Chapter 5

The water-air
heterogeneous system

On-line resource

on-line analytical system that portrays the thermodynamic properties of water vapor and many other gases

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

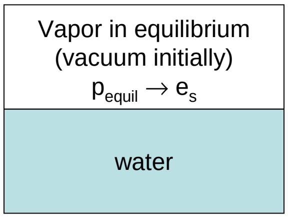
Note: if you are motivated, search the web for resources that relate to this course, and bring them to my attention.

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



Vapor in equilibrium
(vacuum initially)
$p_{equil} \rightarrow e_s$

water

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.

A picture of what we are considering. Water in an initial vacuum will eventually reach an equilibrium.

QuickTime™ and a
TIFF (Uncompressed) decompressor
are needed to see this picture.

Equilibrium is achieved in the saturated state. We will examine this more closely.

Taken from Petty, Fig. 7.1

Motivation

We require an expression for the saturation vapor pressure (or saturation mixing ratio as a function of temperature in order to develop a derivation for the saturated adiabatic lapse rate. It turns out that saturation vapor pressure is a function only of temperture, i.e., $e_s = e_s(T)$.

Fig 7.3. Same as fig. 7.2, except es on the vertical axis is linear.

Fig. 7.2 from Petty. Plot of the functional form of $e_s(T)$. Note the difference between ice and water for T < 0 C. This is important in the growth of ice in clouds.

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.*

The chemical potential of an ideal gas is defined by

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

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

For an ideal gas,

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

* Recall, $dg = -sdT + \alpha dp$ for a reversible transformation (g is Gibbs free energy)

Example (Taken from Wallace and Hobbs, 1977, 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,

$$d\mu_v = \alpha_v de$$

$$d\mu_l = \alpha_l de,$$

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

$$d(\mu_v - \mu_l) = (\alpha_v - \alpha_l)de \cong \alpha_v de \tag{5.1}$$

since $\alpha_v >> \alpha_l$. [Values for α_v and α_l are given below.]

We will apply this approximation ($\alpha_v >> \alpha_l$) many times in subsequent derivations.

The equation of state for water vapor (applied to just <u>one</u> water vapor molecule) is

$$e\alpha_v = kT, \tag{5.2}$$

where k, Boltzmann's constant (1.381×10^{-23} J K^{-1} molecule^{-1}), is used in place of the gas constant to represent one molecule. (Recall that $R_d = 287$ J K^{-1} kg^{-1})

Now solve (5.2) for α_v, and insert the result into (5.1) to get

$$d(\mu_v - \mu_l) = kTde/e. \tag{5.3}$$

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

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

or

$$\mu_v - \mu_l = kT\ln\left(\frac{e}{e_s}\right) \tag{5.4*}$$

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

$$F = C - P + 2 \tag{5.5}$$

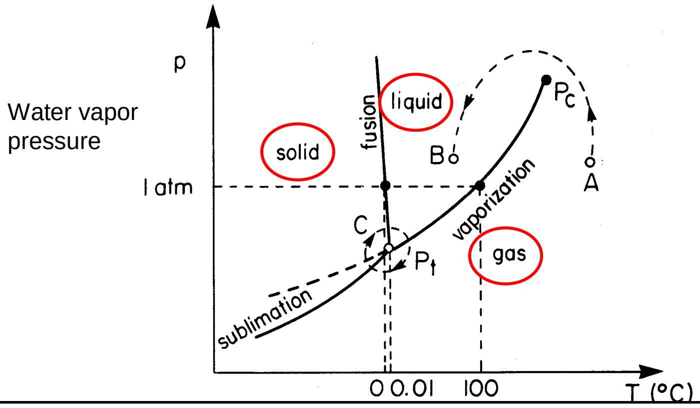
If we deal with a single component system (C=1) such as water then we can form the table below.

P (number of phases)	F (degrees of freedom)	
1	2	Water vapor eq. of state
2	1	Equilibrium: gas-liquid
3	0	Triple point

For a single existing phase (such as water vapor) we may arbitrarily choose p (e) and T (i.e., the equation of state). Then F = 2.

For two phases, the choice of either p or T determines the other (F = 1), and for three phases (i.e., the triple point) there is no choice, i.e., this point has specific values for p and T (F = 0).

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.



A closer look:

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

Equation of state: $e\alpha = R_vT$

Clapeyron Equation
Clausius-Clapeyron Equation: $e_s = f(T)$

No equation (a fixed point)

3-D surface for water

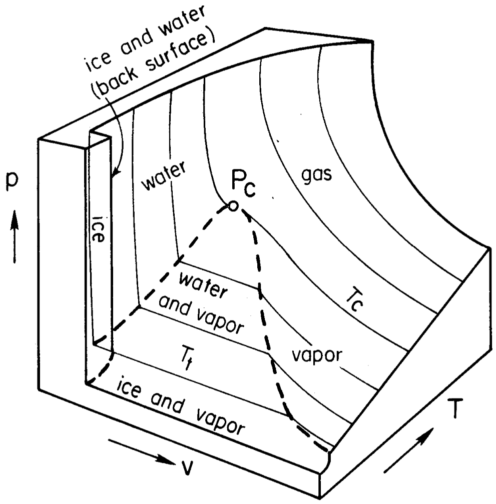


Fig. 5.3 Thermodynamic surface for water. Taken from Iribarne and Godson (1973).

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

triple point:

$p_t = 610.7$ Pa = 6.107 mb;
$T_t = 273.16$ K = 0.01 °C
$\alpha_{it} = 1.091 \times 10^{-3}$ m^3 kg^{-1}
$\alpha_{wt} = 1.000 \times 10^{-3}$ m^3 kg^{-1}
$\alpha_{vt} = 206$ m^3 kg^{-1}

critical point:

$T_c = 647$ K = 366 °C;
$p_c = 218.8$ atm
$\alpha_c = 3.07 \times 10^{-3}$ m^3 kg^{-1}

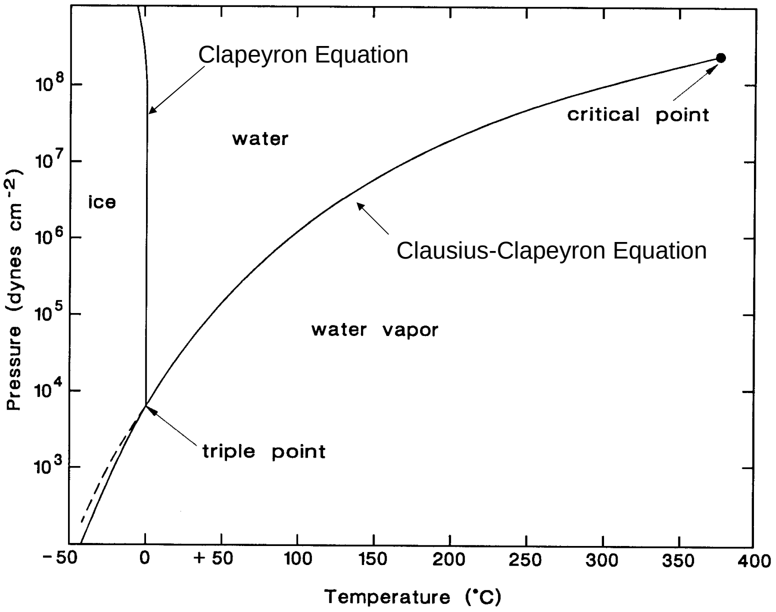


Fig. 5.2. P-T phase diagram for water. Stable phase boundaries are shown by solid lines; metastable phase boundaries are indicated by dashed lines. Note that the ordinate in exponential in pressure, in contrast to the linear p dependence in Fig. 5.1. From Young (1993), p. 401.

5.3.3 Equilibrium between solid (ice) and liquid water - The Clapeyron Eq.

The lines drawn in Figs. 5.1-5.3 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 dg=0, so therefore g(solid) = g(liquid). $[dq = -sdT + \alpha dp]$

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

Define the following:

$$\Delta s = s_{solid} - s_{liquid}$$
$$\Delta\alpha = \alpha_{solid} - \alpha_{liquid}$$

Now combine the terms the multiply dT and dp.

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):

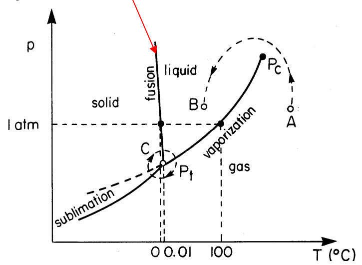
$$dp/dT = \Delta s/\Delta\alpha = -\Delta H_{fusion}/(T\Delta\alpha) \qquad \textit{Clapeyron Equation} \qquad (5.6)$$

where the latter equality is based on the entropy change associated with a phase change (Chap. 4):

$$\Delta s = -\Delta H_{fusion}/T$$

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.

One implication:
If pressure is increased, then melting can occur. An example is the ice skate, which works so well since a water film forms between the skate blade and the ice surface as the pressure (F/A) rapidly increases.



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

In this case

$$\Delta\alpha = \alpha_{liquid} - \alpha_{vapor} \cong -\alpha_{vapor}. \quad (\alpha_{vapor} = 206 \text{ m}^3 \text{ kg}^{-1} ; \alpha_{liquid} = 1.00 \text{ m}^3 \text{ kg}^{-1})$$

Then, from the equation of state, we can write

$$-\alpha_v = -R_vT/e_s$$

(e_s is used in place of p since we are concerned with equilibrium at saturation)

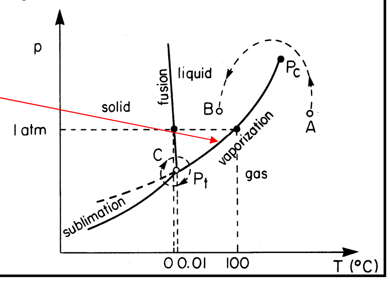
Then

$$de_s/dT = -\Delta H_{vap}/(T\alpha_v) = \Delta H_{vap}e_s/(R_vT^2)$$

or $$d\ln e_s/dT = L_{vl}/(R_vT^2). \qquad (5.7)$$

Clausius-Clapeyron Eq.

(see also Figs. 7.2, 7.3, 5.1, 5.2)



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 $T_0 = 273.1$ K and $e_{s0} = 6.11$ mb (from lab measurements).

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

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

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

But beware:

This form is acceptable to use for quick calculations, but *precise calculations require a derivation that takes into account $L_{vl} = L_{vl}(T)$.*

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 this in Eq (4.10) and integrate.

A more accurate form is (see HW problem)

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

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):

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

The Clausius Clapeyron Eq. is represented by an **exponential function**:

$$e_s(T) = A\exp\left(\frac{BT}{T+C}\right)$$

where B = 17.67 and C = 243.5 (from the Bolton empirical relation on the previous page.

Liquid-vapor equilibrium line

QuickTime™ and a
TIFF (Uncompressed) decompressor
are needed to see this picture.

Know this derivation; also look over Petty Section 7.3, pp. 179-185

Table 5.1. Saturation vapor pressures over water and ice

T (°C)	e_s (Pa)	e_i (Pa)	L_{lv} (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	

Accuracy of $e_s(T) = Ae^{-B/T}$ vs. $e_s(T) = 6.112\exp\left(\frac{17.67T}{T+243.5}\right)$

Relatively accurate (with ~1%)
for the T interval [-20, 20 C]

QuickTime™ and a
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are needed to see this picture.

1% error

Expression for saturation vapor pressure over ice is similar to that over water:

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are needed to see this picture.

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Why do the constants differ?

The difference (e_s - e_i) is important in the growth of ice crystals

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TIFF (Uncompressed) decompressor
are needed to see this picture.

Fig. 7.6

To what temperature can water in a pan be heated?

a) 200 °C
b) 100 °C
c) It depends on ______________

Consider Problem 7.1

To what temperature can water in a pan be heated?

a) 200 °C
b) 100 °C
c) It depends on pressure

Problem 7.1 By consulting Fig. 7.2 and Fig. 1.7, estimate the altitude at which the boiling point of water drops to room temperature (25 C).

Find e_s from Fig. 7.2, or the preceding table: e_s (25 C) = 32 mb

Determine z from the relation: $p(z) = p_0 \exp(-z/H)$

Rewrite to solve for z: $\ln (p/p_0) = -z/H$ $z = -H \ln(p/p_0)$ (let H = 8 km)

$z = -H \ln (32/1013) = -8000\text{ m } (-3.45) \approx 27\text{ km}$

5.4 Water vapor measurement parameters (some previously defined)

Common variables used for measurement of moisture:

mixing ratio (r_v)

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

specific humidity (q_v)

$q_v = m_v/(m_v+m_d) = r_v/r = r_v / (r_d+r_v)$

$= \varepsilon e / [p-(1-\varepsilon)e]$ (using the equation of state for rv and rd) $\cong \varepsilon e/p$

Thus, $q_v \cong r_v$.

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

relative humidity (f)

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

Be careful - f can be expressed in % or as a fraction (e.g., 66% = 0.66)

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

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

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

Some problems to work in class:

Problem 7.7

Problem 7.8

Problem 7.9

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HW Problems

- Notes: 2, 3, 4
- Petty 7.2, 7.6

Note: Section 7.5 and following will be addressed next in my Ch. 6-7 notes.