

Lecture 17 The Clausius-Clapeyron Equation

(Sec.4.5 of Hess)

[Equation editor: ($dq = 0$)]

- 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

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

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.

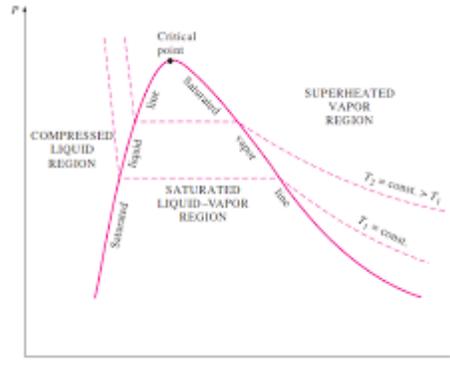


Fig. 4.2

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,

$$\oint Tds = \oint e_s d\alpha, \quad (17.2)$$

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

$$\oint T ds = (\alpha_2 - \alpha_1) \Delta e_s. \quad (17.3)$$

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

$$\oint T ds = - \oint s dT.$$

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

A→B: no heat added, thus s is constant. (4/14/16)

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

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,

$$\oint T ds = (s_2 - s_1) \Delta T. \quad (17.4)$$

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

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

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

$$\frac{de_s}{dT} = \frac{L_{12}}{T\alpha_2}. \quad (17.6)$$

Using the equation of state for ideal gases,

$$e_s \alpha_2 = R_v T \quad \text{or} \quad \alpha_2 = \frac{R_v T}{e_s},$$

we get

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

Therefore,

$$\ln\left(\frac{e_s}{e_{s0}}\right) = \frac{L_{12}}{R_v} \left(\frac{1}{T_o} - \frac{1}{T}\right). \quad (17.8)$$

where e_{s0} is the saturation vapor pressure at T_o .

For evaporation, $e_{s0}=6.11$ mb and $T_o=273$ K, which implies

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

or

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

For sublimation,

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

or

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

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

$$\alpha_i = 1.0908 \times 10^{-3} m^3 kg^{-1}, \quad \alpha_w = 1.001 \times 10^{-3} m^3 kg^{-1}$$

$$L_{melt} = 3.34 \times 10^5 J kg^{-1} \text{ at } 0^\circ C.$$

Solution: Using Clausius-Clapeyron equation,

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

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

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

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 ($e=e_s$).

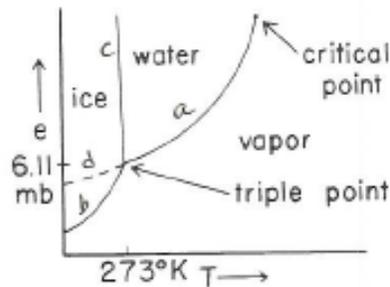


Figure 4.3 (Hess): T , e phase diagram for water substance.

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-Clapyeron 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°C), it is called **supercooled water**. For supercooled water, within a certain temperature range of $T < 0^\circ\text{C}$, $e_{sw} > e_{si}$ (curve d).

Therefore, when an ice crystal is dropped into a cloud of supercooled water 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.

Bergeron-Findeison process: 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)

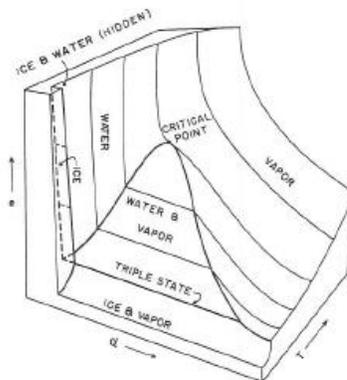


Figure 4.4: (Hess) Three-dimensional thermodynamic surface of water substance.