuity for condensation exists.

## 6.2 Equilibrium phase transformations – latent heat

In the case of a *homogeneous* system undergoing an isobaric transformation that does not result in a phase change the heat

exchanged is proportional to the temperature change (the proportionality constant is  $C_p$ ). In the case of a *heterogeneous* system involving two phases we say that when the two phases are in equilibrium a fixed temperature implies a fixed pressure, meaning that isobaric transformations are also isothermal transformations. Thus, even though the masses of the two phases change, the temperature of the system does not (recall the horizontal stretches in Figure 6.2). In such cases, the amount of heat exchanged depends only on mass changes (which modify the internal energy of each subsystem) and on the work done owing to possible volume changes (the volume can change because the mixture does not obey the ideal gas law). By definition, the latent heat,  $L$ , of a transformation is the heat absorbed (or given away) by the system during an isobaric phase transition

$$L = \delta Q_p = \text{constant}.$$

Recall that enthalpy is defined as  $H = U + pV$ . Differentiation of this equation gives  $dH = dU + pdV + Vdp$ . Since the change of phase takes place at a constant pressure it follows that  $dH = dU + pdV$ . The right-hand side of this equation is according to the first law equal to  $\delta Q$ . It follows that

$$L = dH. \quad (6.2)$$

Thus, the latent heat of a phase change is the change in enthalpy during the transformation. The latent heats of vaporization (liquid  $\leftrightarrow$  vapor), fusion (ice  $\leftrightarrow$  liquid), and sublimation (ice  $\leftrightarrow$  vapor) are denoted by  $L_v$ ,  $L_f$ , and  $L_s$ , respectively. Note that the above latent heats are positive when during the transformation heat is absorbed (liquid  $\rightarrow$  vapor, ice  $\rightarrow$  liquid, ice  $\rightarrow$  vapor) and negative when heat is released (vapor  $\rightarrow$  liquid, liquid  $\rightarrow$  ice, vapor  $\rightarrow$  ice).  $L_v$ ,  $L_f$ , and  $L_s$  are also called the enthalpy of vaporization, fusion, and sublimation, respectively. According to the above,

$$\begin{aligned} L_v &= H_v - H_w = U_v - U_w + p_{wv}(V_v - V_w) \\ L_f &= H_w - H_i = U_w - U_i + p_{wi}(V_w - V_i) \\ L_s &= H_v - H_i = U_v - U_i + p_{vi}(V_v - V_i) \end{aligned} \quad (6.3)$$

where here  $p$  stands for the equilibrium pressure between two phases. At the triple point  $p_{wv} = p_{vi} = p_{wi} = 6.11$  mb. It follows that at the triple point the specific latent heats  $l_v$ ,  $l_f$ , and  $l_s$  satisfy the relationship  $l_s = l_f + l_v$ . Obviously, the latent heats depend on temperature (see Table A.3). Nevertheless, in the range of temperatures observed in the troposphere they do not vary significantly. Because of that it is often assumed that the latent heats are independent of temperature. It is easy to show that the first law in the case of an isobaric change of phase can be written as  $dU = L - pdV$ . For fusion  $dV \approx 0$  and for vaporization and sublimation

$dV = V_{\text{vapor}} - V_{\text{liquid water or ice}} \approx V_{\text{vapor}}$ . Thus, the first law reduces to

$$\begin{aligned} dU &= L && \text{for fusion} \\ dU &= L - mR_v T && \text{for vaporization or sublimation} \end{aligned} \quad (6.4)$$

where  $R_v$  is the gas constant for water vapor.

### 6.3 The Clausius–Clapeyron (C–C) equation

Before we proceed and to avoid confusion with too many subscripts we need to make a change in our notation. From now on we shall represent the water vapor pressure as  $e$ . Furthermore, during phase transitions the equilibrium (saturation) vapor pressure over water will be denoted as  $e_{\text{sw}}$  and equilibrium vapor pressure over ice will be denoted as  $e_{\text{si}}$ .

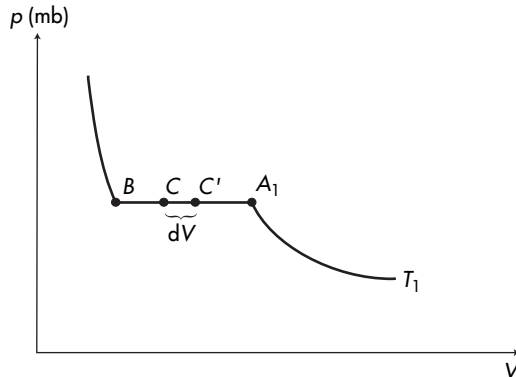
For an ideal gas we saw how the equation of state  $p = f(V, T)$  relates changes of pressure, temperature, and volume. In the case of a heterogeneous system involving two phases we saw that  $p = e_s = f(T)$ . Does this indicate that a relationship similar to the equation of state for ideal gases exists for heterogeneous systems? Let us consider the transformation described by isothermal  $T_1$  in Figure 6.2 and focus our attention on segment  $A_1B$ . Going from  $A_1$  to  $B$  a change of phase takes place (vapor  $\rightarrow$  liquid). As we discussed before, between  $A_1$  and  $B$  vapor is in equilibrium with liquid water and  $p = e_{\text{sw}} = f(T)$ . Because of that any other state variable or function is a function of temperature only. Let us assume that at point  $C$  (Figure 6.3) the mass of the liquid phase is  $m_w$  and the mass of the vapor phase is  $m_v$ . Then the total volume and internal energy of the system at point  $C$  are

$$V = m_w a_w + m_v a_v$$

$$U = m_w u_w + m_v u_v$$

**Figure 6.3**

The isotherm  $T_1$  of Figure 6.2. For any given change  $C \rightarrow C'$  the change in volume is  $dV$ . This causes an amount  $dm$  of liquid water to evaporate.



where  $a_w, a_v, u_w, u_v$  are the specific volumes and internal energies of the two phases. Now assume that the system moves from  $C$  to  $C'$ . This change corresponds to a change in volume  $dV$  and causes an amount  $dm$  of liquid to evaporate. The volume at point  $C'$  will be

$$V + dV = (m_w - dm)a_w + (m_v + dm)a_v$$

or using the previous equation

$$dV = (a_v - a_w)dm. \quad (6.5)$$

Similarly

$$dU = (u_v - u_w)dm. \quad (6.6)$$

Recall from equation (6.3) that during this change

$$u_v - u_w + e_{sw}(a_v - a_w) = l_v. \quad (6.7)$$

Dividing equation (6.6) by (6.5) yields

$$\frac{dU}{dV} = \frac{u_v - u_w}{a_v - a_w}$$

or using equation (6.7)

$$\frac{dU}{dV} = \frac{l_v}{a_v - a_w} - e_{sw}. \quad (6.8)$$

Here is as good a place as any to restate that while general definitions such as the first law (equation (4.5)), the second law (equation (5.12)), enthalpy ( $H = U + pV$ ), specific heat (equation (4.14)), etc. are valid for any system, variations or expressions derived using the ideal gas law (for example, equations (4.22) and (4.18)) *are not* valid for any system but ideal gases. According to problem 6.1, for any system

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial p}{\partial T}\right)_V - p. \quad (6.9)$$

Also, according to problem 6.2, *for an ideal gas*  $(\partial U/\partial V)_T = 0$  (Joule's law). However, water in equilibrium with its vapor is not an ideal gas and  $U$  and  $e_{sw}$  are functions of temperature only. Then since the transformation is isothermal we can write that

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{dU}{dV}$$

and

$$\left(\frac{\partial e_{sw}}{\partial T}\right)_V = \frac{de_{sw}}{dT}.$$

Accordingly, equation (6.9) becomes

$$\frac{dU}{dV} = T \frac{de_{sw}}{dT} - e_{sw}.$$



Combining this equation with equation (6.8) yields

$$T \frac{de_{sw}}{dT} - e_{sw} = \frac{l_v}{a_v - a_w} - e_{sw}$$

or

$$\frac{de_{sw}}{dT} = \frac{l_v}{T(a_v - a_w)}. \quad (6.10)$$

Equation (6.10) is called the Clausius–Clapeyron (C–C) equation. In its general form,

$$\frac{de_s}{dT} = \frac{l}{T\Delta a}, \quad (6.11)$$

it relates the equilibrium pressure between two phases to the temperature of the heterogeneous system. Here  $l$  is the specific latent heat (or specific enthalpy) of the change of phase and  $\Delta a$  is the difference in the specific volumes between the two phases at temperature  $T$ . It is for heterogeneous systems what the equation of state is for ideal gases.

## 6.4 Approximations and consequences of the C–C equation

### • Temperature dependence of enthalpy of vaporization

By differentiating equation (6.3) we have

$$\frac{\partial L_v}{\partial T} = \frac{\partial H_v}{\partial T} - \frac{\partial H_w}{\partial T} = C_{pv} - C_{pw}$$

where  $C_{pv}$  and  $C_{pw}$  are the heat capacities at constant pressure for vapor and liquid water, respectively. Since  $L_v$  is the enthalpy difference between the vapor and liquid water phases at equilibrium, it depends only on temperature. As such the above equation can be written as

$$\frac{dL_v}{dT} = C_{pv} - C_{pw}. \quad (6.12)$$

For a wide range of temperatures ( $-20^\circ\text{C}$  to  $30^\circ\text{C}$ ),  $C_{pv}$  and  $C_{pw}$  vary very little (about 1%). Because of that we can consider them independent of temperature and integrate equation (6.12) to get

$$L_v = L_{v0} + (C_{pv} - C_{pw})(T - T_0)$$

or

$$l_v = l_{v0} + (c_{pv} - c_{pw})(T - T_0) \quad (6.13)$$

where  $l_{v0}$  is the specific latent heat of vaporization at the reference state  $T_0$ . For the reference state  $T_0 = 273\text{ K}$  with  $l_{v0} = 2.5 \times 10^6 \text{ J kg}^{-1}$ ,  $c_{pv} = 1850 \text{ J kg}^{-1} \text{ K}^{-1}$ , and  $c_{pw} = 4218 \text{ J kg}^{-1} \text{ K}^{-1}$ ,

equation (6.13) provides a very good approximation of  $l_v$  over the range from  $-20^\circ\text{C}$  to  $30^\circ\text{C}$ .

We can repeat the above for sublimation and fusion to arrive at

$$\begin{aligned}\frac{dL_s}{dT} &= C_{pv} - C_{pi} \\ \frac{dL_f}{dT} &= C_{pw} - C_{pi}\end{aligned}$$

or

$$\begin{aligned}l_s &= l_{s0} + (c_{pv} - c_{pi})(T - T_0) \\ l_f &= l_{f0} + (c_{pw} - c_{pi})(T - T_0).\end{aligned}\tag{6.14}$$

Recall that the specific heat for constant volume is  $c_v = \delta q/dT$ . Since water vapor is considered an ideal gas (recall Joule's law), it follows that

$$c_{V_v} = \frac{\delta q}{dT} = \frac{du_v}{dT}.$$

For liquid water (not an ideal gas)

$$c_{V_w} = \frac{\delta q}{dT} = \frac{du_w}{dT} + p \frac{da_w}{dT}.$$

Since  $a_w$  varies very little with  $T$  the above equation reduces to

$$c_{V_w} = \frac{du_w}{dT}.$$

Similarly, for ice  $c_{Vi} = du_i/dT$ . Now since  $h = u + pa$  it follows that for water vapor  $c_{pv} = dh_v/dT = du_v/dT + R_v$ . Therefore for water vapor  $c_{pv} \neq c_{V_v}$ . Liquid water and ice do not behave as ideal gases. Therefore  $pa \neq RT$ . In this case

$$c_{pw} = \frac{dh_w}{dT} = \frac{du_w}{dT} + p \frac{da_w}{dT} + a_w \frac{dp}{dT} \approx \frac{du_w}{dT}$$

(because  $dp = 0$  and  $da_w/dT \approx 0$ ). Thus,  $c_{pw} \approx c_{V_w} = c_w$ . Similarly  $c_{pi} \approx c_{Vi} = c_i$ . Using the values of  $c_{pv}$ ,  $c_{V_v}$ ,  $c_w$ , and  $c_i$  at  $T = 0^\circ\text{C}$  (1850, 1390, 4218, and  $2106 \text{ J kg}^{-1} \text{ K}^{-1}$ , respectively) and using equations (6.13) and (6.14) we find that

$$\frac{dl_v}{dT} \approx -2368 \text{ J kg}^{-1} \text{ K}^{-1}$$

$$\frac{dl_s}{dT} \approx -256 \text{ J kg}^{-1} \text{ K}^{-1}$$

$$\frac{dl_f}{dT} \approx 2112 \text{ J kg}^{-1} \text{ K}^{-1}.$$

These rates are small compared with the values of  $l_v$ ,  $l_s$ , and  $l_f$  at  $0^\circ\text{C}$  ( $2.5 \times 10^6$ ,  $2.834 \times 10^6$ , and  $0.334 \times 10^6 \text{ J kg}^{-1} \text{ K}^{-1}$ , respectively).

We can thus conclude that all latent heats vary very little with temperature. As such the above equations justify approximating  $l_v$ ,  $l_s$ , and  $l_f$  as constants. An improvement to this approximation is given by equations (6.13) and (6.14) which express them as linear functions of  $T$ .

• **Temperature dependence of equilibrium (saturation) vapor pressure**

In the case of vaporization,  $a_v \gg a_w$  and C-C equation can be approximated as

$$\frac{de_{sw}}{dT} = \frac{l_v}{T a_v}. \quad (6.15)$$

By combining equations (6.15) and (6.13) and considering vapor as an ideal gas (i.e.  $e_{sw} a_v = R_v T$ ) we obtain

$$\frac{1}{e_{sw}} \frac{de_{sw}}{dT} = \frac{l_{v0} + (c_{pw} - c_{pv})T_0}{R_v T^2} - \frac{c_{pw} - c_{pv}}{R_v T}$$

or

$$\int_{e_{sw} \text{ at } T_0}^{e_{sw} \text{ at } T} \frac{de_{sw}}{e_{sw}} = \frac{l_{v0} + (c_{pw} - c_{pv})T_0}{R_v} \int_{T_0}^T \frac{dT}{T^2} - \frac{c_{pw} - c_{pv}}{R_v} \int_{T_0}^T \frac{dT}{T}$$

or

$$\ln \frac{e_{sw}}{e_{s0}} = \frac{l_{v0} + (c_{pw} - c_{pv})T_0}{R_v} \left( \frac{1}{T_0} - \frac{1}{T} \right) - \frac{c_{pw} - c_{pv}}{R_v} \ln \frac{T}{T_0}.$$

Considering as the reference state the triple point where  $T_0 = 0^\circ\text{C}$ ,  $e_{s0} = 6.11 \text{ mb}$ ,  $l_{v0} = 2.5 \times 10^6 \text{ J kg}^{-1}$ ,  $c_{pv} = 1850 \text{ J kg}^{-1} \text{ K}^{-1}$ , and  $c_{pw} = 4218 \text{ J kg}^{-1} \text{ K}^{-1}$  the above equation reduces to

$$\ln \frac{e_{sw}}{e_{s0}} = 6808 \left( \frac{1}{T_0} - \frac{1}{T} \right) - 5.09 \ln \frac{T}{T_0}$$

or

$$e_{sw} = 6.11 \exp \left( 53.49 - \frac{6808}{T} - 5.09 \ln T \right). \quad (6.16)$$

The above equation provides the relation between  $e_{sw}$  and  $T$ . Another way to establish such a relation would be to integrate equation (6.15) assuming that  $l_v$  is constant and independent of  $T$ . This would result in an approximation to the above equation given by

$$\ln \frac{e_{sw}}{e_{s0}} = \frac{l_v}{R_v T_0} - \frac{l_v}{R_v T}.$$

or

$$e_{sw} = 6.11 \exp \left( 19.83 - \frac{5417}{T} \right). \quad (6.17)$$

In both equations (6.16) and (6.17)  $e_{sw}$  is in mb and  $T$  is in Kelvin. In problem 6.3 you are asked to show that equations (6.16) and

(6.17) are nearly identical for temperatures in the range  $-20^{\circ}\text{C}$  to  $30^{\circ}\text{C}$ .

The corresponding relation to equations (6.16) and (6.17) for sublimation can be derived following the same procedure (here again  $a_v \gg a_i$ ) with  $l_s = 2.834 \times 10^6 \text{ J kg}^{-1}$  and  $c_i = 2106 \text{ J kg}^{-1} \text{ K}^{-1}$ . They are:

$$e_{\text{si}} = 6.11 \exp \left( 26.16 - \frac{6293}{T} - 0.555 \ln T \right) \quad (6.18)$$

and

$$e_{\text{si}} = 6.11 \exp \left( 22.49 - \frac{6142}{T} \right). \quad (6.19)$$

The C-C equation and its simplified versions describe the thermodynamic state of water vapor and liquid water (or water vapor and ice) when the two phases are in equilibrium. When the system's pressure is greater than the equilibrium pressure, equilibrium is approached by condensation (sublimation) of water vapor. This reduces the amount of vapor in the system thereby reducing the vapor pressure. If the system's pressure is lower than the equilibrium pressure, equilibrium is approached by water (ice) evaporating (sublimating). Because of the particular exponential dependence of  $e_{\text{sw}}$  and  $e_{\text{si}}$  on  $T$  in equations (6.17) and (6.19) it follows that for higher temperatures  $e_{\text{sw}}$  is greater than for lower temperatures. As such more water vapor can exist at higher temperatures. For example, for  $T = 300 \text{ K}$  from equation (6.17) we have  $e_{\text{sw}} = 36 \text{ mb}$ . For  $T = 273^{\circ}\text{C}$ ,  $e_{\text{sw}} = 6 \text{ mb}$ . This is a substantial difference. Note that this does necessarily imply that warmer air can hold more water vapor than colder air as it is often wrongly stated. All the above arguments and formulas were derived in the absence of air! We only considered two phases with water evaporating (or vapor condensing) into a vacuum. If you think about it this is consistent with Dalton's law which would indicate that in a mixture of air and water vapor the partial pressures are independent of the mixture. Therefore, keep in mind that when we say that "air at a given temperature is saturated" we do not imply that the air holds as much vapor as it can hold. We strictly mean that at that temperature the amount of vapor that can exist is maximum regardless of the presence of air.

The reason for the relation between equilibrium vapor pressure and temperature arises from purely kinetic reasons. At equilibrium evaporation is zero (strictly speaking it is the net evaporation = evaporation minus condensation that is zero as molecules inside water have as much chance to evaporate as vapor molecules have to condense). At higher temperatures the molecules inside the liquid acquire greater speeds and their chance to escape increases. As a result (net) evaporation increases.

The exponential dependence of  $e_{\text{sw}}$  (or  $e_{\text{si}}$ ) on  $T$  has important consequences for our climate system. Tropical warm water can transfer more water vapor into the atmosphere than colder extratropical water. Most of this water vapor is then precipitated as a result of organized convection in the tropics thereby releasing large amounts of heat. This heat can then be converted to work and generate kinetic energy which helps maintain the general circulation against frictional dissipation.

• **Changes in the melting and boiling points for water**

At boiling point ( $T = 100^\circ\text{C}$ ),  $l_v = 2.26 \times 10^6 \text{ J kg}^{-1}$ ,  $a_v = 1.673 \text{ m}^3 \text{ kg}^{-1}$ , and  $a_w = 0.00104 \text{ m}^3 \text{ kg}^{-1}$ . Then from equation (6.15) it follows that

$$\frac{de_{\text{sw}}}{dT} = 3621 \text{ Pa K}^{-1}$$

or

$$\frac{de_{\text{sw}}}{dT} = 0.03575 \text{ atm K}^{-1}.$$

Accordingly, a decrease in pressure by 0.03575 atm (36.2 mb) lowers the boiling point by  $1^\circ\text{C}$ . Note that if we evaluate the approximate relationship (6.16) at  $T_1 = 373 \text{ K}$  and  $T_2 = 372 \text{ K}$ , we will find that  $e_{\text{sw}}(T_1) \approx 1003 \text{ mb}$  and  $e_{\text{sw}}(T_2) \approx 969 \text{ mb}$ , or  $\Delta e_{\text{sw}} \approx -34 \text{ mb}$ . If we use instead equation (6.17), we will find that  $e_{\text{sw}}(T_1) \approx 1237 \text{ mb}$ ,  $e_{\text{sw}}(T_2) \approx 1190 \text{ mb}$ , and  $\Delta e_{\text{sw}} \approx -47 \text{ mb}$ . The differences are due to the fact that in deriving the approximate expressions we have assumed that the specific heats and latent heats are either constant or linear functions of  $T$ . While in the range of temperature relevant to weather these approximations may be good, for temperatures outside this range the differences may be significant. At melting point ( $T = 0^\circ\text{C}$ ),  $l_f = 0.334 \times 10^6 \text{ J kg}^{-1}$ ,  $a_w = 1.00013 \times 10^{-3} \text{ m}^3 \text{ kg}^{-1}$ , and  $a_i = 1.0907 \times 10^{-3} \text{ m}^3 \text{ kg}^{-1}$ . Substituting these values into equation (6.15) yields

$$\frac{dp_{\text{wi}}}{dT} = -13\,503\,800 \text{ Pa K}^{-1}$$

or

$$\frac{dp_{\text{wi}}}{dT} = -133.3 \text{ atm K}^{-1}.$$

This result indicates that lowering the melting point by just  $1^\circ\text{C}$  will require a tremendous increase in pressure. This is actually rather anomalous as in most cases the melting point increases with increasing pressure. The strange behavior of water and ice is due to the fact that ice is less dense than water whereas in most cases the solid is denser than the liquid. The fact that the melting point of ice is lowered by increasing pressure is very important to geophysics as it explains the motion of glaciers. When a mass of ice encounters

a rock on the glacier bed the high pressure of the ice against the rock lowers the melting point of ice causing the ice to melt and then to flow around the rock. Once behind the rock the pressure is restored and ice freezes again. In this way ice propagates around obstacles.

### Examples

- (6.1) Calculate the work done, the amount of heat absorbed, and the change in the internal energy during (a) melting of 1 g of ice to water at a temperature of  $0^\circ\text{C}$  and under a constant pressure of 1 atmosphere, and (b) evaporation of 1 g of water to water vapor at a temperature of  $100^\circ\text{C}$  and under a constant pressure of 1 atmosphere.

(a) When the effect of absorbing an amount  $Q$  at a constant pressure is a change in the physical state of the system (which also occurs at constant temperature), then  $Q$  is proportional to the mass that undergoes the change. In our case  $Q = ml_f$  where  $l_f$  is the specific latent heat of fusion of  $0^\circ\text{C}$ . For ice  $l_f = 79.7 \text{ cal g}^{-1}$ . Thus,

$$Q = l_f m = 79.7 \text{ cal.}$$

During melting the volume changes. The corresponding work done is

$$W = \int_{\text{ice}}^{\text{water}} p dV = p \int_{\text{ice}}^{\text{water}} dV = p(V_{\text{water}} - V_{\text{ice}}).$$

The density of ice at  $0^\circ\text{C}$  is  $0.917 \text{ g cm}^{-3}$ , so 1 g occupies a volume of  $1.09 \text{ cm}^3$ . The density of water at  $0^\circ\text{C}$  is  $1 \text{ g cm}^{-3}$ . Accordingly, 1 g of water occupies a volume of  $1.0 \text{ cm}^3$ . It follows that

$$W = 1013 \times 10^2 \times (1 - 1.09) \times 10^{-6} \text{ J}$$

or

$$W = -0.00912 \text{ J}$$

or

$$W = -0.0022 \text{ cal.}$$

The work done is negative because the volume of the resulting water is smaller than the volume of ice. From the above we then find that

$$\Delta U = Q - W = 79.7022 \text{ cal.}$$

(b) In this case at  $100^\circ\text{C}$ ,  $l_v = 539 \text{ cal g}^{-1}$ . Thus,

$$Q = l_v m = 539 \text{ cal.}$$

Water at  $100^\circ\text{C}$  has a density of  $0.958 \text{ g cm}^{-3}$  which for  $1 \text{ g}$  gives a volume of  $1.04 \text{ cm}^3$ . The volume of  $1 \text{ g}$  of water vapor at  $100^\circ\text{C}$  is  $1673 \text{ cm}^3$ . As such

$$\begin{aligned} W &= p(V_{\text{vapor}} - V_{\text{water}}) = 1013 \times 10^2 \times (1673 - 1.04) \times 10^{-6} \\ &= 169.37 \text{ J} = 40.47 \text{ cal.} \end{aligned}$$

It then follows that

$$\Delta U = 498.53 \text{ cal.}$$

Note that in both cases the internal energy increases even though the temperature remains constant. This is due to the fact that the degrees of freedom increase. The degrees of freedom of the molecules in  $\text{H}_2\text{O}$  is much greater in the liquid phase than in the ice phase and much greater in water vapor than liquid water.

**(6.2) Can raindrops grow from cloud droplets through condensation alone?**

In order to address this question we have to make some reasonable assumptions. Cloud droplets form over nuclei and begin to grow according to the available water vapor. If the vapor pressure is greater than the equilibrium vapor pressure droplets grow by condensation. So we need to get an idea of how much vapor is available and how many droplets are going to compete for this vapor. Let us assume that the concentration of nuclei is  $100 \text{ cm}^{-3}$  which corresponds to rather clean air. Now we need to estimate the amount of vapor that will be available during the process of growing by condensation. We can get a gross estimate of this amount by assuming that at the level where clouds form (say  $1000 \text{ m}$ ) the air is saturated and the surface temperature is about  $30^\circ\text{C}$ . If this air ascends adiabatically, the temperature decreases. As the temperature decreases the equilibrium (saturation) vapor pressure decreases. This means that not as much vapor is needed for equilibrium or that the vapor pressure becomes greater than the equilibrium vapor pressure. Thus, the droplets begin to grow. If the air ascends to the maximum level (say the top of the troposphere at about  $16 \text{ km}$ ), then we can estimate the equilibrium vapor pressure at that level by assuming that no water vapor condenses

using the equation

$$\ln \frac{e_{\text{sw}}}{6.11} = 19.83 - \frac{5417}{T},$$

where  $T = 30 - (16 \times 9.8) = -126.8^\circ\text{C} = 146.2\text{ K}$ . It follows that at this level  $e_{\text{sw}} = 0$ . At cloud base where the temperature is  $\approx 20.2^\circ\text{C}$ ,  $e_{\text{sw}} \approx 23.7\text{ mb}$ . As such in this scenario the equivalent of 23.7 mb in water vapor will be available to the droplets for growth. How much water vapor is that? From the ideal gas law we find that for  $V = 1\text{ m}^3$

$$m_v = \frac{e_{\text{sw}}V}{R_vT} = 0.0175\text{ kg}.$$

Assuming that a typical raindrop has a radius of 0.5 mm it follows that the mass of a raindrop is  $m_{\text{raindrop}} = V/\rho \approx 0.00052\text{ g}$ . Given the total amount of water vapor available this translates to  $\sim 33\,650$  raindrops. However, in  $1\text{ m}^3$  of air there are  $10^8$  “competitors” with equal rights. Simply, none of them will grow to be a raindrop by condensation only. Other processes must also take place (collision, coalescence, for example).

- (6.3) Consider a sample of 2 moles of supercooled water (i.e. liquid water existing at environmental temperatures less than  $0^\circ\text{C}$ ). Assume that the temperature of the surroundings is  $-10^\circ\text{C}$  and that the supercooled water freezes. In this process the latent heat of fusion (freezing) is lost to the surroundings and finally ice and surroundings return to the original temperature. Calculate  $\Delta U$ ,  $\Delta H$ , and  $\Delta S$  for both supercooled water and surroundings.

Two moles of water equal 36 g. If we neglect volume and pressure variations during phase changes between water and ice it follows from the first law and the definition of enthalpy that for both supercooled water and surroundings

$$\Delta H = \Delta U = Q.$$

There is a correct and a wrong way to calculate  $Q$  and  $\Delta S$  during this process. If we calculate the amount of heat given away from the supercooled water as it freezes at  $-10^\circ\text{C}$ , we find that  $Q_w = -ml_f(-10^\circ\text{C}) = -0.036 \times 0.312 \times 10^6\text{ J} = -11\,232\text{ J}$ . Then, if we use equation (5.7) we will find that  $\Delta S_w = \int \delta Q/T = -42.7\text{ J K}^{-1}$ . The amount of heat released is gained by the surroundings. Thus,  $Q_s = 11\,232$  and  $\Delta S_s = 42.7\text{ J K}^{-1}$ . It follows that the change in entropy of the whole system (surroundings + supercooled water) is zero. But *there*



was a change in the system, which, according to the second law, should increase the entropy of the system. The reason for this violation is that we have indirectly assumed that the spontaneous freezing is a reversible process, which is not.

A correct way would be the following: Start with the supercooled water at  $-10^\circ\text{C}$  and warm it reversibly to  $0^\circ\text{C}$  (step 1), freeze it reversibly at  $0^\circ\text{C}$  (step 2) and then cool it reversibly to  $-10^\circ\text{C}$  (step 3). In this scenario we have

#### Step 1

$$Q_1 = mc_{pw}\Delta T = 1518.5 \text{ J}$$

$$\Delta S_1 = \int_{T_1}^{T_2} mc_{pw} \frac{dT}{T} = 5.67 \text{ J K}^{-1}$$

#### Step 2

$$Q_2 = -ml_f(0^\circ\text{C}) = -12\,013.2 \text{ J}$$

$$\Delta S_2 = \frac{Q_2}{T_2} = -44.0 \text{ J K}^{-1}$$

#### Step 3

$$Q_3 = mc_{pi}\Delta T = -758.2 \text{ J}$$

$$\Delta S_3 = \int_{T_2}^{T_1} mc_{pi} \frac{dT}{T} = -2.83 \text{ J K}^{-1}$$

In the above calculations we have considered that  $T_1 = 263 \text{ K}$ ,  $T_2 = 273 \text{ K}$ ,  $c_{pw} = c_w = 4218 \text{ J kg}^{-1} \text{ K}^{-1}$ ,  $c_{pi} = c_i = 2106 \text{ J kg}^{-1} \text{ K}^{-1}$ , and  $l_f(0^\circ\text{C}) = 0.3337 \times 10^6 \text{ J kg}^{-1} \text{ K}^{-1}$ . It follows that the amount of heat released by the supercooled water is

$$Q_w = Q_1 + Q_2 + Q_3 = -11\,252.9 \text{ J},$$

and the change in entropy of the supercooled water is

$$\Delta S_w = \Delta S_1 + \Delta S_2 + \Delta S_3 = -41.16 \text{ J K}^{-1}.$$

The surroundings ( $T_s = -10^\circ\text{C}$ ) gain the amount that the freezing of supercooled water releases. Thus,

$$\Delta U_s = \Delta H_s = Q_s = -Q_w = 11\,252.9 \text{ J}.$$

At the same time their change of entropy is

$$\Delta S_s = \int \frac{\delta Q_s}{T_s} = \frac{Q_s}{T_s} = 42.79 \text{ J K}^{-1}.$$

It follows that the change in the entropy of the whole system (surroundings + supercooled water) is

$$\Delta S = \Delta S_s + \Delta S_w = 1.63 \text{ J K}^{-1} > 0.$$

## Problems

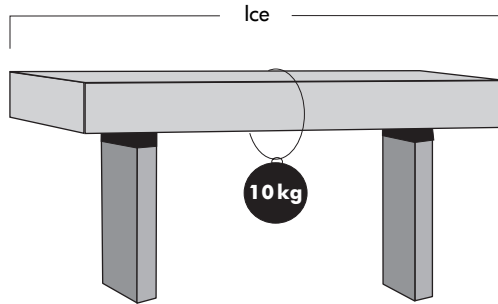
- (6.1) Prove that for any system

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial p}{\partial T}\right)_V - p.$$

(Hint: express  $dU$  using equation (2.1) and substitute into the first law. Then consider the definition of  $dS = \delta Q/T$  and the fact that  $dS$  is an exact differential, perform the partial differentiations and collect terms.)

- (6.2) Using the equation derived in problem 6.1, show that for an ideal gas  $U$  is only a function of temperature and does not depend on  $V$  (Joule's law).
- (6.3) By plotting  $e_{sw}$  against  $T$  show that in the range  $-20^\circ\text{C}$  to  $30^\circ\text{C}$  equations (6.16) and (6.17) are virtually identical. If we were very picky about choosing one over the other which would you choose?
- (6.4) Inside an open container is 500 g of ice with temperature  $T = -20^\circ\text{C}$ . Heat is then provided to the ice at a rate of  $100 \text{ cal min}^{-1}$  for 700 min. Plot (a) the relationship between temperature (in  $^\circ\text{C}$ ) and time (in seconds), (b) the relationship between the heat absorbed by the ice and time, (c) the relationship between the heat absorbed and temperature. Neglect the heat capacity of the container and assume that  $l_f = \text{constant} = 79.7 \text{ cal g}^{-1}$  and  $c_i = \text{constant} = 0.503 \text{ cal g}^{-1} \text{ K}^{-1}$ .
- (6.5) A closed box of volume  $2 \text{ m}^3$  and temperature  $120^\circ\text{C}$  contains  $1 \text{ m}^3$  of water saturated with vapor. Calculate (a) the mass of water vapor, (b) the mass of water vapor that must slowly escape in order for the temperature inside the box to decrease to  $100^\circ\text{C}$  while maintaining saturated conditions. (1.43 kg, 0.71 kg)
- (6.6) An open container of volume 2 liters contains dry air and some quantity of water at standard conditions. After equilibrium is achieved the container is closed and heated to a temperature of  $100^\circ\text{C}$ . What is the least amount of water that must have been added if after the heating the air is saturated? What is the final pressure inside the box? Use equation (6.16). (1.16 g, 2.35 atmospheres)
- (6.7) A substance obeys the equation of state  $pV^{1.2} = 10^9 T^{1.1}$ . A measurement of its internal capacity inside a container

**Figure 6.4**  
Illustration for problem  
6.10.



having a constant volume of 100 liters shows that under these conditions the thermal capacity is constant and equal to  $0.1 \text{ cal K}^{-1}$ . Express the energy and the entropy of the system as function of  $T$  and  $V$ . (Hint: Is the substance an ideal gas?)

- (6.8) How would you have to alter your assumptions in example 6.2 in order to make cloud droplets grow to raindrops by condensation only?
- (6.9) Calculate the change in entropy when 5 kg of water at  $10^\circ\text{C}$  is raised to  $100^\circ\text{C}$  and then converted into steam at that temperature. At  $100^\circ\text{C}$  the latent heat of vaporization of water is  $2.253 \times 10^6 \text{ J kg}^{-1}$ . In the above range of temperatures, the specific heat capacity under constant volume for water is nearly independent of temperature with a value of about  $4.18 \times 10^3 \text{ J kg}^{-1} \text{ K}^{-1}$ . ( $\geq 35\,972 \text{ J K}^{-1}$ )
- (6.10) A block of ice rests as shown in Figure 6.4. A wire on which we attach a weight surrounds the ice. Explain why the wire will go through the ice block without the ice breaking into two pieces.
- (6.11) The warm source of a Carnot cycle has a temperature of  $100^\circ\text{C}$  while the cold source consists of melting ice. When the cycle operates for 1 h it is observed that 1 ton of ice has melted. Calculate (1) the heat absorbed in the cycle from the warm source (2) the heat given away in the cycle to the cold source. The latent heat of fusion at  $100^\circ\text{C}$  is  $0.3337 \times 10^6 \text{ J kg}^{-1}$ . ( $333.7 \times 10^6 \text{ J}$ ,  $244.2 \times 10^6 \text{ J}$ )

