2.7 Equilibrium and the Combined First and Second Laws

By using the first and second laws in combination, we can derive some important results that apply to energy and entropy in the atmosphere and ocean. For any reversible process with expansion work only, we can write the first law as

$$du = dq_{rev} - p\, dv$$

Since $dq_{rev} = T d\eta$ from (2.25), this becomes

$$du = T\, d\eta - p\, dv \tag{2.31}$$

The natural independent variables for internal energy are seen to be entropy and volume. If the enthalpy form of the first law is used, (2.13), we have

$$dh = T\, d\eta + v\, dp \tag{2.32}$$

The natural independent variables for enthalpy are entropy and pressure.

For many applications in the atmosphere and ocean, it is useful to define a new state function whose natural independent variables are temperature and pressure. The *Gibbs energy*, *g*, is defined as

$$g = u - T\eta + pv = h - T\eta \tag{2.33}$$

or in extensive form

$$G = H - T\eta$$

where $\eta = m\eta$ is used to denote extensive entropy and $G = mg$ is the extensive Gibbs energy. In differential form we have

$$dg = -\eta\, dT + v\, dp \tag{2.34}$$

The natural independent variables of the Gibbs energy are temperature and pressure.

Consider the following statement of the combined first and second laws (2.31):

$$du = T\, d\eta - p\, dv$$

Equilibrium is a state of balance between a system and its environment, in which small variations in the system will not lead to a general change in its properties, and the system remains constant with time. In a process that occurs at constant entropy and constant volume, the change in internal energy will be zero. In such a process, the equilibrium state is thus specified for that state for which $du = 0$. It can be shown that under conditions of constant η and v that $d^2u > 0$, which says that internal energy is a minimum at equilibrium. Under conditions of constant internal energy and volume, the same version of the first and second laws combined shows that equilibrium is reached when $d\eta = 0$. It can also be shown that under conditions of constant u and v that $d^2\eta < 0$, which states that entropy is a maximum at equilibrium. The drive of thermodynamical systems toward equilibrium is thus a result of two factors. One is the tendency toward minimum energy. The other is the tendency towards maximum entropy. Only if u is held constant can η achieve its maximum; only if η is held constant can u achieve its minimum.

Since processes are rarely studied under conditions of constant entropy or constant energy, it is desirable to obtain criteria for thermodynamic equilibrium under practical conditions (*e.g.*, constant pressure). The four alternative statements of the combined first and second laws: (2.31), (2.32), (2.34), and (2.36) can be used to establish equilibrium criteria under different boundary conditions. Under conditions of constant η and p, equilibrium is reached for $dh = 0$. Under conditions of constant T and p, equilibrium is specified for the condition $dg = 0$. The thermodynamic equilibrium conditions are thus summarized as

$$
\begin{array}{lll}
\text{At constant } \eta, v & du & = 0,\ d^2u > 0 \\
\text{At constant } \eta, p\text{:} & dh & = 0,\ d^2h > 0 \\
\text{At constant } T, p\text{:} & dg & = 0,\ d^2g > 0
\end{array}
$$

4.3 Phase Equilibria

The Gibbs phase rule allows us to construct qualitatively a phase diagram for water. It now remains to determine the slopes of the $f = 1$ lines in Figure 4.3 that relate pressure and temperature at equilibrium between two phases. To determine the slopes, we consider the combined first and second laws for a heterogeneous system.

Consider the equation for the Gibbs function for a reversible process (2.34) in extensive form:

$$dG = -\eta\, dT + V\, dp \qquad (4.4)$$

where η is here an extensive entropy. This equation applies to a homogeneous system. To extend the equation for the Gibbs function to an open system where a new phase may form in the system or a new component may be added, we write

$$dG = -\eta\, dT + V\, dp + \sum_i \sum_j \frac{\partial G}{\partial n_{ij}}\, dn_{ij} \qquad (4.5)$$

where i is the number of components and j is the number of phases.

The derivative $(\partial G/\partial n)$ is the *chemical potential*, μ:

$$\mu = \frac{\partial G}{\partial n} \tag{4.6}$$

The chemical potential is the change in the Gibbs function of the system with a change in the number of moles of a given component or phase. Note that $\mu = g$. Equation (4.5) applies to an *open system.* We can change the amount of any component i or phase j in an open system by adding or removing dn of the component. Using the definition of chemical potential, we may write (4.5) as

$$dG = -\eta\, dT + V\, dp + \sum_i \sum_j \mu_{ij}\, dn_{ij} \tag{4.7}$$

Under conditions of constant temperature and pressure for a system consisting of one component, we have

$$dG = \sum_j \mu_j\, dn_j \tag{4.8}$$

For a closed system of one component with three phases (*e.g.*, the water example considered in Section 4.2), we allow the number of moles of a given phase to vary under possible phase transitions, but require the total number of moles to remain constant, so that

$$\boxed{n = n_1 + n_2 + n_3 = \text{constant}}$$

and $dn = 0$. For a closed system at constant temperature and pressure, we therefore have

$$dG = \sum_j \mu_j\, dn_j = 0 \tag{4.9}$$

In a system containing several phases, certain thermodynamic requirements for the existence of equilibrium may be derived. The conditions for equilibrium between the two phases, 1 and 2, are:

1) Thermal equilibrium: $T_1 = T_2$. If $T_1 \neq T_2$, then heat would flow from one phase to the other and there would be no equilibrium.

2) Mechanical equilibrium: $p_1 = p_2$. If $p_1 \neq p_2$, then one phase would be expanding at the expense of the other and there would be no equilibrium.

3) Chemical equilibrium: $\mu_1 = \mu_2$. If $\mu_1 \neq \mu_2$, then a transfer of n moles of phase 1 to phase 2 would change the Gibbs function.

As seen from Figure 4.3, if we fix the pressure and then heat a condensed phase, the temperature will increase until the equilibrium value is reached where two phases may coexist. The temperature and pressure remain constant until one of the phases disappears. During a phase change, heat is added to (or removed from) the system without changing the temperature or pressure of the system. During this phase transition, entropy and the specific volume will increase. The enthalpy change during the phase transition is

$$\Delta h = L \tag{4.10}$$

where L is the *latent heat* of the phase transition (sometimes called the *molar heat*). The *latent heat of fusion*, $L_{il} = h_l - h_i$ is the latent heat associated with the solid-liquid phase transition, where the subscript l refers to liquid and the subscript i to ice. The *latent heat of vaporization*, $L_{lv} = h_v - h_l$ is associated with the liquid-vapor phase transition; and the *latent heat of sublimation*, L_{iv} is associated with the solid-vapor phase transition. Note that $L_{il} = L_{iv} - L_{lv}$. In a phase change process at constant pressure, the entropy change can easily be shown from (4.10) to be

$$\Delta \eta = \frac{\Delta h}{T} = \frac{L}{T} \tag{4.11}$$

A molecular interpretation of the latent heat provides additional insight. Consider first the vaporization of a liquid. By virtue of the differences in density between the liquid and vapor and thus the average distance between molecules, the molecular interactions are large in a liquid and small in a gas. "Large" and "small" are here defined with respect to the average kinetic energy in the dilute gas, $(3/2)kT$ per molecule (Section 1.6). Thus the latent heat of vaporization should be a very rough measure of the average intermolecular potential energy in the liquid. During vaporization, the majority of the latent heat is used to overcome the cohesive forces holding the molecules together in the liquid form. The latent heat of fusion is much less than the heat of vaporization, since the density difference between a solid and a liquid is relatively small, and the cohesive forces holding the solid together do not differ greatly from those holding the liquid together.

We are now able to derive the slopes of the $f = 1$ lines in Figure 4.3. Chemical equilibrium ($\mu_1 = \mu_2$) implies that $G_1 = G_2$ at equilibrium and $dg_1 = dg_2$, so that

$$\begin{aligned} dg_1 &= -\eta_1\, dT + v_1\, dp \\ dg_2 &= -\eta_2\, dT + v_2\, dp \end{aligned} \tag{4.12}$$

Since $dg_1 = dg_2$ at equilibrium, we may write

$$-\eta_1\, dT + v_1\, dp = -\eta_2\, dT + v_2\, dp \tag{4.13}$$

Collecting terms we have

$$\frac{dp}{dT} = \frac{\eta_2 - \eta_1}{v_2 - v_1} = \frac{\Delta \eta}{\Delta v} = \frac{\Delta h}{T \Delta v} = \frac{L}{T \Delta v} \tag{4.14}$$

which is known as the *Clapeyron equation* or the *first latent heat equation*. This equation can be used to evaluate the slopes of the $f = 1$ lines on the p, T phase diagram (Figure 4.3).

First, consider the solid-liquid equilibrium line. Equation (4.14) may then be written as

$$\frac{dp}{dT} = \frac{L_{il}}{T(v_l - v_i)} \tag{4.15}$$

Inverting this equation gives the variation of the melting point with pressure:

$$\frac{dT}{dp} = \frac{T(v_l - v_i)}{L_{il}} \tag{4.16}$$

Because the specific volume of liquid water is less than the specific volume of ice, the melting point decreases with increasing pressure.

For the liquid-vapor equilibrium,

$$\frac{dp}{dT} = \frac{L_{lv}}{T(v_v - v_l)} \tag{4.17}$$

At the triple point $v_v = 206\ \mathrm{m^3\ kg^{-1}}$ and $v_l = 10^{-3}\ \mathrm{m^3\ kg^{-1}}$, so that $v_v >> v_l$ and v_l can be neglected relative to v_v. We may then write the Clapeyron equation as

$$\frac{dp}{dT} \approx \frac{L_{lv}}{T v_v} \tag{4.18}$$

If we substitute the ideal gas law for v_v, we obtain

$$\frac{dp}{dT} = \frac{L_{lv} p}{R_v T^2} \tag{4.19}$$

Equation (4.~~21~~19) is the *Clausius-Clapeyron equation.*

The *boiling point temperature* is defined to be the temperature at which the vapor pressure is equal to the atmospheric pressure. Equation (4.19) can be inverted to determine the variation of the boiling point temperature with atmospheric pressure:

$$\frac{dT}{dp} = \frac{R_v T^2}{L_{lv} p} \tag{4.20}$$

This equation clearly shows the well-known decrease of boiling point temperature with decreasing pressure — something all high-altitude cooks are aware of.

Integration of (4.19) requires that some assumption be made about $L_{lv}(T)$. The variation of L_{lv} with temperature is slow, so we incur little error if we assume that L_{lv} is constant over a small range of temperature variation. Using the notation that e denotes the water vapor pressure, and assuming that L_{lv} is constant, (4.19) is easily integrated:

$$\int_{e_1}^{e_2} d\ln e = \int_{T_1}^{T_2} \frac{L_{lv}}{R_v T^2}\, dT \tag{4.21}$$

to yield

$$\ln \frac{e_2}{e_1} = -\frac{L_{lv}}{R_v}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{4.22}$$

or

$$e_2 = e_1 \exp\left[-\frac{L_{lv}}{R_v}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right] \tag{4.23}$$

The values of e_1 and e_2 are referred to as the *saturation vapor pressure* at T_1 and T_2, respectively. Recall that in arriving at (4.23), we have assumed that the vapor phase obeys the ideal gas law and that L_{lv} is constant.

Analogously, the sublimation-pressure curve, which defines equilibrium between the vapor and ice phases, may be determined from

$$\frac{de}{dT} = \frac{L_{iv}}{T\left(v_v - v_i\right)} \tag{4.24}$$

Since $v_i = 1.091 \times 10^{-3}$ m^3 kg^{-1} at the triple point, $v_v >> v_i$, and we have

$$\frac{de}{dT} \approx \frac{L_{iv}}{Tv_v} \tag{4.25}$$

Again, using the ideal gas law and assuming that L_{iv} is constant, we can integrate to obtain

$$e_2 = e_1 \exp\left[-\frac{L_{iv}}{R_v}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right] \tag{4.26}$$

where e_1 and e_2 are the *saturation vapor pressures with respect to ice* at T_1 and T_2, respectively. As can be seen from Figure 4.3, the saturation vapor pressure with respect to ice is less than the saturation vapor pressure with respect to water. This difference is a consequence of the latent heat of sublimation being larger than the latent heat of vaporization.

To integrate the Clausius-Clapeyron equation more precisely, we must include the variation of L_{lv} and L_{iv} with T. The latent heat of vaporization is defined by (4.10) to be the difference in enthalpies, Δh, between the two phases. For any process, the change of Δh with temperature and pressure can be represented by the general equation

$$d\Delta h = \left(\frac{\partial \Delta h}{\partial T}\right)_p dT + \left(\frac{\partial \Delta h}{\partial p}\right)_T dp \tag{4.27}$$

and hence

$$\frac{d\Delta h}{dT} = \left(\frac{\partial \Delta h}{\partial T}\right)_p + \left(\frac{\partial \Delta h}{\partial p}\right)_T \frac{dp}{dT} = \Delta c_p + \left(\frac{\partial \Delta h}{\partial p}\right)_T \frac{dp}{dT} \tag{4.28}$$

The last term on the right-hand side of the equation is small, and we have

$$\frac{dL_{lv}}{dT} = c_{pv} - c_{pl} \tag{4.29}$$

Thus the rate of change of the latent heat of vaporization with absolute temperature is equal to the difference between the specific heat at constant pressure of the vapor and the specific heat of the liquid. Equation (4.29) is *Kirchoff's law* or *the second latent heat equation*. The variation of the latent heat of fusion with temperature can be shown analogously to be

$$\frac{dL_{il}}{dT} = c_{pl} - c_{pi} \tag{4.30}$$

Equations (4.29) and (4.30) can be integrated by assuming that the specific heats are constant. Although the specific heat capacities depend weakly on both temperature and pressure, c_{pv} and c_{pl} vary by only 1% over the temperature range 0°C to 30°C (Table 4.2). The latent heat of vaporization is seen to decrease with increasing temperature. At the triple-point temperature, T_{tr}, the latent of vaporization becomes zero as the specific heats of water vapor and liquid become equal.

Table 4.2 Latent heats of condensation and sublimation for water, and specific heat capacities of ice (c_{pi}), water (c_{pl}), and vapor (c_{pv}).

T (°C)	L_{lv} (10^6 J kg^{-1})	L_{iv} (10^6 J kg^{-1})	c_{pi} (J kg^{-1} K^{-1})	c_{pl} (J kg^{-1} K^{-1})	c_{pv} (J kg^{-1} K^{-1})
-40	2.603	2.839	1814	4773	1856
-30	2.575	2.839	1885	4522	1858
-20	2.549	2.838	1960	4355	1861
-10	2.525	2.837	2032	4271	1865
0	2.501	2.834	2107	4218	1870
10	2.477			4193	1878
20	2.453			4182	1886
30	2.430			4179	1898
40	2.406			4179	1907

The Clausius-Clapeyron equation describes the equilibrium between gaseous and condensed phases. Because the Clausius-Clapeyron equation was derived from the combined first and second laws, the equilibrium that is described is a statistical equilibrium. Consider a system consisting of a layer of liquid water overlain by a layer of water vapor (Figure 4.5). If the vapor pressure is equal to the saturation vapor pressure of the liquid, then there is equilibrium between the two phases. This does not mean that an individual water molecule cannot undergo a phase transition. Due to random molecular motions, some liquid molecules will leave the surface (becoming vapor) and some vapor molecules will return. While individual water molecules can undergo phase transitions, the net migration of vapor molecules to the liquid phase and liquid molecules to the vapor phase is zero under equilibrium conditions. If the overlying vapor pressure is less than the saturation vapor pressure of the liquid, there will be a net migration of molecules from the liquid to vapor phase. This is called *evaporation*. Conversely, *condensation* is defined as a net migration of water molecules from the vapor to the liquid, when the vapor pressure exceeds the saturation vapor pressure of the liquid. During condensation the entropy decreases since liquid is a "less random" state, while during evaporation the entropy increases.

More generally, we have the following terms for the phase transitions:

liquid	—>	vapor	:	*evaporation*
vapor	—>	liquid	:	*condensation*
solid	—>	vapor	:	*sublimation*
vapor	—>	solid	:	*deposition*
solid	—>	liquid	:	*melting*
liquid	—>	solid	:	*freezing*

4.4 Atmospheric Humidity Variables

In the previous section, the gaseous phase under consideration was taken to be pure water vapor. In the atmosphere we have a mixture of dry air gases and water vapor. In the following, we refer to the partial pressure of the water vapor by e, the partial pressure of dry air by p_d, and the total atmospheric pressure by p. The saturation vapor pressure with respect to liquid water is denoted by e_s and the saturation vapor pressure with respect to ice is e_{si}. If we write the integrated forms of the Clausius-Clapeyron equation for atmospheric water vapor (assuming that the latent heat does not vary with temperature), we have

$$e_s = e_{s,tr} \exp\left[\frac{L_{lv}}{R_v}\left(\frac{1}{T_{tr}} - \frac{1}{T}\right)\right] \tag{4.31}$$

$$e_{si} = e_{s,tr} \exp\left[\frac{L_{lv}}{R_v}\left(\frac{1}{T_{tr}} - \frac{1}{T}\right)\right] \tag{4.32}$$

where the reference pressure and temperature referring to the triple point are commonly used ($e_{s,tr}$ = 6.11 hPa; T_{tr} = 273.16 K).

Application of the Clausius-Clapeyron equation to determining the saturation vapor pressure in the atmosphere is not strictly valid because:

1) the total pressure is not the sum of the partial pressures of two ideal gases (*i.e.*, Dalton's law of partial pressures is not strictly valid);

2) the condensed phase is under a total pressure that is augmented by the presence of dry air; and

3) the condensed phase is not purely liquid water, but contains dissolved air.

The departure from the ideal case can be shown to be less than 1%. Departures 2 and 3 stated above result in a triple point temperature of 273.15 K for water in the presence of an atmosphere, compared with 273.16 K for the pure water system.

As a result of the departures from an ideal gas, and because of the variations in the latent heat with temperature, values of the saturation vapor pressure calculated from the Clausius-Clapeyron equation, especially in its simplest integrated form (Equation 4.31), are not exact. Empirical values (Appendix E) of the saturation vapor pressure are used when high accuracy is needed.

A sixth-order polynomial can be shown to fit to observations to within their accuracy:

$$e_s = a_1 + \sum_{n=2}^{7} a_n (T - T_{tr})^{n-1} \tag{4.33}$$

where the coefficients for the saturation vapor pressure over water and over ice are given in Table 4.3 and where T_{tr} = 273.15 K. This expression provides the increased accuracy needed for numerical cloud models.

Table 4.3 Coefficients of the sixth-order polynomial fits to saturation vapor pressure for the temperature range -50° to 50°C for both liquid water and ice (after Flatau *et al.*, 1992).

Coefficient	liquid water	ice
a_1	6.11176750	6.10952665
a_2	0.443986062	0.501948366
a_3	0.143053301E-01	0.186288989E-01
a_4	0.265027242E-03	0.403488906E-03
a_5	0.302246994E-05	0.539797852E-05
a_6	0.203886313E-07	0.420713632E-07
a_7	0.638780966E-10	0.147271071E-09

Values of the saturation vapor pressure are used in the determination of some of the commonly used atmospheric humidity variables. The *relative humidity*, $\mathcal{H}$, is defined as

$$\mathcal{H} = \frac{e}{e_s} \tag{4.34a}$$

and $\mathcal{H}_i$, the *relative humidity with respect to ice saturation*, is defined as

$$\mathcal{H}_i = \frac{e}{e_{si}} \tag{4.34b}$$

The relative humidity is the ratio of the actual partial pressure of water vapor in the air to the saturation vapor pressure, and is a function only of e and T. It is commonly multiplied by 100 and expressed as a percentage. At temperatures below 0°C, it is necessary to specify whether the relative humidity is being evaluated relative to the saturation vapor pressure over liquid water or over ice.

Comparing (4.32a) and (4.32b) for water and ice shows that, at a given subfreezing temperature,

$$\frac{e_s(T)}{e_{si}(T)} = \exp\left\{\frac{L_{il}}{R_v T_{tr}}\left(\frac{T_{tr}}{T} - 1\right)\right\} \tag{4.35}$$

This relation indicates that $e_s(T)/e_{si}(T) > 1$ for all subfreezing temperatures and that the ratio increases as the temperature decreases. Table 4.4 shows that an atmosphere saturated with respect to liquid water is supersaturated with respect to ice, and that the degree of supersaturation increases with the supercooling.

Table 4.4 Variation of $\mathcal{H}_i$ with T for constant $\mathcal{H} = 1$

T (°C)	$\mathcal{H}$	$\mathcal{H}_i$
0	1.0	1.0
-10	1.0	1.10
-20	1.0	1.22
-30	1.0	1.34
-40	1.0	1.47

The *water vapor mixing ratio*, w_v, is the ratio of the mass of water vapor present to the mass of dry air. It is thus defined, after substituting from the ideal gas law, as

$$w_v = \frac{m_v}{m_d} = \frac{\rho_v}{\rho_d} = \varepsilon \frac{e}{p-e} \tag{4.36}$$

where $\varepsilon = M_v / M_d = 0.622$ (Section 1.7). A value of the *saturation mixing ratio*, w_s, is given by

$$w_s = \varepsilon \frac{e_s}{p - e_s} \tag{4.37}$$

Since $p >> e$ and $p >> e_s$,

$$\mathcal{H} \approx \frac{w_v}{w_s} \tag{4.38}$$

is an approximate definition of the relative humidity.

The water vapor mixing ratio can be related to the specific humidity, q_v, which was originally defined in Section 1.7, as

$$q_v = \frac{m_v}{m_d + m_v} = \varepsilon \frac{e}{p - (1 - \varepsilon)e} = \frac{w_v}{1 + w_v} \tag{4.39}$$

Since both w_v and q_v are always smaller than 0.04, $q_v \approx w_v$.

In summary, given T, p, and one of the humidity variables (for example, e), all of the other humidity variables ($\mathcal{H}$, w_v, q_v, *etc.*) can easily be determined.

The total mass of water vapor in a column of unit cross-sectional area extending from the surface to the top of the atmosphere is called the *precipitable water*, W_v:

$$W_v = \int_0^\infty \rho_v \, dz \tag{4.40}$$

The term precipitable water is used because if all the vapor in the column were to be condensed into a pool of liquid at the base of the column, the depth of the pool would be $D = W_v/\rho_l$. To obtain a relationship between precipitable water and specific humidity, we can write (4.40) in terms of pressure by incorporating the hydrostatic equation, (1.33):

$$W_v = \frac{1}{g} \int_p^{p_0} \frac{\rho_v}{\rho_a} dp = \frac{1}{g} \int_p^{p_0} q_v \, dp \tag{4.41}$$

where p_0 is the surface pressure, corresponding to z=0.

Chapter 6 Thermodynamic Transformations of Moist Air

In this chapter we consider the thermodynamic processes that result in the formation and dissipation of clouds. Based on microphysical considerations, we found in Chapter 5 that the liquid phase is nucleated at relative humidities only slightly greater than 100%. For simplicity, we assume here that clouds form in the atmosphere when the water vapor reaches its saturation value and $\mathcal{H} = 100\%$.

In a closed system consisting of moist air, the water vapor mixing ratio remains constant through the course of thermodynamic transformations as long as condensation does not occur. However, vapor pressure and relative humidity do not remain the same during such transformations. For example, in an adiabatic expansion the vapor pressure decreases since it remains proportional to atmospheric pressure.

The relative humidity was defined in Section 4.4 as

$$\mathcal{H} = \frac{w_v}{w_s(T)}$$

where w_v is the water vapor mixing ratio and w_s is the saturation mixing ratio. For initially unsaturated air to become saturated, the relative humidity must increase. An increase in relative humidity can be accomplished by increasing the amount of water vapor in the air (*i.e.*, increasing w_v), and/or by cooling the air, which decreases $w_s(T)$. The amount of water vapor in the air can increase by evaporation of water from a surface or via evaporation of rain falling through unsaturated air. The temperature of the atmosphere can decrease by isobaric cooling (e.g., radiative cooling) or by adiabatic cooling of rising air. An additional mechanism that can increase the relative humidity is the mixing of two unsaturated parcels of air.

In this chapter, we begin by writing the combined first and second laws of thermodynamics for a system that consists of moist air plus condensed water. To understand the changes in thermodynamic state associated with the formation and dissipation of clouds, we apply the combined first and second laws to the following idealized thermodynamic reference processes associated with phase changes of water:

- isobaric cooling
- adiabatic isobaric processes
- adiabatic expansion
- adiabatic isobaric freezing

Although real clouds are not truly adiabatic and nearly always involve more than one of these reference processes in their formation, consideration of the individual reference processes provides a convenient framework for understanding mechanisms that cause clouds to form and dissipate.

6.1 Enthalpy of moist air plus liquid water

The enthalpy of a system consisting of moist air and a liquid water cloud is not only a function of temperature (as was the ideal gas), but also a function of the latent heat associated with the phase change. Enthalpy is the sum of the dry air enthalpy, the enthalpy of water vapor, the enthalpy of the liquid water, plus the latent heat associated with any phase change between the liquid and vapor phases. We can therefore write the enthalpy as

$$dH = \left(m_d c_{pd} + m_v c_{pv} + m_l c_l\right) dT + L_{lv}\, dm_v \tag{6.2b}$$

where the subscripts d, v, l represent dry air, water vapor, and liquid water, respectively. In the atmosphere, the mass of water vapor is only a few percent of the mass of dry air (Section 1.1), and the mass of condensed water is a small fraction of the mass of water vapor. Thus $m_d >> m_v >> m_l$ and we can approximate (6.2b) by

$$dH \approx m_d c_{pd}\, dT + L_{lv}\, dm_v \tag{6.3}$$

In intensive form, we have

$$dh \approx c_{pd}\, dT + L_{lv}\, dw_v \tag{6.4}$$

In a similar manner, we can write an equation for internal energy as

$$du = \left(c_{vd} + w_v c_{vv} + w_l c_l\right) dT + L_{lv}\, dw_v \tag{6.5}$$

and an approximate form as

$$du \approx c_{vd}\, dT + L_{lv}\, dw_v \tag{6.6}$$

Depending on how the thermodynamic system is defined, the term $L_{lv} dw_v$ may be included as part of the enthalpy, or it may constitute an external heat source. For a closed system, we can write

$$dq = c_{pd}\, dT + L_{lv}\, dw_v - v\, dp \tag{6.7a}$$

and for an adiabatic process,

$$0 = c_{pd}\, dT + L_{lv}\, dw_v - v\, dp \tag{6.7b}$$

Now consider a system that consists of moist air, with an external heat source associated with evaporation from a water source (such as moist air over a lake). The first law of thermodynamics can be written as

$$dq = dh - v\,dp$$

where $dh = c_{pd}\,dT$ and $dq = L_{lv}\,dw_l = -L_{lv}\,dw_v$. where w_l is *liquid water mixing ratio,* which is defined analogously to the water vapor mixing ratio (4.36) as

$$w_l = \frac{m_l}{m_d}$$

We can then write

$$-L_{lv}\,dw_v = c_{pd}\,dT - v\,dp \tag{6.8}$$

Note that (6.7) and (6.8) are mathematically equivalent; however, in (6.7b) the term $L_{lv}\,dw_v$ is part of the enthalpy, while in (6.8) the term $L_{lv}\,dw_v$ is a heat source. This example illustrates the care that must be taken to interpret correctly the thermodynamic equation in the context in which the system is defined.

We can also define w_t as the *total water mixing ratio* ($w_t = w_v + w_l$).

6.2 Isobaric Cooling

A thermodynamic process can be approximated as isobaric if vertical motions are small and there is only a small departure from a reference pressure. In the absence of condensation, the first law of thermodynamics for an isobaric process in moist air is written (following 2.16) as

$$dq = dh = c_p\,dT$$

where c_p can be approximated as the dry air value, or alternatively the contribution from water vapor can be incorporated following (2.65). As moist air cools, relative humidity increases: w_v remains the same, but as the temperature decreases then w_s decreases. If the cooling continues, w_s will become equal to w_v and $\mathcal{H}$ will equal unity; at this point, the air has reached saturation. Further cooling beyond saturation results in condensation.

The temperature at which saturation is reached in an isobaric cooling process is the *dew-point temperature*, which is illustrated in Figure 6.1a. The dew-point temperature, denoted by T_D, can be defined by

$$e = e_s(T_D) \tag{6.14}$$

or equivalently by

$$w_v = w_s(T_D) \tag{6.15}$$

We can determine the dew-point temperature by inverting either (6.14) or (6.15), which can be done using (4.31) and (4.36).

Analogously to the dew-point temperature, we define the *frost point temperature* as the temperature at which ice saturation occurs. The frost point temperature, T_F, is thus defined as

$$e = e_{si}\left(T_F\right) \tag{6.16}$$

or equivalently as

$$w_v = w_{si}\left(T_F\right) \tag{6.17}$$

In Figure 6.1b, it is seen that if the vapor pressure is initially below the triple point pressure of water (point 1), isobaric cooling results in deposition once the frost point is reached (point 2). As described in Section 5.3, saturation with respect to ice is not sufficient to initiate the ice phase in the atmosphere. Deposition occurs at the frost point only if ice crystals already exist in the atmosphere. Since $T_F > T_D$, the formation of frost on the ground must occur by deposition rather than by freezing of condensed water vapor; grass and other structures provide a good substrate for initiating the ice phase by deposition.

Although the units of the dew-point temperature are Kelvins, the dew-point temperature is a measure not of temperature but of atmospheric humidity. By examining Figure 6.1 and the Clausius-Clapeyron relationship (4.21), it is seen that

$$\frac{d(\ln e)}{dT_D} = \frac{L_{lv}}{R_v T_D^2} \tag{6.18}$$

and that e and T_D give equivalent information about the amount of water vapor in the atmosphere.

A relationship between T_D and $\mathcal{H}$ can be obtained by integrating (6.18) between T and T_D

$$\ln \frac{e_s}{e} = -\ln \mathcal{H} = \frac{L_{lv}}{R_v}\left(\frac{1}{T_D} - \frac{1}{T}\right)$$

or equivalently

$$\mathcal{H} = \exp\left[-\frac{L_{lv}}{R_v}\left(\frac{T - T_D}{T\,T_D}\right)\right] \tag{6.19}$$

The term $T - T_D$ in (6.19) is called the *dew point depression.* Figure 6.2 illustrates that dew point depression is inversely proportional to relative humidity and that a relative humidity of 100% corresponds to a dew point depression of zero.

Thus, through (6.14), (6.15), and (6.19), the dew-point temperature is shown to be a humidity variable. If temperature, dew-point temperature and pressure are given, then the values of mixing ratio, relative humidity, and vapor pressure can be calculated. Analogously, the frost point temperature can be related to all of the other humidity variables. In an isobaric process in the absence of condensation, the dew-point and frost point temperatures are conservative; that is, they do not change during the cooling process until condensation is reached.

Once the air is cooled slightly below the dew point temperature, condensation begins. After condensation begins, the first law of thermodynamics for an isobaric process is written following (6.4) in the approximate form

$$dq = dh = c_p\, dT + L_{lv}\, dw_v \tag{6.20}$$

Assuming that condensation occurs at saturation ($\mathcal{H}$=1) and that the water vapor mixing ratio is equal to the saturation vapor mixing ratio $w_v = w_s$, we can write

$$w_t = w_s + w_l \tag{6.21}$$

In a closed system, w_t remains constant, so

$$dw_l = -dw_s$$

Using the approximation $w_s \sim \varepsilon e_s / p$ from Section 4.4 and the Clausius-Clapeyron relation (4.21), we can write

$$dw_l = -dw_s = -\varepsilon \frac{de_s}{p} = -\frac{\varepsilon L_{lv} e_s}{p R_v T^2}\, dT \tag{6.22a}$$

Incorporating (6.22a) into (6.20) and using $R_d = R_v/\varepsilon$, we obtain

$$dw_l = -\left[\frac{L_{lv}e_s}{c_p p R_d T^2 + L_{lv}e_s}\right] dq \tag{6.22b}$$

Combination of (6.22b) with (6.20) gives a relationship between dq and dT during isobaric condensation

$$dq = \left[c_p + \frac{L_{lv}^2 e_s}{pR_d T^2}\right] dT \tag{6.22c}$$

Integration of (6.22b) (which is most easily done numerically, since e_s is a function of T) allows determination of the amount of isobaric cooling, Δq, required to condense an amount of liquid water, Δw_l. Analogously, integration of (6.22c) allows determination of the temperature change, ΔT, in response to the isobaric cooling, Δq. Before condensation occurs, we have $\Delta q = -c_p \Delta T$. Once condensation begins, it is seen from (6.22c) that the temperature drops much more slowly in response to the isobaric cooling, because the heat loss is partially compensated by the latent heat released during condensation.

Once condensation begins, the dew-point temperature decreases, since the water vapor mixing ratio is decreasing as the water is condensed. Relative humidity remains constant, at $\mathcal{H} = 1$.

Isobaric cooling is a primary formation mechanism for certain types of fog and stratus clouds (see Section 8.4). The equations derived in this section are equally applicable to isobaric heating. In this instance, an existing cloud or fog can be dissipated by evaporation that ensues from isobaric heating (e.g. solar radiation).

6.3 Cooling and Moistening by Evaporation of Water

Consider a system comprised of unsaturated moist air plus rain falling through the air. Because the air is unsaturated, the rain will evaporate. If there are no external heat sources ($dq = 0$), and the evaporation occurs isobarically ($dp = 0$), we can write an adiabatic isobaric (or *isenthalpic*) form of the enthalpy equation (6.20) as

$$0 = dh = c_p\, dT - L_{lv}\, dw_l = c_p\, dT + L_{lv}\, dw_s \tag{6.23}$$

where c_p can be approximated as the dry air value, or alternatively the contributions from water vapor and liquid water can be incorporated following (6.2a). Since $dh = 0$, (6.23) can be used to determine a relationship between temperature and humidity variables for isenthalpic processes in the atmosphere that involve a phase change of water.

If we allow just enough liquid water from the rain to evaporate so that the air becomes saturated, we can integrate (6.23)

$$c_p \int_T^{T_w} dT = -L_{lv} \int_{w_l}^{0} dw_s$$

where w_l represents the amount of water that must be evaporated to bring the air to saturation. During the evaporation process, latent heat is drawn from the atmosphere, and the final temperature, referred to as the *wet-bulb temperature* (T_w), is cooler than the original temperature. Integration gives

$$c_p\,(T_w - T) = -L_{lv}\,[w_s\,(T_w) - w_v]$$

or alternatively

$$T_w = T - \frac{L_{lv}}{c_p}\left[w_s\,(T_w) - w_v\right] \tag{6.24}$$

where the temperature dependence of L_{lv} has been neglected. Given w_v and T, this expression is implicit for T_w and must be solved numerically. However, if T and T_w are given, then w_v is easily determined. T_w can be measured using a *wet-bulb thermometer*, whereby a wetted muslin wick is affixed to the bulb of a thermometer. Concurrent measurement of the "dry bulb" temperature by a normal thermometer can then provide a means of determining the water vapor mixing ratio and therefore atmospheric humidity. For this reason, (6.24) is often referred to as the *wet-bulb equation*.

The wet bulb temperature is thus defined as the temperature to which air would cool isobarically as the result of evaporating sufficient liquid water into the air to make it saturated. As such, the wet bulb temperature in the atmosphere is conservative with respect to evaporation of falling rain. Calculations for given values of T and w show that $T_D < T_w < T$. This can be shown graphically. Since e increases while T decreases during the approach to T_w, the Clapeyron diagram looks like

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If ice is the evaporating phase, we can determine an analogous *ice-bulb temperature* , T_I, to be

$$T_I = T - \frac{L_{iv}}{c_p}\left[w_{si}(T_I) - w_v\right] \tag{6.25}$$

It is easily shown that $T_I > T_w$.

6.4 Saturation by Adiabatic, Isobaric Mixing

We have seen in Sections 6.2 and 6.3 how unsaturated air can be brought to saturation by isobaric cooling and by the adiabatic, isobaric evaporation of falling rain. There is an additional isobaric process that can bring unsaturated air to saturation. Under some circumstances, the isobaric mixing of two samples of unsaturated air can lead to saturation. One example of this process occurs when your breath produces a puff of cloud on a cold day.

Consider the isobaric mixing of two moist air masses, with different temperatures and humidities but at the same pressure. Condensation is assumed not to occur. For adiabatic, isobaric mixing, we can write the first law of thermodynamics from (2.16) as

$$0 = dH \approx m_1\, c_{pd}\, dT_1 + m_2\, c_{pd}\, dT_2$$

where dT_1 and dT_2 correspond to the temperature change of the air masses upon mixing and we have ignored the heat capacity of the water vapor in accordance with (6.4). Upon integration from an initial state where the air masses are unmixed to a final state where the air masses both have the same final temperature, T, we have

$$m_1 c_{pd}\left(T - T_1\right) + m_2 c_{pd}\left(T - T_2\right) = 0$$

Solving for T we obtain

$$T \approx \frac{m_1}{m_1+m_2} T_1 + \frac{m_2}{m_1+m_2} T_2$$

The total mass $m = m_1 + m_2$ remains constant during the mixing process, so the specific humidity is a mass-weighted average of q_{v1} and q_{v2}

$$q_v = \frac{m_1}{m_1+m_2} q_{v1} + \frac{m_2}{m_1+m_2} q_{v2}$$

Thus, both the temperature and specific humidity mix linearly if the heat capacity of the water vapor is neglected. Since $q_v \sim w_v$, we can also assume that the mixing ratios mix linearly. If we further assume that $w_v \sim \varepsilon e/p$, then vapor pressure mixes linearly as well.

Because of the nonlinearity of the Clausius-Clapeyron equation, adiabatic isobaric mixing results in an increase in relative humidity. This mixing process is illustrated in Figure 6.13 using a T, e diagram. If Y_1 and Y_2 are the image points for the two air masses, the image point for the mixture lies on a straight line joining Y_1 and Y_2. If $m_1 = m_2$, then T and e will lie midpoint on this line. Because of the exponential relationship between e_s and T, the mixing process increases the relative humidity. In the example shown in Figure 6.3, the mixing process results in the image point Y having a relative humidity that exceeds 100%, crossing the $f = 1$ line into the liquid phase (see also Figure 4.3). Water will condense and latent heat will be released, with the final equilibrium image point at Y' on the $f = 1$ line.

The slope of the line between Y and Y' can be determined from the first law of thermodynamics for an adiabatic isobaric process in which condensation occurs (6.23):

$$dh = 0 \approx c_p\, dT + L_{lv}\, dw_s$$

Using the definition of the saturated water vapor mixing ratio, $w_s = \varepsilon e_s /p$, we can write

$$0 = c_p\, dT + \frac{L_{lv}\,\varepsilon}{p}\, de$$

or

$$\frac{de}{dT} = -\frac{p c_p}{\varepsilon L_{lv}} \qquad (6.26)$$

The value of (e, T) at Y' can be found by simultaneously solving (6.26) with the Clausius-Clapeyron equation (4.21). The amount of liquid water condensed during the mixing is

$$\Delta w_l = \frac{\varepsilon}{p}\left[e(Y) - e(Y')\right] \tag{6.27}$$

A notable example of the formation of clouds by adiabatic, isobaric mixing occurs when the exhaust gases from the combustion of fuels by an aircraft mixes with the ambient atmosphere. The trail of clouds often formed by an aircraft in flight at high altitude are referred to as condensation trails, or *contrails*. In the exhaust, the aircraft ejects heat and water vapor, the temperature of the exhaust typically 600 K. Figure 6.4 indicates that for an aircraft flying at 200 mb, atmospheric temperatures below about – 47°C will form contrails. Once contrails form, their persistence depends on the atmospheric humidity and the rate at which the exhaust trail is diffused. If the particles are ice, atmospheric humidity in excess of the ice saturation value will result in growth of the contrails.

6.5 Saturated Adiabatic Cooling

Adiabatic cooling is the most important mechanism by which moist air is brought to saturation. As described in Sections 2.1 and 2.10, adiabatic expansion in the atmosphere occurs when a dry air mass rises due to mechanical lifting (*e.g.*, orographic, frontal), large-scale low-level convergence, turbulent mixing, and buoyancy caused by surface heating.

Recall from Section 2.4 that the first law of thermodynamics for an adiabatic process for moist air in the absence of condensation is written as (2.19b)

$$c_p\, dT - v\, dp = 0$$

from which we derived an expression for the potential temperature (2.62)

$$\theta = T\left(\frac{1000}{p}\right)^{R/c_p}$$

and the dry adiabatic lapse rate (2.68)

$$\Gamma_d = \frac{g}{c_p} \approx 10\ °\mathrm{C\ km^{-1}}$$

Recall that the potential temperature, θ, is conserved in reversible, dry adiabatic processes in the atmosphere.

As air expands adiabatically and cools, the relative humidity increases as the temperature and saturation mixing ratio decrease. The water vapor mixing ratio remains constant during adiabatic ascent. At some point, the relative humidity reaches 100%, and further cooling results in condensation. To determine the temperature and pressure at which saturation is reached, we logarithmically differentiate $\mathcal{H} = e/e_s$

$$d(\ln \mathcal{H}) = d(\ln e) - d(\ln e_s) \tag{6.28a}$$

Using Dalton's law of partial pressure (1.13), we have $d(\ln p) = d(\ln e)$, and we can write the first law of thermodynamics for an adiabatic process in enthalpy form (2.19b) as

$$d(\ln e) = \frac{c_p}{R_d} d(\ln T) \tag{6.28b}$$

Using the Clausius-Clapeyron equation (4.21), we can write

$$d(\ln e_s) = \frac{L_{lv}}{R_v T} d(\ln T) \tag{6.28c}$$

Incorporating (6.28b) and (6.28c) into (6.28a), we can integrate (6.28a) from the initial condition to conditions where saturation is attained, indicated by $\mathcal{H} = 1$ and $T = T_s$, where T_s is *the saturation temperature*

$$\int_{\mathcal{H}}^{1} d(\ln \mathcal{H}') = \int_{T}^{T_s} \left(\frac{c_p}{R_d} - \frac{\varepsilon L_{lv}}{R_d T}\right) d(\ln T')$$

to obtain

$$-\ln \mathcal{H} = \frac{c_p}{R_d} \ln\left(\frac{T_s}{T}\right) + \frac{\varepsilon L_{lv}}{R_d}\left(\frac{1}{T_s} - \frac{1}{T}\right) \tag{6.29}$$

Equation (6.29) can be solved numerically to obtain T_s. An approximate but simpler equation for T_s, given initial values of T (in Kelvins) and $\mathcal{H}$, is given by (Bolton, 1980)

$$T_s = \frac{1}{\dfrac{1}{T-55} - \dfrac{\ln\mathcal{H}}{2840}} + 55 \qquad (6.30)$$

The *saturation pressure*, p_s, can be obtained from (2.22) to be

$$\ln\frac{p_s}{p} = \frac{c_p}{R_d}\ln\frac{T_s}{T}$$

or, taking anti-logs,

$$p_s = p\left(\frac{T_s}{T}\right)^{c_p/R_d} \qquad (6.31)$$

The coordinate (T_s, p_s) is known as the *saturation point* of the air mass.

During ascent, the water vapor mixing ratio, w_v, remains constant until saturation occurs. The dew-point temperature, however, decreases slightly during the ascent as pressure decreases. Recall from (6.18) that

$$d(\ln e) = \frac{L_{lv}}{R_v T_D^2}\, dT_D \qquad (6.32)$$

Using Dalton's law of partial pressure (1.13), we can write the hypsometric equation (1.46) as

$$d(\ln e) = -\frac{g}{R_d T}\, dz \qquad (6.33)$$

Combining (6.32) and (6.33), we obtain

$$\frac{dT_D}{dz} = -\frac{T_D^2 g}{\varepsilon L_{lv} T} = \frac{T_D^2 c_p}{\varepsilon L_{lv} T}\Gamma_d \qquad (6.34a)$$

For typical atmospheric values, dT_D/dz is approximately one-sixth of the dry adiabatic lapse rate. At saturation level, T becomes equal to T_D and to T_s. The *lifting condensation level*, z_s, corresponds to the level of the saturation pressure, p_s.

Using (6.34a) and the definition of the dry adiabatic lapse rate, $\Gamma_d = g/c_p$, we can write

$$\frac{d(T-T_D)}{dz} = \left(1 + \frac{T_D^2 c_p}{\varepsilon L_{lv} T}\right)\Gamma_d \qquad (6.34b)$$

When $T = T_D$, the saturation level has been reached, and a value of z_s can be determined by integrating (6.34b)

$$\int_{T_0 - T_{D0}}^{0} d(T - T_D) = \int_0^{z_s} \left[\left(1 + \frac{T_D^2\, c_p}{\varepsilon L_{lv} T}\right) \Gamma_d \right] dz \tag{6.34c}$$

where T_0 - T_{D0} is the dewpoint depression at the surface. For a parcel of air lifted from the surface, the value of z_s can be estimated from (6.34c) to be

$$z_s \approx 0.12\ (T_0 - T_{D0}) \quad \text{(km)} \tag{6.35}$$

This relation is an approximate expression of the height of the lifting condensation level achieved in an adiabatic ascent where T_0 and T_{D0} represent the initial temperature and dew-point temperature of the air mass that is being lifted. Note that z_s can be determined directly from (1.45) if p_s and T_s are known. Calculation of the lifting condensation level provides a good estimate of the cloud base height for clouds that form by adiabatic ascent.

Once saturation occurs, further lifting of the air mass results in condensation. Because of the latent heat released during condensation, the decrease of temperature with height will be smaller than that in dry adiabatic ascent. In addition, the potential temperature, θ, which was conserved in a reversible dry adiabatic ascent, is no longer be conserved once condensation occurs.

A derivation of an approximate form of the *saturated adiabatic lapse rate*, Γ_s, is given here by starting with the adiabatic entropy equation (6.12) in the following approximate form:

$$0 = c_{pd}\, d(\ln T) - R_d\, d(\ln p) + \frac{L_{lv}}{T}\, dw_s \tag{6.36}$$

Using the hypsometric equation (1.46)

$$\frac{dp}{p} = -\frac{g}{R_d T}\, dz$$

and logarithmically differentiating the equation for saturation mixing ratio (4.37)

$$\frac{dw_s}{w_s} = \frac{de_s}{e_s} - \frac{dp}{p}$$

we can rewrite (6.36) as

$$-L_{lv}w_s\left(\frac{de_s}{e_s}-\frac{dp}{p}\right)=c_p\,dT+g\,dz \tag{6.37}$$

Dividing by an incremental dz and solving for $-dT/dz$, we obtain

$$-\frac{dT}{dz}=\frac{L_{lv}}{c_p}w_s\left(\frac{1}{e_s}\frac{de_s}{dz}+\frac{g}{RT}\right)+\frac{g}{c_p} \tag{6.38}$$

Using the chain rule, we can write the term de_s/dz as

$$\frac{de_s}{dz}=\frac{de_s}{dT}\frac{dT}{dz} \tag{6.39}$$

and substitute into (6.38) to obtain

$$-\frac{dT}{dz}\left(1+\frac{de_s}{dT}\frac{L_{lv}}{c_p}\frac{w_s}{e_s}\right)=\frac{g}{c_p}\left(\frac{L_{lv}w_s}{RT}+1\right)$$

Incorporating the Clausius-Clapeyron equation (4.21), solving for $dT/dz = -\Gamma_s$ and noting that $\Gamma_d = -g/c_p$ (2.68), we obtain finally

$$\Gamma_s=\Gamma_d\left[\frac{1+\dfrac{L_{lv}w_s}{R_dT}}{1+\dfrac{\varepsilon L_{lv}^2w_s}{c_{pd}R_dT^2}}\right] \tag{6.40}$$

The denominator of (6.40) is larger than the numerator, and thus $\Gamma_s < \Gamma_d$. Table 6.1 shows values of Γ_s for selected values of T and p. It is seen that the temperature variation of Γ_s exceeds the pressure variation. At low temperatures and high pressures, Γ_s approaches Γ_d.

Values of Γ_s determined from (6.40) are within about 0.5% of the values determined from a more exact form of the entropy equation (6.11). Because of the approximate nature of (6.40), Γ_s is sometimes called the *pseudo-adiabatic lapse rate*.

The amount of water condensed in saturated adiabatic ascent, called the *adiabatic liquid water content*, can be determined from the adiabatic enthalpy equation (6.7b):

$$0=c_p\,dT-L_{lv}\,dw_l-v\,dp$$

Solving for dw_l and incorporating the hydrostatic equation (1.33), we obtain

$$dw_l = \frac{c_p}{L_{lv}}\left[\frac{dT}{dz} + \frac{g}{c_p}\right] dz$$

Substituting $\Gamma_d = g/c_p$ and $\Gamma_s = -dT/dz$ yields

$$dw_l = \frac{c_p}{L_{lv}}\left[\Gamma_d - \Gamma_s\right] dz \tag{6.41}$$

Integrating (6.41) from cloud base to height z gives the liquid water content at height z. Because of the complicated form of Γ_s, this equation must be integrated numerically. Integration of (6.41) shows that the adiabatic liquid water content increases with height above the cloud base and increasing cloud base temperature

Because of the variation of Γ_s with temperature, clouds with warmer bases have larger values of $\Gamma_d - \Gamma_s$ and thus larger values of the adiabatic liquid water content. The adiabatic liquid water content represents an upper bound on the liquid water that can be produced in a cloud by rising motion.

Table 6.1 Γ_s for selected values of temperature and pressure.

	p (mb)		
T (°C)	1000	700	500
-30	9.2	9.0	8.7
-20	8.6	8.2	7.8
-10	7.7	7.1	6.4
0	6.5	5.8	5.1
10	5.3	4.6	4.0
20	4.3	3.7	3.3

Processes such as precipitation and mixing with dry air reduce the cloud liquid water content relative to the adiabatic value.

6.6 The Ice Phase

As isobaric or adiabatic cooling proceeds, the cloud may eventually cool to the point where ice crystals form. Assuming that a water cloud is present initially, then the formation of ice crystals releases latent heat during fusion. Once the cloud glaciates, it is supersaturated with respect to ice, and deposition occurs on the ice crystals, releasing the latent heat of sublimation, until the ambient relative humidity is at ice saturation. Further cooling will result in the increase of ice water content in the cloud and the release of the latent heat of sublimation into the atmosphere.

Assuming that the thermodynamic system consists of moist air plus the condensate, and that the freezing and subsequent deposition occur isobarically and adiabatically, then the enthalpy of the system will not change during this transformation. Since enthalpy is an exact differential, the enthalpy change depends only on the initial and final states (but not on the path). Consider the following path for the warming of the system associated with the phase change:

Step 1: Water freezes at constant T_1

$$\Delta h_1 = -L_{il} w_l \tag{6.42}$$

Step 2: Vapor deposits on the ice at constant T_1, until the water vapor pressure reaches the saturation value over ice at T_2

$$\Delta h_2 = -L_{iv}\left[w_s(T_1) - w_{si}(T_2)\right] = -L_{iv}\frac{\varepsilon}{p}\left[e_s(T_1) - e_{si}(T_2)\right]$$

Assuming that $(T_2 - T_l)$ is small enough to treat as a differential, we can approximate $e_{si}(T_2)$ as

$$e_{si}(T_2) = e_{si}(T) + \frac{L_{iv}\, e_{si}(T_1)}{R_v T^2}(T_2 - T_1)$$

and Δh_2 becomes

$$\Delta h_2 = -w_s L_{iv}\left[1 - \frac{e_{si}(T_1)}{e_s(T_1)}\right] + \frac{L_{iv}^2\, w_{si}(T_1)}{R_v T^2}(T_2 - T_1) \tag{6.43}$$

where w_s has been adopted in favor of e_s using $w_s \sim \varepsilon e_s/p$.

Step 3: The system is heated from T_1 to T_2

$$\Delta h_3 = c_p (T_2 - T_1) \tag{6.44}$$

Since $\Delta h_1 + \Delta h_2 + \Delta h_3 = 0$, we can incorporate (6.42), (6.43), and (6.44) and solve for $\Delta T = T_2 - T_1$

$$\Delta T=\frac{L_{il}w_l+L_{iv}w_s\left(1-\frac{e_{si}}{e_s}\right)}{c_p+\frac{\varepsilon w_i L_{iv}^2}{R_d T^2}} \tag{6.45}$$

Equation (6.45) gives the increase in temperature due to the freezing of cloud water and the subsequent deposition of water vapor onto the ice crystals. In clouds that cool by adiabatic ascent, the freezing does not occur isobarically, but gradually over a temperature interval.

Once the cloud has glaciated, further adiabatic ascent results in deposition of water vapor onto the ice crystals. Analogously to (6.40), the *ice-saturation adiabatic lapse rate* is determined to be

$$\Gamma_{\mathrm{si}}=\Gamma_{\mathrm{d}}\left[\frac{1+\frac{L_{iv}w_{si}}{R_d T}}{1+\frac{\varepsilon L_{iv}^2 w_{si}}{c_{pd}R_d T^2}}\right] \tag{6.46}$$

The melting process is distinctly different from the freezing process. Melting may occur as ice particles fall to temperatures that are above the melting point. In contrast to freezing which may be distributed through a considerable vertical depth, melting of ice particles can be quite localized, occurring in a very narrow layer around the freezing point. Cooling of the atmosphere from the melting can result in an isothermal layer near 0°C. Because of their large size and density, hail stones do not melt at the freezing level in the same manner as a small ice crystal or a snowflake with a low density, but melt over a deeper layer. If atmospheric relative humidities are low in the atmosphere below the melting level, then the melting water will evaporate, cooling the hailstone and retarding the melting.

6.7 Conserved Moist Thermodynamic Variables

As shown in Section 3.1, conserved variables are commonly used in time-dependent equations. The concept of potential temperature becomes less useful when applied to a cloud, since potential temperature is not conserved during phase changes of water. Derivation of a potential temperature that is conserved in moist adiabatic ascent eliminates the need to include latent heat source terms in the time-dependent thermodynamic equation. Additionally, a potential temperature that is conserved in moist adiabatic ascent can be used to interpret graphically numerous cloud processes and characteristics (see Sections 6.8, 7.3, and 8.5).

Recall that for a reversible, adiabatic process in dry air, the entropy equation is written as (2.26b)

$$0 = c_{pd}\, d\left(\ln T\right) - R_d\, d\left(\ln p\right)$$

It was shown in Section 2.4 that integration of the above equation gives the potential temperature (2.62)

$$\theta = T\left(\frac{p_0}{p}\right)^{R_d/c_{pd}}$$

which is conserved for dry adiabatic motions.

We seek an analogous variable that is conserved for a cloud in adiabatic ascent so that the variation of temperature with pressure can be determined in a saturated adiabatic process. The simplest possible case is that in which saturation conditions are maintained, ice is not present, and heat capacity of the water vapor and condensed water are neglected relative to that of dry air. Using these approximations, the entropy equation (6.13) becomes:

$$0 = c_{pd}\, d(\ln T) - R_d\, d(\ln p) + d\left(\frac{L_{lv}\, w_s}{T}\right) \qquad (6.47)$$

Recall that we have for a dry adiabatic process from (2.63)

$$c_{pd}\, d\ln\theta = c_{pd}\, d\ln T - R_d\, d(\ln p)$$

Equating (2.63) with (6.47) yields

$$-\, d\left(\frac{L_{lv}\, w_s}{T}\right) = c_{pd}\, d(\ln\theta)$$

This expression is integrated to a height in the atmosphere where all of the water vapor has been condensed out by adiabatic cooling. The corresponding temperature is called the *equivalent potential temperature*, θ_e. Integration of

$$-L_{lv}\int_{w_s}^{0} d\left(\frac{w_s}{T}\right) = c_p\int_{\theta}^{\theta_e} d(\ln\theta)$$

yields

$$\frac{L_{lv} w_s}{T} = c_{pd} \ln\left(\frac{\theta_e}{\theta}\right)$$

or

$$\theta_e = \theta \exp\left(\frac{L_{lv} w_s}{c_{pd} T}\right) \tag{6.48}$$

It is easily determined that $\theta_e > \theta$, which arises from the latent heat released from the condensation of water vapor. Because of the approximations made in (6.47), the equivalent potential temperature is only approximately conserved in a saturated adiabatic process. Although approximate, (6.48) retains the essential physics of the process, whereby the condensation of water vapor provides energy to the moist air and increases its temperature relative to what the temperature would have been in dry adiabatic ascent.

In this chapter, we have considered numerous temperatures and potential temperatures, which are defined in the context of their conservative properties regarding certain moist atmospheric processes. Table 6.2 summarizes how various temperature, humidity, and other thermodynamic parameters vary in response to certain types of moist processes.

Table 6.2 Conservative properties of several parameters (C = conservative; N = nonconservative).

parameter	isobaric cooling no condensation	isobaric cooling with condensation	adiabatic expansion no condensation	adiabatic expansion with condensation
w_v	C	N	C	N
$\mathcal{H}$	N	C	N	C
T_D	C	N	N	N
θ	N	N	C	N
θ_e	N	N	C	C
η	N	N	C	C

6.8 Aerological Diagrams

The principal function of a thermodynamic diagram is to provide a graphical display of a thermodynamic process. The following examples of thermodynamic diagrams have been used thus far in the text: (T, s) diagram (Section 1.9); (p, V)

diagram (Sections 2.4 and 4.2); and (e, T) diagram (Section 4.2). Here we consider a special class of thermodynamic diagrams called aerological diagrams. An *aerological diagram* is used to represent the vertical structure of the atmosphere and major types of processes to which moist air may be subjected, including isobaric cooling, dry adiabatic processes, and saturated adiabatic processes.

The simplest and most common form of the aerological diagram has pressure as the ordinate and temperature as the abscissa. While the temperature scale is linear, it is usually desirable to have the ordinate approximately representative of height above the surface. Thus the ordinate may be proportional to $-\ln p$ (the *Emagram*) or to p^{R/c_p} (the *Stuve diagram*). The emagram has the advantage over the Stuve diagram in that area on the diagram is proportional to energy. Before the advent of computers, aerological diagrams were used widely in weather forecasting applications and the energy-area equivalence of the diagram was an important consideration. For the present purposes, we use the aerological diagram to illustrate certain moist atmospheric processes, and the energy-area equivalence is not an important consideration. Because of the simplicity of its construction, we use the Stuve diagram (sometimes referred to as a *pseudo-adiabatic chart*) to illustrate the utility of aerological diagrams in understanding moist thermodynamic processes.

The construction of the pseudo-adiabatic chart is illustrated in Figure 6.5 (see also Appendix...*TBD*). The temperature scale is linear, while the pressure scale is proportional to p^{R/c_p}. From (2.62), it is easily seen that the dry adiabats or lines of constant potential temperature are straight lines. Pseudo-adiabats (θ_e = constant), are shown by the curved dashed lines. Lines of constant water vapor mixing ratio (w_v = constant) are given by the thin solid lines in Figure 6.5. The ordinate p^{R/c_p} can be interpreted in terms of altitude, z, using (1.45). The use of the pseudo-adiabatic chart is illustrated with the following examples.

Figure 6.6 illustrates vertical profiles of temperature and dew-point temperature plotted on an aerological diagram. Such observations are obtained using balloons, aircraft or remote sensing. From the definition of dew-point temperature (6.15), it is easily seen that by reading off the saturation mixing ratio at the dew-point temperature at a given level on the diagram, one obtains the actual water vapor mixing ratio. Conversely, if the mixing ratio is given, the dew-point temperature may be read off the diagram. The saturation mixing ratio is determined by reading off the mixing ratio corresponding to the temperature at that level.

The adiabatic ascent of a parcel from the surface is represented schematically in Figure 6.7. Consider a parcel with $p = p_0$, $T = T_0$, and $w_v = w_0$. The potential temperature of this parcel corresponds to the value of the dry adiabat that passes through T_0, p_0. In adiabatic ascent, the parcel will be lifted dry adiabatically along an isopleth of constant θ, that passes through p_0, T_0. In this ascent, the temperature and saturation mixing ratio decrease while the actual mixing ratio remains the same. The level where the saturation mixing ratio equals the actual mixing ratio (the intersection of the constant θ line with the constant w_0 line) corresponds to T_s, p_s, z_s; the saturation temperature and pressure and the lifting condensation level. The thermodynamic properties of air that continues to ascend above the saturation point is found by following the pseudo-adiabat (line of constant θ_e) that passes through T_s, p_s. The mixing ratio of the parcel in pseudo-adiabatic ascent corresponds to the saturation mixing ratio at that level (the intersection of the pseudo-adiabat that passes through T_s, p_s with the constant mixing ratio line). The adiabatic liquid water content at a given level above the saturation point is approximated by subtracting the saturation mixing ratio from the original mixing ratio, w_0.

The equivalent potential temperature, θ_e, corresponding to T_0, p_0, is determined by following the pseudo-adiabat through T_s, p_s, to very low pressure, until the pseudo-adiabat is essentially parallel to the dry adiabat. By following the dry adiabat down to a pressure of p_0 and reading off the corresponding temperature, the equivalent temperature, T_e, is obtained; by continuing to follow this dry adiabat down to $p = 1000$ mb, the equivalent potential temperature, θ_e, is obtained. The *equivalent temperature* is related to the equivalent potential temperature analogously to (2.62) as

$$\theta_e = T_e \left(\frac{p_0}{p}\right)^{R/c_p}$$

The wet bulb temperature, T_w, can be approximated by following the pseudo-adiabat that passes through p_s, T_s down to the level of p_0 and reading the corresponding temperature. By continuing to follow this pseudo-adiabat down to $p = 1000$ mb, the equivalent wet bulb temperature, θ_w, is determined. Note that while the pseudo-adiabatic wet bulb temperature is almost numerically equivalent to the adiabatic isobaric wet bulb temperature defined in Section 6.3, they are slightly different. In the case of the pseudo-adiabatic wet bulb temperature, water is evaporated into the air through pseudo-adiabatic descent, while water is evaporated isobarically in the atmosphere in the determination of the adiabatic isobaric wet bulb temperature.

While aerological diagrams are useful for illustrating schematically the results of thermodynamic transformations of moist air, their use as a computational tool has been superseded by computers.

2.10 Dry Adiabatic Processes in the Atmosphere

In Section 2.4, the following relationship between pressure and temperature was derived for a reversible adiabatic process for an ideal gas:

$$\frac{T_0}{T} = \left(\frac{p_0}{p}\right)^{R/c_p} \tag{2.61}$$

The lifting of air parcels by processes such as orographic lifting, frontal lifting, low-level convergence, and vertical mixing causes pressure to decrease, with a corresponding temperature decrease that is specified by (2.61). The lifting of air parcels can be considered a dry adiabatic process as long as condensation does not occur.

If we choose $p_0 = 1000$ mb to correspond to a temperature θ, (2.61) becomes

$$\theta = T\left(\frac{p_0}{p}\right)^{R/c_p} \qquad (2.62)^{*****}$$

where R/c_p for dry air is evaluated to be

$$\frac{R}{c_p} = \frac{R}{c_v + R} = \frac{R}{\frac{5}{2}R + R} = \frac{2}{7} = 0.286$$

The temperature θ is called the *potential temperature.* It is the temperature a sample of gas would have if it were compressed (or expanded) in an adiabatic reversible process from a given state, p and T, to a pressure of 1000 mb. Since θ is a function of two variables of state (p and T), it is itself a variable of state. θ is thus a characteristic of the gas sample which is invariant during a reversible adiabatic process. Such a quantity is known as a *conservative quantity*. Because it is conserved for reversible adiabatic processes in the atmosphere, θ is a useful parameter in atmospheric thermodynamics. Potential temperature and other conserved variables will be used throughout the text, to simplify the thermodynamic equations and in the context describing air and water mass characteristics.

Consider an atmospheric temperature profile with a lapse rate Γ=6°C km^{-1}. For atmospheric pressures less than 1000 mb, the potential temperature of a sample of air is greater than the physical temperature, since adiabatic compression must be done to lower the parcel to 1000 mb. Conversely, the potential temperature of a sample of air with pressure greater than 1000 mb will be less than the physical temperature. At a pressure level of 1000 mb, $\theta = T$.

Equation (2.62) does not account for water vapor. The specific heat of moist air is

$$c_p = \left(1 - q_v\right)c_{pd} + q_v c_{pv} \approx c_{pd}\left(1 + 0.87q_v\right) \tag{2.65}$$

where the subscripts d and v refer to dry air and water vapor, respectively. The ratio R/c_p for moist air can then be determined from (1.23) to be

$$\theta(s,T,p;p_0)=T_0+\int_p^{p_0}\Gamma(s,\theta(s,T,p;p_0),p)\,dp \tag{2.74}$$

where p_0 and T_0 are the reference pressure and temperature. An expression was derived by Bryden (1973) using experimental compressibility data to give θ (°C) as a function of T (°C), s (psu), and p (bars):

$$\begin{aligned}\theta(s,T,p) &= T-p(3.604\times10^{-4}+8.3198\times10^{-5}T-5.4065\times10^{-7}T^2\\ &\quad+4.0274\times10^{-9}T^3)-p(s-35)(1.7439\times10^{-5}-2.9778\times10^{-7}T)\\ &\quad-p^2(8.9309\times10^{-7}-3.1628\times10^{-8}T+2.1987\times10^{-10}T^2\\ &\quad+4.1057\times10^{-9}(s-35)p^2-p^3(-1.6056\times10^{-10}+5.0484\times10^{-12}T)\end{aligned} \tag{2.75}$$

where θ (25, 10, 1000) = 8.4678516°C can be used as a check value.

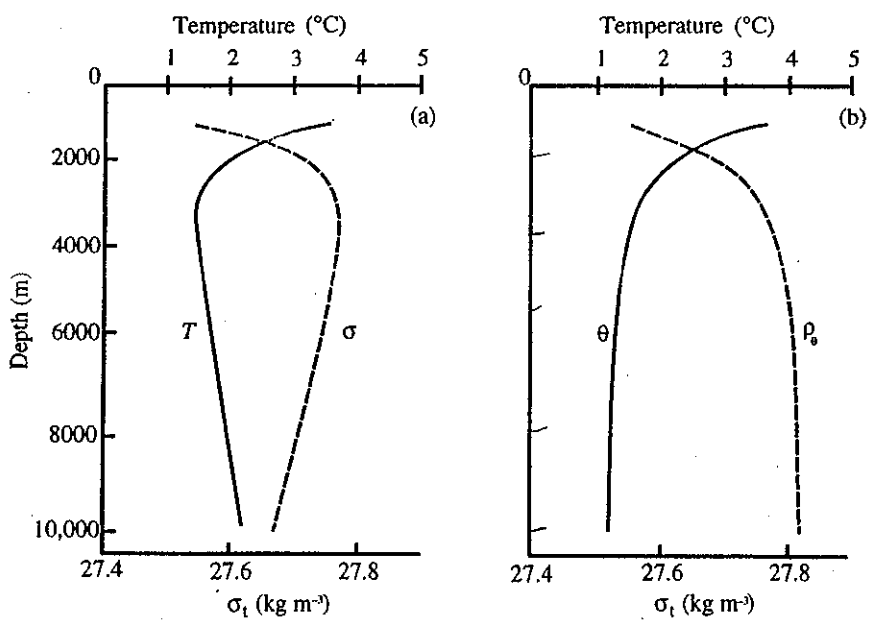

Figure 2.9 (a) Temperature and density profiles, representative of typical values found in the ocean. The nearly adiabatic profiles in the deep ocean produce constant values of potential temperature and potential density, as shown in (b).