Atmospheric Thermodynamics

Lecture 4: Thermodynamics of Moist Air

Part2. Phase change, Latent Heat, and Glousius Claperon Equation

4.1 Phase Change and Latent Heat

So far, we have learned that adding thermal energy by heat, increases the temperature of a substance. But surprisingly, there are situations where adding energy does not change the temperature of a substance at all! Instead, the thermal energy acts to loosen bonds between molecules or atoms and causes a **phase change**.

Because this energy enters or leaves a system during a phase change without causing a temperature change in the system, it is known as **latent heat** (latent means hidden).

The three phases of matter that you frequently encounter are solid, liquid and gas (see Fig. 4.1). Solid has the least energetic state; atoms in solids are in close contact, with forces between them that allow the particles to vibrate but not change position with neighboring particles. (These forces can be thought of as springs that can be stretched or compressed, but not easily broken.) Liquid has a more energetic state, in which particles can slide smoothly past one another and change neighbors, although they are still held together by their mutual attraction. Gas has a more energetic state than liquid, in which particles are broken free of their bonds. Particles in gases are separated by distances that are large compared with the size of the particles.

The most energetic state of all is **plasma**. Stars are made up of plasma, as is lightning. The plasma state is reached by heating a gas to the point where particles are pulled apart, separating the electrons from the rest of the particle. This produces an ionized gas that is a combination of the negatively charged free electrons and positively charged ions, known as plasma.

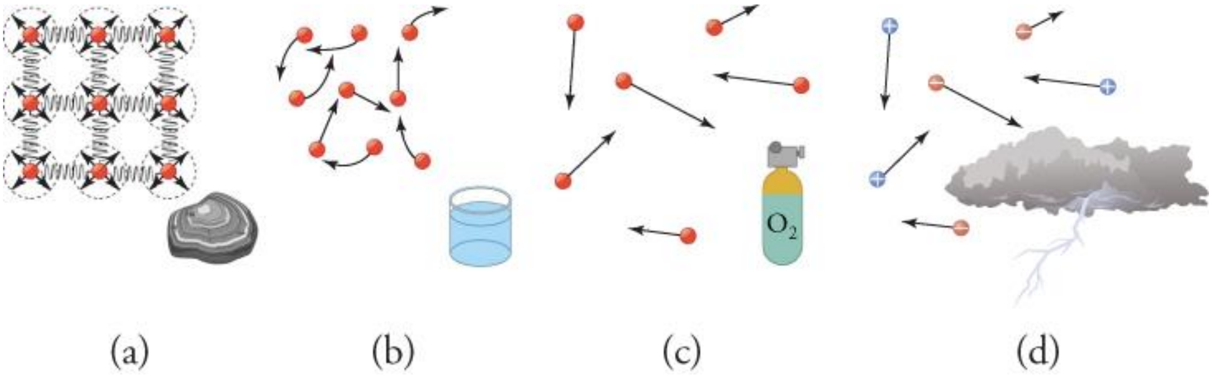

Figure (4.1) States of particles (a) solid, (b) liquid, (c) gas, and (d) plasma

During a phase change, matter changes from one phase to another:

(1) Phase changes to a *more energetic state* include the following:

- Melting - Solid to liquid
- Vaporization - Liquid to gas (included boiling and evaporation)
- Sublimation - Solid to gas
- Ionization - Gas to plasma

(2) Phase changes to a *less energetic state* are as follows:

- Condensation - Gas to liquid
- Freezing - Liquid to solid
- Recombination - Plasma to gas
- Deposition - Gas to solid

The heat, Q, required to change the phase of a sample of mass m is:

$$Q = m\,L_f \qquad (4.1) \qquad \text{(for melting/freezing),}$$

$$Q = m\,L_v \qquad (4.2) \qquad \text{(for vaporization/condensation),}$$

where $\boldsymbol{L_f}$ is the **latent heat of fusion**, and $\boldsymbol{L_v}$ is the **latent heat of vaporization**. The latent heat of fusion is the amount of heat needed to cause a phase change between solid and liquid. The latent heat of vaporization is the amount of heat needed to cause a phase change between liquid and gas. L_f and L_v are coefficients that vary from substance to substance, depending on the strength of intermolecular forces, and both have standard units of J/kg (or kJ/kg). See Table (4.1) for values of L_f and L_v of different substances.

Table (4.1) values of L_f and L_v of different substances.

Substance	**Melting Point (°C)**	L_f (kJ/kg)	**Melting Point (°C)**	L_v (kJ/kg)
Nitrogen	–210.0	25.5	–195.8	201
Oxygen	–218.8	13.8	–183.0	213
Water	0.00	334	100.0	2256
Gold	1063	64.5	2660	1578
Copper	1083	134	2595	5069
Uranium	1133	84	3900	1900
Tungsten	3410	184	5900	4810

Let’s consider the example of adding heat to ice to examine its transitions through all three phases (Figure 4.2). The ice starts out at −30 °C, and its temperature rises linearly, absorbing heat at a constant rate until it reaches 0 °C. Once at this temperature, the ice gradually melts, absorbing 334 kJ/kg. The temperature remains constant at 0 °C during this phase change. Once all the ice has melted, the temperature of the liquid water rises, absorbing heat at a new constant rate. At 100 °C, the water begins to boil and the temperature again remains constant while the water absorbs 2256 kJ/kg during this phase change. When all the liquid has become vapor, the temperature rises again at a constant rate.

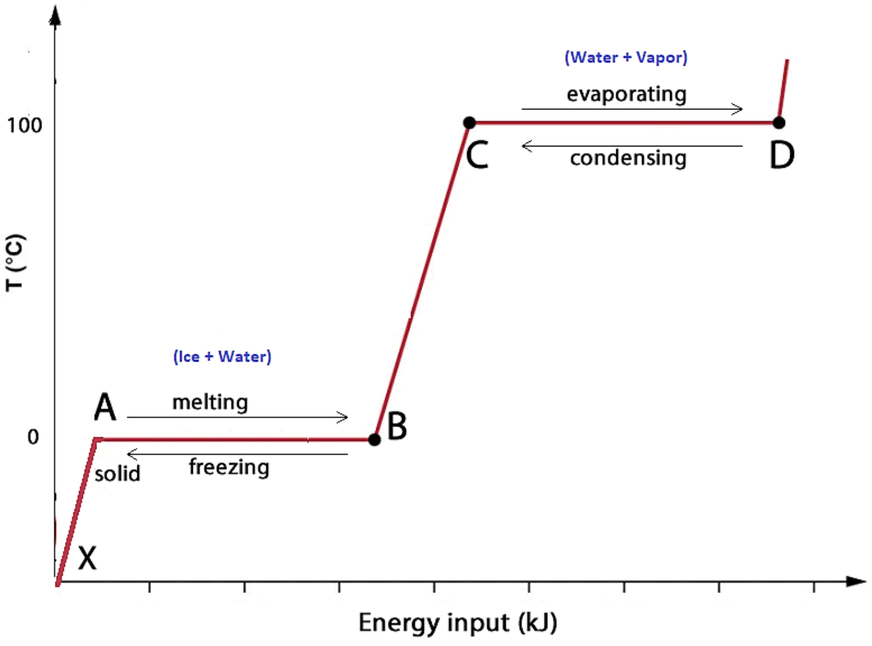

Figure 4.2 A graph of temperature versus added energy

- Vaporization requires heat transfer to a substance from its surroundings. Condensation is the reverse process, where heat in transferred *away from* a substance *to* its surroundings.
- This release of latent heat increases the temperature of the surroundings. Energy must be removed from the condensing particles to make a vapor condense. The heat transfers energy away from the warm vapor to the cold surface. The energy is exactly the same as that required to cause the phase change in the other direction, from liquid to vapor, and so it can be calculated from $Q = m\,L_v$. Latent heat is also released into the environment when a liquid freezes, and can be calculated from $Q = m\,L_f$.

Example

Calculate (a) how much energy is needed to melt 1 kg of ice at 0 °C (freezing point), and (b) how much energy is required to vaporize 1 kg of water at 100 °C (boiling point).

Sol.

(a) The energy to melt 1 kg of ice is

$$Q = m\,L_f = (1\,kg)(334\,kJ/kg) = 334\,kJ$$

(b) The energy to vaporize 1 kg of liquid water is

$$Q = m\,L_v = (1\,kg)(2256\,kJ/kg) = 2256\,kJ$$

Discussion

The amount of energy need to melt a kilogram of ice (334 kJ) is the same amount of energy needed to raise the temperature of 1 kg of liquid water from 0 °C to 79.8 °C. This example shows that the energy for a phase change is enormous compared to energy associated with temperature changes. It also demonstrates that the amount of energy needed for vaporization is even greater.

Practice Problems

(1) How much energy is needed to melt 2 kg of ice at 0 °C ?

a. 334 kJ
b. 336 kJ
c. 167 kJ
d. 668 kJ

(2) If 2500kJ of energy is just enough to melt 3 kg of a substance, what is the substance's latent heat of fusion?

(a) 7500 kJ/kg
(b) 7500 kJ/kg
(c) 830 kJ/kg
(d) 830 kJ/kg

Check Your Understanding

(1) What is latent heat?

a. It is the heat that must transfer energy to or from a system in order to cause a mass change with a slight change in the temperature of the system.
b. It is the heat that must transfer energy to or from a system in order to cause a mass change without a temperature change in the system.
c. It is the heat that must transfer energy to or from a system in order to cause a phase change with a slight change in the temperature of the system.
d. It is the heat that must transfer energy to or from a system in order to cause a phase change without a temperature change in the system.

(2) In which phases of matter are molecules capable of changing their positions?

a. gas, liquid, solid
b. liquid, plasma, solid
c. liquid, gas, plasma
d. plasma, gas, solid

4.2 The Clausius - Clapeyron Equation

Clausius-Clapeyron equation calculates the change of the saturation vapor pressure with temperature (*des/dT*) during a phase change.

$$\frac{de_s}{dT} = \frac{L_{12}}{T(\alpha_2 - \alpha_1)} \qquad (4.3)$$

If L_{12}, α_1 and α_2 are known functions of T, then (4.3) can be integrated to obtain a relation between saturation vapor pressure and T.

Since $\alpha_2 \gg \alpha_1$ (specific volume of water vapor is much greater than specific volume of liquid water or ice), equation 4.3 becomes:

$$\frac{de_s}{dT} = \frac{L_{12}}{T\alpha_2} \qquad (4.4)$$

From the equation of state ($\alpha_2 = R_v T/e_s$) we get:

$$\frac{de_s}{e_s} = \frac{L_{12}}{R_v}\frac{dT}{T^2} \qquad (4.5)$$

Therefore,

$$\ln\left(\frac{e_s}{e_{s0}}\right) = \frac{L_{12}}{R_v}\left(\frac{1}{T_0} - \frac{1}{T}\right) \qquad (4.6)$$

Where e_{s0} is the saturation vapor pressure at T_0.

For evaporation, $e_{s0} = 6.11$ hPa and $T_0 = 273\ K$, which implies,

$$\ln\left(\frac{e_s}{6.11\ mb}\right) = \frac{L_{evap}}{R_v}\left(\frac{1}{273} - \frac{1}{T}\right) \qquad (4.7)$$

$$\text{or} \qquad e_s = 6.11\ mb\ \exp[\frac{L_{evap}}{R_v}\left(\frac{1}{273} - \frac{1}{T}\right)] \qquad (4.8)$$

For sublimation,

$$\ln\left(\frac{e_s}{6.11\ mb}\right) = \frac{L_{sub}}{R_v}\left(\frac{1}{273} - \frac{1}{T}\right) \qquad (4.9)$$

$$\text{or} \qquad e_s = 6.11\ mb\ \exp[\frac{L_{sub}}{R_v}\left(\frac{1}{273} - \frac{1}{T}\right)] \qquad (4.10)$$

Ex: Calculate the change in the melting point of ice if the pressure is increased from 1 to 2 atm, given that: $\alpha_i = 1.0908\ \times 10^{-3}\ m^3kg^{-1},\ \alpha_w = 1.001 \times 10^{-3}\ m^3kg^{-1}$

$$L_{melt} = 3.34 \times 10^5\ Jkg^{-1} \quad at\ 0^oC$$

Solution: Using Clausius-Clapeyron equation,

$$dT = T(\alpha_w - \alpha_i)\frac{dp}{L_{melt}}$$

$$= 273 \times (1.001 - 1.0908) \times 1.013 \times 10^5/3.34 \times 10^5$$

$$= -0.00744\ deg$$

Therefore, an increase in pressure of 1 atm decreases the melting point of ice by about 0.007 deg. Usually, the melting point increases with increasing pressure. But ice is unusual because $\alpha_w < \alpha_i$.

Equations (4.7) and (4.9) plus a similar equation for melting allow us to plot the curves of saturation pressure versus temperature. These curves describe the *T*-*e* relations during phase changes ($e=e_s$).

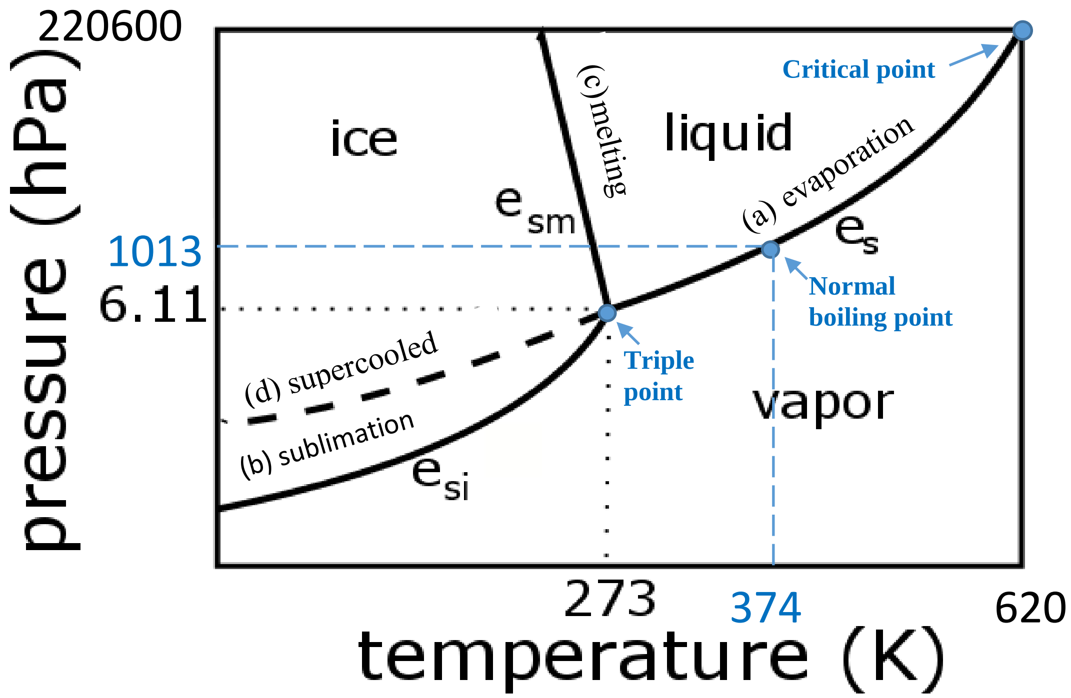

Figure 4.1 *T*, *e* phase diagram for water substance

All curves begin at the triple point.

(a) Evaporation curve a: curves upward exponentially to the right according to Eq. (4.7) ($T > 273$ K, and $e_s > 6.11$ mb). Along this curve, water and vapor are in equilibrium until it reaches the critical point ($T = 374\ C$) where only vapor can exist. At some point along this curve, water starts to boil. That is the point when $e_s=p_{atm}$.

(b) Sublimation curve b: curves downward exponentially to the left of the triple point ($T < 273\ K$, $e_s < 6.11$ mb). This curve is steeper than the evaporation curve because $L_{sub} > L_{evap}$.

(c) Melting curve c: since $\alpha_w - \alpha_i$ is almost zero (a very small negative number), de_s/dT is almost $-\infty$, based on the Clausius-Clapeyron equation. Thus the curve is almost vertical, but tilts very slightly to the left.

(d) Supercooled water d: When water which does not freeze below 273 K (0ºC), it is called supercooled water. For supercooled water, within a certain temperature range of T < 0 ºC, $e_{sw} > e_{si}$ (curve d). Therefore, in a cloud with mixture of ice crystals and supercooled water (cloud) droplets, water vapor will first condense on the ice because e_{si} is smaller than e_{sw}.

In other words, in the competition for water vapor, ice will win over supercooled water. This leads to the well-known Bergeron-Findeison process. That is, ice crystal in a cloud of supercooled water droplets will grow faster than the water droplets.