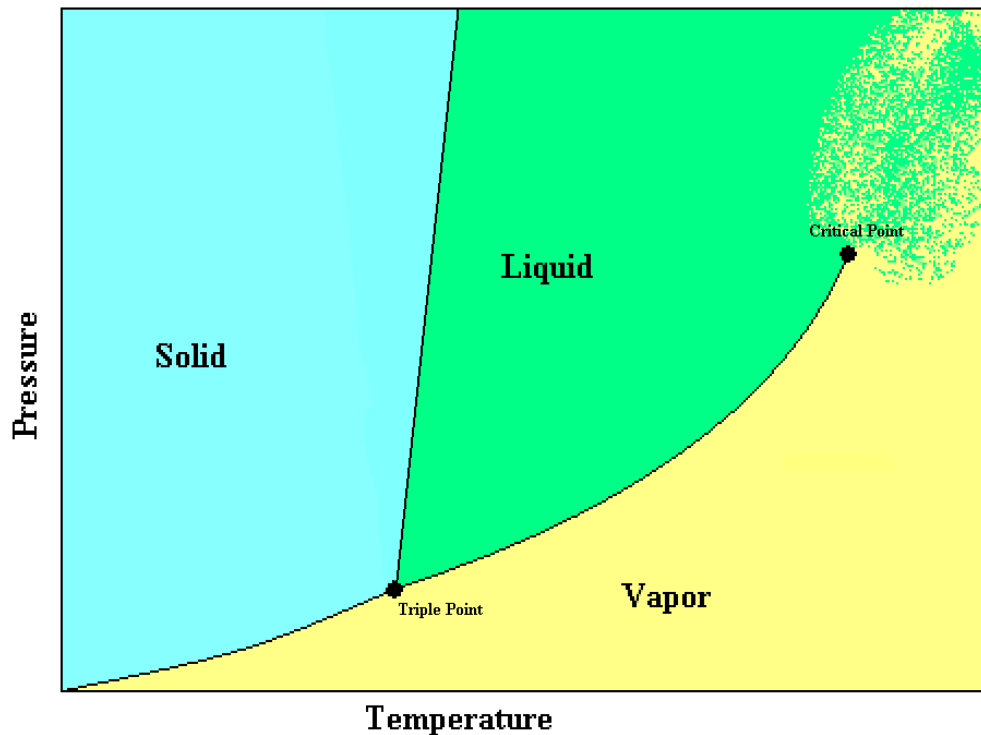


ESCI 341 – Atmospheric Thermodynamics
Lesson 13 – Phase Changes
Dr. DeCaria

References: *Thermodynamics and an Introduction to Thermostatistics*, Callen
Physical Chemistry, Levine

GENERAL

- A phase change is a change between solid, liquid, or vapor (gas).
- A system may even have more than one solid or liquid phase
 - Carbon has several solid phases, including graphite and diamond
- The phase of a system in equilibrium can be represented on a phase diagram.
- A typical phase diagram is shown below

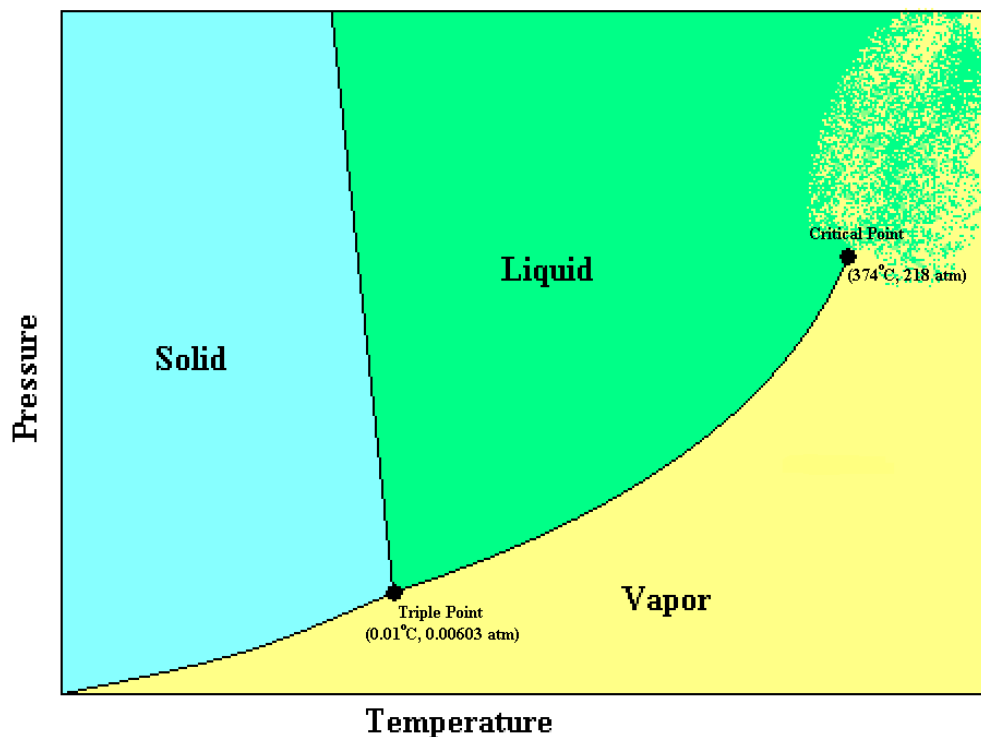


- The lines separating the phases represent points where the two phases can coexist.
- The *triple point* represents the one and only point on the diagram where all three phases can coexist.
- The *critical point* occurs at the end of the vapor-to-liquid transition line. At temperatures above the critical temperature, or pressures above the critical pressure there is no distinction between the liquid and vapor phases.

- If you go from the vapor to liquid phase at temperatures or pressures exceeding the critical values, condensation does not occur. Instead, there is a gradual increase in density and a continuous transition from vapor to liquid.
- The slope of the solid-to-liquid transition line shows how the melting point changes with pressure.
- The diagram above is typical for substances such as CO₂. In this case, an increase in pressure will increase the melting point.
 - If you are near the solid-to-liquid transition line in this case, squeezing the substance will cause it to solidify.
 - The triple-point temperature and pressure for CO₂ are -57°C and 5.1 atm. Therefore, at room temperatures dry ice is a gas, and if it is cooled below -57°C it will deposit into the solid phase, without ever going through the liquid phase. This is why solid CO₂ is referred to as “dry ice.”

PHASE DIAGRAM FOR H₂O

- Water is one of the few substances that can exist in all three phases at the temperatures and pressures found in the Earth’s atmosphere.
- The phase diagram for water is



- The triple point of water is at 0.01°C and 6.03×10^{-3} atm (611 Pa).
- A unique feature of water is that the solid-to-liquid transition line slopes upward to the left, instead of to the right.

GIBBS FREE ENERGY AND MATERIAL EQUILIBRIUM

- We have previously shown the following inequalities for closed systems

$$\begin{aligned}
 dU &\leq TdS - pdV \\
 dH &\leq TdS + Vdp \\
 dF &\leq -SdT - pdV \\
 dG &\leq -SdT + Vdp
 \end{aligned}
 \tag{1}$$

- These inequalities are valid for all processes in a closed system that is in mechanical and thermal equilibrium, but not material equilibrium¹.

- For a multi-component system the Gibbs free energy is a function of T, p , and the masses of each component, m_i . The differential of G is therefore

$$dG = \left(\frac{\partial G}{\partial T} \right)_{p, m_i} dT + \left(\frac{\partial G}{\partial p} \right)_{T, m_i} dp + \sum_i \left(\frac{\partial G}{\partial m_i} \right)_{T, p} dm_i
 \tag{2}$$

- We also know that for a closed system with fixed composition ($dm_i = 0$) that is also in equilibrium, that

$$dG = -SdT + Vdp,
 \tag{3}$$

and comparing Eqs. (2) and (3) shows that

$$\begin{aligned}
 \left(\frac{\partial G}{\partial T} \right)_{p, m_i} &= -S \\
 \left(\frac{\partial G}{\partial p} \right)_{T, m_i} &= V
 \end{aligned}$$

so Eq. (2) can be written as

$$dG = -SdT + Vdp + \sum_i \left(\frac{\partial G}{\partial m_i} \right)_{T, p} dm_i.
 \tag{4}$$

- We also know that the total Gibbs free energy of a substance is equal to the specific Gibbs free energy of each constituent multiplied by its mass,

¹ See Levine, Chapter 4 (particularly Section 4.4) if more details are desired.

$$G = \sum_i g_i m_i . \quad (5)$$

Differentiating Eq. (5) shows that²

$$\left(\frac{\partial G}{\partial m_i} \right)_{T,p} = g_i .$$

Using this in Eq. (4) yields

$$dG = -SdT + Vdp + \sum_i g_i dm_i . \quad (6)$$

- **Going back to Eq. (1) we know that**

$$dG \leq -SdT + Vdp . \quad (7)$$

- **Combining Eqs. (6) and (7) gives**

$$-SdT + Vdp + \sum_i g_i dm_i \leq -SdT + Vdp$$

which reduces to

$$\sum_i g_i dm_i \leq 0 . \quad (8)$$

- **Equation (8) tells us that if a multi-component system is not in material equilibrium, that it will then spontaneously evolve until**

$$\sum_i g_i dm_i = 0 . \quad (9)$$

- **Equation (9) is the condition for material equilibrium.**
- **Note that even though the equilibrium condition of Eq. (9) is in terms of the specific Gibbs free energy, it is not limited to constant pressure, constant temperature processes. It is the material equilibrium condition without any restrictions.**

MATERIAL EQUILIBRIUM IN A TWO COMPONENT SYSTEM

² Note that the specific Gibbs free energy, g_i , of a constituent does not depend on the mass of itself or any other constituents, so that $\frac{\partial g_i}{\partial m_j} = 0$ for any values of i or j . However, this is not true for the other

intensive state variables, i.e., $\frac{\partial u_i}{\partial m_j} \neq 0$. So, although $\frac{\partial G}{\partial m_i} = g_i$, it is not necessarily true that

$$\frac{\partial U}{\partial m_i} = u_i .$$

- In a system with two components, Equation (8) becomes

$$g_1 \frac{dm_1}{dt} + g_2 \frac{dm_2}{dt} \leq 0. \quad (10)$$

- Any mass lost from component 1 must be gained by component 2, so we have

$$\frac{dm_1}{dt} = -\frac{dm_2}{dt}$$

and Eq. (10) becomes

$$(g_1 - g_2) \frac{dm_1}{dt} \leq 0. \quad (11)$$

- Let's examine what happens if the two components are not in material equilibrium, so that $g_1 \neq g_2$. There are two possible scenarios:
 - *Case 1:* $g_1 > g_2$
 - This case requires $dm_1/dt < 0$ so the mass of component 1 will decrease while the mass of component 2 will increase.
 - *Case 1:* $g_1 < g_2$
 - This case requires $dm_1/dt > 0$ so the mass of component 1 will increase while the mass of component 2 will decrease.
- In either case, the result is that the component that has the lowest specific Gibbs free energy will increase at the expense of the component with the higher Gibbs free energy.
- Another way to state this is that equilibrium favors the component with the lowest specific Gibbs free energy.
- The only way the two components can be in material equilibrium is if they have the same specific Gibbs free energy, $g_1 = g_2$.

THE CLAPEYRON EQUATION

- If we have two phases present, the condition for equilibrium from Eq. (9) is

$$g_1 = g_2. \quad (12)$$

- The equilibrium condition says that *at equilibrium the specific Gibbs free energies of the two phases will be equal.*
- Differentiating Eq. (12) gives

$$dg_1 = dg_2. \quad (13)$$

- From the Gibbs equations we have

$$dg = -sdT + \alpha dp.$$

so we can write Eq. (13) as

$$-s_1dT + \alpha_1dp = -s_2dT + \alpha_2dp.$$

which can be rearranged to give

$$\frac{dp}{dT} = \frac{s_2 - s_1}{\alpha_2 - \alpha_1} = \frac{\Delta s}{\Delta \alpha}. \quad (14)$$

- From the first law of thermodynamics we have

$$dh = Tds + \alpha dp.$$

which, if the temperature and pressure are constant, integrates to

$$\Delta h = T\Delta s = L,$$

where L is the latent heat of the phase change (units of energy per mass).

- Equation (14) then becomes

$$\frac{dp}{dT} = \frac{L}{T\Delta \alpha}, \quad (15)$$

which is known as the *Clapeyron Equation*.

- The Clapeyron equation is completely general. It applies to any equilibrium phase change.

LIQUID – VAPOR EQUILIBRIUM

- If we apply the Clapeyron equation to the phase change between liquid and vapor, then the pressure is just the saturation vapor pressure ($p = e_s$) and we get

$$\frac{de_s}{dT} = \frac{L_v}{T(\alpha_v - \alpha_l)}. \quad (16)$$

- Since the specific volume of a vapor is so much greater than the specific volume of a liquid, we can approximate the difference between the two as $\alpha_v - \alpha_l \cong \alpha_v$.

This makes Eq. (16)

$$\frac{de_s}{dT} \cong \frac{L_v}{T\alpha_v}. \quad (17)$$

- If the vapor is an ideal gas, then

$$\alpha_v = \frac{R'T}{e_s},$$

and Eq. (17) becomes

$$\frac{1}{e_s} \frac{de_s}{dT} = \frac{L_v}{R'T^2}, \quad (18)$$

which is known as the *Clausius-Clapeyron* equation.

- Integrating the Clausius-Clapeyron equation will give an equation for the interface of the solid-liquid phase change on the phase diagram. Integrating between a known reference vapor pressure and temperature, e_0 and T_0 (assuming that the latent heat is independent of temperature and pressure) gives

$$e_s = e_0 \exp \left[\frac{L_v}{R'} \left(\frac{1}{T_0} - \frac{1}{T} \right) \right]. \quad (19)$$

- A visualization as to why saturation vapor pressure depends on temperature can be found at this link: <http://phy.mtu.edu/vpt/>

SOLID – VAPOR EQUILIBRIUM

- For the phase change from solid to vapor we only need to replace the latent heat of vaporization with the latent heat of sublimation, L_s in Eq. (19). Thus, over an ice surface the saturation vapor pressure is

$$e_s = e_0 \exp \left[\frac{L_s}{R'} \left(\frac{1}{T_0} - \frac{1}{T} \right) \right]. \quad (20)$$

SOLID – LIQUID EQUILIBRIUM

- For solid – liquid equilibrium we must return to the Clapeyron equation [Eq. (15)]

$$\frac{dp}{dT} = \frac{L}{T(\alpha_l - \alpha_s)}.$$

- For most substances the solid is more dense than the liquid, so that $\alpha_l > \alpha_s$. Thus, for most substances, the solid-liquid line on the phase diagram will tilt upward to the right.

- Water is unique in that its solid phase (ice) is less dense than the liquid phase, so that $\alpha_s < \alpha_l$. This is why the solid-liquid line on the water phase diagram tilts upward to the left.

THE EFFECT OF AIR PRESSURE ON THE SATURATION VAPOR PRESSURE

- Up to now we've assumed that the only substances we had in our system was water. What happens if we also have an inert gas, such as air present?
- The equilibrium condition, Eq. (9), still requires that

$$\sum_i g_i dm_i = 0,$$

but now we have three constituents: liquid water (m_l), water vapor (m_v), and dry air (m_d).

- The equilibrium condition is therefore

$$g_l dm_l + g_v dm_v + g_d dm_d = 0.$$

- Since the air is inert, $dm_d = 0$ and $dm_l = -dm_v$. So as before, the equilibrium condition is

$$dg_l = dg_v. \quad (21)$$

- At first glance this looks like we are going to get an exactly equivalent answer to what we had without air present. However, there is a difference. Although the air does not have any effect on the Gibbs free energy of the water vapor (since both are ideal gases, and therefore don't influence each other), the air does increase the pressure on the liquid. So, we have

$$-s_l dT + \alpha_l dp = -s_v dT + \alpha_v de_s$$

(note that if air were not present, then $p = e_s$ and we would just get the Clapeyron equation as before).

- We want to know what affect changing p has on e_s , so if we hold the temperature constant we get

$$\alpha_l dp = \alpha_v de_s \text{ if temperature held constant}$$

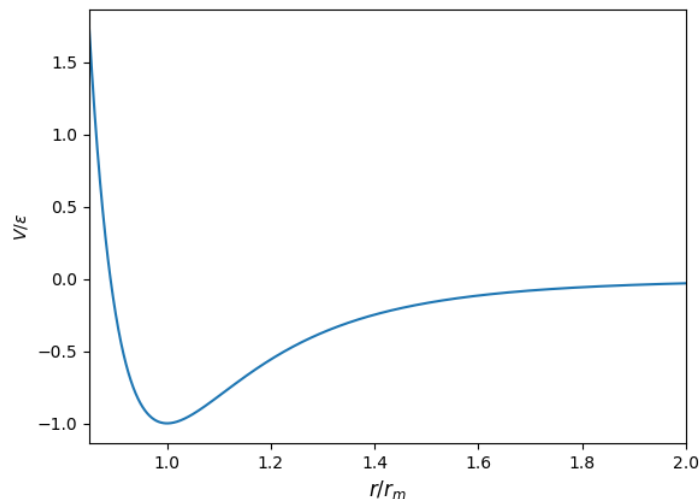
which can be written as

$$\left(\frac{\partial e_s}{\partial p} \right)_T = \frac{\alpha_l}{\alpha_v}. \quad (22)$$

- Equation (22) is called the *Poynting Equation*.
- The Poynting Equation says that an increase in pressure will increase the saturation vapor pressure. This implies that it is easier for water molecules to escape from the liquid to the vapor phase if the liquid is under pressure.
- The physical explanation for this phenomena is not straight-forward, however it is likely due the fact that repulsive forces between molecules dominate at short distances, while attractive forces dominate at larger distance..
- Molecular attractions and repulsions are often modeled by the Lennard-Jones potential, which is given by

$$V = \varepsilon \left[\left(\frac{r_m}{r} \right)^{12} - 2 \left(\frac{r_m}{r} \right)^6 \right], \quad (23)$$

where ε is the depth of the potential well. A plot of the Lennard-Jones potential is shown here



- The term raised to the twelfth power represents short-range repulsive forces that push the molecules apart.
- The term raised to the sixth power represents longer-range attractive forces which try to bring the molecules together.
- When $r = r_m$ the potential is a minimum.
- The thought is that pressure squeezes the molecules closer to each other, enhancing their repulsive forces and allowing molecules on the surface of the fluid to escape more readily into the vapor outside of the liquid.

- Unless pressures are very high or temperatures are very low, $\alpha_v \gg \alpha_l$.

Therefore, for most atmospheric applications

$$\left(\frac{\partial e_s}{\partial p} \right)_T \cong 0,$$

and we can ignore the effects of ambient air pressure on the saturation vapor pressure.

- However, we will see in the next lesson that in a curved droplet the interior pressure is very greatly enhanced, and the effects of the Poynting Equation cannot be dismissed in this situation.
- It is important to note that the presence of air does not significantly alter the saturation vapor pressure.
 - *We often speak of the air “holding” the water vapor, and of warm air somehow being able to “hold more” water vapor. This notion is actually pretty silly, since the air is doing nothing. There would be the same amount of water vapor present regardless of whether or not air was present.*

THE MYTH OF THE ICE SKATER

- The anomalous slope of the solid-liquid equilibrium line for water has led many to attribute the ability to ice skate on ‘pressure melting’, whereby as a skater passes over the ice, the increased pressure on the ice shifts the equilibrium from the solid phase to the liquid phase.
- It turns out that, although the explanation sounds plausible, it is incorrect.
- The true nature of the slipperiness of ice is much more complex, and involves a process called ‘surface melting.’ The details are beyond the scope of this course, but an overview of the subject can be found in Rosenberg (2005)³.

³ Rosenberg, R, 2005: “Why is ice slippery?”, *Physics Today*, December issue, pp. 50-55