

MOIST THERMODYNAMIC PROCESSES

As most of the rest of this book is concerned with the dynamics of moist convective processes, it is fitting to pause to review the elementary thermodynamics of atmospheres with variable water vapor content and with phase changes of water substance. The latter makes a very major contribution to atmospheric thermodynamics and introduces a variety of new dynamical processes with no analogs in dry convection.

It is assumed that the student has had a college-level course in thermodynamics and has been or will be exposed to the fundamentals of cloud microphysics. A detailed treatment of moist thermodynamics can be found in the work of Iribarne and Godson (1973), while the student is referred to Rogers and Yau (1989) or Pruppacher and Klett (1978) for expositions on cloud microphysical processes. The present chapter should be considered an overview of these subjects.

This chapter begins with a brief exposition of water vapor variables and moist thermodynamic variables and constants. Section 4.2 describes the thermodynamics of moist but unsaturated air. “Virtual” temperatures that are useful in describing density fluctuations in moist and in cloudy and precipitation-filled air are described in Section 4.3, while phase equilibrium is the subject of Section 4.4. In Section 4.5, we derive certain conserved moist thermodynamic variables. The various physical processes that lead to phase change are described in Section 4.6 and the thermodynamics of cloudy, saturated air are reviewed in Section 4.7. The chapter concludes with brief reviews of cloud microphysical processes and of the thermodynamics of the ice phase.

4.1 Moisture variables

The amount of water vapor in the atmosphere may be described by a number of related variables, the most commonly used of which are the *mixing ratio* (r), which is the mass of water vapor per unit mass of dry air; the *specific humidity* (q), the mass of water vapor per unit mass of air (including the vapor); the *vapor pressure* (e),¹ the partial pressure of water vapor; and the *vapor density* (ρ_v), the mass of vapor per unit volume.

¹ Logically, the vapor pressure should be labeled p_v . Here we retain e to conform to widespread usage, and for greater ease of notation.

These and other moist thermodynamic variables are listed in Appendix 1. The mixing ratio is related to vapor density by

$$r = \frac{\rho_v}{\rho_d}, \quad (4.1.1)$$

where ρ_d is the mass of dry air per unit volume, while use of the ideal gas law in the above gives a relation between r and e :

$$r = \frac{e/R_v T}{p_d/R_d T} = \frac{R_d}{R_v} \frac{e}{p - e} \equiv \epsilon \frac{e}{p - e}, \quad (4.1.2)$$

where p_d is the partial pressure of dry air, R_d is the weighted mean gas constant for all the constituents of air other than water vapor, and R_v is the gas constant for water vapor. We have also used Dalton's law, $p = p_d + e$. We define ϵ as the ratio of R_d to R_v ; it is also the ratio of the molecular weight of water to the mean molecular weight of dry air, where the latter is defined

$$\bar{m}_d \equiv \frac{\sum M_i}{\sum \frac{M_i}{m_i}}, \quad (4.1.3)$$

where M_i is the mass of the i th constituent of dry air and m_i is its molecular weight.

The specific humidity, q , is related to vapor pressure and mixing ratio by

$$q = \frac{\rho_v}{\rho_d + \rho_v} = \frac{r}{1 + r} = \frac{\epsilon e}{p - e(1 - \epsilon)}. \quad (4.1.4)$$

The mixing ratio, specific humidity, and vapor pressure that would obtain if the atmosphere were saturated at the same temperature and pressure are denoted, respectively, as the *saturation mixing ratio* (r^*), *saturation specific humidity* (q^*), and *saturation vapor pressure* (e^*). Since e^* is a function of temperature alone (see Section 4.4), all these are *state variables*; that is, they are functions of temperature and pressure alone.

The *relative humidity* (\mathcal{H}) is the ratio between the actual and saturation vapor pressure²:

$$\mathcal{H} \equiv \frac{e}{e^*}. \quad (4.1.5)$$

In terms of mixing ratios, we have, from (4.1.2),

$$\mathcal{H} = \frac{r}{r^*} \left(\frac{1 + r^*/\epsilon}{1 + r/\epsilon} \right). \quad (4.1.6)$$

Condensed water may virtually always be considered to be in suspension in the air; that is, all water drops and ice crystals or pellets can be

² The relative humidity is sometimes defined as the ratio of the actual mixing ratio to the saturation mixing ratio.

considered to be falling at their terminal velocities. We may describe the liquid water content by the *liquid water mixing ratio* (r_l), which is the mass of liquid per unit mass of *dry* air. We also define a *total water content* (r_t)³ by

$$r_t \equiv r + r_l. \quad (4.1.7)$$

r_t is therefore the total water content (except ice) per unit mass of dry air.

The ice content can be described by the *ice mixing ratio* (r_i), and the sum of the vapor and ice contents is r_{t_i} . We may also define a *net water content* $r_T \equiv r + r_l + r_i$. Since the saturation vapor pressure over ice is different from that over water, we define $e^\#$ as the former and also define $r^\#, q^\#,$ and \mathcal{H}_i based on $e^\#$.

In addition to the above, there are other density and thermodynamic variables listed in Appendix 1 that are defined as they are introduced in subsequent sections. The student is advised that, although it is tedious, committing these to memory will greatly facilitate the comprehension of the rest of this book as well as research papers on the subject of moist convection and phase changes in the atmosphere.

4.2 Thermodynamics of unsaturated moist air

The thermodynamics of dry and moist (but unsaturated) air differ in that the effective heat capacities are influenced by the presence of water vapor. Water vapor is a triatomic molecule whose state may be described by three translational and three rotational coordinates, giving six quadratic terms in the expression of its kinetic energy. The equipartition theorem would give

$$c_{vv} = 3R_v = 1384.53 \text{ J kg}^{-1} \text{ K}^{-1}$$

and

$$c_{pv} = 4R_v = 1846.04 \text{ J kg}^{-1} \text{ K}^{-1},$$

where c_{vv} and c_{pv} are the heat capacities of water vapor at constant volume and constant pressure, respectively. Here it is assumed that the molecule is in the ground state; that is, that vibrational energy does not contribute to heat capacity. But at atmospheric temperatures and pressures, vibrational states do occur so that experimental values of the heat capacities exceed these by an amount that depends on temperature and pressure. Over the range of tropospheric conditions, these variations are less than 3% and will be ignored here, so that as listed in Appendix 2,

$$c_{vv} \simeq 1410 \text{ J kg}^{-1} \text{ K}^{-1},$$

$$c_{pv} \simeq 1870 \text{ J kg}^{-1} \text{ K}^{-1}.$$

³ The total water content is sometimes denoted by Q .

The effective heat capacities of a mixture of dry air and water vapor may be deduced from the first law of thermodynamics, which may be written

$$dQ = dU + p dV, \quad (4.2.1)$$

where dQ is the total heat input,⁴ U is the total internal energy, and V is the volume. At constant volume, we may write the above as

$$(M_v + M_d) dQ = (M_d c_{vd} + M_v c_{vv}) dT, \quad (4.2.2)$$

where dQ is the specific heat input; M_v and M_d are the masses of water vapor and dry air, respectively; and c_{vd} is the heat capacity of dry air at constant volume. Dividing through by M_d and making use of the definition of mixing ratio, we have

$$\left(\frac{\partial Q}{\partial T} \right)_v = c_{vd} \left(\frac{1 + r c_{vv}/c_{vd}}{1 + r} \right) \equiv c'_v, \quad (4.2.3)$$

where we have defined c'_v as the effective heat capacity. Since r is always much smaller than 1 in the atmosphere, the above is approximately

$$c'_v \simeq c_{vd} \left[1 + r \left(\frac{c_{vv}}{c_{vd}} - 1 \right) \right] \simeq c_{vd} (1 + 0.94r). \quad (4.2.4)$$

By a similar procedure, the effective heat capacity at constant pressure is

$$\begin{aligned} c'_p &= c_{pd} \left[\frac{1 + r \frac{c_{pv}}{c_{pd}}}{1 + r} \right] \simeq c_{pd} \left[1 + r \left(\frac{c_{pv}}{c_{pd}} - 1 \right) \right] \\ &\simeq c_{pd} (1 + 0.85r). \end{aligned} \quad (4.2.5)$$

Using these quantities, the first law becomes

$$dQ = c'_v dT + p d\alpha \quad (4.2.6)$$

or, equivalently,

$$dQ = c'_p dT - \alpha dp, \quad (4.2.7)$$

where α is the *specific volume*; that is, the volume per unit mass of (moist) air. This may be expressed

$$\begin{aligned} \alpha &= \frac{V}{M_d + M_v} = \frac{\alpha_d}{1 + r} = \frac{R_d T}{p_d} \frac{1}{1 + r} \\ &= \frac{R_d T}{p} \frac{p_d + e}{p_d} \frac{1}{1 + r} = \frac{R_d T}{p} \frac{1 + r/\epsilon}{1 + r} \\ &\equiv R' \frac{T}{p}, \end{aligned} \quad (4.2.8)$$

⁴ In general, dQ is not a perfect differential!

where α_d is the volume per unit mass of dry air and R_d is the gas constant for dry air. Thus, we have derived the *effective gas constant* (R'):

$$R' \equiv R_d \frac{1 + r/\epsilon}{1 + r}. \quad (4.2.9)$$

Since $\epsilon < 1$, the effective gas constant is larger than R_d .

In an adiabatic process, the temperature varies with pressure, from (4.2.7) and (4.2.8), according to

$$c'_p dT = R' \frac{T}{p} dp,$$

which may be written

$$d \ln T = \frac{R'}{c'_p} d \ln p. \quad (4.2.10)$$

Since r is constant in a reversible, unsaturated process, this may be exactly integrated (ignoring the small temperature dependence of c'_p) to define a *potential temperature*:

$$\begin{aligned} \theta &\equiv T \left(\frac{p_0}{p} \right)^{R'/c'_p} \\ &= T \left(\frac{p_0}{p} \right)^{\frac{R_d}{c_{pd}} \frac{1+r/\epsilon}{1+r}} \\ &\simeq T \left(\frac{p_0}{p} \right)^{\frac{R_d}{c_{pd}} (1-0.24r)}, \end{aligned} \quad (4.2.11)$$

where p_0 is a reference pressure usually taken to be 1000 millibars. The potential temperature (θ) thus defined is conserved in adiabatic displacements of unsaturated air. This shows that, due to the increased heat capacity of moist air, the temperature will change less rapidly with pressure in moist air. Since r is generally less than 0.04 in the atmosphere, the exponent in (4.2.11) varies by less than 1%; this variation is usually ignored.

4.3 Virtual and density temperatures

According to (4.2.8) the specific volume ($1/\rho$) of air varies with water vapor content at constant temperature and pressure, so that moist air is lighter than dry air at the same p and T . (Some scientists during the nineteenth century thought that this was responsible for updrafts in cumulus clouds.) It has become conventional to absorb this water vapor dependence of density into a modified temperature, called *virtual temperature* (T_v), so that

$$R_d T_v \equiv R' T,$$

or

$$T_v \equiv T \frac{1 + r/\epsilon}{1 + r} \simeq T(1 + 0.608r). \quad (4.3.1)$$

The virtual temperature is therefore greater than the temperature. It can be thought of as the temperature dry air would have to have to yield the same density as moist air at the same pressure.

The *virtual potential temperature* is defined by neglecting the water vapor dependence of the exponent of (4.2.11) and replacing the temperature by the virtual temperature:

$$\theta_v \equiv T_v \left(\frac{p_0}{p} \right)^{R_d/c_{pd}} \quad (4.3.2)$$

A comparison of two air masses of differing θ_v at the same pressure will thus yield a comparison of their virtual temperatures and, therefore, their densities. Since r and θ are conserved in reversible processes, θ_v is a (*very nearly*) conserved variable in unsaturated air and is also directly related to density. For this reason, the vertical gradient of θ_v is the relevant stability parameter in moist unsaturated air, as shown in Chapter 6. The convective atmospheric boundary layer is therefore characterized by nearly constant θ_v .

When air is filled with cloud droplets, ice crystals, and/or precipitation of any type, the particles may always be considered to be falling at their terminal velocities, to a good approximation. From this point of view, *cloud and precipitation may be considered to be in suspension*. For many purposes, the mixture of air and condensed water may be considered as a single, heterogeneous system rather than as two coupled systems, though there are exceptions to this rule. But if the scale of density-driven motions that we are interested in is much larger than typical distances between condensed water particles, as is usually the case, then it is natural to consider the condensed water as contributing to the density of the heterogeneous system. We can then write the specific volume of the system as

$$\alpha = \frac{V_a + V_l + V_i}{M_d + M_v + M_l + M_i}, \quad (4.3.3)$$

where V_a , V_l , and V_i are the volumes occupied by moist air, liquid water, and ice, respectively, and the M 's are the masses of dry air, vapor, liquid water, and ice. Dividing through by M_d gives

$$\alpha = \alpha_d \left[\frac{1 + r_l (\alpha_l/\alpha_d) + r_i (\alpha_i/\alpha_d)}{1 + r_T} \right], \quad (4.3.4)$$

where α_l and α_i are the specific volumes of liquid water and ice, respectively, and r_T is the net water mixing ratio, $r_T = r + r_l + r_i$. Since the specific volumes of liquid and ice are each about 3 orders of magnitude less

than the specific volume of air, and since r_l and r_i are typically of order 10^{-3} , the last two terms in the numerator of (4.3.4) are negligible. Using this and the ideal gas law, together with the definition of vapor mixing ratio (4.1.2), gives

$$\alpha \simeq \frac{R_d T}{p_d} \frac{1}{1 + r_T} = \frac{R_d T}{p} \frac{p_d + e}{p_d} \frac{1}{1 + r_T} = R_d \frac{T}{p} \frac{1 + r/\epsilon}{1 + r_T}. \quad (4.3.5)$$

This leads naturally to the definition of *density temperature* (T_ρ):

$$T_\rho \equiv T \frac{1 + r/\epsilon}{1 + r_T}. \quad (4.3.6)$$

T_ρ may be thought of as the temperature dry air would have to have to yield the same density as moist, cloudy air. Depending on the relative amounts of condensed water and water vapor, T_ρ may be either greater than or less than the actual temperature. Once again, when used in the ideal gas law, T_ρ reflects the actual density of the heterogeneous system; that is, $\alpha = R_d T_\rho / p$. Note that T_v is a special case of T_ρ , since when condensed water is absent $r_T = r$.

4.4 Phase equilibrium of water substance

The phase diagram for water substance is presented in Figure 4.1. The features of this diagram are as follows:

- 1) The triple point of water substance lies at O; here all three phases are in equilibrium. This is characterized by

$$T_0 = 273.16 \text{ K} = 0.01^\circ \text{C},$$

$$e_0 = 6.112 \text{ millibars.}$$

- 2) The vapor–liquid curve ends at C, the critical point, beyond which there is no phase discontinuity between vapor and liquid. This occurs at

$$T_{\text{cr}} = 647 \text{ K},$$

$$e_{\text{cr}} = 221,000 \text{ millibars.}$$

- 3) The portion of the curve A–C below the triple point represents equilibrium between supercooled water and vapor.
- 4) The curve O–B represents phase equilibrium between vapor and solid; liquid–ice equilibrium is represented by O–D.
- 5) The liquid–solid transition has a negative slope as a consequence of the fact that ice is less dense than water. This is a relatively unusual property of materials, and has important geophysical consequences (e.g., ice floats and glaciers move since greater pressure lowers the freezing point). The slope of this curve is so nearly vertical, however,

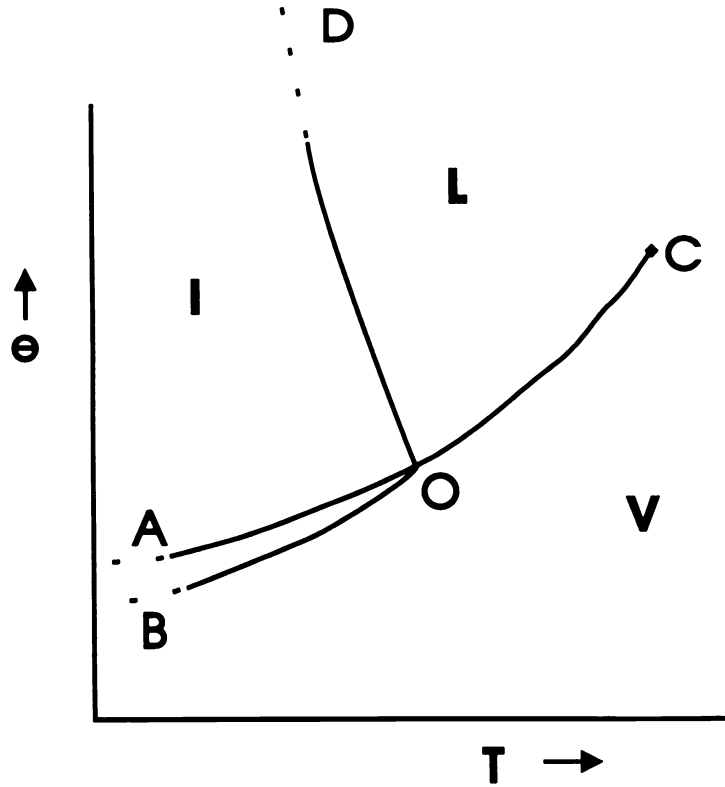


Fig. 4.1 Phase diagram for water substance. The letters L , V , and I denote liquid, vapor, and ice phases, respectively. O is the triple point and “ C ” is the critical point. The curves $O-C$, $O-D$, and $O-B$ represent phase equilibria for liquid–vapor, liquid–ice, and ice–vapor. The curve $A-O$ represents equilibrium between ice and supercooled water.

that the equilibrium may be considered to occur at 0°C over a large range of atmospheric pressures.

The phase equilibria are determined by integration of the *Clausius-Clapeyron equation*, which is derived from the definition of latent heat and from the chemical, mechanical, and thermal equilibria conditions.

The latent heat pertaining to the phase transition of a substance is defined as the difference between the heat contents, or *enthalpies*, of the two phases:

$$L_{i,ii} \equiv k_{ii} - k_i, \quad (4.4.1)$$

where k is the *specific enthalpy* and the subscripts (i) and (ii) refer to the two phases. The dependence of $L_{i,ii}$ on temperature and pressure may be obtained by differentiating (4.4.1):

$$\begin{aligned} dL_{i,ii} &= dT \left[\left(\frac{\partial k_{ii}}{\partial T} \right)_p - \left(\frac{\partial k_i}{\partial T} \right)_p \right] + dp \left[\left(\frac{\partial k_{ii}}{\partial p} \right)_T - \left(\frac{\partial k_i}{\partial p} \right)_T \right] \\ &= dT (c_{p_{ii}} - c_{p_i}) + dp \left\{ \alpha_{ii} - \alpha_i + p \left[\left(\frac{\partial \alpha_{ii}}{\partial p} \right)_T - \left(\frac{\partial \alpha_i}{\partial p} \right)_T \right] \right\}, \quad (4.4.2) \end{aligned}$$

where we have used the definition of enthalpy

$$k \equiv u + p\alpha,$$

where u is the specific internal energy. From the definition of c_p ,

$$\left(\frac{\partial k}{\partial T}\right)_p = \left(\frac{\partial Q}{\partial T}\right)_p \equiv c_p.$$

Directing our attention to the term determining the pressure dependence of $dL_{i,ii}$, we first note that for an ideal gas $\alpha = -p(\partial\alpha/\partial p)_T$. Also, for liquid water and ice, both α and $\partial\alpha/\partial p$ are very small. Thus, to a good approximation, we may neglect the pressure dependence of L in (4.4.2), resulting in *Kirchhoff's equation*:

$$\frac{dL_{i,ii}}{dT} = c_{pii} - c_{pi}. \quad (4.4.3)$$

Since the heat capacities of liquid water and water vapor do not vary much over the range of atmospheric temperatures, (4.4.3) may be integrated to get

$$L_{i,ii} \simeq L_{i,ii0} + (c_{pii} - c_{pi})(T - 273.16 \text{ K}), \quad (4.4.4)$$

where $L_{i,ii0}$ is the latent heat at the triple point.

The phase equilibria are determined by requiring that the two phases be in thermal, mechanical, and chemical equilibrium:

$$\begin{aligned} T_i &= T_{ii}, \\ p_i &= p_{ii}, \\ g_i &= g_{ii}, \end{aligned} \quad (4.4.5)$$

where g is the *Gibbs free energy*:

$$g \equiv u + p\alpha - Ts = k - Ts, \quad (4.4.6)$$

where s is the *specific entropy*. If we produce a reversible, infinitesimal change while maintaining equilibrium, it follows that

$$dg_i = dg_{ii}, \quad (4.4.7)$$

or substituting (4.4.6),

$$\alpha_i dp - s_i dT = \alpha_{ii} dp - s_{ii} dT, \quad (4.4.8)$$

where we have made use of the first law of thermodynamics:

$$T ds = du + p d\alpha.$$

It follows from (4.4.8) that

$$\left(\frac{dp}{dT}\right)_{i,ii} = \frac{s_{ii} - s_i}{\alpha_{ii} - \alpha_i}. \quad (4.4.9)$$

We also have, from (4.4.6) and (4.4.1), together with (4.4.5),

$$L_{i,ii} = k_{ii} - k_i = T(s_{ii} - s_i),$$

so that (4.4.9) can be written

$$\left(\frac{dp}{dT}\right)_{i,ii} = \frac{L_{i,ii}}{T(\alpha_{ii} - \alpha_i)}. \quad (4.4.10)$$

This is the Clausius-Clapeyron equation.

For liquid-ice equilibrium, the specific volumes are nearly constant and (4.4.10) is approximately

$$\left(\frac{dp}{dT}\right)_{\text{ice,vapor}} \simeq -1.344 \times 10^5 \text{ millibars K}^{-1},$$

showing that the melting temperature changes by only 0.007 K for a 1000 millibars change in pressure.

In the case of liquid-vapor equilibrium, we can, to a good approximation, ignore α_{liquid} compared to α_{vapor} , and using the ideal gas law,

$$\frac{de^*}{dT} = \frac{L_v e^*}{R_v T^2}, \quad (4.4.11)$$

where e^* is the saturation vapor pressure and L_v the *latent heat of vaporization*. If we use (4.4.4) to approximate the temperature dependence of L_v , then integration of (4.4.11) gives

$$\ln \frac{e^*}{6.107} = \frac{L_{v0} - (c_{pv} - c_l)T_0}{R_v} \left(\frac{1}{T_0} - \frac{1}{T}\right) + \frac{c_{pv} - c_l}{R_v} \ln \frac{T}{T_0}, \quad (4.4.12)$$

where c_l is the heat capacity of liquid water, L_{v0} is the latent heat of vaporization at $T_0 = 273.15$ K, and e^* is in millibars. Several approximations are involved in (4.4.12), including ignoring the specific volume of liquid water in (4.4.10), treating water vapor as an ideal gas, and ignoring the temperature dependence of the heat capacities. Moreover, in the derivation (4.4.10) we have neglected the influence of the pressure exerted by dry air and also the fact that the liquid phase contains dissolved gas. Even so, (4.4.12) is accurate to within 0.5% of experimental values in the range $-20^\circ\text{C} \leq T \leq 30^\circ\text{C}$. An improvement can be made to (4.4.12) pertaining to pure phase equilibrium (without dry air) by slightly modifying the coefficients. This gives

$$\ln e^* = 53.67957 - \frac{6743.769}{T} - 4.8451 \ln T, \quad (4.4.13)$$

with e^* in millibars and T in K. This matches the values given in the Smithsonian Meteorological Tables (List, 1951) to better than 0.006% in the range $0^\circ\text{C} \leq T \leq 40^\circ\text{C}$. Measurements of equilibrium below 0°C between supercooled water and vapor are not entirely accurate, but the above fits the values in the Smithsonian tables to within 0.3% down to -30°C and within 0.7% as low as -40°C . A somewhat simpler, if slightly less accurate, formula has been suggested by Bolton (1980) as a modification of Tetens's (1930) formula:

$$e^* = 6.112 \exp\left(\frac{17.67T}{T + 243.5}\right), \quad (4.4.14)$$

with T in degrees Celsius. In the range $-35^\circ\text{C} \leq T \leq 35^\circ\text{C}$ this is accurate to within 0.3%.

The phase equilibrium between water vapor and ice may be found from the Clausius-Clapeyron equation (4.4.10) with similar approximations made to arrive at an equation like (4.4.11) but with L_s , the *latent heat of sublimation*, and thence to a relation analogous to (4.4.12) but with L_{s0} , and c_i replacing c_l . Once again, a slight modification of the coefficients gives a better fit to the values in the Smithsonian tables, with the equation

$$\ln e^\# = 23.33086 - \frac{6111.72784}{T} + 0.15215 \ln T, \quad (4.4.15)$$

accurate to within 0.14% in the range $-80^\circ\text{C} \leq T \leq 0^\circ\text{C}$.

The effects of the departures of water vapor from an ideal gas, the partial pressure of dry air, and the presence of dissolved gas in equilibrium introduce a slight pressure dependence of $e^\#$ and e^* . These can be accounted for by an empirical correction factor, f , such that

$$e^{*'} = f e^*$$

and

$$e^{\#'} = f_i e^\#, \quad (4.4.16)$$

where $e^{*'}$ and $e^{\#}'$ are the corrected saturation pressures. Some values of f are listed in Table 4.1. Using a mean value of 1.003 will result in total errors less than 0.3% over a large range of tropospheric conditions.

4.5 Conserved moist thermodynamic variables

We will find it useful to define several thermodynamic variables that are conserved under several thermodynamic processes. First consider a system that undergoes phase changes of water *at constant pressure*. Then if no heat is added other than latent heat associated with the phase changes, the *total enthalpy* is conserved since

$$dQ = dk - \alpha dp.$$

Table 4.1 Some values of the empirical correction factors. [From Iribarne and Godson (1973)]

T ($^{\circ}\text{C}$)	p (millibars)		
	30	100	1100
	f		
-40	1.0002	1.0006	1.0060
0	1.0005	1.0008	1.0047
40	—	1.0019	1.0054
	f_i		
-80	1.0002	1.0008	1.0089
-40	1.0002	1.0006	1.0061
0	1.0005	1.0008	1.0048

The enthalpy, k ,⁵ of the heterogeneous system consists of the specific enthalpies of dry air, water vapor, and liquid water (ice is considered later):

$$M_d k = M_d k_d + M_v k_v + M_l k_l, \quad (4.5.1)$$

where k is the total enthalpy per unit mass of *dry* air and the M 's denote masses of each phase denoted by d (dry air), v (vapor), and l (liquid water), respectively. Dividing through by M_d gives

$$k = k_d + r_v k_v + r_l k_l. \quad (4.5.2)$$

By the definition of latent heat, (4.4.1), we have

$$L_v(T) = k_v - k_l,$$

so that (4.5.2) may be written

$$k = k_d + L_v r + k_l r_t, \quad (4.5.3)$$

where r_t is the total water content. Substituting the definitions of k_d and k_l and using the ideal gas law gives

$$k = (c_{pd} + r_t c_l)T + L_v r. \quad (4.5.4)$$

⁵ Enthalpy is often denoted by h . Here we use k to avoid confusion with h , which is widely used to denote the moist static energy.

This is usually referred to as the *moist enthalpy*, but we refer to it merely as the *enthalpy*.

Since the quantity

$$L_{v0} - (c_{pv} - c_l)T_0 = L_v - (c_{pv} - c_l)T$$

is a constant, and since r_t is a constant, we can form another conserved variable by subtracting $r_t [L_{v0} - (c_{pv} - c_l)T_0]$ from (4.5.4), giving

$$k_w \equiv (c_{pd} + r_t c_{pv})T - L_v r_t. \quad (4.5.5)$$

This is called the *liquid water enthalpy*. It is important to realize that k and k_w are conserved under an isobaric process as long as no external heat is applied or mass lost from the system, *regardless of whether the transformations are reversible*, since we have used only the first law of thermodynamics.

We next consider quantities conserved under *reversible moist adiabatic processes*. As we assume reversibility, the heterogeneous system must be in phase equilibrium at all times. In this case the *total entropy* (s) is conserved.

By analogy to (4.5.2), the total specific entropy (entropy per unit mass of dry air) may be written

$$s = s_d + r s_v + r_l s_l, \quad (4.5.6)$$

where s_d is the specific entropy of dry air, s_v is the specific entropy of water vapor, and s_l is the specific entropy of liquid water.

Writing the Clausius-Clapeyron equation as

$$L_v = T(s_v^* - s_l),$$

where s_v^* is the specific entropy of water vapor *in equilibrium* with liquid water, and substituting this into (4.5.6) gives

$$s = s_d + r_t s_l + \frac{L_v r}{T} + r(s_v - s_v^*). \quad (4.5.7)$$

Using the definitions of specific entropies:

$$\begin{aligned} s_d &= c_{pd} \ln T - R_d \ln p_d, \\ s_v &= c_{pv} \ln T - R_v \ln e, \\ s_v^* &= c_{pv} \ln T - R_v \ln e^*, \end{aligned}$$

and

$$s_l = c_l \ln T, \quad (4.5.8)$$

(4.5.7) may be written

$$s = (c_{pd} + r_t c_l) \ln T - R_d \ln p_d + \frac{L_v r}{T} - r R_v \ln(\mathcal{H}). \quad (4.5.9)$$

Note that the last term vanishes when the air is saturated ($\mathcal{H} = 1$) and also in the limit of $r \rightarrow 0$, reaching its maximum magnitude for intermediate \mathcal{H} . The quantity s , defined by (4.5.9), is conserved under *reversible* moist adiabatic transformations.

It has become conventional to express entropy in terms of an *equivalent potential temperature* θ_e , which is defined so that

$$(c_{pd} + r_t c_l) \ln \theta_e \equiv s + R_d \ln p_0, \quad (4.5.10)$$

where p_0 is a reference pressure. Substituting (4.5.9) gives

$$\theta_e = T \left(\frac{p_0}{p_d} \right)^{R_d / (c_{pd} + c_l r_t)} (\mathcal{H})^{-r R_v / (c_{pd} + c_l r_t)} \exp \left[\frac{L_v r}{(c_{pd} + c_l r_t) T} \right]. \quad (4.5.11)$$

When $r = 0$, $\theta_e = \theta$, the potential temperature.

It is of interest to note the conditions under which entropy, as represented by s or θ_e , is not conserved. Obviously, s will change when external sensible heating such as radiation or conduction is applied, or when latent heating is applied externally as occurs, for example, when water evaporates into air from oceans and lakes. Even when transformations are adiabatic, however, small entropy increases will occur due to irreversible effects. An important example of this is the evaporation of rain into *unsaturated* air. By differentiating (4.5.9) and using the first law of thermodynamics, the Clausius-Clapeyron relation, and Kirchhoff's relation, it can be shown that there is an irreversible increase of entropy associated with this process, given by

$$(ds)_{\text{irr}} = -R_v \ln(\mathcal{H}) dr. \quad (4.5.12)$$

This is always nonnegative since $\mathcal{H} \leq 1$ and $dr > 0$, the latter being the case since it is impossible for condensation to occur in subsaturated

transformations. Comparing this term with the internal energy term of the first law of thermodynamics, we can calculate that the evaporation of 10 g kg^{-1} of liquid water into air at 50% relative humidity increases the entropy by an amount equivalent to a diabatic temperature increase of about 1°C . Thus, bringing dry air to saturation by evaporating rain into it increases its entropy by a small, but not always negligible, amount.

There are two other entropy variables that we shall find useful: the *liquid water potential temperature* θ_l and the *liquid water virtual potential temperature* θ_{lv} . Starting again with (4.5.6),

$$\begin{aligned} s &= s_d + r s_v + r_l s_l \\ &= s_d + r_t s_v + r_l (s_l - s_v) \\ &= s_d + r_t s_v + r_l (s_l - s_v^*). \end{aligned} \quad (4.5.13)$$

The last equality results because in thermodynamic equilibrium $s_v = s_v^*$ whenever $r_l \neq 0$. Using the definitions of entropies, (4.5.8), the Clausius-Clapeyron equation,

$$L_v = T(s_v^* - s_l),$$

and the relations

$$\begin{aligned} e &= \left(\frac{r p}{\epsilon + r} \right), \\ p_d &= \left(\frac{p}{1 + \frac{r}{\epsilon}} \right), \end{aligned}$$

and also making use of the relation $r = r_t - r_l$, (4.5.13) becomes

$$\begin{aligned} s_w &= (c_{pd} + r_t c_{pv}) \ln T - (R_d + r_t R_v) \ln p \\ &+ (R_d + r_t R_v) \ln \left(1 + \frac{r_t - r_l}{\epsilon} \right) - r_t R_v \ln \left(\frac{r_t - r_l}{\epsilon} \right) - \frac{L_v r_l}{T}. \end{aligned} \quad (4.5.14)$$

By adding the conserved quantity

$$(R_d + r_t R_v) \ln p_0 - (R_d + r_t R_v) \ln \left(1 + \frac{r_t}{\epsilon} \right) + r_t R_v \ln \left(\frac{r_t}{\epsilon} \right)$$

to (4.5.14), dividing the result through by $(c_{pd} + r_t c_{pv})$ and then taking the exponent of the resulting quantity, we arrive at the definition of the liquid water potential temperature, θ_l :

$$\begin{aligned} \theta_l \equiv T &\left(\frac{p_0}{p} \right)^x \left(1 - \frac{r_l}{\epsilon + r_t} \right)^x \\ &\times \left(1 - \frac{r_l}{r_t} \right)^{-\gamma} \exp \left[\frac{-L_v r_l}{(c_{pd} + r_t c_{pv}) T} \right], \end{aligned} \quad (4.5.15)$$

in which

$$\begin{aligned}\chi &\equiv \left(\frac{R_d + r_t R_v}{c_{pd} + r_t c_{pv}} \right), \\ \gamma &\equiv \left(\frac{r_t R_v}{c_{pd} + r_t c_{pv}} \right).\end{aligned}\tag{4.5.16}$$

This quantity is also conserved under reversible, adiabatic transformations. It has the virtue of reducing exactly to potential temperature (4.2.11) when $r_l = 0$. This can also be expressed in terms of virtual temperature, or virtual potential temperature, by making use of the definition of the former and the relation $r = r_t - r_l$:

$$T = T_v \left(\frac{1+r}{1+\frac{r}{\epsilon}} \right) = T_v \left(\frac{1+r_t-r_l}{1+\frac{r_t-r_l}{\epsilon}} \right).\tag{4.5.17}$$

(Note that we have used virtual temperature, not density virtual temperature.) Substituting (4.5.17) in (4.5.15) and dividing the result by the conserved variable $(1+r_t)/(1+r_t/\epsilon)$ gives the definition of *liquid water virtual potential temperature*:

$$\begin{aligned}\theta_{lv} &\equiv T_v \left(\frac{p_0}{p} \right)^\chi \left(1 - \frac{r_l}{1+r_t} \right) \left(1 - \frac{r_l}{\epsilon+r_t} \right)^{\chi-1} \\ &\quad \times \left(1 - \frac{r_l}{r_t} \right)^{-\gamma} \exp \left[\frac{-L_v r_l}{(c_{pd} + r_t c_{pv}) T} \right],\end{aligned}\tag{4.5.18}$$

with χ and γ given by (4.5.16). This quantity reduces to the virtual potential temperature (4.3.2) when $r_l = 0$.

One further thermodynamic quantity will prove to be useful in dealing with moist convective processes: the *static energy* h . It is conserved in adiabatic displacements *in which the pressure change is entirely hydrostatic*. We derive it using the adiabatic form of the first law together with Kirchhoff's relation (4.4.3):

$$0 = (c_{pd} + r_t c_l) dT + d(L_v r) - \alpha_d dp.\tag{4.5.19}$$

We also have, from (4.3.4),

$$\alpha_d \simeq \alpha(1+r_t),\tag{4.5.20}$$

where we have neglected the very small contributions of the specific volume of liquid water. For a strictly hydrostatic pressure change,

$$\alpha dp = -g dz,\tag{4.5.21}$$

where z is altitude. Combining (4.5.19) to (4.5.21) gives

$$0 = (c_{pd} + r_t c_l) dT + d(L_v r) + (1 + r_t)g dz \equiv dh. \quad (4.5.22)$$

If r_t is also conserved, the above may be integrated to yield

$$h \equiv (c_{pd} + r_t c_l)T + L_v r + (1 + r_t)gz, \quad (4.5.23)$$

where z is now the *geopotential height*, which is defined to account for variations in the gravitational acceleration, g . Note that we have made no assumptions about the existence of two phases in deriving h , so that h is conserved for *adiabatic, saturated or unsaturated transformations in which mass is conserved and in which the pressure change is strictly hydrostatic*. We can also define a dry static energy, h_d ,⁶ conserved under hydrostatic unsaturated transformations:

$$h_d \equiv (c_{pd} + r c_{pv})T + (1 + r)gz. \quad (4.5.24)$$

Also, by subtracting the conserved variable

$$r_t [L_{v0} - (c_{pv} - c_l)T_0] = r_t [L_v - (c_{pv} - c_l)T]$$

from (4.5.23), we obtain a new conserved variable called the *liquid water static energy*:

$$h_w \equiv (c_{pd} + r_t c_{pv})T - L_v r_l + (1 + r_t)gz. \quad (4.5.25)$$

The static energies h , h_d , and h_w are very closely related to the entropy variables θ_e , θ , and θ_l , respectively. Their distributions in the atmosphere look very similar.

Finally, it will prove useful to deduce certain differential relations among several of the thermodynamic variables we have defined. We begin with the definitions of enthalpy and entropy, (4.5.4) and (4.5.8), and

⁶ The symbol s is often used to denote dry static energy; here we adhere to the notation h_d to avoid confusion with entropy.

consider the relationship between small increments of each quantity, with entropy increments assumed to occur in phase equilibrium:

$$dk = (c_{pd} + rc_{pv} + r_l c_l) dT + c_l T dr_t + L_v dr \quad (4.5.26)$$

and

$$T ds = (c_{pd} + rc_{pv} + r_l c_l) dT + c_l T \ln T dr_t + L_v dr - \alpha_d dp, \quad (4.5.27)$$

from which we may write

$$dk = T ds + c_l T(1 - \ln T) dr_t + \alpha_d dp. \quad (4.5.28)$$

Here we have allowed for the possibility of an *open system* from which water mass may be added or subtracted. We can then deduce the following:

$$\begin{aligned} \left(\frac{\partial k}{\partial s} \right)_{p, r_t} &= T, \\ \left(\frac{\partial k}{\partial p} \right)_{s, r_t} &= \alpha_d, \\ \left(\frac{\partial k}{\partial r_t} \right)_{s, p} &= c_l T(1 - \ln T). \end{aligned} \quad (4.5.29)$$

By cross-differentiating the expressions in (4.5.29), one may obtain certain *Maxwell's relations* for moist thermodynamic processes:

$$\left(\frac{\partial T}{\partial p} \right)_{s, r_t} = \left(\frac{\partial \alpha_d}{\partial s} \right)_{p, r_t}, \quad (4.5.30)$$

$$\left(\frac{\partial T}{\partial r_t} \right)_{p, s} = -c_l \ln T \left(\frac{\partial T}{\partial s} \right)_{p, r_t}, \quad (4.5.31)$$

$$\left(\frac{\partial \alpha_d}{\partial r_t} \right)_{p, s} = -c_l \ln T \left(\frac{\partial T}{\partial p} \right)_{s, r_t}. \quad (4.5.32)$$

Several of these will prove useful later in deriving stability properties of moist atmospheres.

4.6 Processes leading to saturation in the atmosphere

There are several physical processes that can lead to saturation of previously unsaturated air. While by far the most important of these is cooling by adiabatic expansion, other processes occasionally come into play and are briefly reviewed here.

4.6.1 Diabatic cooling at constant pressure

Close to the surface and near the tops of clouds, the radiative flux divergence can be large and the atmosphere may cool appreciably. Near the surface, this process may be approximated as occurring at constant pressure. If enough cooling occurs, the saturation vapor pressure may drop as low as the actual vapor pressure and saturation will occur, leading to dew, frost, or ground fog. The temperature at which saturation is achieved by isobaric cooling is called the *dew-point temperature* (T_d), while the equivalent temperature at which ice saturation occurs is the *frost point temperature* (T_f). They are defined by the relations

$$e^*(T_d) = e \quad (4.6.1)$$

and

$$e^\#(T_f) = e.$$

Note that e itself is conserved in an isobaric, unsaturated process since the conserved variable is r , and $r = \epsilon e/p - e$. We can find T_d and T_f by inverting (4.6.1), though this cannot be done in closed form using (4.4.13) or (4.4.15). But an excellent approximation can be obtained by inverting Bolton's formula (4.4.14), giving

$$T_d \simeq \frac{243.5}{\left(\frac{17.67}{\ln e/6.112}\right) - 1}, \quad (4.6.2)$$

where e is given in millibars and T_d is in degrees Celsius.

4.6.2 Cooling and moistening by evaporation of water

If rain falls into unsaturated air and evaporates, the vapor pressure will increase at the same time that the saturation vapor pressure decreases, since the heat of vaporization in this case must be supplied by the air. If the process continues long enough, the air asymptotically approaches saturation. The idealized process is considered to occur at constant pressure. The temperature ultimately achieved at saturation is called the *wet-bulb temperature* (T_w), and can be measured by ventilating a thermometer whose sensing bulb is kept wet by a piece of damp cloth (thus the term "wet bulb"). Since the process is isobaric, the total enthalpy of the air-water system is kept constant, so that from (4.5.4) we have

$$(c_{pd} + r_t c_l)(T_w - T) + L_v(T_w)r^*(T_w) - L_v(T)r = 0, \quad (4.6.3)$$

where T and r are the ambient temperature and mixing ratio and $L_v(T_w)$ and $r^*(T_w)$ are the latent heat and saturation mixing ratio evaluated at $T = T_w$. Here r_t is the total water content, which is the initial amount of vapor together with the amount of liquid necessary to saturate the air. This sum must equal the final mixing ratio, $r^*(T_w)$, so that (4.6.3) can be written

$$[c_{pd} + r^*(T_w)c_l](T - T_w) = L_v(T_w)r^*(T_w) - L_v(T)r. \quad (4.6.4)$$

This is a highly implicit relation for T_w , given r and T . Alternatively, if T_w and T are known from wet-bulb and dry-bulb thermometers, then r can be recovered directly from (4.6.4). This is a convenient way of measuring water vapor content.

4.6.3 Saturation by isobaric mixing

Consider two samples of moist unsaturated air of masses M_1 and M_2 . It is possible that mixing of these masses will lead to saturation. To see this, it is first necessary to point out that the vapor pressure and temperature mix very nearly linearly. From the first law we have

$$c'_{p1}M_1dT_1 + c'_{p2}M_2dT_2 = 0, \quad (4.6.7)$$

where c'_p is defined by (4.2.5), and dT_1 and dT_2 are the changes in temperature of each sample upon mixing. From this we have

$$T_m = \frac{c'_{p1}M_1T_1 + c'_{p2}M_2T_2}{c'_{p1}M_1 + c'_{p2}M_2}, \quad (4.6.8)$$

where T_m is the final temperature of the mixture. If we neglect the water vapor dependence of c'_p , the above becomes

$$T_m \simeq \frac{M_1T_1 + M_2T_2}{M_1 + M_2}. \quad (4.6.9)$$

Similarly, the specific humidity, q , mixes linearly:

$$q_m = \frac{M_{v1} + M_{v2}}{M_1 + M_2} = \frac{q_1M_1 + q_2M_2}{M_1 + M_2}, \quad (4.6.10)$$

where M_{vi} is the mass of water vapor in sample i . Thus, as shown in Figure 4.2, the mixture will lie very nearly on a straight line on a diagram with specific humidity on one axis and temperature on the other. Since q^* is a nonlinear function of T (at constant pressure), it is possible that the

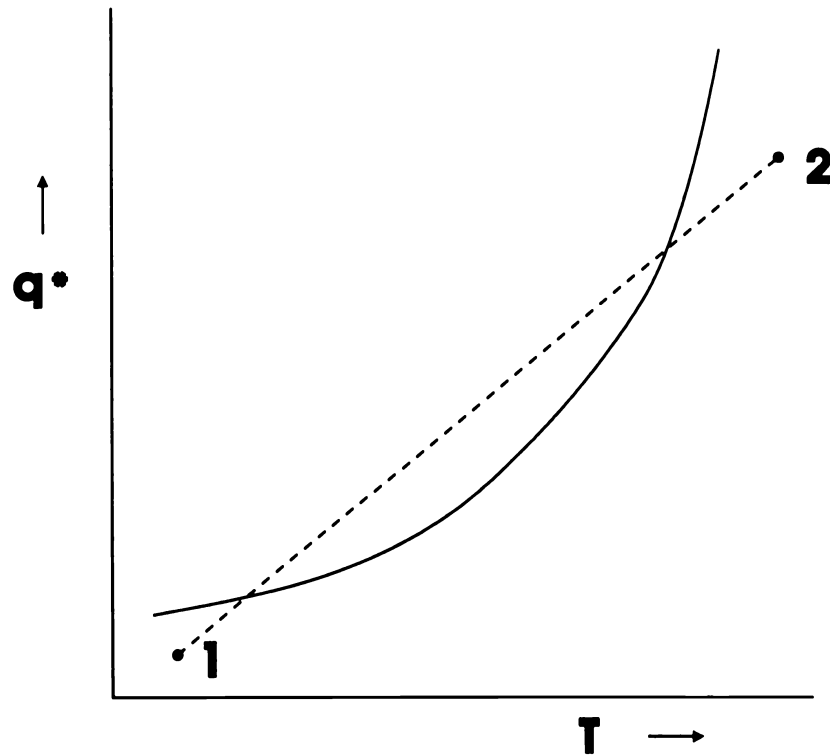


Fig. 4.2 Schematic phase diagram at constant pressure, where the curve represents the saturation specific humidity, q^* , and two samples of unsaturated air are indicated by points 1 and 2. Since q and T mix nearly linearly, the mixture will lie on a straight line connecting samples 1 and 2. The mixture may be supersaturated.

mixture of two unsaturated samples will produce condensation of water vapor.

An example of saturation by this process occurs when very cold air flows out over relatively warm water. Right next to the water surface, a thin layer of nearly saturated air forms, having about the same temperature as the water. Due to unstable stratification and mechanical mixing, some of this air is stirred upward into the cold, dry air above. If the difference between the water and air temperature is sufficiently large, the mixture will saturate, resulting in *steam fog* or, if the water droplets are supercooled, *arctic sea smoke*. Another form of cloud resulting from mixing is the condensation trail behind high-flying jet aircraft. Since water vapor is one by-product of the combustion process, the exhaust gases contain water vapor at high temperature. When these mix with the surrounding cold air, condensation may result, depending on the ambient temperature and humidity.

4.6.4 Saturation by adiabatic expansion (ascent)

By far the most important means by which saturation is achieved in the atmosphere is by adiabatic cooling, which is produced by a variety of mechanisms, including free convective ascent, large-scale dynamic instabilities, and forced ascent over topography. As air rises adiabatically, it cools ac-

ording to the first law of thermodynamics, so that the saturation vapor pressure falls. Since the mixing ratio is conserved, however, the actual vapor pressure falls as well. Saturation can only occur if e^* falls faster than e . The change in relative humidity can be written

$$[d \ln(\mathcal{H})]_{r,s} = [d \ln e]_{r,s} - [d \ln e^*]_{r,s}, \quad (4.6.11)$$

where the subscripts denote a process at constant entropy and mixing ratio. From the definition of mixing ratio we can express e as

$$e = \frac{p_d r}{\epsilon},$$

and we have

$$[d \ln e]_{r,s} = \frac{r}{\epsilon e} dp_d = d \ln p_d. \quad (4.6.12)$$

From the Clausius-Clapeyron equation (4.4.11), we have

$$[d \ln e^*]_{r,s} = \frac{L_v}{R_v T} [d \ln T]_{r,s}, \quad (4.6.13)$$

while the first law of thermodynamics can be expressed, for adiabatic processes

$$\begin{aligned} 0 &= (c_{pd} + r c_{pv}) dT - \alpha_d dp \\ &= (c_{pd} + r c_{pv}) dT - \alpha_d dp_d - \alpha_d de \\ &= (c_{pd} + r c_{pv}) dT - \alpha_d \left(1 + \frac{r}{\epsilon}\right) dp_d, \end{aligned} \quad (4.6.14)$$

since $e = p_d r / \epsilon$ and r is conserved. Using (4.6.14) and the ideal gas law in (4.6.13) gives

$$[d \ln e^*]_{r,s} = \frac{\epsilon L_v}{c_{pd} T} \frac{1 + r/\epsilon}{1 + r \frac{c_{pv}}{c_{pd}}} d \ln p_d. \quad (4.6.15)$$

We can therefore write (4.6.11) as

$$[d \ln(\mathcal{H})]_{r,s} = d \ln p_d \left[1 - \frac{\epsilon L_v}{c_{pd} T} \frac{1 + r/\epsilon}{1 + r \frac{c_{pv}}{c_{pd}}} \right], \quad (4.6.16)$$

whereupon we note that relative humidity will increase with decreasing p_d if

$$T < \frac{\epsilon L_v}{c_{pd}} \frac{1 + r/\epsilon}{1 + r \frac{c_{pv}}{c_{pd}}}. \quad (4.6.17)$$

For saturation to occur, (4.6.17) must continue to be true right up through the saturation point, that is, T must be less than

$$T_{cr} = \frac{\epsilon L_v(T_{cr})}{c_{pd}} \frac{1 + r^*(T_{cr})/\epsilon}{1 + r^*(T_{cr}) \frac{c_{pv}}{c_{pd}}}. \quad (4.6.18)$$

The critical temperature given by (4.6.18) will be a function of pressure since r^* is a function of T and p . Since T_{cr} turns out to be very large, however, r^* will be very much larger than unity and we can neglect unity in the numerator and denominator of (4.6.18); that is,

$$T_{cr} \simeq \frac{L_v(T_{cr})}{c_{pv}}. \quad (4.6.19)$$

This is not a function of pressure and turns out to be the critical point of water, that is, $T_{cr} = 647$ K. We may thus conclude that adiabatic expansion of moist air will always ultimately lead to saturation in the earth's atmosphere.

Given the temperature, pressure, and mixing ratio of an air parcel, it is possible to find the temperature, pressure, and altitude at which saturation will occur through adiabatic expansion. These will be denoted, respectively, the *saturation temperature*, T^* ; *saturation pressure*, p^* ; and *lifted condensation level*, z^* . The saturation temperature may be found by first substituting the first law (4.6.14) into (4.6.16):

$$[d \ln \mathcal{H}]_{r,s} = \frac{c_{pd}}{R_d} \frac{1 + r \frac{c_{pv}}{c_{pd}}}{1 + r/\epsilon} d \ln T - \frac{L_v}{R_v T^2} dT. \quad (4.6.20)$$

Using Kirchhoff's relation (4.4.3) for L_v , this can be directly integrated between the actual state and the saturation state at which $\mathcal{H} = 1$, giving

$$-\ln(\mathcal{H}) = \left(\frac{c_{pd}}{R_d} \frac{1 + r c_{pv}/c_{pd}}{1 + r/\epsilon} + \frac{c_l - c_{pv}}{R_v} \right) \ln \frac{T^*}{T} + \left[\frac{L_{v0} + (c_l - c_{pv})T_0}{R_v} \right] \left(\frac{1}{T^*} - \frac{1}{T} \right), \quad (4.6.21)$$

where \mathcal{H} , r , and T are the actual relative humidity, mixing ratio, and temperature, and T_0 is 273.15 K. This can be solved numerically for T^* . Once T^* is obtained, the saturation pressure can be obtained by integrating the first law:

$$\ln \frac{p^*}{p} = \frac{c_{pd} + r c_{pv}}{R_d(1 + r/\epsilon)} \ln \frac{T^*}{T}, \quad (4.6.22)$$

while the lifted condensation level can be determined by integrating the hydrostatic equation:

$$d \ln p = -\frac{g}{R_d T} \frac{1 + r}{1 + r/\epsilon} dz,$$

or from the first law,

$$\frac{c_{pd} + r c_{pv}}{1 + r} dT = -g dz,$$

giving

$$z^* - z = \frac{c_{pd}}{g} \frac{1 + r \frac{c_{pv}}{c_{pd}}}{1 + r} (T - T^*). \quad (4.6.23)$$

Bolton (1980) has derived somewhat simpler forms than (4.6.21) for the saturation temperature, T^* . These are

$$T^* = \frac{2840}{3.5 \ln T - \ln e - 4.805} + 55 \quad (4.6.24)$$

or

$$T^* = \frac{1}{\frac{1}{T-55} - \frac{\ln(\mathcal{H})}{2840}} + 55. \quad (4.6.25)$$

These are accurate to within 0.1°C in the typical range of atmospheric temperatures.

It should be noted that the definition of T^* , p^* , and z^* can be generalized to air samples that contain condensed water, in which case they are the temperature, pressure, and altitude at which all the condensed water has just evaporated following reversible adiabatic descent of the sample. The coordinates (T^*, p^*) are known as the *saturation point* of an air sample.

4.7 Reversible and pseudoadiabatic processes

When saturated air is displaced reversibly and adiabatically, the moist entropy defined by (4.5.9) is conserved. This implies that the moist entropy of a given state is a function of temperature, pressure, and liquid water mixing ratio, r_l . Since a saturated adiabatic expansion involves the release of latent heat, the temperature will not fall as rapidly as in an unsaturated expansion. The moist adiabatic lapse rate therefore has a smaller magnitude than the dry adiabatic lapse rate. A comparison between the two lapse rates can be found by differentiating (4.5.9). We can write this in terms of pressure and temperature changes alone by noting that, from the definition of r ,

$$dr = \frac{r}{p - e} \left(\frac{p}{e} de - dp \right). \quad (4.7.1)$$

Using the Clausius-Clapeyron equation (4.4.11), this may be expressed

$$dr^* = \frac{r^*}{p - e} \left(p \frac{L_v}{R_v T^2} dT - dp \right). \quad (4.7.2)$$

Substituting (4.7.2) into the differential of (4.5.9) and using the hydrostatic

equation gives, for a saturated reversible adiabatic displacement,

$$\begin{aligned}
 - \left(\frac{dT}{dz} \right)_s \equiv \Gamma_m &= \frac{g}{c_{pd}} \frac{1 + r_t}{1 + r \frac{c_{pv}}{c_{pd}}} \\
 &\times \left[\frac{1 + \frac{L_v r}{R_d T}}{1 + r_l \frac{c_l}{c_{pd} + r c_{pv}} + \frac{L_v^2 r (1 + r/\epsilon)}{R_v T^2 (c_{pd} + r c_{pv})}} \right], \quad (4.7.3)
 \end{aligned}$$

where Γ_m is called the *moist adiabatic lapse rate*. From the first law for moist but unsaturated adiabatic displacement we have

$$- \left(\frac{dT}{dz} \right)_{s_d} \equiv \Gamma_d = \frac{g}{c_{pd}} \frac{1 + r}{1 + r \frac{c_{pv}}{c_{pd}}}, \quad (4.7.4)$$

where Γ_d is the *dry adiabatic lapse rate*. Comparing (4.7.3) with (4.7.4) gives

$$\frac{\Gamma_m}{\Gamma_d} = \frac{1 + \frac{L_v r}{R_d T}}{1 + r_l \frac{c_l}{c_{pd} + r c_{pv}} + \frac{L_v^2 r (1 + r/\epsilon)}{R_v T^2 (c_{pd} + r c_{pv})}}. \quad (4.7.5)$$

In the absence of liquid water, r_l , this ratio will be smaller than unity if $T < T_{cr}$, with T_{cr} defined by (4.6.18). It can also be seen that this ratio approaches unity as r_l and r become small. When the atmosphere is very moist, this ratio is appreciably smaller than unity. For example, for air saturated at $T = 25^\circ\text{C}$, $p = 950$ millibars, and with no liquid water content, $\Gamma_m/\Gamma_d = 0.381$.

Since entropy is a function of pressure, temperature, and liquid water content, it cannot be represented on a single two-dimensional thermodynamic diagram. For this reason it is convenient to define a *pseudoadiabatic process* as one in which the heat capacity of liquid water (or ice) is neglected. The moist adiabatic lapse rate in this case is found simply by dropping the small r_l term in the denominator of (4.7.3) and (4.7.5). The resulting lapse rates differ from the reversibly defined lapse rates by less than 1%.

A pseudoadiabatically defined entropy, s_p , may be derived from (4.5.9) with the liquid water term omitted:

$$\begin{aligned}
 T ds_p &= (c_{pd} + r c_{pv}) dT + L_v dr - \alpha_d dp \\
 &= (c_{pd} + r c_l) dT + d(L_v r) - \alpha_d dp, \quad (4.7.6)
 \end{aligned}$$

where Kirchhoff's relation (4.4.3) has been used. By using the Clausius-Clapeyron relation and the ideal gas law, (4.7.6) may be shown to be

equivalent to

$$ds_p = (c_{pd} + rc_l) d \ln T + d \left(\frac{L_v r}{T} \right) - R_d d \ln p_d - R_v d [r \ln(\mathcal{H})]. \quad (4.7.7)$$

Were it not for the mixing ratio dependence of the first term on the right side of (4.7.7), the latter could be integrated exactly. As it is, we must integrate numerically, with the result that

$$s_p = s + c_l \left[\int_1^T r d(\ln T) - r_t \ln T \right], \quad (4.7.8)$$

with s the reversibly defined entropy given by (4.5.9). It is readily seen that $s_p \leq s$ since $r \leq r_t$, reflecting the neglect of heat carried by condensed water.

Bolton (1980) has evaluated (4.7.8) rather accurately in order to arrive at a *pseudoequivalent potential temperature*, θ_{ep} . With some curve-fitting, Bolton obtains

$$\theta_{ep} = T \left(\frac{1000}{p} \right)^{0.2854(1-0.28r)} \times \exp \left[r(1 + 0.81r) \left(\frac{3376}{T^*} - 2.54 \right) \right], \quad (4.7.9)$$

with T^* given by (4.6.24) or (4.6.25). In the range of atmospheric conditions this is accurate to within 0.3°C.

Sometimes isopleths of θ_{ep} are labeled in terms of their temperature at the reference pressure of 1000 millibars. The quantity is then referred to as the *wet-bulb potential temperature*, θ_w . The relationship between θ_{ep} and θ_w is, from (4.7.9),

$$\theta_{ep} = \theta_w \exp \left[r'(1 + 0.81r') \left(\frac{3376}{\theta_w} - 2.54 \right) \right], \quad (4.7.10)$$

where

$$r' \equiv r^*(p = 1000 \text{ millibars}, T = \theta_w).$$

The pseudoequivalent potential temperature may be interpreted as the actual temperature achieved by an air parcel under the following thermodynamic process:

Table 4.2 Temperatures achieved by a parcel lifted reversibly (T) and pseudoadiabatically (T_p) starting from saturation at $p = 950$ millibars and $T = 25^\circ\text{C}$. Also shown is the difference between the density temperatures resulting from each process

p (mb)	T (K)	T_p (K)	$T - T_p$ (K)	$T_\rho - T_{\rho p}$ (K)
950	298.15	298.15	0.0	0.0
800	292.36	292.35	0.01	-1.04
700	287.77	287.73	0.04	-1.75
600	282.32	282.22	0.10	-2.44
500	275.59	275.36	0.23	-3.07
400	266.78	266.27	0.51	-3.51
300	254.10	252.90	1.21	-3.39
200	233.30	230.32	2.98	-1.76
100	195.77	189.96	5.81	1.70

- 1) Pseudoadiabatic ascent to zero pressure
- 2) Dry adiabatic descent to 1000 millibars

Note that *no similar meaning can be attached to the reversibly defined θ_e in Eq. (4.5.11)*. Thus the two quantities cannot be directly compared. In Table 4.2 we list the temperatures of a parcel starting at 950 millibars and 25°C saturated, but with no liquid water, subject to pseudoadiabatic ascent and to reversible ascent. This is a very moist parcel by atmospheric standards. The reversibly lifted parcel is progressively warmer than the pseudoadiabatic parcel due to the heat-carrying capacity of the liquid water. No allowance has been made for freezing effects. By the time the parcel reaches the upper troposphere the difference is quite substantial.

Also shown in Table 4.2 is the difference between the density temperatures [defined by (4.3.6)] resulting from reversible and pseudoadiabatic ascent. In the former case all the condensate is carried by the airstream, while in the latter it is all removed as it is formed. Thus the reversibly lifted parcel has the *greater* density through most of the troposphere due to the weight of the condensate. But above about 150 millibars the heat capacity effect overwhelms the condensate loading and the reversibly lifted parcel becomes the less dense of the two.

4.8 Microphysical considerations

4.8.1 Nucleation

Up to this point we have tacitly assumed that condensation of water vapor will occur at nominal water saturation and we have ignored the ice phase altogether. Here we briefly consider microphysics as it bears on the problem of condensation, sublimation, freezing, and formation of precipitation. We emphasize that the following is a superficial treatment; discussion in later

chapters reveals that complex microphysical processes can have important effects on convective dynamics.

The saturation vapor pressure expressed by Eqs. (4.4.13) and (4.4.15) together with (4.4.16) pertains to equilibrium between vapor and a planar water or ice surface. In the atmosphere, the condensate appears as very small droplets or crystals whose surface energy per unit mass depends inversely on the radius of the particle. The creation of this surface energy must be accounted for in formulating the Clausius-Clapeyron equation. Specifically, in (4.4.5), it is no longer true that the pressure within the droplet equals the pressure just outside it; for mechanical equilibrium, the pressure must be larger within the droplet to compensate for surface tension. When this is accounted for, the actual saturation vapor pressure is given by *Kelvin's law*:

$$e_a^* = e^* \exp\left(\frac{2\sigma\alpha_l}{R_v T a}\right), \quad (4.8.1)$$

where e_a^* is the actual saturation vapor pressure over a droplet of radius a , e^* is the nominal saturation vapor pressure over a flat surface, and σ is the surface tension. The actual saturation vapor pressure increases with decreasing droplet radius.

The phase equilibrium of a droplet of radius a given by (4.8.1) is an unstable one. If the droplet were to evaporate by a small fraction, its radius would decrease and the saturation vapor pressure would increase, allowing for more evaporation. Conversely, if its radius were to increase slightly, the saturation vapor pressure would decrease and the environment would be supersaturated with respect to the droplet. Thus to create a water droplet or ice crystal in a given environment it is necessary to form a droplet of at least the critical radius a_c given by setting the actual vapor pressure equal to the saturation value e_a^* in (4.8.1).

Were there no *aerosols* (small solid or liquid particles) in the atmosphere, the only means of creating a small particle of the critical radius would be by the random clumping of water molecules that occurs in a gas. This is called *homogeneous nucleation* and in practice would require supersaturations of up to several hundred percent. In nature, however, there is a large number of aerosols consisting of combustion products, dust, products of photochemical reactions involving sulfides, ash, and sea salt. Those particles that are wettable, and particularly those that are water soluble, serve as nuclei on which water may condense. These are called *cloud condensation nuclei (CCN)* and their presence allows *heterogeneous nucleation* to occur. The distribution of CCN varies greatly in space and time, with largest concentrations in urban areas and near the earth's surface, and smallest concentrations over the oceans and away from the surface.

The presence of a water-soluble CCN reduces the supersaturation needed for nucleation since some of the surface energy of a droplet is provided by molecules of the solute. The reduction of saturation vapor pressure

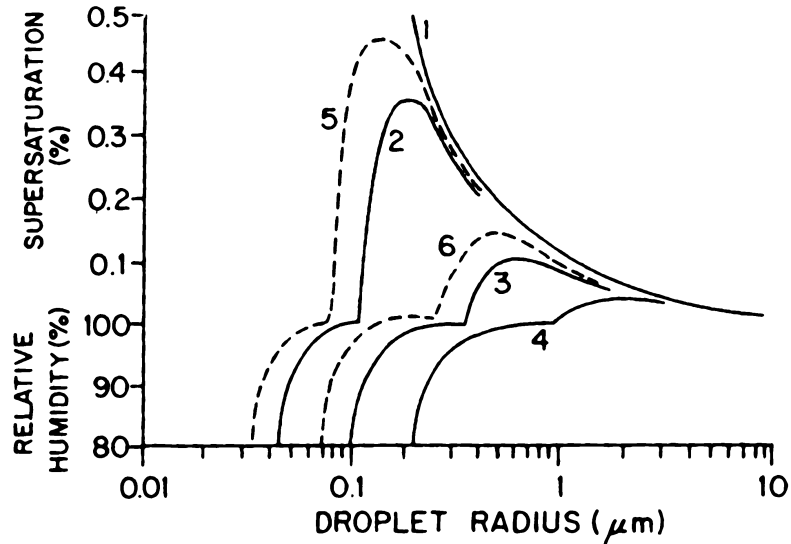


Fig. 4.3 Variations of the relative humidity and supersaturation of the air adjacent to droplets of (1) pure water and solution droplets containing the following fixed masses of salt, (2) 10^{-19} kg of NaCl, (3) 10^{-18} kg of NaCl, (4) 10^{-17} kg of NaCl, (5) 10^{-19} kg of $(\text{NH}_4)_2\text{SO}_4$, and (6) 10^{-18} kg of $(\text{NH}_4)_2\text{SO}_4$. [Adapted from S. I. Rasool (ed.), *Chemistry of the Lower Atmosphere*, Plenum Press, New York, 1973, p. 16.]

is given by

$$\frac{e_s^*}{e_a^*} = f, \quad (4.8.2)$$

where f is the kilomole fraction; that is, the number of kilomoles of H_2O per kilomole of water plus solute. In terms of droplet radius this is given by

$$f = \frac{\left(\frac{4}{3}\pi a^3 \rho_l - M_s\right) / m_v}{\left(\frac{4}{3}\pi a^3 \rho_l - M_s\right) / m_v + i M_s / m_s}, \quad (4.8.3)$$

where M_s is the mass of solute, m_s its molecular weight, and i is the number of solute ions. Combining (4.8.3) with (4.8.1) and (4.8.2) gives

$$e_s^* = \left[1 + \frac{i M_s \frac{m_v}{m_s}}{\frac{4}{3}\pi a^3 \rho_l - M_s}\right]^{-1} \exp\left(\frac{2\sigma\alpha_l}{R_v T a}\right). \quad (4.8.4)$$

A plot of e_s^* given by (4.8.4) is shown in Figure 4.3. The curves on this plot are known as *Köhler curves*. Wherever the slope of these curves is positive, the droplets are in a state of stable equilibrium; otherwise, the equilibrium is unstable and the droplets will grow. A droplet that reaches the peak of its Köhler curve is said to be *nucleated*.

In nature, CCN are plentiful enough that supersaturations required for nucleation seldom exceed 1%. Thus, in practice, we may consider that condensation occurs whenever the actual vapor pressure exceeds its nominal saturation value.

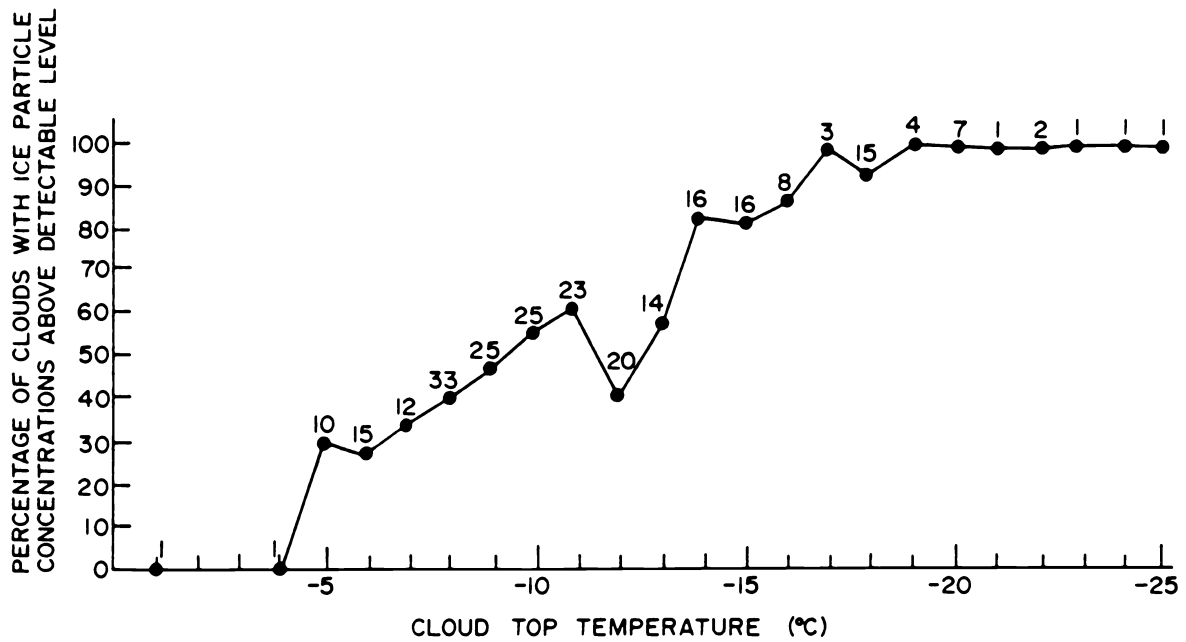


Fig. 4.4 Percentage chance of ice being detected in clouds as a function of the cloud top temperature. Results are based on field observations of 30 orographic cloud systems. The number above each point is the total number of cloud samples for that temperature. [From Proc. Amer. Met. Soc. 1st National Conf. on Weather Modification, Albany, N. Y., 1968, p. 306; Quart. J. Roy. Met. Soc., **96**, 487 (1970); Proc. Intern. Conf. on Weather Modification, Canberra, Australia, 1971, p. 5.]

On the other hand, it is not possible to state that freezing will occur whenever the temperature falls below 0°C . The same considerations apply as to the nucleation of water vapor; namely, that a surface energy must be accounted for to get ice nucleation within a water drop. Homogeneous nucleation is efficient at temperatures below about -40°C ; otherwise freezing can be initiated at higher temperatures if *freezing nuclei* are present. These consist of atmospheric aerosols with molecular structures similar to that of ice and they are considerably rarer than CCN. Depending on their relative abundance and other factors, freezing may commence at temperatures anywhere from -4°C to -40°C . Figure 4.4 shows the frequency with which ice occurs in clouds whose tops are at a given temperature.

4.8.2 Growth of cloud droplets and ice crystals

Condensation or *deposition* (transfer of water from the vapor to the ice phase) is responsible for the initial growth of cloud droplets and ice crystals. The rate of change of radius of condensate by condensation or deposition varies inversely with radius, however, so that after some time the process becomes inefficient. The amount of time required for cloud droplets to grow to a size at which their terminal velocities are appreciable compared to air motion is many orders of magnitude greater than the observed time for precipitation formation.

There are several more efficient mechanisms by which cloud droplets

may grow to precipitation-size particles (raindrops). In clouds that contain no ice, droplets grow principally by collision, due mostly to differing terminal velocities. Depending on the sizes of both droplets, one may be swept around the other in the airflow, it may collide with the other but bounce off, or it may coalesce with the other to form a larger drop. The net fraction of droplets within a cross-sectional area intercepted by a larger drop that coalesces with the latter is called the *collection efficiency* and is a sensitive function of the radii of both drops.

For a given initial size distribution of CCN, the chance coalescence of droplets may be considered as a statistical process by which precipitation forms in warm clouds (clouds that contain no ice) and also operates to some extent in cold clouds. Since continental CCN are roughly 5 times more prevalent than maritime CCN, more but smaller droplets will form in continental clouds, all other conditions being equal. For this reason, stochastic coalescence is less efficient in continental clouds. It is observed that marine clouds precipitate more easily than do continental clouds. The end product of stochastic coalescence is a nearly log-normal distribution of raindrops known as a *Marshall-Palmer distribution*, which has the form

$$N(a) = N_0 e^{-\lambda a}, \quad (4.8.5)$$

where N_0 and λ are constants that may depend on the nature of the environment in which the microphysical processes occur.

The amount of time required to form raindrops by stochastic coalescence in an updraft is quite sensitive to the updraft speed, temperature, and CCN distribution. For convective clouds, the time scale is on the order of tens of minutes, which is not negligible compared to the time scales characteristic of the convection itself. This lack of separation between dynamical and microphysical time scales has important but not fully understood consequences for the dynamics of convective clouds.

When the top of a cloud is cold enough to contain ice crystals, another important mechanism for condensate growth comes into play. If some of the ice crystals fall into a supercooled water cloud, they find themselves in an environment that is saturated with respect to liquid, which is up to 21% supersaturated with respect to ice. The result is rapid growth of the ice crystals at the expense of the water droplets. This mechanism for rapid ice-crystal growth is known as the *Bergeron-Findeisen process*. Once the ice crystal is large enough, it may grow faster by *riming*, that is, by collision with supercooled water droplets that freeze on impact. When taken to an extreme in large thunderstorms, riming produces hailstones. Ice crystals that collide with each other may stick together, or *aggregate*, leading to a larger particle.

At the time of the writing of this book, investigations of cloud microphysical processes and of cloud dynamics remain somewhat separate. The author cannot emphasize enough the importance of understanding the

interplay between precipitation formation and cloud dynamics. This lack of understanding will return to haunt us in subsequent chapters. For example, we show in Chapter 14 that the tropical troposphere is often in a state of near neutrality to a *reversibly* lifted parcel from the top of the subcloud layer. But what relevance does an adiabatic parcel have in a precipitating convective cloud? Is it an accident that the tropical troposphere is neutral to a parcel with its adiabatic condensed water intact? It should become clear that microphysical processes have an important bearing on the thermodynamic structure of convecting atmospheres.

4.9 Thermodynamics of the ice phase

As saturated air ascends within convective clouds, it may eventually cool to the point that ice-crystal formation begins and it is then necessary to account for the heat released during fusion. At just what temperature this occurs depends critically on the nature of the convection. In an updraft whose velocity is small compared to the fall velocity of snowflakes ($\simeq 2 \text{ m s}^{-1}$), the latter will fall through the updraft (assuming the latter is upright) and the ascending air will encounter ice very near the freezing point (0°C). In this case very little supercooled water may be found. At the other extreme, a very intense updraft may carry liquid water upward so rapidly that freezing does not occur until the temperature falls below about -35°C .

We must account for the latent heat of fusion in two ways. First, we will assume that at some temperature T_1 the existing condensate freezes, thereby raising the temperature to T_2 . Subsequent ascent will then take place along a reversible or pseudoadiabatic ascent path relevant to deposition rather than to condensation.

The relation between T_1 and T_2 may be found by assuming that the (irreversible) freezing occurs at constant pressure. In that case, enthalpy is conserved. The total enthalpy may be written

$$k = k_d + rk_v + r_l k_l + r_i k_i, \quad (4.9.1)$$

where k_i is the specific enthalpy of ice. This is equivalent to

$$\begin{aligned} k &= k_d + r(k_v - k_l) + (r + r_l + r_i)k_l + r_i(k_i - k_l) \\ &= k_d + rL_v + r_T k_l - r_i L_f \\ &= (c_{pd} + c_l r_T)T + rL_v - r_i L_f, \end{aligned} \quad (4.9.2)$$

where L_f is the latent heat of fusion. Equating the enthalpies of the first state of vapor–liquid equilibrium at $T = T_1$ and the second state of vapor–ice equilibrium at $T = T_2$ gives

$$(c_{pd} + c_l r_T)(T_2 - T_1) + L_v(T_2)r^\#(T_2) - L_v(T_1)r^*(T_1) - L_f r_i = 0, \quad (4.9.3)$$

where r_i is the ice content of state 2. We make the approximation that $T_2 - T_1$ is small so that $L_v(T_2) \simeq L_v(T_1) \equiv L_v$. In addition we relate $r^\#(T_2)$ to $r^\#(T_1)$ by linearizing the Clausius-Clapeyron relation:

$$\begin{aligned} r^\#(T_2) &= \frac{e^\#(T_2)}{e^*(T_2)} r^*(T_2) \\ &= \frac{e^\#(T_2)}{e^*(T_2)} \left[r^*(T_1) + \frac{L_v r^*(T_1)}{R_v T_1^2} (T_2 - T_1) \right]. \end{aligned} \quad (4.9.4)$$

Substituting (4.9.4) into (4.9.3) and solving for $(T_2 - T_1)$ gives

$$T_2 - T_1 \simeq \frac{L_f r_i + L_v r^*(1 - e^\# / e^*)}{c_{pd} + c_l r_T + \frac{L_v^2 r^\#}{R_v T^2}}. \quad (4.9.5)$$

Subsequent to freezing, we may regard the further ascent of the ice-vapor mixture as being reversible or pseudoadiabatic. In the former case, the two conserved quantities are $r_T (= r_t + r_i)$ and s_s , the total entropy of the dry-air, vapor, and ice mixture. In analogy to the derivation of (4.5.9), s_s is given by

$$s_s = (c_{pd} + r_T c_i) \ln T + \frac{L_s r}{T} - R_d \ln p_d, \quad (4.9.6)$$

where c_i is the heat capacity of ice and L_s is the latent heat of sublimation. Conservation of s_s can yield temperatures several degrees Celsius higher than conservation of s in typical atmospheric situations.

EXERCISES

4.1 Which of the following quantities are conserved in reversible, adiabatic *unsaturated* transformations?

$$r, q, r_t, r_T, q_t, q_T, e, \rho_v, r^*, q^*, e^*, r^\#, q^\#, e^\#, \mathcal{H}, p^*, T^*, z^*, \rho, T_w, \theta, \theta_v, \theta_e, \theta_{ep}, \theta_w, \theta_l, \theta_{lv}, k, k_d, k_w, h, h_d, h_w.$$

4.2 Which of the quantities listed in Exercise 4.1 are conserved in reversible, adiabatic, *saturated* transformations?

4.3 Which of the quantities listed in Exercise 4.1 are conserved in adiabatic, unsaturated, isobaric transformations?

4.4 Which of the quantities listed in Exercise 4.1 are conserved in adiabatic, saturated, isobaric transformations?

- 4.5 Calculate and compare the virtual temperature and density temperatures of air with an actual temperature of 25°C , pressure of 950 millibars, and the following characteristics:
- No water vapor or condensed water
 - Saturated with water vapor and with no condensed water
 - Saturated with water vapor and with 2 g kg^{-1} of condensed water
 - At 50% relative humidity and with 2 g kg^{-1} of condensed water
- 4.6 Repeat Exercise 4.5, but at an air temperature of -40°C and pressure of 300 millibars.
- 4.7 By differentiating (4.5.4), show that enthalpy is conserved during adiabatic, isobaric transformations whether or not the air is saturated.
- 4.8 The inviscid equations of motion may be written in vector form

$$\frac{d\mathbf{V}}{dt} = -\alpha\nabla p - g\hat{k} - f\hat{k} \times \mathbf{V},$$

where \hat{k} is the unit vector along the direction of net gravity.

By taking the dot product of \mathbf{V} with the above and making use of the identity

$$\mathbf{V} \cdot \nabla p = \frac{dp}{dt} - \frac{\partial p}{\partial t},$$

as well as (4.5.19) and (4.5.20), show that the quantity

$$\frac{1}{2}|\mathbf{V}|^2(1 + r_t) + h$$

is conserved along streamlines in adiabatic, inviscid *steady* flow. Estimate the error made in calculating temperature changes by assuming that just h is conserved. (This shows you why h is called the *static energy*.)

- 4.9 Under what atmospheric conditions can we “see our breath”? Assume that the air we exhale is at $T = 36^\circ\text{C}$ and $\mathcal{H} = 80\%$ at a pressure of 1000 millibars, and find the maximum atmospheric temperature at which condensation will occur when the atmospheric relative humidity is (a) 99.9%, and (b) 0%. An electronic calculator will be most helpful.
- 4.10 Show that the entropy per unit *total* mass,

$$s' \equiv [c_{pd}(1 - q_t) + q_t c_l] \ln T + \frac{L_v q}{T} - R_d(1 - q_t) \ln p_d - qR_v \ln \mathcal{H}$$

is conserved following reversible adiabatic displacements of moist air in which freezing does not occur.

- 4.11 Neglect of the effect of water substance on heat capacities, the gas constant, and density on the entropy defined in Exercise 4.10 gives

$$s' \simeq c_{pd} \ln T + \frac{L_v q}{T} - R_d \ln p - qR_v \ln \mathcal{H}.$$

Show that the use of L_{v0} is necessary for consistency.

- 4.12 If the air is never very far from saturation, we may neglect the last term in the equation in Exercise 4.11 and write

$$s' \simeq c_{pd} \ln T + \frac{L_{v0}q}{T} - R_d \ln p,$$

while to the same level of approximation, for unsaturated air,

$$s'_d \simeq c_{pd} \ln T - R_d \ln p.$$

(*Note:* These approximations are rather crude and should not be used when quantitatively accurate results are desired!) The first law of thermodynamics may be written in either of the two forms

$$dQ_m \simeq T ds'$$

or

$$dQ \simeq T ds'_d,$$

where dQ_m denotes heating other than by latent heat release, while dQ denotes total heating, including that owing to latent heat release. Show that to the level of approximation applied here,

$$dQ = dQ_m - L_{v0} dq.$$

Now consider a *closed* thermodynamic cycle that returns a sample of moist air to its original thermodynamic state (T, p, q) . Show that to the level of approximation employed here, the amount of mechanical energy available from such a cycle is

$$E = \oint T ds' = \oint T ds'_d,$$

where \oint denotes integration over the closed thermodynamic cycle.

- 4.13 Consider the thermodynamic cycle of a mature hurricane, illustrated in Figure E4.1. The cycle consists of four legs:

- (a) Leg a–c: Isothermal expansion at temperature T_s and addition of water vapor from the ocean, with heat of vaporization supplied by the latter.
- (b) Leg c–o: Moist adiabatic expansion to temperature T_0 . Water is lost by precipitation.
- (c) Leg o–o': Isothermal compression at temperature T_0 .
- (d) Leg o'–a: Compression under the influence of radiative cooling, with water vapor added due to the mixing effects of shallow cumulus clouds. But since the air's temperature closely follows a moist adiabat along this leg, the amount of heat lost and water

gained is nearly the same as if this leg represented moist adiabatic compression.

Describe the contribution of *each* leg to the total mechanical energy given at the end of Exercise 4.12, first using

$$E = \oint T ds'$$

and then using

$$E = \oint T ds_d.$$

Then comment on and compare the following two statements:

- 1) "Hurricanes are driven by the latent heat released in cumulus clouds near the center of the storm."
- 2) "Hurricanes are driven by the thermodynamic disequilibrium between the tropical oceans and atmosphere."

4.14 Derive the following expression for the *ice specific pseudoentropy*:

$$s_{pi} \equiv s_s + c_i \left[\int_1^T r d(\ln T) - r_T \ln T \right].$$

4.15 Show that the *ice water specific entropy*,

$$s_f \equiv (c_{pd} + r_T c_{pv}) \ln T - (R_d + r_T R_v) \left[\ln p - \ln \left(1 + \frac{r_T - r_i}{\epsilon} \right) \right] - r_T R_v \ln \left(\frac{r_T - r_i}{\epsilon} \right) - \frac{L_s r_i}{T},$$

is conserved under reversible adiabatic transformations at temperatures below 0°C.

4.16 Show that the *ice phase specific enthalpy*,

$$k_s \equiv (c_{pd} + r_T c_i)T + L_s r,$$

is conserved in adiabatic isobaric transformations, provided all the condensed water is in the ice phase, and that mass is conserved.

4.17 Show that the *condensed water specific enthalpy*,

$$k_T \equiv (c_{pd} + r_T c_{pv})T - L_v r_l - L_s r_i,$$

is conserved under all adiabatic isobaric transformations in which mass is conserved.

4.18 Show that the *frozen water static energy*,

$$h_f \equiv (c_{pd} + r_T c_{pv})T - L_s r_i + (1 + r_t)gz,$$

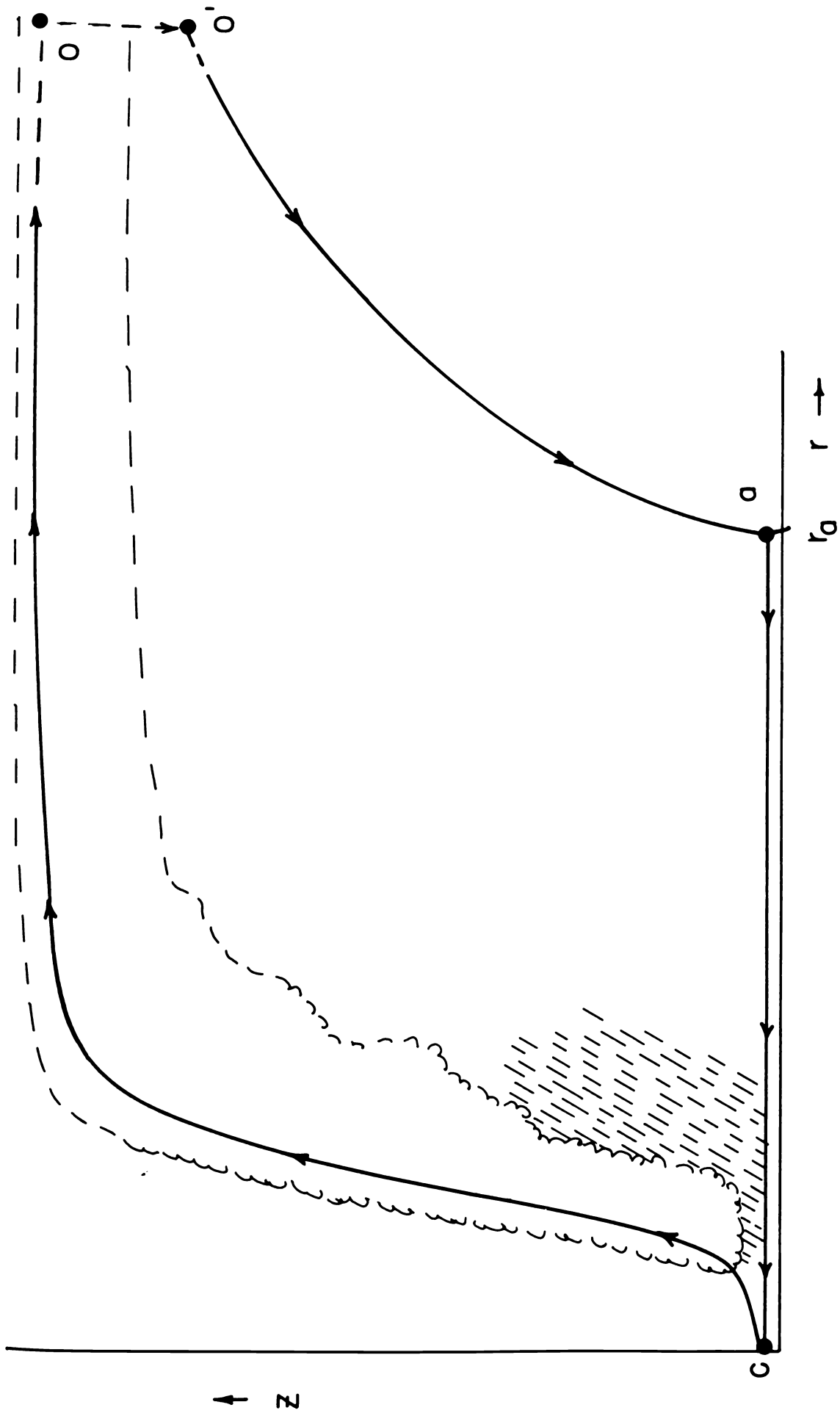


Fig. E4.1 Vertical cross section through mature hurricane, showing Carnot cycle.

is conserved in adiabatic, hydrostatic transformations, provided all condensed water is in the ice phase, and that mass is conserved.

4.19 Show that the *condensed water static energy*,

$$h_T \equiv (c_{pd} + r_T c_{pv})T - L_v r_l - L_s r_i + (1 + r_T)gz,$$

is conserved in adiabatic, hydrostatic transformations for which mass is conserved.

4.20 By dividing the definitions of h_w , h_f , and h_T [Eq. (4.5.25) and Exercises 4.18 and 4.19] through by $1 + r_T$ and making use of the definition of T_ρ (4.3.6), show that the quantities

$$h_{w\rho} \equiv \frac{(c_{pd} + r_t c_{pv})T_\rho}{1 + r/\epsilon} - \frac{L_v r_l}{1 + r_t} + gz,$$

$$h_{f\rho} \equiv \frac{(c_{pd} + r_T c_{pv})T_\rho}{1 + r/\epsilon} - \frac{L_s r_i}{1 + r_T} + gz,$$

and

$$h_{T\rho} \equiv \frac{(c_{pd} + r_T c_{pv})T_\rho}{1 + r/\epsilon} - \frac{L_v r_l + L_s r_i}{1 + r_T} + gz$$

are conserved under the same conditions that h_w , h_f , and h_T are, respectively, conserved. Also show that, to the same degree of approximation used in deriving the virtual potential temperature (4.3.2), the above reduce, respectively, to

$$h_{w\rho} = h_{f\rho} = h_{T\rho} \simeq c_{pd}T_\rho + gz,$$

when no condensed water is present.

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