

5. The water-air heterogeneous system

Aside: The following is an on-line analytical system that portrays the thermodynamic properties of water vapor and many other gases.

<http://webbook.nist.gov/chemistry/fluid/>

5.1 Preliminaries

a) Review on equilibrium:

thermodynamic equilibrium -- a system is in thermal equilibrium (no temperature difference)

mechanical equilibrium -- a system in which no pressure difference exists between it and its environment

chemical equilibrium -- condition in which two phases coexist (water in this case) without any mass exchange between them

b) For a homogeneous system, 2 intensive properties describe the thermodynamic state (consider the eq. of state $p\alpha = RT$); this is not the case for a heterogeneous system consisting of dry air, water vapor and condensed water.

c) Consider an extensive property Z of the water-air system and define it as

$$Z_{\text{tot}} = Z_g(p, T, n_d, n_v) + Z_c(p, T, n_c)$$

The total differential of this property is the following:

$$dZ_{g,\text{tot}} = \left(\frac{\partial Z_{g,\text{tot}}}{\partial T} \right)_{p,n} dT + \left(\frac{\partial Z_{g,\text{tot}}}{\partial p} \right)_{T,n} dp + \left(\frac{\partial Z_{g,\text{tot}}}{\partial n_d} \right)_{T,p,n} dn_d + \left(\frac{\partial Z_{g,\text{tot}}}{\partial n_v} \right)_{T,p,n} dn_v$$

$$dZ_{c,\text{tot}} = \left(\frac{\partial Z_{c,\text{tot}}}{\partial T} \right)_{p,n} dT + \left(\frac{\partial Z_{c,\text{tot}}}{\partial p} \right)_{T,n} dp + \left(\frac{\partial Z_{c,\text{tot}}}{\partial n_c} \right)_{T,p,n} dn_c$$

Example of chemical equilibrium

A closed container initially filled partly with water in a vacuum will be in chemical equilibrium when $p = e_s$ (the saturation vapor pressure). At this point, the number of molecules passing from liquid to vapor equals the number passing from vapor to liquid.

| |
|--|
| Vapor in equilibrium (vacuum initially) $p_{\text{equil}} \rightarrow e_s$ |
| water |

5.2 Chemical potential

If a single molecule is removed from a material in a certain phase, with the temperature and pressure remaining constant, the resulting change in the Gibbs free energy is called the chemical potential of that phase. In other words, *the chemical potential can be defined as the Gibbs free energy per molecule*. (Recall, $dg = -sdT + \alpha dp$ for a reversible transformation.)

The chemical potential of an ideal gas is defined by

$$\mu = \mu^0 + RT \ln p, \quad [d\mu = RT d \ln p = RT dp/p = \alpha dp]$$

where μ^0 is the chemical potential for $p = 1$ atm.

For an ideal gas,

$$\Delta g = \mu_2 - \mu_1 = RT \ln(p_2/p_1) \quad [= -w_{\max}]$$

Example (Taken from Wallace and Hobbs, pp. 101-102): Derive an expression for the difference in chemical potential between water vapor and liquid water, $\mu_v - \mu_l$, in terms of the bulk thermodynamic properties: e (the partial pressure of water vapor) and T .

For a (vapor) pressure change de , we have (from $dg = -sdT + \alpha dp$), for vapor and liquid, respectively,

$$\begin{aligned} d\mu_v &= \alpha_v de, \\ d\mu_l &= \alpha_l de, \end{aligned}$$

where α_v is the specific volume of a water vapor molecule and α_l is the specific volume of a liquid water molecule. Then it follows, by combining the equations above, that

$$d(\mu_v - \mu_l) = (\alpha_v - \alpha_l)de \cong \alpha_v de \quad (5.1)$$

since $\alpha_v \gg \alpha_l$. The equation of state applied to just one water vapor molecule is

$$e\alpha_v = kT, \quad (5.2)$$

where k , Boltzmann's constant whose value is $1.381 \times 10^{-23} \text{ J K}^{-1} \text{ molecule}^{-1}$, is used in place of the gas constant to represent one molecule. Upon solving (5.2) for α_v , we can write (5.1) as

$$d(\mu_v - \mu_l) = kT \frac{de}{e}. \quad (5.3)$$

Since $\mu_v = \mu_l$ at $e = e_s$ (saturation, which is equilibrium) we can integrate (5.3) as follows:

$$\int_0^{\mu_v - \mu_l} d(\mu_v - \mu_l) = \int_{e_s}^e kT de/e,$$

or

$$\mu_v - \mu_l = kT \ln \left(\frac{e}{e_s} \right) \quad (\text{for one molecule}). \quad (5.4)^*$$

This result will be used later in development of the theory of nucleation of water droplets from the vapor phase. [Nucleation is therefore closely related to thermodynamics.]

5.3 Changes in state

We will now consider various equilibria for water in the atmosphere.

5.3.1 Gibbs phase rule

For a system of C independent species and P phases, the Gibbs phase rule states that the number of degrees of freedom F (i.e., the number of state properties that may be arbitrarily selected) is

$$F = C - P + 2 \quad (5.5)$$

If we deal with a single component system ($C=1$) such as water then we can form the table below:

| P (number of phases) | F (degrees of freedom) |
|----------------------|------------------------|
| 1 | 2 |
| 2 | 1 |
| 3 | 0 |

Thus, for a single existing phase (such as water vapor) we may arbitrarily choose p (e) and T (i.e., the equation of state). For two phases, the choice of either p or T determines the other, and for three phases (i.e., the triple point) there is no choice, i.e., this point has specific values for p and T . The phase diagram for water is depicted in Figs. 5.1 and 5.2. Along the two coexisting phase lines, one degree of freedom is possible, within each phase two degrees of freedom exists, and with three coexisting phases (the so-called *triple point*) there are none. We will now consider the phase lines.

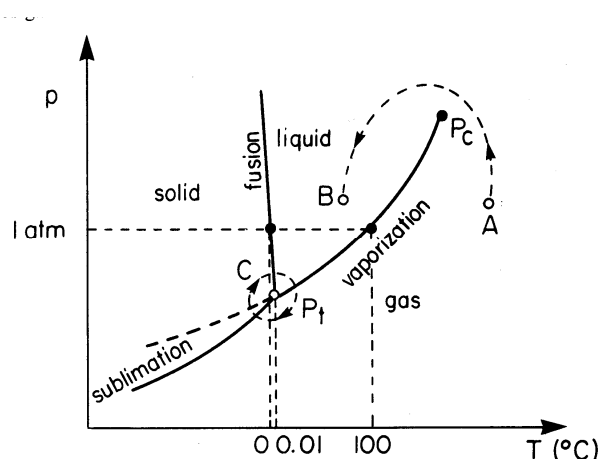


Fig. 5.1. Phase transition equilibria for water. P_t is the triple point, and P_c is the critical point, above which no distinction between the liquid and vapor phases exists. From Iribarne and Godson (1973).

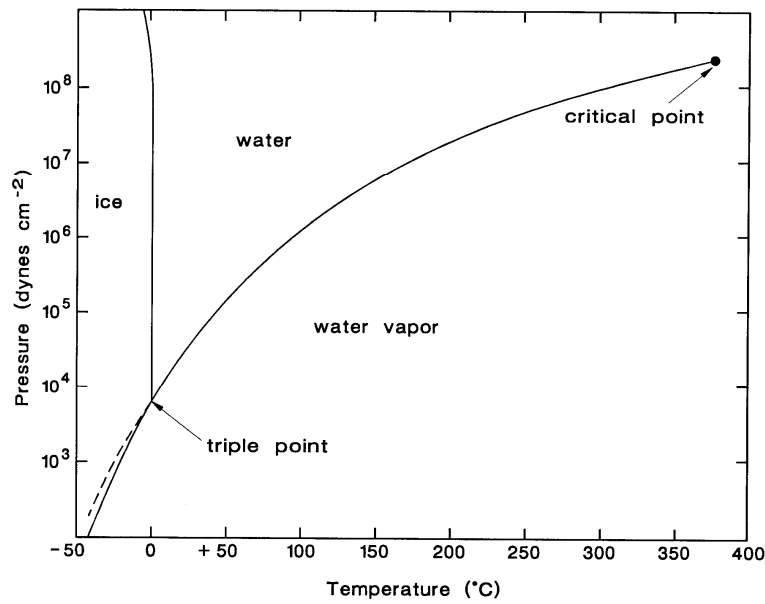


Fig. 5.2. PT phase diagram for water. Stable phase boundaries are shown by solid lines; metastable phase boundaries are indicated by dashed lines. Note that the ordinate is exponential in pressure, in contrast to the linear p dependence in Fig. 5.1. From Young (1993), p. 401.

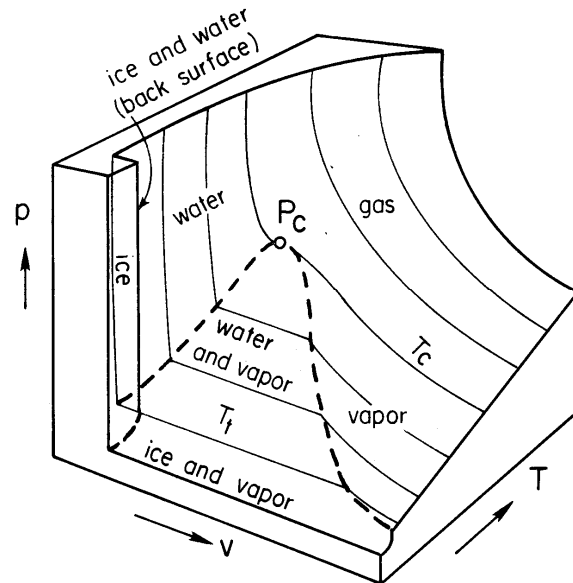


Fig. 5.3 Thermodynamic surface for water. Taken from Iribarne and Godson (1973).

5.3.2 Thermodynamic characteristics of water

Key points on a p-T diagram for water (Figs. 5.1, 5.2 and 5.3):

- a) triple point: $p_t = 610.7 \text{ Pa} = 6.107 \text{ mb}$; $T_t = 273.16 \text{ K} = 0.01 \text{ }^\circ\text{C}$;
 $\alpha_{it} = 1.091 \times 10^{-3} \text{ m}^3 \text{ kg}^{-1}$; $\alpha_{wt} = 1.000 \times 10^{-3} \text{ m}^3 \text{ kg}^{-1}$; $\alpha_{vt} = 206 \text{ m}^3 \text{ kg}^{-1}$
- a) critical point: $T_c = 647 \text{ K}$; $p_c = 218.8 \text{ atm}$; $\alpha_c = 3.07 \times 10^{-3} \text{ m}^3 \text{ kg}^{-1}$

5.3.3 Equilibrium between solid and liquid - The Clapeyron Eq.

The lines drawn in Figs. 5.1-5.3 are represent the equilibrium condition between two phases of water. These are important in our study of thermodynamics, and the equilibrium line between the liquid and vapor phase is particularly valuable. These equilibrium conditions can be expressed analytically, and the basis for the functions derived in the following is the First Law, from the the Gibbs free energy is derived.

At equilibrium we have $dg=0$, so therefore $g(\text{solid}) = g(\text{liquid})$.

$$-s_{\text{liquid}}dT + \alpha_{\text{liquid}}dp = -s_{\text{solid}}dT + \alpha_{\text{solid}}dp$$

Define the following:

$$\Delta s = s_{\text{solid}} - s_{\text{liquid}}$$

$$\Delta \alpha = \alpha_{\text{solid}} - \alpha_{\text{liquid}}$$

Then

$$\Delta s dT = \Delta \alpha dp.$$

We solve this as follows, and utilize the definition of entropy change for a phase transition (Ch. 4):

$$dp/dT = \Delta s / \Delta \alpha = -\Delta H_{\text{fusion}} / (T \Delta \alpha) \quad \text{Clapeyron Equation} \quad (5.6)$$

where the latter equality is based on the entropy change associated with a phase change, defined in Chap. 4: $\Delta s = -\Delta H_{\text{fusion}} / T$.

This expression is the Clapeyron Equation. Since $\Delta H > 0$ (heat is liberated upon freezing) and $\Delta \alpha > 0$ (freezing water expands), the slope $dp/dT < 0$ as shown in Figs. 5.1 and 5.2.

5.3.4 Liquid/vapor equilibrium - the Clausius-Clapeyron Eq.

In this case $\Delta \alpha = \alpha_{\text{liquid}} - \alpha_{\text{vapor}} \cong -\alpha_{\text{vapor}}$. Then, from the equation of state, we can write

$$-\alpha_v = -R_v T / e_s \quad (e_s \text{ is used in place of } p \text{ since we are concerned with equilibrium at saturation})$$

Then

$$de_s/dT = -\Delta H_{\text{vap}}/(T\Delta\alpha) = \Delta H_{\text{vap}}e_s/(R_v T^2)$$

$$\text{or} \quad d\ln e_s/dT = L_{vl}/(R_v T^2). \quad (5.7)$$

Recall that L_{vl} is not a constant, but varies by ~10% over the temperature interval (0, 100 °C), and by about 6% over the interval (-30, 30 °C). (See Table 5.1) However, to a first approximation, we can assume that L_{vl} is constant and integrate Eq. (5.7):

$$\int_{e_{so}}^{e_s} d\ln e_s = \frac{L_{lv}}{R_v} \int_{T_o}^T \frac{dT}{T^2}$$

which is solved as

$$\ln\left(\frac{e_s}{e_{so}}\right) = \frac{L_{vl}}{R_v} \left(\frac{1}{T_o} - \frac{1}{T}\right)$$

where $T_o = 273.1$ K and $e_{so} = 6.11$ mb (from lab measurements).

Rewriting this expression and grouping the constants into new constants A and B yields the simple, *approximate* expression:

$$e_s(T) = Ae^{-B/T}, \quad (5.8)$$

where $A = 2.53 \times 10^8$ kPa and $B = 5.42 \times 10^3$ K.

A more elegant derivation of the Clausius-Clapeyron equation given in Rogers and Yau, pp 12-16. We will also consider this.

In order to get a more accurate representation of $e_s(T)$, the temperature dependence can be incorporated using a linear correction term involving T in an expression for L_{vl} , and then substitute in Eq (4.10) and integrated.

A more accurate form is (see HW problem)

$$\log_{10} e_s = -2937.4/T - 4.9283\log_{10} T + 23.5471 \quad (e_s \text{ in mb and } T \text{ in K})$$

Bolton (1980) determined the following empirical relation by fitting a function to tabular values of $e_s(T)$. This form is accurate to within 0.1% over the temperature interval (-35 C, +35 C):

$$e_s(T) = 6.112 \exp\left(\frac{17.67T}{T + 243.5}\right) \quad (5.9)$$

Table 5.1. Saturation vapor pressures over water and ice, and latent heats of condensation and sublimation.

| T (°C) | e _s (Pa) | e _i (Pa) | L _{iv} (10 ³ J kg ⁻¹) | L _{iv} (10 ³ J kg ⁻¹) |
|--------|---------------------|---------------------|---|---|
| -40 | 19.05 | 12.85 | 2603 | 2839 |
| -35 | 31.54 | 22.36 | | |
| -30 | 51.06 | 38.02 | 2575 | 2839 |
| -25 | 80.90 | 63.30 | | |
| -20 | 125.63 | 103.28 | 2549 | 2838 |
| -15 | 191.44 | 165.32 | | |
| -10 | 286.57 | 259.92 | 2525 | 2837 |
| -5 | 421.84 | 401.78 | | |
| 0 | 611.21 | 611.15 | 2501 | 2834 |
| 5 | 872.47 | | 2489 | |
| 10 | 1227.94 | | 2477 | |
| 15 | 1705.32 | | 2466 | |
| 20 | 2338.54 | | 2453 | |
| 25 | 3168.74 | | 2442 | |
| 30 | 4245.20 | | 2430 | |
| 35 | 5626.45 | | 2418 | |
| 40 | 7381.27 | | 2406 | |
| | | | | |

5.4 Moisture parameters

Common variables used for measurement of moisture:

a) mixing ratio (r_v)

$$r_v = m_v/m_d = \epsilon e / [p - e] \cong \epsilon e/p \quad (5.10)$$

b) specific humidity (q_v)

$$\begin{aligned} q_v &= m_v/(m_v + m_d) = r_v/r = r_v / (r_d + r_v) \\ &= \epsilon e / [p - (1 - \epsilon)e] \quad (\text{using the equation of state for } r_v \text{ and } r_d) \\ &\cong \epsilon e/p \\ \text{Thus, } q_v &\cong r_v. \end{aligned}$$

c) vapor pressure (e) (connection to Clausius-Clapeyron Eq.) -- Don't confuse e with e_s

d) relative humidity (f)

$$f = r_v / r_{vs}(T, p) \approx e/e_s(T) = r_{vs}(T_d)/r_{vs}(T) \quad (5.11)$$

Be careful - f can be expressed in % or in fraction

e) virtual temperature (T_v) (defined previously; not really used to measure water vapor)

$$T_v \cong T(1 + 0.608r_v)$$

f) dewpoint temperature (T_d): temperature at which saturation occurs; defined as a process in Chap. 6.

Which of these are absolute and relative?

Which are conserved for a substaturated parcel that is not experiencing mixing with its surroundings?

Problems

1. Prove that pure water vapor can reach saturation in the following processes:
 - a) isothermal compression
 - b) adiabatic expansion

2. Using the relation

$$L(T) = L_0 - (c - c_{pv})(T - T_0)$$

for the dependence of the latent heat of vaporization on temperature, integrate Eq. (5.7) for obtaining the expression for $e_s(T)$. This result is sometimes call the Magnus equation or Kiefer's formula. Over the range $-30^\circ\text{C} \leq T \leq +30^\circ\text{C}$, compare $e_s(T)$ from this equation with the simpler approximation (5.8), with Bolton's empirical formula

$$e_s(T) = 6.112 \exp\left(\frac{17.67T}{T + 243.5}\right)$$

where e_s is in mb and T is in $^\circ\text{C}$. Also compare with data in Table 5.1.

3. A sample of moist air has a temperature of -5°C , a pressure of 80 kPa, and a relative humidity of 65%. Solve for the following properties of the sample by calculations, using approximations only when necessary. Confirm your answers with a skew-T diagram wherever possible.
 - a) Potential temperature
 - b) Mixing ratio
 - c) Dew point
 - d) Saturation point temperature (temp. of the LCL)
 - e) Equivalent potential temperature
 - f) Virtual temperature
 - g) Density
4. Determine the water vapor pressure and mixing ratio for a dew point temperature of 90°F and a pressure of 1 atm. (1 atm = 1013 mb). ($^\circ\text{F} = 9/5^\circ\text{C} + 32$)
5. From the equation $\log_{10} e_s = -2937.4/T - 4.9283 \log_{10} T + 23.5518$ for the saturation vapor pressure (in mb), derive the latent heat of vaporization at 10°C .