

Thermodynamics with Applications to the Atmosphere (continued)

CLIM 710

Introduction to the Physical Climate System

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6 The Perfect Gas

6.1 Equation of State.

The variables p , ρ and T for a perfect gas are related to one another by the following equation of state:

$$p = \rho RT \quad (1)$$

$$pv = RT \quad (2)$$

where v is the volume per unit mass, and the constant R has the dimensions of $m^2sec^{-2}deg^{-1}$ but has a different numerical value for each perfect gas, that is it depends on the constituent molecules. Atmospheric gases obey these laws quite closely, as does water vapor.

We define the *molecular weight* of a molecule by the non-dimensional quantity m_w :

$$m_w = 12 \frac{m}{m_c} \quad (3)$$

where m is the mass of the molecule in question and m_c is the mass of a carbon atom (isotope C^{12}).

An empirical result called “Avogadro’s Hypothesis” states that under conditions of equal temperature and pressure, equal volumes of any gases contain the same number of molecules. Replacing ρ in equation 1 by $M/V = Nm/V$, where N is the number of molecules in volume V , it is easy to show that:

$$\frac{pV}{NT} = mR = \frac{m_c}{12} R m_w \quad (4)$$

By Avogadro’s Hypothesis, the quantity mR must be a universal constant. Defining

$$R^* \equiv R m_w \quad (5)$$

it is clear that R^* does not depend on the composition of the perfect gas. Since

$$\frac{m_c}{12} R m_w = \frac{m_c}{12} R^* = k \quad (6)$$

where k is our good friend Boltzmann's constant, the perfect gas equation of state [4](#) can also be written as:

$$p = nkT \quad (7)$$

where $n = N/V$ is the number of molecules per unit volume. Using equation [6](#) to evaluate R^* numerically, we get:

$$\begin{aligned} R^* &= 8.314 \times 10^7 \text{ erg gm}^{-1} \text{ deg}^{-1} \\ R^* &= 8.314 \times 10^4 \text{ j kg}^{-1} \text{ deg}^{-1} \end{aligned}$$

The appearance of k in the equation of state is not a coincidence of course. A closer study of statistical mechanics would make its appearance here more clear.

6.2 Specific Heats.

In a famous experiment performed by Joule, a gas was confined in one part of a two-chamber insulated vessel, and allowed to expand irreversibly into the evacuated second chamber, where it eventually reaches a new equilibrium state.

Since the gas does no work and receives no heat, the internal energy U cannot change. Since the initial and final states are in equilibrium, we can write $U = U(T, V)$, and then:

$$0 = U_f - U_i = \Delta U = \left(\frac{\partial U}{\partial T} \right)_V \Delta T + \left(\frac{\partial U}{\partial V} \right)_T \Delta V \quad (8)$$

While clearly $\Delta V \neq 0$, Joule found empirically that $\Delta T \approx 0$. Hence U only depends on T . Since by the definition of the specific heat at constant volume $C_v = \left(\frac{\partial u}{\partial T} \right)_V$ where now C_v and u are taken per unit mass, we can write:

$$u = \int_{T_0}^T dT' C_v(T') \quad (9)$$

where the energy is measured relative to the energy at some standard temperature T_0 . However, for atmospheric temperatures it is a good approximation to take C_v as a constant, whence:

$$u = C_v T \quad (10)$$

6.3 Mixture of Ideal Gases.

Of course air is not a single ideal gas, but a mixture of ideal gases with different constituents. Consider a collection of perfect gases, each at the same p and T

but with different total masses, total volumes and gas constants, which we denote by M_i , V_i and R_i , where i is an index for the individual constituents. If these gases are allowed to mix, it is observed that the resultant mixture has the same p and T and also behaves like a perfect gas, and has a final volume given by the sum of the constituent volumes (and a final mass given by the sum of constituent masses):

$$V_f = \sum_i V_i \quad (11)$$

$$M_f = \sum_i M_i \quad (12)$$

We can write the gas constant R_f for the final mixture from equation 2:

$$\begin{aligned} R_f &= pv/T = pV_f/(TM_f) \\ &= p \left(\sum_i V_i \right) / (TM_f) \\ &= \sum_i ((pV_i)/T) / M_f \\ &= \sum_i (M_i R_i) / \sum_i M_i = \sum_i \chi_i R_i \end{aligned} \quad (13)$$

where χ_i is the fractional part *by mass* of the i-th constituent. (Note that in the last line of equation 13 we have used equation 1 for the i-th constituent in the form $pV_i = M_i R_i T$.) Note that since $R_i = R^*/m_{w,i}$ with R^* a universal constant, we can write the equation of state of the final mixture of gases equally well in terms of an effective molecular weight m_w :

$$\frac{1}{m_w} = \sum_i \left(\frac{\chi_i}{m_{wi}} \right) \quad (14)$$

where m_{wi} is the molecular weight of the i-th constituent. The atmosphere is predominantly made up of Nitrogen molecules (78% by volume), with $m_{w1} = 28$, while the other major constituent is Oxygen molecules (21% by volume), with $m_{w2} = 32$. A careful calculation involving all constituents using equation 14 gives an effective molecular weight for dry air of 28.966, whence the effective gas constant R is:

$$R = R^*/m_w = 287 \text{ j kg}^{-1} \text{ deg}^{-1} = 287 \text{ m}^2 \text{ sec}^{-2} \text{ deg}^{-1} \quad (15)$$

If the *partial pressure* p_i of the i-th constituent in this mixture of perfect gases is defined as the pressure that would occur if this constituent alone occupied the entire final volume, we have:

$$p_i = \frac{M_i}{V_f} R_i T \quad (16)$$

Summing over i just gives

$$\sum_i p_i = \sum_i \frac{M_i R_i}{V_f} T = \frac{M_f R_f}{V_f} T = p \quad (17)$$

where we have used equation 13. This is *Dalton's law of partial pressures*. Note that the last equality just gives $pv = RT$, where v is the volume per unit mass of the mixture.

If we write the mass of the i -th constituent $M_i = m_i N_i$ in equation 16 (where m_i is the molecular weight), and use the fact that by Avogadro's Hypothesis $mR = k$, we obtain:

$$p_i = \frac{N_i m_i}{V_f} R_i T = \frac{N_i k}{V_f} T = n_i k T \quad (18)$$

$$= \frac{1}{v_i} R_i T \quad (19)$$

where n_i is just the number density per unit volume of the i -th constituent, and v_i , the volume per unit mass of the i -th constituent, is given by the total volume divided by the total mass of that constituent. Thus in this mixture, the equation of state of each component also follows the ideal gas law, with the pressure replaced by the partial pressure, but the volume given by the total final volume.

In the mixture process described above, no *external* work is done on the system of gases, since the original pressure of each constituent remains unchanged. Since no heat is added or taken away from the system, we expect the internal energy to remain unchanged. The initial energy is given by $\sum_i M_i C_{vi} T$ and the final energy by $M_f C_{vf} T$. Equating them we see that:

$$C_{vf} = \frac{\sum_i M_i}{M_f} C_{vi} = \sum_i \chi_i C_{vi} \quad (20)$$

so that the specific heat of the mixture is the mass-weighted average of the specific heat of each constituent. For dry air,

$$C_v = 717 \text{ j kg}^{-1} \text{ deg}^{-1} = \frac{5}{2} R \quad (21)$$

Numerically, C_v is seen to be close to $5/2R$. The equality indicated above is a more rigorous result from statistical mechanics, valid for *diatomic* molecules¹.

We have already defined the specific enthalpy (enthalpy per unit mass) h :

$$h = u + pv = (C_v + R) T \quad (22)$$

¹When more than one atom exists in the molecule of ideal gas, we have to take into account vibrational and rotational modes in computing the specific heat. For most diatomic molecules, the spacing between rotational levels is small compared to kT for ordinary atmospheric temperatures, while the spacing between vibrational levels is large compared to kT . Thus we can assume that all rotational levels are equally likely, but that the molecules are found in only the lowest vibrational energy level.

where we have used the equation of state of the mixture from equation 17. Thus:

$$C_p = \left(\frac{\partial h}{\partial T} \right)_p = C_v + R = \frac{7}{2}R \quad (23)$$

so that with C_v effectively constant, so is C_p , and :

$$h = C_p T \quad (24)$$

6.4 Entropy of Ideal Gas Mixture.

From the earlier lecture on thermodynamics, we know that we can relate the heat incrementally added to a system δq in a reversible process to the change in entropy (per unit mass) ds :

$$\delta q = T ds = du + p dv \quad (25)$$

where we have also used the first law. Using equation 10 this becomes:

$$ds = C_v d \ln T + R d \ln v \quad (26)$$

$$= C_v d \ln T - R d \ln \rho \quad (27)$$

$$= C_v d \ln p + C_p d \ln v \quad (28)$$

$$= C_v d \ln p - C_p d \ln \rho \quad (29)$$

$$= C_p d \ln T - R d \ln p \quad (30)$$

In an *isentropic* process, $ds = 0$, and these relationships show how the change in any one of the basic state variables for a perfect gas mixture determine the change of all others. The next to last can be rearranged:

$$\left(\frac{\partial p}{\partial \rho} \right)_s = \frac{C_p p}{C_v \rho} = \frac{C_p}{C_v} RT \equiv \gamma RT \quad (31)$$

Note that we have defined γ as the ratio of specific heats. For dry air, $\gamma \simeq 7/5$. From the theory of sound waves we also have the result that $\left(\frac{\partial p}{\partial \rho} \right)_s = c^2$ where c is the speed of sound.

Equation 30 is used to define the *potential temperature*. Recasting this equation (with $ds = 0$) as:

$$\frac{\partial \ln T}{\partial \ln p} = \frac{R}{C_p} \equiv \kappa \quad (32)$$

we can integrate this equation from a given state (p, T) to a reference pressure p_0 (usually 1000 mb). The resulting temperature (call it T_0) is then obtained from:

$$\begin{aligned}\ln T_0 - \ln T &= \kappa (\ln p_0 - \ln p) \\ \ln \left(\frac{T_0}{T} \right) &= \kappa \ln \left(\frac{p_0}{p} \right) \\ T_0 &= T \left(\frac{p_0}{p} \right)^\kappa \equiv \Theta\end{aligned}\tag{33}$$

where T_0 is defined as the potential temperature, or the temperature a parcel would have if it were brought to 1000 mb adiabatically (without addition of heat). It is usually denoted by Θ .

Starting again from equation 30, we have

$$\begin{aligned}ds &= C_p d \ln T - R d \ln p \\ &= C_p (d \ln T - d \ln p^\kappa)\end{aligned}$$

But from equation 33 we have

$$d \ln \Theta = d \ln T - d \ln p^\kappa\tag{34}$$

whence:

$$ds = C_p d \ln \Theta\tag{35}$$

so that:

$$s = C_p \ln \Theta \quad (36)$$

give the fundamental relationships between entropy and potential temperature.

The entropy of a mixture of ideal gases is mass additive; that is, the total entropy of the mixture is given by:

$$S = \sum_i M_i s_i \quad (37)$$

where s_i is the specific entropy for each constituent. To see why this assertion makes sense, remember that the definition of entropy in statistical mechanics was just:

$$S = k \ln \Omega \quad (38)$$

where Ω is the number of available states to the entire system consistent with any constraints (such as total volume and total energy). Since in a mixture of ideal gases, each individual constituent acts to a large extent independent of the other constituents, the number of available states of the whole system is just given by the number of states of constituent 1, times the number of states of constituent 2, and so on:

$$\Omega_f = \Omega_1 \times \Omega_2 \times \dots \quad (39)$$

From equations 38 and 39 we have

$$S_f = \sum_i S_i \quad (40)$$

from which 37 follows.

6.5 Change in the composition of the mixture

Collecting equations 37, its equivalent for internal energy U , equation 17, the statement that the volume per unit mass of the i -th constituent is just the total volume divided by M_i , and finally equation 25 expressed for the i -th constituent:

$$\begin{aligned} S &= \sum_i M_i s_i \\ U &= \sum_i M_i u_i \\ p &= \sum_i p_i \\ v_i &= V/M_i \\ T ds_i &= du_i + p_i dv_i \end{aligned} \quad (41)$$

Allowing the masses of each constituent M_i to change as well as the entropy, volume and internal energy, 41 becomes:

$$T dS = T \sum_i (M_i ds_i + s_i dM_i) \quad (42)$$

$$= \sum_i M_i \left(du_i + p_i d \left(\frac{V}{M_i} \right) \right) + \sum_i T s_i dM_i \quad (43)$$

But we also have:

$$dU = \sum_i M_i du_i + \sum_i u_i dM_i \quad (44)$$

$$\begin{aligned} \sum_i M_i p_i d \left(\frac{V}{M_i} \right) &= \sum_i -\frac{p_i}{M_i} V dM_i + \sum_i p_i dV \\ &= -\sum_i dM_i (p_i v_i) + p dV \end{aligned} \quad (45)$$

Using equations 44 and 45 in equation 43, and collecting the terms proportional to dM_i gives:

$$T dS = dU + p dV - \sum_i (u_i + p_i v_i - T s_i) dM_i \quad (46)$$

Defining the Gibbs's potential (or Gibbs free energy) per unit mass as:

$$g_i = u_i + p_i v_i - T s_i \quad (47)$$

we just have:

$$T dS = dU + p dV - \sum_i g_i dM_i \quad (48)$$

For simplicity let us consider one unit of the total mass, so that $M = \sum_i M_i = 1$. Then S , U , and V can be replaced by s , u , and v , while M_i can be replaced by χ_i , the mass fraction. We then obtain:

$$T ds = du + p dv - \sum_i g_i d\chi_i \quad (49)$$

Now this was derived only for a mixture of perfect gases. However, the most important change in composition will be when water vapor either condenses into liquid or solid water, in which case one constituent certainly will not be an ideal gas. The generalization of equation 49 is:

$$T ds = du + p dv - \sum_i \mu_i d\chi_i \quad (50)$$

where the quantity μ_i is the *chemical potential* for constituent i .

Thus we can state that for a mixture of perfect gases, the chemical potential of each constituent is just g_i , and is only a function of the state of the i -th constituent itself.

7 Changes of Phase.

7.1 General Results.

A substance may exist in several phases. Water, as the prime example here, can exist in vapor, liquid or (several forms of) solid. If we fix two thermodynamic variables, say p and T , then each phase is associated with a distinct, separate mathematical function representing the other state variables v , u , h and s . Changes of phase in equilibrium generally occur along one-dimensional subspaces (lines) in the thermodynamic diagram. A change of a small mass from one phase to another at fixed (p, T) will involve both a change in u and v , and so according to the first law will be associated with the absorption or release of heat. This heat is called *latent heat*. The latent heats associated with the phase changes of water play an important role in the atmosphere.

We assume that phase changes occur as reversible processes. (Later on we will

consider departures from this assumption in the real world.) Since a reversible process is a succession of equilibrium states, we start by examining the conditions under which two phases of the same substance may exist in equilibrium.

Consider an insulated container of fixed volume V , containing mass M_1 of phase 1 and mass M_2 of phase 2. The pressure and temperature must define a point in the thermodynamic diagram which lies along one of the special lines allowing the co-existence of two phases. Physically, you can think of water vapor in the container, in the presence of liquid water below, or in the presence of small drops of liquid water. (More on this later.)

Let us assume that the two phases have *different* temperature and pressure, but that the mixture is at equilibrium. Then the entropy $S = M_1s_1 + M_2s_2$ must be a maximum, and any small physical perturbation of the system must, to first order, lead to no change in the total entropy. For this hypothetical perturbation to be physical, it must also conserve total mass, total energy, and total volume. From these constraints (no change in energy, entropy, mass and volume) we will derive conditions on the pressures and temperatures, and one more condition will emerge.

Conservation of mass, internal energy, volume and entropy can be expressed in

the following system of equations:

$$dM_1 + dM_2 = 0 \quad (51)$$

$$M_1 du_1 + M_2 du_2 + u_1 dM_1 + u_2 dM_2 = 0 \quad (52)$$

$$M_1 dv_1 + M_2 dv_2 + v_1 dM_1 + v_2 dM_2 = 0 \quad (53)$$

$$M_1 ds_1 + M_2 ds_2 + s_1 dM_1 + s_2 dM_2 = 0 \quad (54)$$

Also, we can replace ds_i in the last equation by $T_i^{-1} (du_i + p_i dv_i)$ from the first law. We are assuming that the work of volume expansion against a pressure is the only reversible work that is relevant. (In particular, we ignore work against the surface tension in small drops. We will revisit this later.)

Using equation 51 to replace dM_2 in the other constraints above, we obtain:

$$M_1 du_1 + M_2 du_2 + dM_1 (u_1 - u_2) = 0 \quad (55)$$

$$M_1 dv_1 + M_2 dv_2 + dM_1 (v_1 - v_2) = 0 \quad (56)$$

$$\frac{M_1}{T_1} (du_1 + p_1 dv_1) + \frac{M_2}{T_2} (du_2 + p_2 dv_2) + dM_1 (s_1 - s_2) = 0 \quad (57)$$

Now, multiplying equation 55 by $\frac{1}{T_1}$ and equation 56 by $\frac{p_1}{T_1}$:

$$\frac{M_1}{T_1} du_1 + \frac{M_2}{T_1} du_2 + \frac{1}{T_1} dM_1 (u_1 - u_2) = 0 \quad (58)$$

$$\frac{M_1 p_1}{T_1} dv_1 + \frac{M_2 p_1}{T_1} dv_2 + \frac{p_1}{T_1} dM_1 (v_1 - v_2) = 0 \quad (59)$$

Simply taking equation 58 plus 59 minus equation 57:

$$\begin{aligned} & \left(\frac{1}{T_1} - \frac{1}{T_2} \right) M_2 du_2 + \left(\frac{p_1}{T_1} - \frac{p_2}{T_2} \right) M_2 dv_2 \\ & + \left(-(s_1 - s_2) + \frac{1}{T_1} (u_1 - u_2) + \frac{p_1}{T_1} (v_1 - v_2) \right) dM_1 = 0 \end{aligned} \quad (60)$$

Now we have set up this perturbation with all the constraints explicitly written, so that du_2 , dv_2 and dM_1 are all independent. Thus equation 60 leads to:

$$\begin{aligned} T_1 &= T_2 \\ p_1 &= p_2 \\ g_1 &= g_2 \end{aligned} \quad (61)$$

where we have again defined the *Gibbs free energy* (per unit mass) as:

$$g = u + pv - Ts = h - Ts \quad (62)$$

In this equilibrium, we find that not only are T and p equal in the two phases, but g must be the same also. Since $g_1(p, T)$ and $g_2(p, T)$ are two different functions of p and T , the required equality of $g_1 = g_2$ means that p and T are not independent, but form a *curve* in the (p, T) thermodynamic diagram. Another way of putting this is that the pressure at which the two phases are in equilibrium, p_{eq} is a function of the temperature.

From equation 62 we have:

$$\begin{aligned}
 dg &= du + (p dv + v dp) - (T ds + s dT) \\
 &= (T ds - p dv) + (p dv + v dp) - (T ds + s dT) \\
 &= v dp - s dT
 \end{aligned} \tag{63}$$

where we have used the first law. From this we see that:

$$\left(\frac{\partial g}{\partial p} \right)_T = v \tag{64}$$

$$\left(\frac{\partial g}{\partial T} \right)_p = -s \tag{65}$$

For the two-phase equilibrium we have $g_1 = g_2$, so that as we move along the

curve $p_{eq}(T)$, we have $dg_1 - dg_2 = 0$, or:

$$\left[\frac{\partial}{\partial p}(g_1 - g_2) \right]_T dp_{eq} + \left[\frac{\partial}{\partial T}(g_1 - g_2) \right]_p dT = 0 \quad (66)$$

Using equations 64 and 65 this is just:

$$(s_2 - s_1) dT = + (v_2 - v_1) dp_{eq} \quad (67)$$

The *latent heat* $L_{1,2}$ is the heat necessary to change reversibly a unit mass from phase 1 at temperature T and pressure p_{eq} to phase 2 at the same value of T and p :

$$L_{1,2} = \int_1^2 dq = \int_1^2 T ds = T(s_2 - s_1) \quad (68)$$

Combining this with equation 67 we arrive at:

$$L_{1,2} = T(v_2 - v_1) \frac{dp_{eq}}{dT} \quad (69)$$

which is known as the *Clausius - Clapeyron equation*, relating the latent heat to the slope of the phase equilibrium curve in the (p, T) thermodynamic diagram. Note that since the right-hand side is a function of T (in general), so is the latent heat.

Another expression of $L_{1,2}$ is readily obtained from equation 68 by recalling that $g = h - Ts$ with g the Gibb's free energy per unit mass, and h the enthalpy per unit mass, and by noting that $g_1 = g_2$ and $T_2 = T_1$ in a two-phase equilibrium:

$$L_{1,2} = T(s_2 - s_1) = (T_2s_2 - T_1s_1) = (h_2 - g_2) - (h_2 - g_1) = h_2 - h_1 \quad (70)$$

Thus the latent heat $L_{1,2}$ is the heat required to change the enthalpy (or “sensible heat”) from that characteristic of phase 1 to that characteristic of phase 2.

A Note on Metastable Phases. The line of argument just developed does not forbid the existence of any phase, by itself, at any value of T and p . We have merely derived some conditions for the mutual existence of two phases in equilibrium.

An example of a metastable phase is *supersaturated water vapor*. This is water vapor which remains gaseous even after the temperature is decreased (and/or the pressure of the vapor is increased) past the point that the vapor would normally become liquid. This can occur if the air containing the water vapor is very pure, and in particular has no nuclei on which the water vapor can condense. Another example is supercooled liquid, i.e. liquid cooled below the T at which it normally freezes. Supersaturated air and supercooled water are not strictly

speaking in thermodynamic equilibrium, since eventually we would expect the vapor to condense, and the liquid to condense. But these conditions are referred to as meta-stable equilibria; the entropy is a maximum with respect to infinitesimally small deviations, yet a larger entropy maximum of entropy exists a finite distance away at the normal state. The sudden freezing of supercooled water, for example, is an irreversible jump from a local maximum to a global entropy maximum.

7.2 Properties of Phase Transitions of Water.

Since all three phases of water exist under atmospheric-like conditions, there are three equilibrium lines giving $p_{eq}(T)$ in the $p - T$ thermodynamic diagram (see Figure 1 below).

The point O is called the *triple point*, at which all three phases can coexist in equilibrium. It occurs at temperature $T = 273.16K$ and at a pressure of $e = 0.611\text{ cb} = 6.11\text{ mb} = 611\text{ Pa}$, where $1\text{ Pa} = 1\text{ Nm}^{-2}$. We use the symbol e for pressure, since we will eventually consider the mixture of water vapor with dry air, so that the relevant pressure becomes the partial pressure of the mixture.

The vapor-liquid curve AC ends at point C, the *critical point*. Beyond this point, there is no difference between liquid and vapor. It is located at $T = 647K$ and

a pressure of $e = 22,100cb$. The slope of ACD is positive, as is the *latent heat of vaporization* L_v , also called the latent heat of condensation. L_v has a mild temperature dependence:

$$\begin{aligned} L_v &= 2.501 \times 10^6 \text{ j/kg} & T &= 273.15 \\ L_v &= 2.382 \times 10^6 \text{ j/kg} & T &= 323.15 \end{aligned}$$

The portion of AC below the triple point represents the equilibrium between vapor and super-cooled liquid.

The Clausius-Clapeyron equation (69) can be simplified in the case of the vapor-liquid transition by ignoring the volume per unit mass of the liquid compared to that of the vapor, and by using the ideal gas law for the water vapor. Thus if 2 refers to the vapor phase and 1 to the liquid phase in equation 69, and writing the pressure as the saturation vapor pressure of water vapor e_s , we have:

$$\frac{de_s}{dT} = \frac{L_v}{T(v_2 - v_1)} = \frac{L_v}{T} \frac{1}{v_2} = \frac{L_v}{T} \frac{e_s}{R_v T} = \frac{e_s L_v}{R_v T^2} \quad (71)$$

The liquid-solid transition OD has a *negative* slope,

$$\frac{dp_{eq}}{dT} < 0 \quad (72)$$

although on a carefully drawn phase diagram the deviation of the line from a vertical line corresponding to $dp_{eq}/dT = 0$ is too small to be seen. With reference to the Clausius-Clapeyron equation 69, If we consider going from solid to liquid (from a state of lower entropy to one of higher entropy), the corresponding latent heat, called the *latent heat of fusion* L_f , is positive. Then the negative slope of the equilibrium line requires that:

$$v_2 - v_1 = v_i - v_l < 0$$

or that ice (denoted by subscript i) is *less dense* than liquid water (denoted by subscript l) at the transition temperature. Thus ice floats on water. Two values of L_f are:

$$L_f = 0.334 \times 10^6 \text{ j/kg} \quad T = 273.15$$

$$L_f = 0.203 \times 10^6 \text{ j/kg} \quad T = 223.15$$

The curve OB is the vapor-solid, or *sublimation* curve. The heat of sublimation L_s is very close to constant over a range of temperature:

$$L_s = 2.835 \times 10^6 \text{ j/kg} \quad T = 273.15$$

$$L_s = 2.838 \times 10^6 \text{ j/kg} \quad T = 223.15$$

7.3 Properties of Water Vapor, Liquid Water and Ice.

Water vapor is close to a perfect gas. Its molecular weight $m_w = 18.016$, so that its gas constant R_v is given by:

$$R_v = \frac{R^*}{m_w} = \frac{8314.36}{18.016} = 461.5$$

in units of $j \text{ kg}^{-1} \text{ deg}^{-1}$. We use the symbol $R_d = 287j \text{ kg}^{-1} \text{ deg}^{-1}$ for the gas constant of dry air. The ratio of the gas constants for dry air and water vapor is denoted by ϵ :

$$\epsilon = \frac{R_d}{R_v} = 0.622 = (1.609)^{-1} \quad (73)$$

The specific heat at constant pressure, taken at a temperature of 10 K and saturation pressure for the vapor $e = e_s$, is:

$$C_{pv} = 1876.5j \text{ kg}^{-1} \text{ deg}^{-1} \simeq 4.07R_v$$

Note that this is quite different from the ideal gas result given in equation [23](#) for diatomic molecules. However, since for an ideal gas we have in general $C_v = C_p - R$:

$$C_{vv} = C_{pv} - R = 1415j \text{ kg}^{-1} \text{ deg}^{-1} \simeq 3.07R_v$$

Liquid water has an almost constant volume per unit mass $v = 1 \text{ cm}^3 \text{ gm}^{-1}$. The specific heat of liquid is nearly constant over ranges of temperature of interest:

$$C_l = 4187 \text{ j kg}^{-1} \text{ deg}^{-1}$$

Note that the distinction between the specific heat at constant pressure and at constant volume is *not* important for the liquid and solid phases of water. For, borrowing a result from an earlier lecture:

$$C_p = C_v + \left(\frac{\partial v}{\partial T} \right)_p \left[\left(\frac{\partial u}{\partial v} \right)_T + p \right] \quad (74)$$

and the derivative of volume (per unit mass) with temperature at constant pressure is very small for liquid and solid water over the temperature range of interest. (This is clearly not the case for water vapor.)

Ice also has an almost constant volume per unit mass: $v = 1.09 \text{ cm}^3 \text{ gm}^{-1}$. Its specific heat C_i varies somewhat more than does C_l :

$$\begin{aligned} C_i &= 2106 \times 10^6 \text{ j kg}^{-1} \text{ deg}^{-1} & T &= 273.15 \\ C_i &= 1738 \times 10^6 \text{ j kg}^{-1} \text{ deg}^{-1} & T &= 223.15 \end{aligned}$$

7.4 Relationships Between the Three Phases of Water (not complete)

It is convenient to have a mathematical model of the relationships between the three phases of water which is thermodynamically consistent, reasonably accurate and fairly simple.

We begin by making some reasonable approximations:

1. For liquid and solid, assume the specific volumes are constant and equal $v_i = v_l$, and assume that the specific heats C_l and C_i are also constant (but not equal.)
2. Consistently ignore the specific volumes of ice and water compared to that of the vapor: $v_v - v_i$ and $v_v - v_l$ are both approximated by v_v .
3. Treat water vapor as a perfect gas with constant specific heats C_{pv} and C_{vv} .

For solid and liquid forms, we then have

$$\delta q = T ds = du = C dT \quad (75)$$

$$ds = C d \ln T \quad (76)$$

so that u and s are functions only of T . (The constancy and equality of v_v and v_i together eliminate the appearance of the pressure.)

For thermodynamic equilibrium between ice (phase 1) and liquid (phase 2), we have as in general:

$$\begin{aligned} T_1 &= T_2 \\ p_1 &= p_2 \\ g_1 &= g_2 \end{aligned}$$

but with $g = u + pv - Ts$, the constancy and equality of the v_1 and v_2 means that

$$T(s_2 - s_1) + (u_1 - u_2) + p(v_1 - v_2) = 0 \quad (77)$$

becomes:

$$T(s_l - s_i) = u_l - u_i = L_f \quad (78)$$

But with s_l and s_i being different functions of temperature, this can be satisfied only at one temperature, which must be T_3 , the triple point temperature. Hence the curve OD in Figure 1 is completely vertical in this approximation, and L_f is a constant.

Now we consider the case of equilibrium between the solid phase (1) and the vapor phase (2). The general equilibrium conditions of equality of temperature and pressure of course still hold while the equality of the Gibb's free energy

(equation 77) becomes:

$$T(s_v - s_i) + (u_i - u_v) - pv_v = 0 \quad (79)$$

where we have neglected v_i compared to v_v . Then the latent heat of sublimation L_s is just:

$$L_s = T(s_v - s_i) = u_v + e_v v_v - u_i \quad (80)$$

where we now use the letter e to denote pressure. Now $u_v + e_v v_v = h_v$, the enthalpy, which is simply equal to $C_{pv}T$ for an ideal gas. Putting this all together, we obtain:

$$L_s = T(s_v - s_i) = C_{pv}T - u_i \quad (81)$$

$$L_v = T(s_v - s_l) = C_{pv}T - u_l \quad (82)$$

where we have also written the equivalent result based on the liquid phase to vapor phase transition. (to be continued)

8 Moist Thermodynamics

8.1 Effect of dry air on saturation of water vapor.

Now we consider what happens to the liquid - vapor transition of water in the atmosphere, that is in the presence of dry air. We expect the purely mechanical effect of dry air molecules on vapor molecules to be extremely small (since moist air is nearly an ideal gas). Here we focus on the thermodynamic effects.

As before, we assume that the vapor and liquid water have *different* temperature and pressure, but that the mixture is at equilibrium in a closed system (fixed volume and insulated). Any small physical perturbation of the system in which a small amount of water vapor becomes liquid (or vice-versa) must, to first order, lead to no change in the total entropy. For this hypothetical perturbation to be physical, a number of conservation laws must be satisfied. Remembering that the

dry air is not perturbed in this process, we arrive at:

$$M_d = \text{constant} \quad (83)$$

$$M_v + M_l = \text{constant} \quad (84)$$

$$M_l u_l + M_v u_v = \text{constant} \quad (85)$$

$$M_l v_l + M_v v_v = \text{constant} \quad (86)$$

$$M_d v_d = M_v v_v \quad (87)$$

where the subscripts d, v and l refer to dry air, water vapor and liquid water. The first two equations express conservation of mass, the third conservation of energy, and the fourth equation the conservation of volume. The fifth equation states that there is a single volume co-occupied by the two gases, water vapor and dry air.

Following the same logic used following equations 51 - 54, one can show that the condition that $dS = 0$ leads to:

$$\begin{aligned} T_l &= T_v = T_d \\ p_l &= p_v + p_d \\ g_l &= g_v \end{aligned} \quad (88)$$

which generalizes our result in the absence of dry air given in equations 61 and

62.

p_v is the saturation vapor pressure of the moist air in the presence of dry air, which we now call e'_s , for reasons which will become clear. The question we want to ask is: At a *fixed temperature* T , how much does e'_s differ from e_s , the saturation vapor pressure we have defined in the absence of dry air? In the following, the symbol Δ refers to the difference in any thermodynamic quantity that the presence of dry air makes.

We have the equality $g_l = g_v$ in both cases (with and without dry air), so the change in g_l when dry air is introduced must be equal to the change in g_v when dry air is introduced. If we consider g as a function of T and p , we have:

$$\Delta g = v\Delta p - s\Delta T \quad (89)$$

so that under conditions of constant temperature $\Delta g = v\Delta p$. For the liquid, $\Delta p_l = p_d + e'_s - e_s$, while for the vapor, $\Delta p_v = e'_s - e_s$. Since the change $v\Delta p$ for liquid and vapor must be the same:

$$v_l(p_d + e'_s - e_s) = v_v(e'_s - e_s) \quad (90)$$

$$(e'_s - e_s)(v_l - v_v) = -v_l p_d \quad (91)$$

$$(e'_s - e_s)v_v = v_l p_d \quad (92)$$

where we have neglected v_l compared to v_v , as before. Now, using the appropriate equations of state:

$$p_d = \frac{R_d T}{v_d} = (0.622) \frac{R_v T}{v_d}$$

$$v_v = \frac{R_v T}{e_s}$$

one easily gets:

$$\frac{e'_s - e_s}{e_s} = (0.622) \frac{v_l}{v_d}$$

Since the fraction on the right-hand side is very small, the fractional change in the saturation vapor pressure due to the inclusion of dry air is indeed small.

8.2 Humidity Variables.

Both dry air and water vapor are ideal gases, and so have the equations of state:

$$p_d v_d = R_d T \tag{93}$$

$$p_v v_v = R_v T \tag{94}$$

where the volume per unit mass in each case is the given by the ratio of the total (joint) volume to the mass of dry air or vapor. Also, recall equation 73:

$$\epsilon = \frac{R_d}{R_v} = 0.622 = (1.609)^{-1}$$

Applying equations 13 and 20 to the mixture of dry air and water vapor:

$$R = \chi_v R_v + \chi_d R_d \quad (95)$$

$$C_v = \chi_v C_{vv} + \chi_d C_{vd} \quad (96)$$

$$C_p = \chi_v C_{pv} + \chi_d C_{pd} \quad (97)$$

where χ_v and χ_d are the mass fractions of vapor and dry air. Here R is the gas constant of moist air: $pv = RT$ where p is the total pressure and v the volume per mass of moist air. The last equation follows from that the expression for enthalpy $h = u + pv = (C_v + R)T = C_p T$ for an ideal gas.

It is often convenient to consider R as fixed, and to use the numerical value R_d . This can be achieved by defining the *virtual temperature* T^* such that:

$$RT = R_d T^* \quad (98)$$

The *mixing ratio* r is the ratio of the mass of water vapor to the mass of the *dry*

air in a sample of moist air:

$$r = \frac{M_v}{M_d} = \frac{\rho_v}{\rho_d} = \frac{v_d}{v_v} = \frac{R_d p_v}{R_v p_d} = \epsilon \frac{e}{p - e} \quad (99)$$

where we have used p for total pressure, e for vapor pressure and by Dalton's Law, $p - e$ for the pressure of the dry air.

The *specific humidity* q is the ratio of the mass water vapor to the *total mass* of a sample of moist air:

$$q = \frac{M_v}{M_v + M_d} = \frac{r}{1 + r} \quad (100)$$

From above, the gas constant R for moist air is just:

$$R = \frac{M_d}{M_v + M_d} R_d + \frac{M_v}{M_v + M_d} R_v = (1 - q) R_d + q R_v = \frac{1 + (1.609)r}{1 + r} R_d \quad (101)$$

To determine the specific heats of moist air, recall that while for dry air (composed almost entirely of diatomic molecules), $C_{vd} = \frac{5}{2} R_d$ and that therefore $C_{pd} = C_{vd} + R_d = \frac{7}{2} R_d$. However, as we saw earlier, for water vapor we have $C_{vv} = 3.07 R_v$ so that $C_{pv} = 4.07 R_v$.

We can also write $C_{vv} = 3.07 \times 1.609 \times R_d = 3.07 \times 1.609 \times \frac{2}{5} C_{vd} = 1.976 C_{vd}$.

Thus we have that for moist air:

$$\begin{aligned} C_v &= (1 - q)C_{vd} + qC_{vv} \\ &= \frac{1}{1 + r} (1 + (1.976)r) C_{vd} \end{aligned} \quad (102)$$

and a similar calculation for C_p of moist air leads to:

$$C_p = \frac{1}{1 + r} (1 + (1.87)r) C_{pd} \quad (103)$$

We are now in a position to relate the virtual temperature to the mixing ratio using equations 98 and 101:

$$T^* = \frac{R}{R_d} T = \left(\frac{1 + (1.609)r}{1 + r} \right) T \quad (104)$$

which shows that the virtual temperature is always greater than or equal to the temperature.

Air is saturated when the vapor pressure $e = e_s(T)$. Using equation 99. The *saturation mixing ratio* is therefore defined as

$$r_s(p, T) = \epsilon \frac{e_s(T)}{p - e_s(T)} \quad (105)$$

which leads to the definition of the *relative humidity* \hat{R} as the ratio of r to r_s :

$$\hat{R} = \frac{r}{r_s} \quad (106)$$

In terms of specific humidity q we have $q = r/(1 + r)$. Thus $q_s = r_s/(1 + r_s)$ defines the *saturation specific humidity*, which we can relate to \hat{R} as follows:

$$q = \frac{r}{1 + r} = \frac{r_s \hat{R}}{1 + r} = \frac{r_s}{1 + r_s} \frac{1 + r_s}{1 + r} \hat{R} = q_s \frac{1 + r_s}{1 + r} \hat{R} \approx q_s \hat{R}$$

where we make use of the fact that both r and r_s are typically small, less than 0.01 kilograms of vapor per kilogram of dry air.

Using equation 105, we have:

$$q_s = \frac{\epsilon e_s / (p - e_s)}{1 + \epsilon e_s / (p - e_s)} = \frac{\epsilon e_s}{p - (1 - \epsilon) e_s} \quad (107)$$

8.3 Isobaric condensation

Several processes by which moist air is brought to saturation at constant pressure are of interest. Two that will be described here are diabatic cooling, and the adiabatic mixing of two moist air masses.

Diabatic cooling at constant pressure occurs when a sample of moist air (with $e < e_s$) is cooled by radiation or conduction without a change in pressure. Since p and r remain unchanged, by equation 99 so is the vapor pressure e . If the temperature of the sample is lowered sufficiently, $e = e_s$ since e_s falls with the temperature. The *dew point* temperature T_d is defined as the temperature at which this equality occurs, that is the temperature at which the sample of air becomes saturated:

$$e_s(T_d) = e \quad (108)$$

$$r_s(T_d, p) = r \quad (109)$$

where T_d is defined in terms of the pressure p and mixing ratio r of the sample.

A second isobaric process of producing saturated air is that of mixing of two samples of moist air under adiabatic conditions. We treated the case of the mixing of two ideal gases under adiabatic and isobaric conditions in Section 1.4, and discovered that the enthalpy of the final mixture is just the sum of the enthalpies of the original masses. This still holds, so that $H_3 = H_1 + H_2$, where 1 and 2 denote the original masses and 3 the final mixture.

Either of the moist samples can be treated as a mixture of dry air and water

vapor, and the total enthalpies are additive:

$$H = H_d + H_v \quad (110)$$

Dividing by the total mass $M_d + M_v$ and using the definition of the mixing ratio r , we obtain:

$$h = \frac{h_d + rh_v}{1 + r} \quad (111)$$

for the enthalpy per unit mass. Using the fact that $r \ll 1$, we will approximate $h = h_d = C_{pd}T$ for both samples of moist air.

Returning to the mixing of the two samples with masses M_1 and M_2 , since the total enthalpies are again additive:

$$h_3 = \frac{M_1h_1 + M_2h_2}{M_1 + M_2} \quad (112)$$

and we are approximating h by C_{pd} for each sample:

$$T_3 = \frac{M_1T_1 + M_2T_2}{M_1 + M_2} \quad (113)$$

Further, using the definition of mixing ratio for samples 1 and 2 and for the mixture 3, it is easy to show that:

$$r_3 = \frac{M_{v3}}{M_{d3}} = \frac{M_{d1}r_1 + M_{d2}r_2}{M_{d1} + M_{d2}} \approx \frac{M_1r_1 + M_2r_2}{M_1 + M_2} \quad (114)$$

Finally, we approximate equation 99 as follows: remembering that $e = p_v$, the partial pressure of moist air:

$$\epsilon \frac{e}{p} = \epsilon \frac{e}{p_d + e} = \epsilon \frac{e}{p_d (1 + e/p_d)} = \epsilon \frac{e}{p_d (1 + r/\epsilon)} \approx \epsilon \frac{e}{p_d} = r \quad (115)$$

where we have used the fact that $r \ll 1$. Since the total pressure p is fixed, equation 114 becomes:

$$e_3 \approx \frac{M_1 e_1 + M_2 e_2}{M_1 + M_2} \quad (116)$$

so that *both the vapor pressure e and temperature T of the final mixture are simply mass weighted sums of the individual samples.*

Figure 3 shows two samples of moist air (marked 1 and 2) at constant pressure in a thermodynamic diagram in which the independent variables are T and e . The final vapor pressure e_3 and temperature T are each linear combinations of the sample variables, with the same weighting. Thus the final state 3 lies along a straight line, as shown. The heavy curve shown is that for the saturation vapor pressure e_s . The key point is that this curve is concave upward, that is:

$$\frac{d^2 e_s}{dT^2} > 0 \quad (117)$$

a result which is not hard to show, using equation 71.

Thus even if the original samples 1 and 2 are unsaturated, the mixed final sample 3 may be saturated.

8.4 Adiabatic cooling to saturation

We consider adiabatic reduction in the pressure of a sample of *unsaturated* moist air, as would occur if a parcel of air was rising. Recalling that $ds = C_p d \ln T - R d \ln p$, the change in T with pressure p for no change in entropy can be written as:

$$\left(\frac{dT}{dp} \right)_{un} = \frac{T R}{p C_p} \approx \frac{T R_d}{p C_{pd}} \quad (118)$$

Since no condensation takes place, the masses of the dry air and water vapor stay the same, so r is constant. From equation 99 and the fact that $e \ll p$, we see that the reduction in p will mean a reduction in e . Thus the reduction in p will bring the parcel to saturation only if the reduction in T brings the sample to the saturation curve $e_s(T)$ quickly enough to overcome the decrease in e .

Consider a line of constant saturated mixing ratio r_s in the $p - T$ plane:

$$r_s(p, T) = \epsilon \frac{e_s(T)}{p - e_s(T)} \quad (119)$$

To find a line of constant r_s , set $dr_s = 0$, giving:

$$\frac{de_s}{p - e_s} - \frac{e_s}{(p - e_s)^2} (dp - de_s) = 0 \quad (120)$$

which gives:

$$p de_s = e_s dp \quad (121)$$

Thus the lines of constant r_s are given by:

$$\left(\frac{dT}{dp} \right)_{r_s} = \frac{dT}{de_s} \frac{de_s}{dp} = \frac{dT}{de_s} \frac{e_s}{p} = \frac{T R_v T}{p L_v} \quad (122)$$

where in the last step we have used equation 71.

Refer to Figure 4, which shows an unsaturated sample at point O, where we assume the parcel is unsaturated. It moves to lower pressure along the dashed line of constant r with the slope being given by the inverse of $\left(\frac{dT}{dp} \right)_{un}$. The dashed line will intersect the line of constant $r = r_s$ (given by solid lines in the figure), with slope given by the inverse of $\left(\frac{dT}{dp} \right)_{r_s}$, if the latter slope is bigger. Thus the condition for intersection becomes:

$$\left(\frac{dT}{dp} \right)_{un}^{-1} > \left(\frac{dT}{dp} \right)_{r_s}^{-1} \quad (123)$$

which can be easily reduced to:

$$T < \frac{R}{R_v} \frac{L_v}{C_p} \sim 1000$$

which is satisfied for the atmosphere.

8.5 The reversible saturated adiabatic process.

We consider a moist parcel that rises, and reaches the saturation point, as just discussed. It is then assumed that all condensed water (which we take to be liquid) stays with the saturated air, that no heat of mass is exchanged with the environment, and that all changes are reversible.

This process is therefore one of constant *total* entropy and *total* mixing ratio $r_v + r_l = \frac{M_v + M_l}{M_d}$.

We can express the total entropy S as:

$$s = \frac{M_d s_d + M_v s_v + M_l s_l}{M}$$

where $M = M_d + M_v + M_l$ is the total mass, and the subscripts d , v , and l refer to dry air, water vapor, and liquid water respectively. Dividing numerator and

denominator by M_d , we obtain:

$$\begin{aligned} s &= \frac{s_d + r_v s_v + r_l s_l}{1 + r_v + r_l} \\ &= \frac{s_d + r_v(s_v - s_l) + (r_v + r_l)s_l}{1 + r_v + r_l} \end{aligned} \quad (124)$$

We determine s_d by integrating the relationship $ds_d = C_{pd} d \ln T - R_d d \ln p_d$ from a reference state of temperature T_0 and pressure p_0 to a state (p, T) :

$$s_d = C_{pd} \ln \left(\frac{T}{T_0} \right) - R_d \ln \left(\frac{p - e_s}{p_0} \right) \quad (125)$$

where the use of $p - e_s$ for p_d makes it clear that we are *explicitly assuming that the moist parcel is saturated*. From the definition of L_v we have:

$$(s_v - s_l) = \frac{L_v}{T} \quad (126)$$

and we also have

$$r_v = \epsilon \frac{e_s(T)}{p - e_s(T)} \quad (127)$$

Setting $ds = 0$ in equation 124, and using equations 125, 126, and 127, we obtain (after a great deal of work, and some relationships given in the Appendix):

$$\left(\frac{dT}{dp}\right)_{rev} = \frac{R_d T + L_v r_v}{(p - e) \left[C_{pd} + \frac{\epsilon L_v^2}{R_d T^2} \left(\frac{p}{p-e}\right) r_v + C_l r_l + C_{pv} r_v \right]} \quad (128)$$

where $e_s(T)$ is written as simple e . The right-hand side is a function of p and T and of r_l . Since the moist air is assumed to be saturated, r_v is given by the saturation mixing ratio, and is determined by T and p .

Since the dimensionless quantities r_l and r_v are both typically quite small compared to 1, we can neglect the last two terms in square brackets in the denominator, and also replace $p - e$ with p everywhere to get:

$$\left(\frac{dT}{dp}\right)_{rev} \approx \left(\frac{R_d T}{p C_{pd}}\right) \frac{\left(1 + \frac{L_v r_v}{R_d T}\right)}{\left(1 + \frac{\epsilon L_v}{C_{pd} T} \frac{L_v r_v}{R_d T}\right)} \quad (129)$$

8.6 Pseudo-Moist Adiabats

The exact expression in equation 128 is a function of p , T , and r_l as mentioned. It is useful to have an expression for the change of T with p that only depends on

T and p . Such an expression is called a *pseudo-moist adiabat*. While equation 129 is one example, the official formula (quoted by Phillips as being due to von Bezold) is slightly different, and is given by:

$$C_{pd} d \ln T - R_d d \ln p + d \left(\frac{L_v r_v}{T} \right) + r_v C_l d \ln T = 0 \quad (130)$$

Note that the left-hand side is not an exact differential, because of the dependence of the saturated r_v on T and p . This approximation can be derived from the exact reversible expression equation 128 if the term involving r_l in the denominator is ignored. This also can be re-written (with some work) as:

$$(1 + r_v) [C_p dT - RT d \ln p] = -L_v dr_v \quad (131)$$

Please note the C_p and R here refer to the values for moist saturated air. Equation 131 has a simple physical interpretation: the presence of liquid water is ignored in the exchange of heat within the saturated sample, and all the released heat of condensation (the right-hand side) is absorbed by the moist air.

8.7 Lapse rates

. Note that the limit of equations 128, 129 and 130 in which there is no moisture ($r_v = r_l = 0, e = 0$) yields the expected expression for the adiabatic process of

dry air:

$$\left(\frac{dT}{dp}\right) = \left(\frac{R_d T}{p C_{pd}}\right) \quad (132)$$

Using the hydrostatic relationship and the equation of state for dry air, this can be easily re-written in terms of the *dry adiabatic lapse rate*:

$$\Gamma = -\frac{dT}{dz} = +\frac{g}{C_{pd}} \equiv \Gamma_d \quad (133)$$

From the above, it is not hard to see that if we use the approximate equation [129](#) for the saturated moist process, the lapse rate becomes:

$$\Gamma = -\frac{dT}{dz} = \Gamma_d \frac{\left(1 + \frac{L_v r_v}{R_d T}\right)}{\left(1 + \frac{\epsilon L_v}{C_{pd} T} \frac{L_v r_v}{R_d T}\right)} \quad (134)$$

which is often called the *pseudo - moist adiabatic lapse rate*.

8.8 Thermodynamic Diagrams.

It is often convenient to portray graphically either the evolution of the thermodynamic state of a given parcel of air, or the variation with pressure of the vertical

air column located above a particular location at one time. (The latter is used to plot the observations of p , T and moisture obtained by, for example, a radiosonde ascent.)

The coordinates in two-dimensional diagram can be picked in a number of ways. One property that is useful is that the area defined by a closed reversible cycle is proportional to the work done by the sample during the cycle. In a $v - p$ diagram, the work done by a cycle is just given by $\oint p dv$, where the direction around the cycle is shown in the left hand panel of Figure 5.

In a more general thermodynamic diagram in which the abscissa is x and the ordinate y , this cycle will be represented by another set of curves. In order to study what the the integral $\oint p dv$ will be in this new diagram, consider a number of infinitesimally small boxes, as shown in the right hand panel of Figure 5. Although the boxes are pictured separated slightly for clarity, they are meant to be touching along all common sides.

It is not hard to see that the line integral of any quantity along the path going clockwise around the outer edge of the four box complex is simply the sum of the four line integrals of the same quantity computed for each box around the clockwise paths shown in the figure. This is because the portion of the line integral

going to the right along the top of box A has exactly the same magnitude but the opposite sign as the line integral going to the left along the bottom of box C. Similarly, the line integrals along the portions of the remaining touching interior boundaries cancel.

Since these boxes are extremely small, *we can compute the integral $\oint p dv$ around an arbitrary shape in the $x - y$ plane as a sum of a very large number of these elemental boxes.*

Going back to a single box (say A), the line integral of the work done by the sample is:

$$\oint_A p dv = \int_1 p \frac{\partial v}{\partial x} dx + \int_3 p \frac{\partial v}{\partial x} dx + \int_2 p \frac{\partial v}{\partial y} dy + \int_4 p \frac{\partial v}{\partial y} dy \quad (135)$$

where

- \int_1 denotes the integral along the top of box A, with (direction of integration to the right)
- \int_3 denotes the integral along the bottom of box A, with (direction of integration to the left)
- \int_2 denotes the integral along the left of box A (direction of integration up-

ward)

- \int_4 denotes the integral along the right of box A (direction of integration downward)

We have made use of the fact that along parts (1) and (3) of the path, y is constant, while along parts (2) and (4) of the path, x is constant. The four components are now ordinary one-dimensional integrals, but only if we take into account the path direction:

$$\begin{aligned}
 \oint_A p \, dv &= \int p_1 \frac{\partial v}{\partial x} dx - \int p_3 \frac{\partial v}{\partial x} dx + \int p_2 \frac{\partial v}{\partial y} dy - \int p_4 \frac{\partial v}{\partial y} dy \\
 &= \int (p_1 - p_3) \frac{\partial v}{\partial x} dx + \int (p_2 - p_4) \frac{\partial v}{\partial y} dy \\
 &= \int \frac{\partial p}{\partial y} dy \frac{\partial v}{\partial x} dx + \int \frac{\partial p}{\partial x} dx \frac{\partial v}{\partial y} dy \\
 &= \int J(v, p|x, y) \, dx \, dy \tag{136}
 \end{aligned}$$

where the last integral is just an ordinary area integral over the tiny box. We are able to replace the finite differences in pressure with the appropriate partial derivatives because the box is infinitesimally small. The last line defines notation

for the *Jacobian* of p and v with respect to x and y :

$$J(v, p|x, y) \equiv \frac{\partial v}{\partial x} \frac{\partial p}{\partial y} - \frac{\partial p}{\partial x} \frac{\partial v}{\partial y} \quad (137)$$

where the partial derivative with respect to x means that y is held constant, and the partial derivative with respect to y means that x is held constant.

If the Jacobian is equal to a constant (call it C), then when we compute the work done by the sample along any arbitrary closed cycle in the $x - y$ plane by adding up a large number of small boxes (each labeled by i) we obtain:

$$\oint p dv = \sum_i \oint_i p dv = \sum_i \int_i J(v, p|x, y) dx dy = C \sum_i \int_i dx dy = C A \quad (138)$$

where A is the area of the closed curve in the $x - y$ plane.

Thus the condition of having the Jacobian constant leads to equal work done around closed paths for equal areas in the new $x - y$ diagram. Thus the transformation from a $p - v$ diagram to the new $x - y$ diagram is area preserving.

Note The previous development, encompassing equations 136 - 138 can be repeated, computing the area in the $x - y$ plane in terms of the area in the $v - p$

plane. In this case we obtain:

$$\oint x dy = \oint \left(\frac{\partial x}{\partial v} \frac{\partial y}{\partial p} - \frac{\partial x}{\partial p} \frac{\partial y}{\partial v} \right) p dv = \oint J(x, y|v, p) p dv \quad (139)$$

The partial derivative $\frac{\partial}{\partial p}$ is taken holding v constant, while the partial derivative $\frac{\partial}{\partial v}$ is taken holding p constant. Thus $\frac{\partial p}{\partial x}$ in equation 137 is *not* the inverse of $\frac{\partial x}{\partial p}$ in equation 139 because different variables are kept constant.

Examples of coordinates used in thermodynamic diagrams are given below. All but one are area preserving. Can you find out which one is not?

- Emagram ($x = T, y = -\ln p$)
- Tephigram ($x = T, y = s = C_p \ln T - R \ln p$)
- Skew T - log p Diagram ($x = K \ln p, y = -\ln p$)
- Stueve Diagram ($x = T, y = -p^{R/C_p}$)

8.9 Appendix: Relationships between phases of water.

Future versions of these notes will have a complete derivation of an approximate mathematical model due to Phillips for the thermodynamics of the three phases

of water relevant for ordinary atmospheric conditions.

Two expressions which are needed to derive equation 128 relate to the specific entropy of liquid water s_l and the temperature dependence of the latent heat of vaporization L_v .

$$s_l = s_{i3} + \frac{L_f}{T_3} + C_l \ln\left(\frac{T}{T_3}\right) \quad (140)$$

where T_3 is the triple point of water, s_{i3} is a constant, and the latent heat of freezing L_f is effectively a constant.

$$L_v = L_{v3} + (C_{pv} - C_l)(T - T_3) \quad (141)$$

here L_{v3} is the latent heat of vaporization at the triple point.

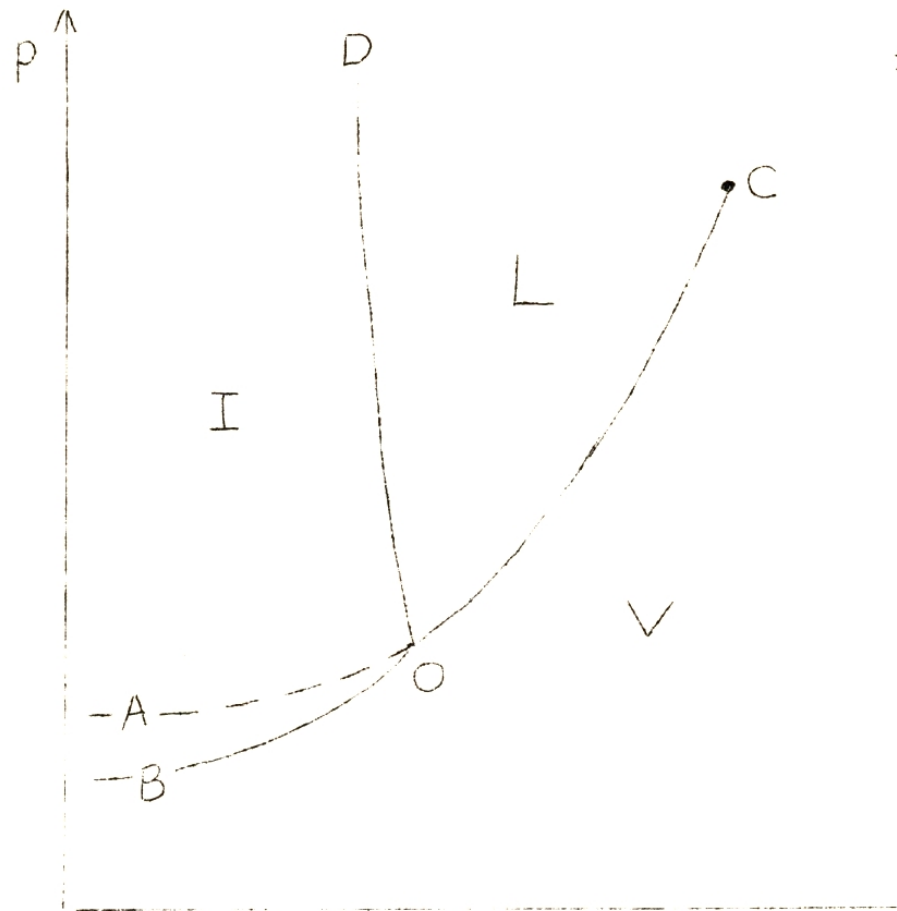


Figure 2.5

Schematic vapor pressure diagram for water

Figure 1: Schematic vapor pressure diagram of water. The ordinate is pressure, the abscissa is temperature. V denotes vapor, I solid (or ice), and L liquid. AC is the vapor-liquid transition curve, OD the liquid- solid transition curve, and OB the vapor-solid transition curve (from Phillips).

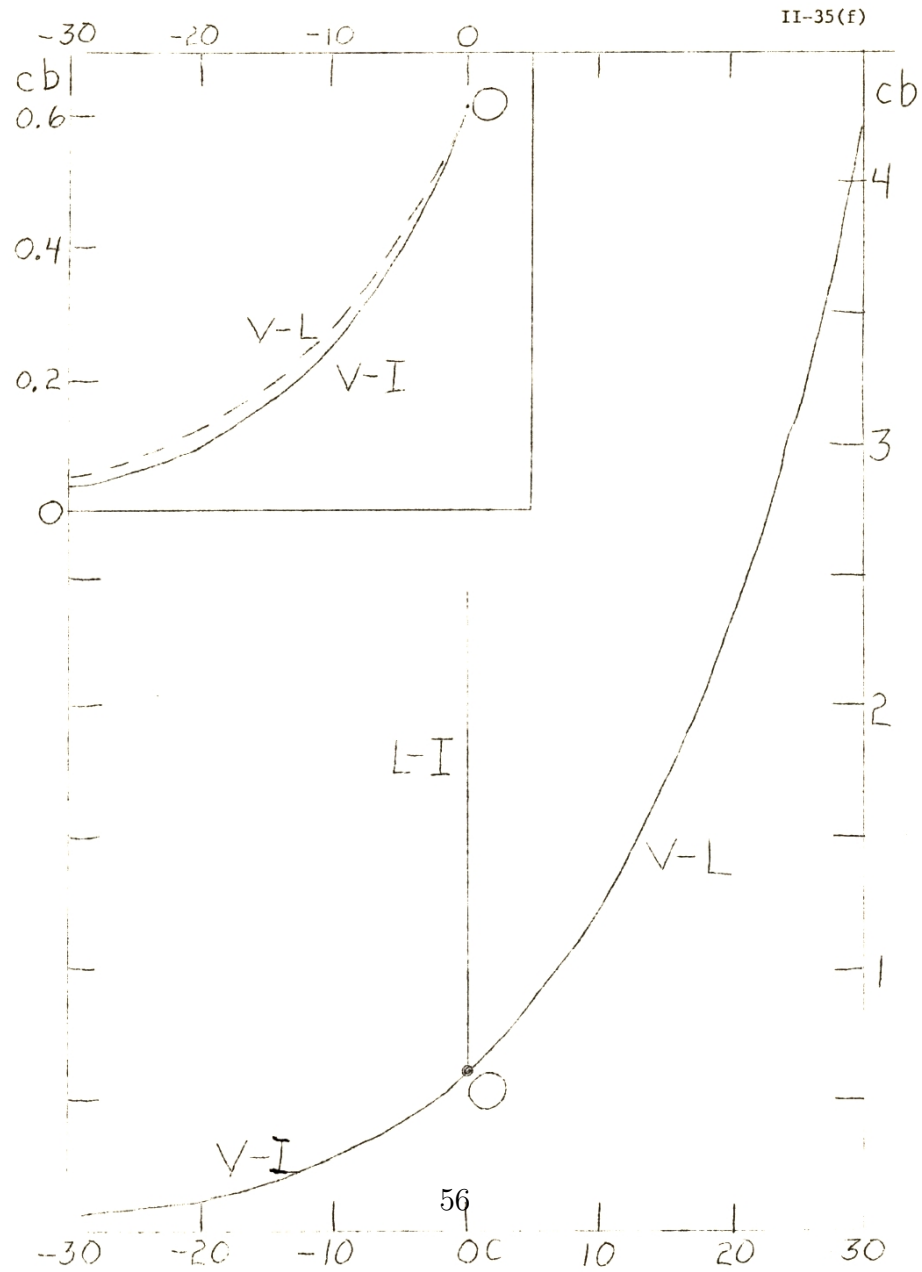


Figure 2: More detailed vapor pressure diagram for water (from Phillips).

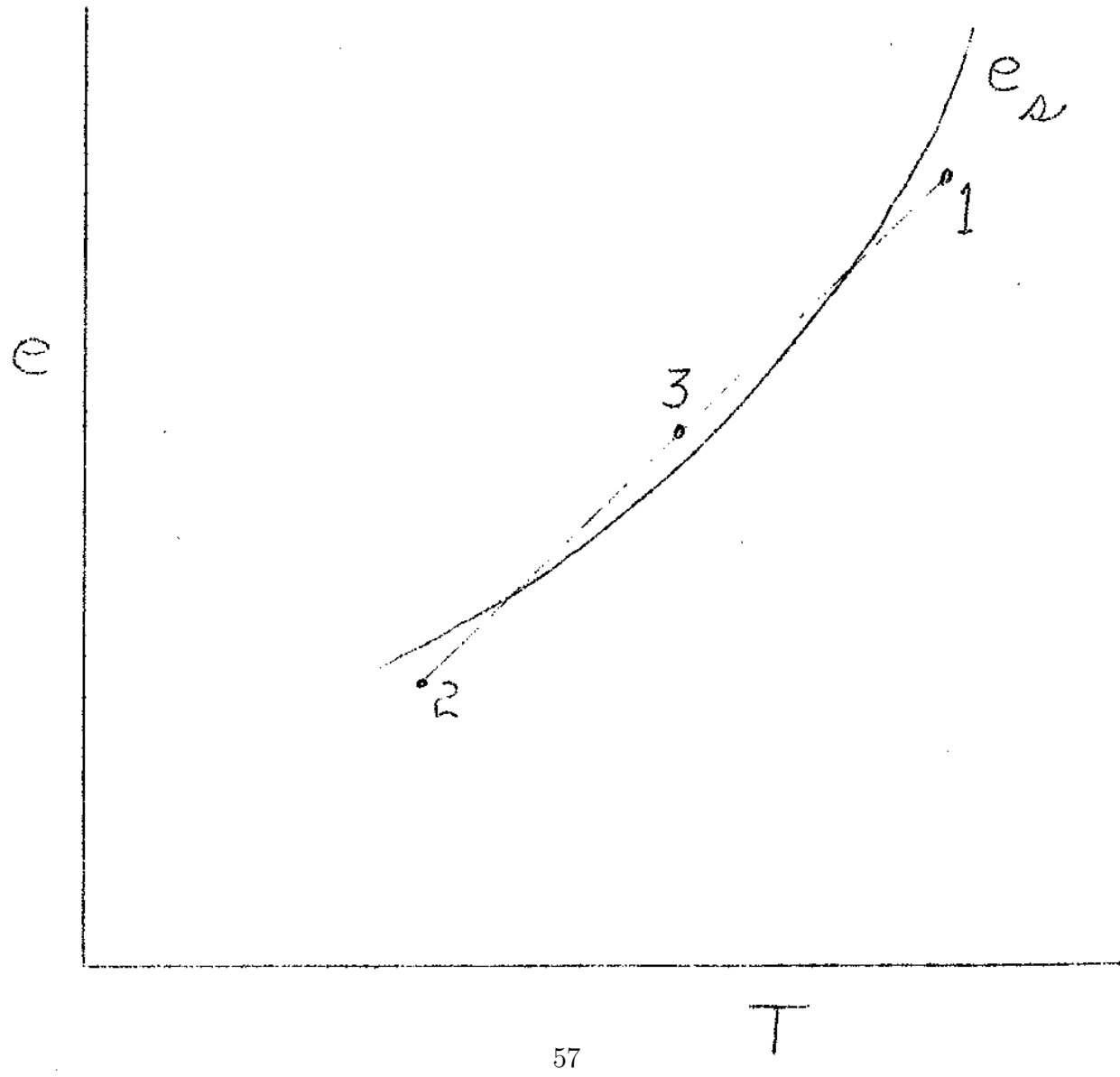


Figure 3: Isobaric mixing of unsaturated air (from Phillips).

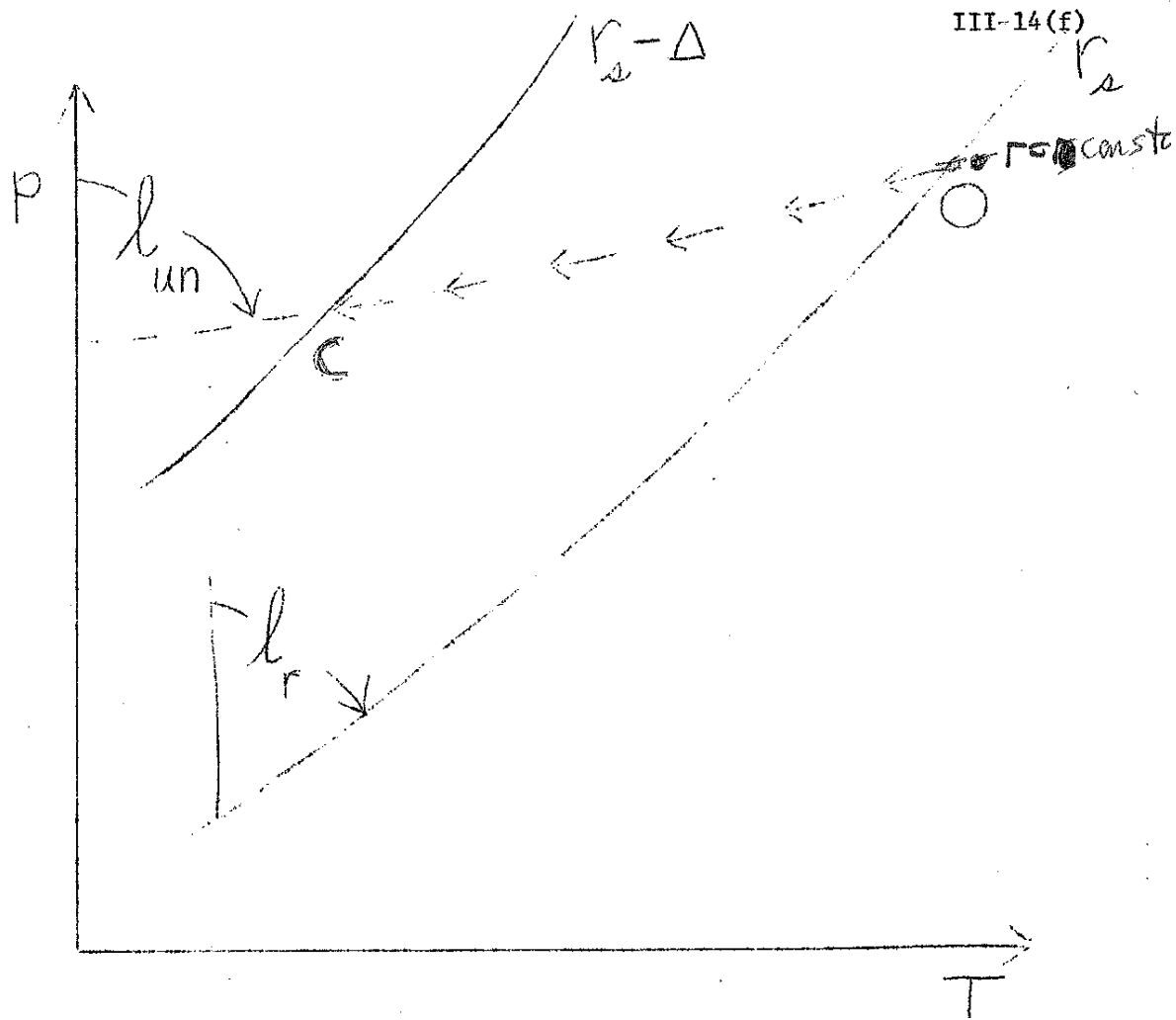


Figure 4: Lines of constant r and r_s (from Phillips).

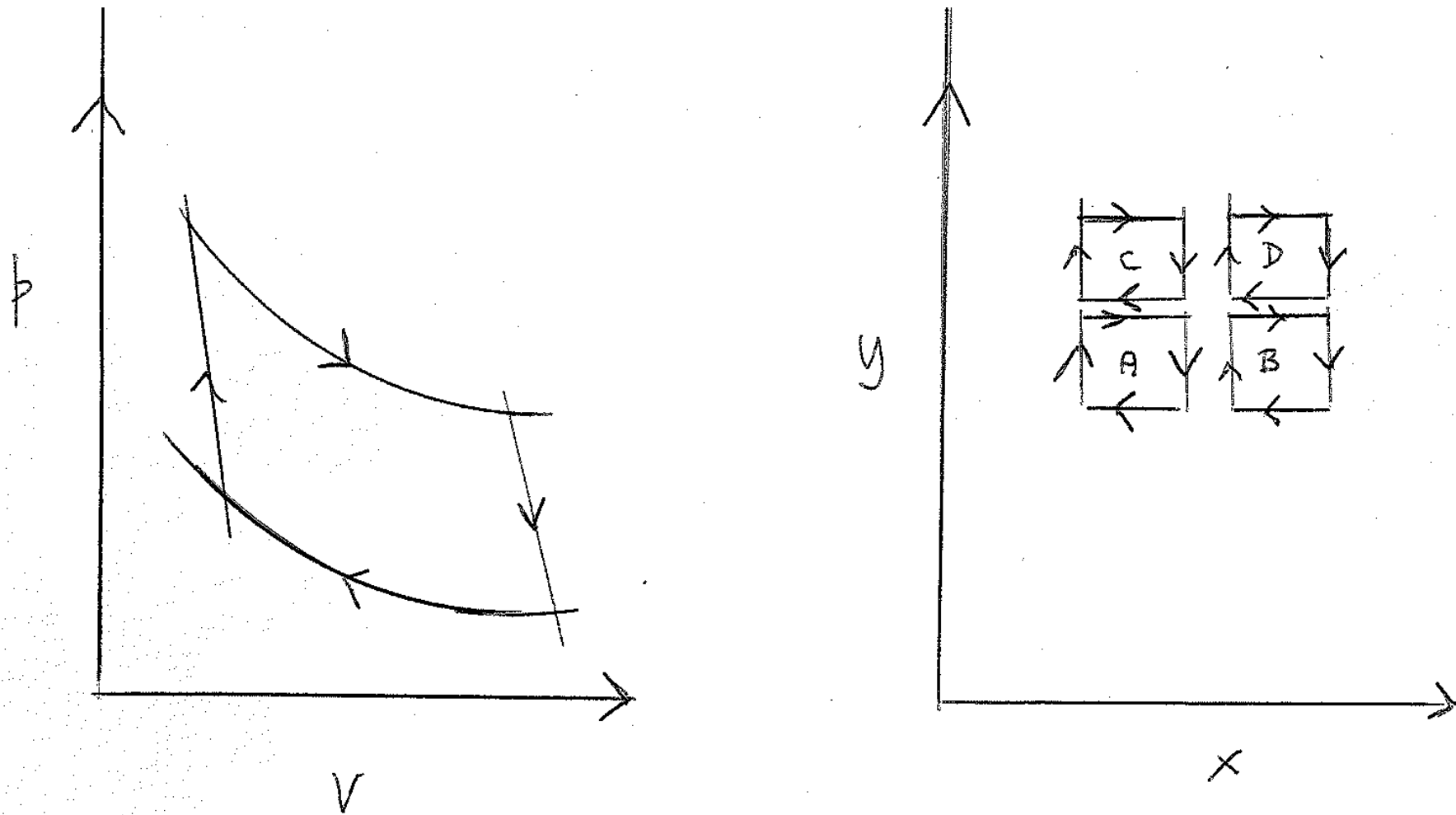


Figure 5: Left hand panel: Path of line integral $\oint p dv$ in the $p - v$ thermodynamic plane. Right hand panel: 4 infinitesimally small integration boxes in the $x - y$ plane.