ASME231 Atmospheric Thermodynamics NC A&T State U
Department of Physics Dr. Yuh-Lang Lin
https://mesolab.org ylin@ncat.edu

Lecture 17 The Clausius-Clapeyron Equation

(Ref.: Sec.4.5 of Hess)

- In this lecture, we will derive an important equation, the Clausius-Clapeyron equation, which calculates the change of the saturation vapor pressure with temperature (de_s/dT) during a phase change.
- Based on observations and experiments, a phase change is reversible and isothermal.

  The latent heat for a reversible process may be calculated by

$$L_{12} = \int_1^2 dq = \int_1^2 T ds = T(s_2 - s_1)\,. \qquad (17.1)$$

  Thus, in order to relate L_{12} to saturation pressure, we need to relate entropy s_2 and s_1 to saturation pressure.

- Consider the following cyclic process in an α-e diagram.

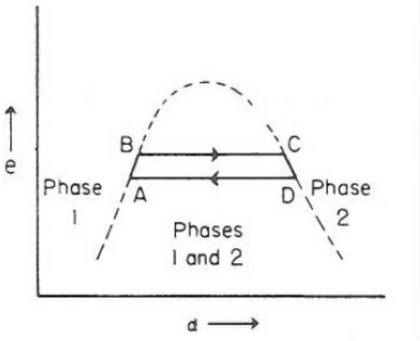


Fig. 4.2

A→B: A slight increase in temperature, ΔT, without any change in phase leading to state B: ($e_s+\Delta e_s$, $\alpha_1+\Delta\alpha_1$, $T+\Delta T$)

B→C: an isothermal phase change leading to state C: ($e_s+\Delta e_s$, $\alpha_2+\Delta\alpha_2$, $T+\Delta T$)

C→D: A slight decrease in temperature, $-\Delta T$, without any change of phase, leading to state D: (e_s, α_2, T)

D→A: an isothermal change of phase back to state A: (e_s, α_1, T)

- Apply the first law to the above processes,

$$dq = Tds = du + e_s d\alpha.$$

Thus, for the whole cyclic process,

$$\oint Tds = \oint e_s d\alpha, \tag{17.2}$$

because for a closed line integral du is zero (du is an exact differential).

The right side of (17.2) is nothing but the area enclosed by the curves, which is approximately equal to $(\alpha_2 - \alpha_1)\Delta e_s$.

Thus, we have

$$\oint Tds = (\alpha_2 - \alpha_1)\Delta e_s. \tag{17.3}$$

Since $d(Ts)$ is an exact differential, we have

$$\oint Tds = -\oint sdT.$$

We now evaluate this integral, $-\oint sdT$, along each of the four parts of the cycle.

A→B: no heat added, thus s is a constant.

$$-\int_A^B s\, dT = -s_1 \Delta T.$$

B→C: Isothermal process,

$$-\int_B^C s\, dT = 0.$$

C→D: no heat added, similar to A→B,

$$-\int_C^D s\, dT = s_2 \Delta T.$$

D→ *A*: Isothermal process,

$$-\int_D^A s\,dT = 0.$$

As a result,

$$\oint T ds = (s_2 - s_1)\Delta T \cdot \qquad (17.4)$$

Combining Eqs. (17.3) and (17.4) leads to

$$(s_2 - s_1)\Delta T = (\alpha_2 - \alpha_1)\Delta e_s$$

or

$$s_2 - s_1 = (\alpha_2 - \alpha_1)\frac{de_s}{dT}.$$

Substituting the above equation into (17.1) leads to

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

or

$$\frac{de_s}{dT} = \frac{L_{12}}{T(\alpha_2 - \alpha_1)}. \qquad (17.5)$$

This is called Clausius-Clapeyron equation. If L_{12}, α_1, and α_2 are known functions of *T*, then (17.5) can be integrated to obtain a relation between saturation vapor pressure and *T*.

It gives the slope of the curves of saturation vapor pressure versus temperature as a function of the latent heat, temperature and the difference in specific volume of the two phases.

- We will consider two special cases: evaporation and sublimation. Since for these two cases, α_2 is the specific volume for water vapor which is much greater than α_1 (for liquid water or ice), and L_{12} is nearly a constant for each processes.

Thus, the Clausius-Clapeyron equation may be approximated by

$$\frac{de_s}{dT} = \frac{L_{12}}{T\alpha_2}. \tag{17.6}$$

Using the equation of state for ideal gases,

$$e_s\alpha_2 = R_vT \quad or \quad \alpha_2 = \frac{R_vT}{e_s},$$

we get

$$\frac{de_s}{e_s} = \frac{L_{12}}{R_v}\frac{dT}{T^2}. \tag{17.7}$$

Therefore,

$$\ln\left(\frac{e_s}{e_{so}}\right) = \frac{L_{12}}{R_v}\left(\frac{1}{T_o} - \frac{1}{T}\right). \tag{17.8}$$

where e_{so} is the saturation vapor pressure at T_o.

For evaporation, e_{so}=6.11 mb and T_o=273 K, which implies

$$\ln\left(\frac{e_s}{6.11\,mb}\right) = \frac{L_{evap}}{R_v}\left(\frac{1}{273} - \frac{1}{T}\right). \tag{17.9}$$

or

$$e_s = 6.11mb\exp\left[\frac{L_{evap}}{R_v}\left(\frac{1}{273} - \frac{1}{T}\right)\right]. \tag{17.10}$$

For sublimation,

$$\ln\left(\frac{e_s}{6.11\,mb}\right) = \frac{L_{sub}}{R_v}\left(\frac{1}{273} - \frac{1}{T}\right), \tag{17.11}$$

or

$$e_s = 6.11mb\exp\left[\frac{L_{sub}}{R_v}\left(\frac{1}{273} - \frac{1}{T}\right)\right]. \tag{17.12}$$

Example: Calculate the change in the melting point of ice if the pressure is increased from 1 to 2 atm, given that

$$\alpha_i = 1.0908x10^{-3}\, m^3 kg^{-1},\ \ \alpha_w = 1.001x10^{-3}\, m^3 kg^{-1}$$

$$L_{melt} = 3.34x10^5\, J\ kg^{-1}\ at\ 0^o C.$$

Solution: Using Clausius-Clapeyron equation,

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

$$= 273x(1.001 - 1.0908)x1.013x10^5 / 3.34x10^5$$

$$= -0.00744 \text{ deg}$$

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 (17.9) and (17.11) 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 ($e = e_s$).

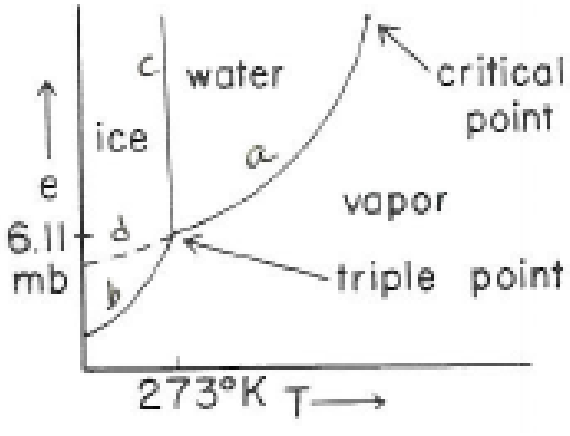
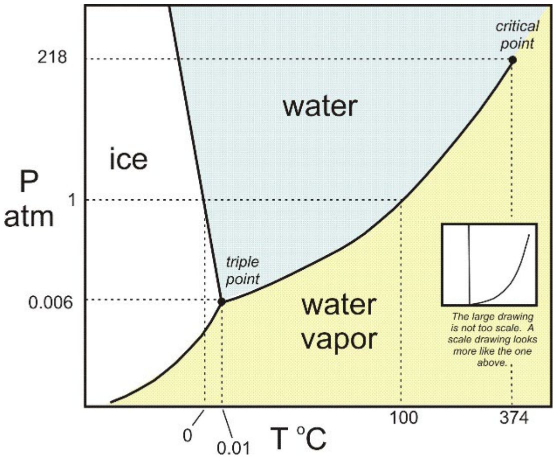


Figure 4.3 (Hess): *T, e* phase diagram for water substances.



[Ref]

All curves begin at the triple point.

(a) Evaporation curve a: curves upward exponentially to the right according to Eq. (17.9) ($T > 273$ K, and $e_s > 6.11$ mb). Along this curve, water and vapor are in equilibrium until it reaches the critical point ($T = 374$ K) 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 (0^oC), it is called supercooled water. For supercooled water, within a certain temperature range of $T < 0^\circ C$, $e_{sw} > e_{si}$ (curve d).

Therefore, in a cloud with mixture of ice crystals and supercooled water (cloud) droplets, water vapor will first sublime 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-Findeisen process.

That is, ice crystal in a cloud of supercooled water droplets will grow faster than the water droplets.

- Since for each temperature (T), there is a relation (2-D curve) between e and α, for all possible T, these curves become a three-dimensional surface (Figure 4.4)

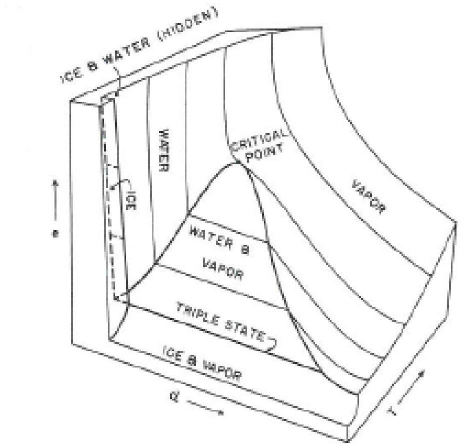
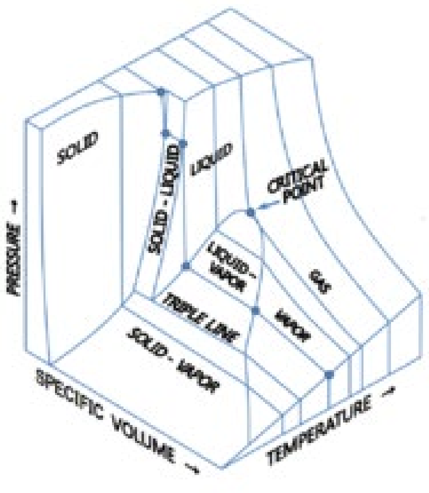


Figure 4.4: (Hess) 3D thermodynamic surface of water substance.



[Reference]