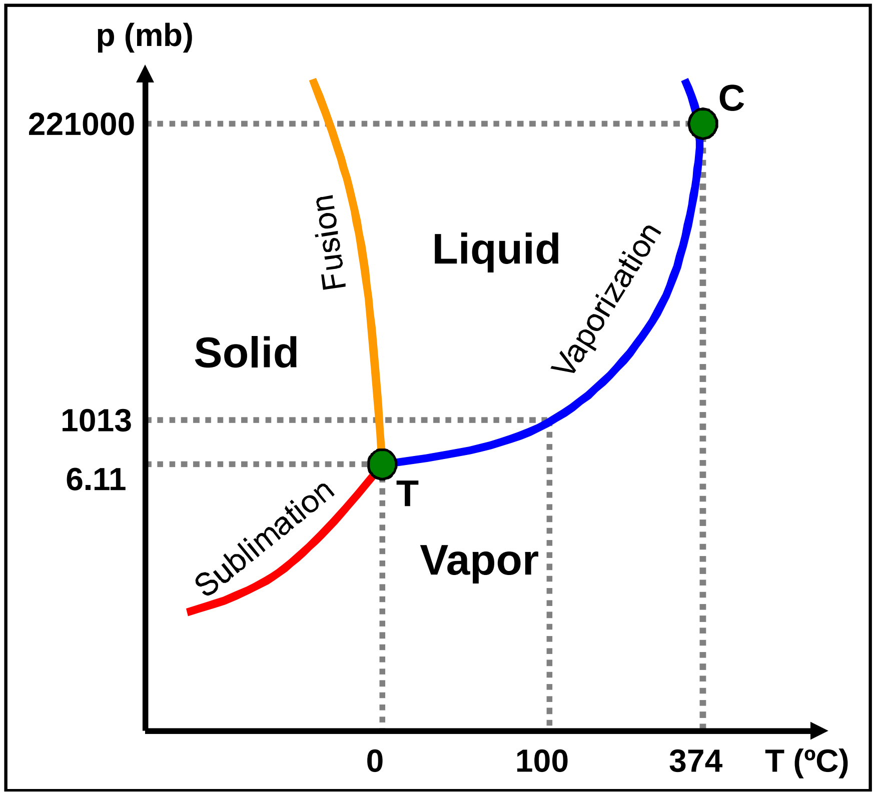
Clausius-Clapeyron Equation



Cloud drops first form when the vaporization equilibrium point is reached (i.e., the air parcel becomes saturated)

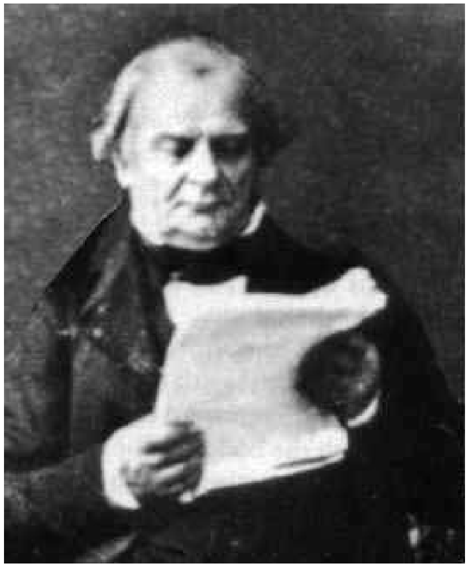
Here we develop an equation that describes how the vaporization/condensation equilibrium point changes as a function of pressure and temperature

Clausius-Clapeyron Equation

Who are these people?

Rudolf Clausius
1822-1888
German
Mathematician / Physicist

"Discovered" the Second Law
Introduced the concept of entropy



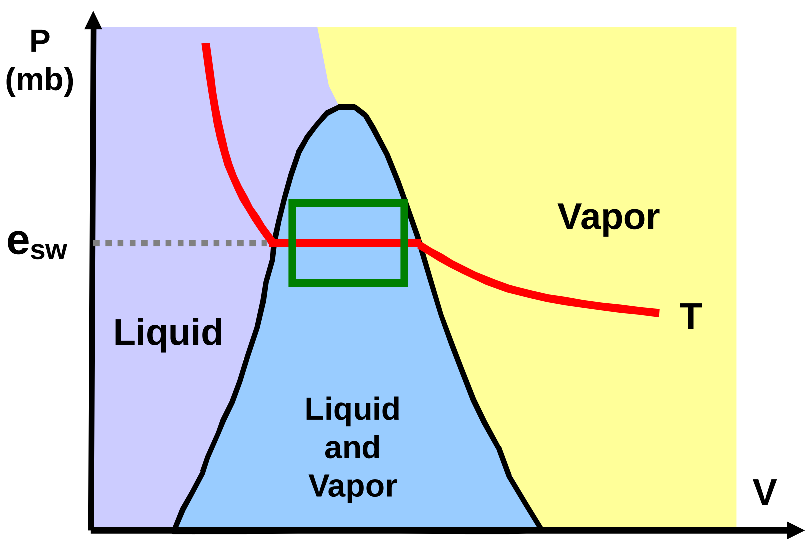
Benoit Paul Emile Clapeyron
1799-1864
French
Engineer / Physicist

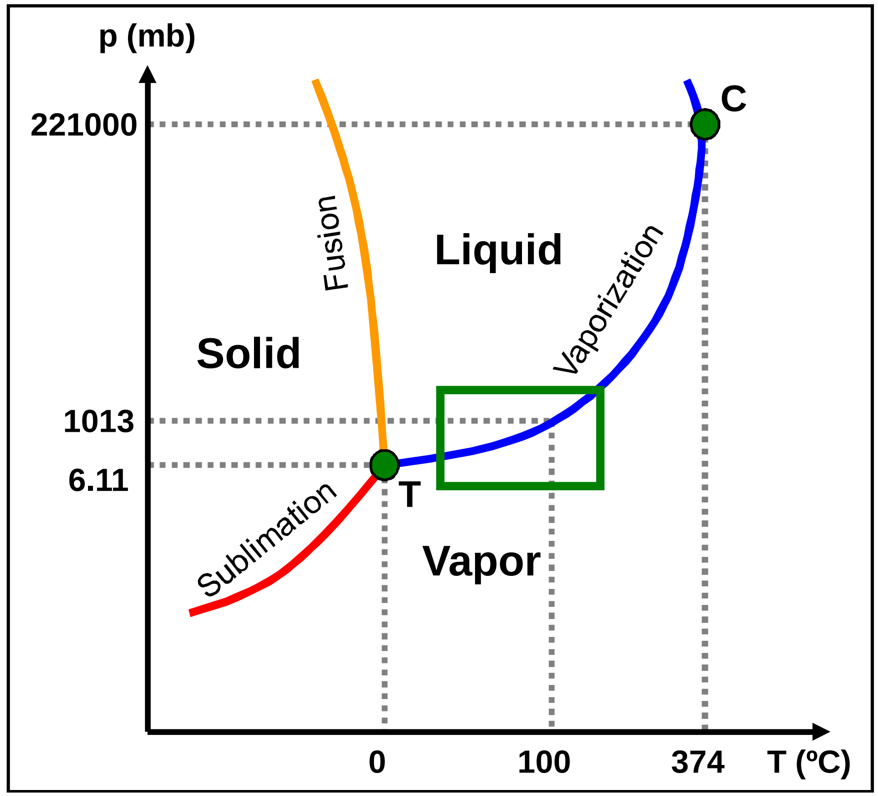
Expanded on Carnot's work

Clausius-Clapeyron Equation

Basic Idea:

- Provides the mathematical relationship (i.e., the equation) that describes **any** equilibrium state of water as a function of temperature and pressure.
- Accounts for phase changes at **each** equilibrium state (<u>each temperature</u>)





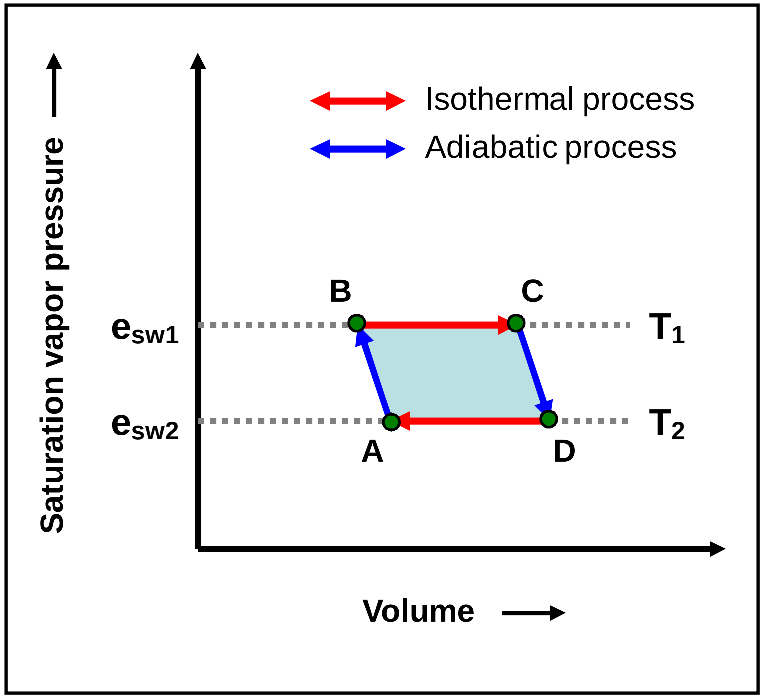
Sections of the P-V and P-T diagrams for which the Clausius-Clapeyron equation is derived in the following slides

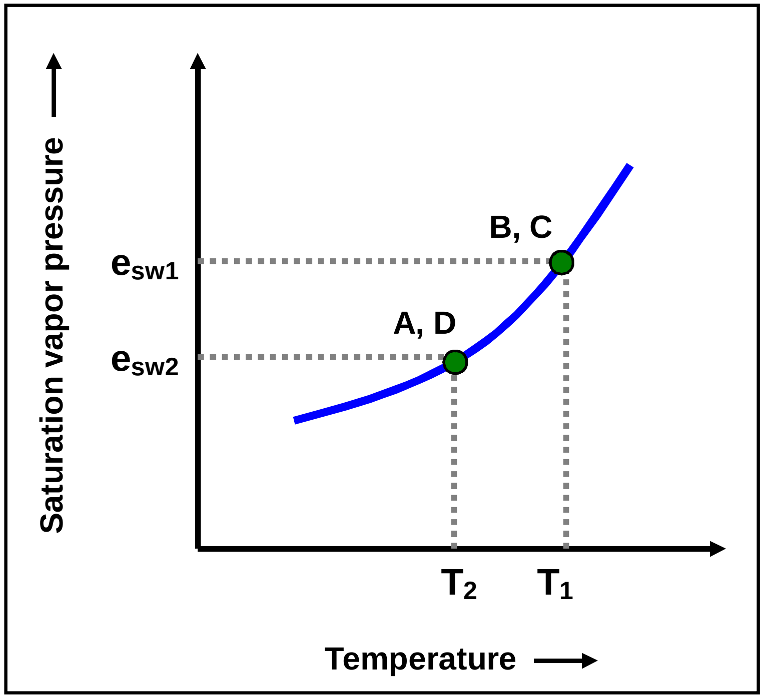
Clausius-Clapeyron Equation

Mathematical Derivation:

Assumption: Our system consists of liquid water in equilibrium with water vapor (at saturation)

- We will return to the Carnot Cycle…





Clausius-Clapeyron Equation

Mathematical Derivation:

- Recall for the Carnot Cycle:

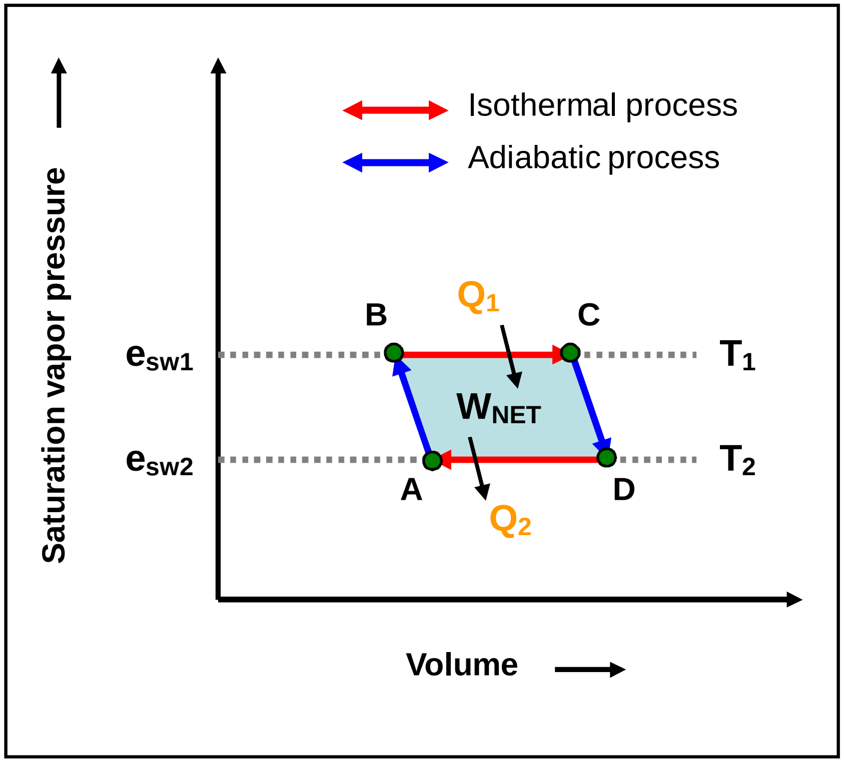
$$W_{NET} = Q_1 + Q_2$$

$$\frac{Q_1 + Q_2}{Q_1} = \frac{T_1 - T_2}{T_1}$$

where: $Q_1 > 0$ and $Q_2 < 0$

- If we re-arrange and substitute:

$$\frac{Q_1}{T_1} = \frac{W_{NET}}{T_1 - T_2}$$



Clausius-Clapeyron Equation

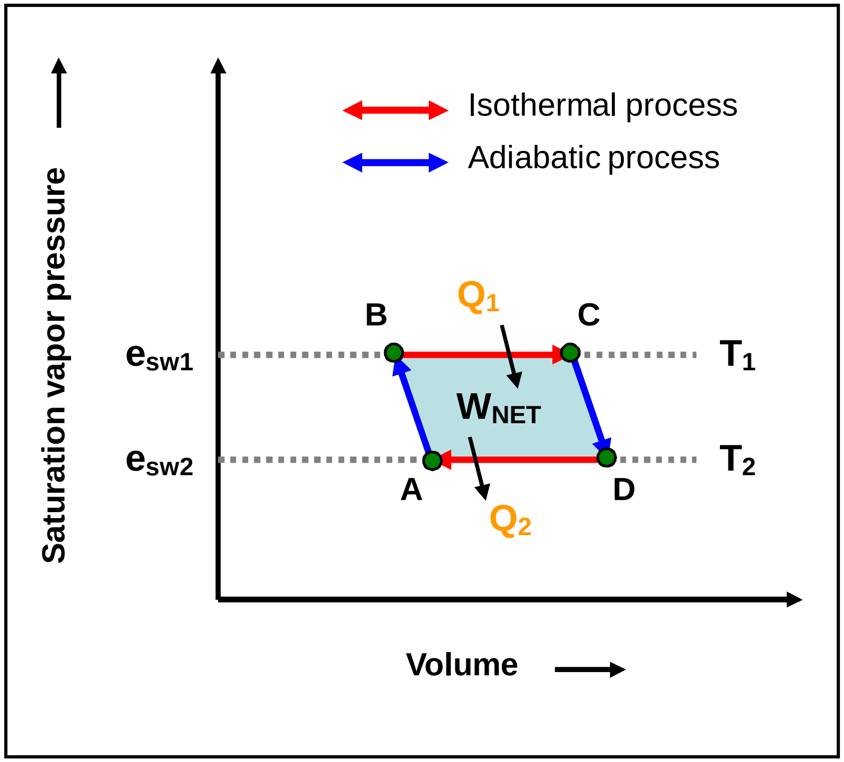
Mathematical Derivation:

Recall:

- During phase changes, Q = L
- Since we are specifically working with vaporization in this example,

$$Q_1 = L_v$$

$$\frac{Q_1}{T_1} = \frac{W_{NET}}{T_1 - T_2}$$



- Also, let:

$$T_1 = T$$

$$T_1 - T_2 = dT$$

Clausius-Clapeyron Equation

Mathematical Derivation:

Recall:

- The net work is equivalent to the **area** enclosed by the cycle:

$$W_{NET} = dV \times dp$$

- The change in pressure is:

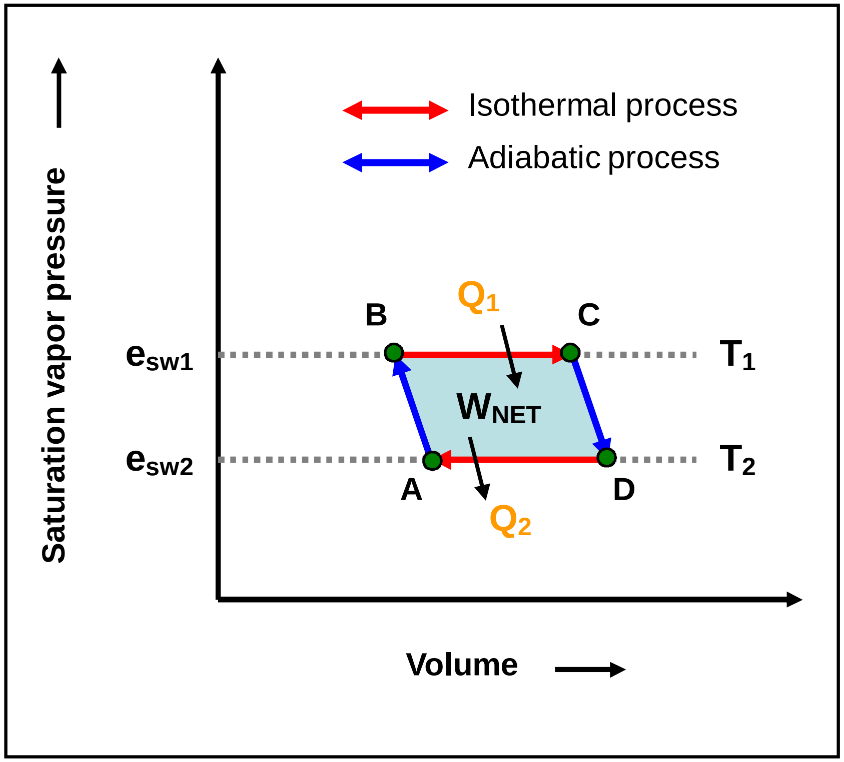
$$de_{sw} = e_{sw1} - e_{sw2}$$

- The change in volume of our system at each temperature (T_1 and T_2) is:

$$dV = (\alpha_v - \alpha_w)dm$$

where: α_v = specific volume of vapor
α_w = specific volume of liquid
dm = total mass converted from vapor to liquid

$$\frac{Q_1}{T_1} = \frac{W_{NET}}{T_1 - T_2}$$



Clausius-Clapeyron Equation

Mathematical Derivation:

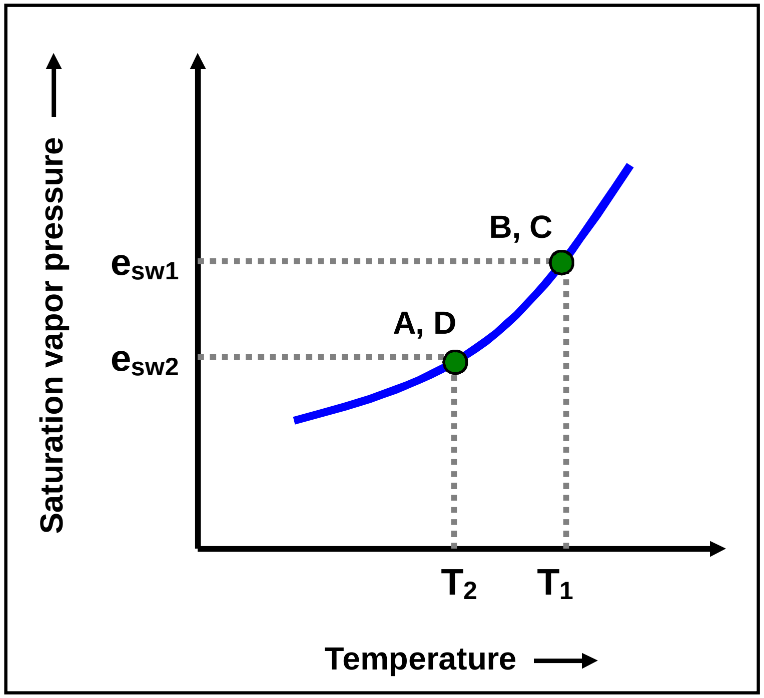
- We then make all the substitutions into our Carnot Cycle equation:

$$\frac{Q_1}{T_1} = \frac{W_{NET}}{T_1 - T_2} \Rightarrow \frac{L_v}{T} = \frac{(\alpha_v - \alpha_w)\, dm\, de_{sw}}{dT}$$

- We can re-arrange and use the definition of specific latent heat of vaporization ($l_v = L_v / dm$) to obtain:

$$\frac{de_{sw}}{dT} = \frac{l_v}{T(\alpha_v - \alpha_w)}$$

Clausius-Clapeyron Equation for the equilibrium vapor pressure with respect to liquid water



Clausius-Clapeyron Equation

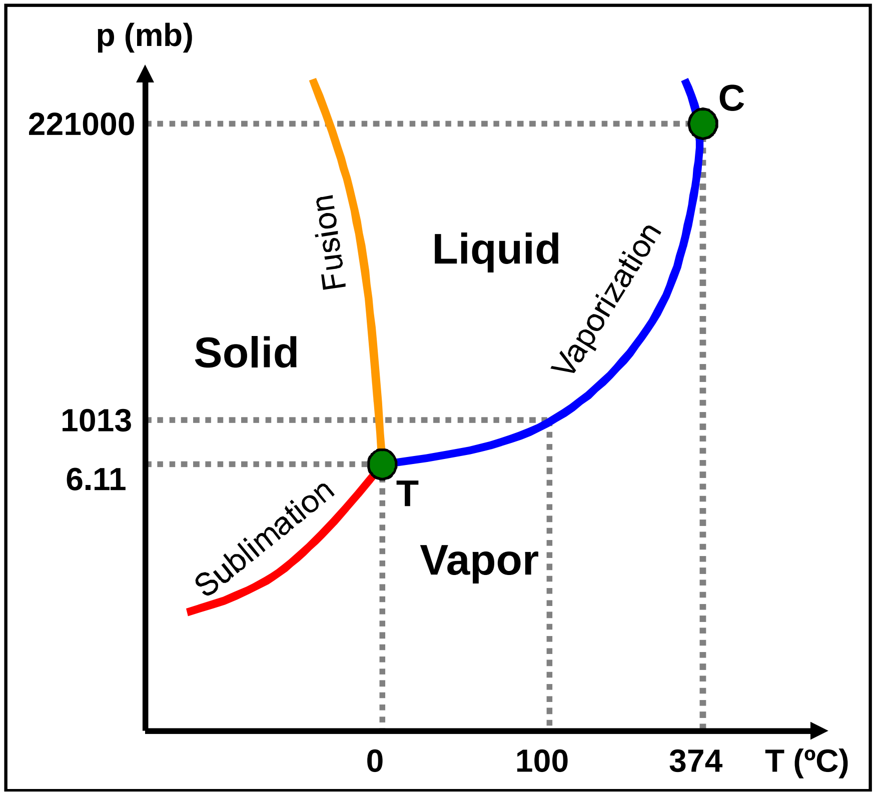
General Form:

- Relates the equilibrium pressure between two phases to the temperature of the heterogeneous system

$$\frac{dp_s}{dT} = \frac{l}{T\Delta\alpha}$$

where:
T = Temperature of the system
l = Latent heat for given phase change
dp_s = Change in system pressure at saturation
dT = Change in system temperature
$\Delta\alpha$ = Change in specific volumes between the two phases

Equilibrium States for Water
(function of temperature and pressure)



Clausius-Clapeyron Equation

Application: Saturation vapor pressure for a given temperature

Starting with:

$$\frac{de_{sw}}{dT} = \frac{l_v}{T(\alpha_v - \alpha_w)}$$

Assume: $\alpha_v >> \alpha_w$ [valid in the atmosphere]

and using: $e_{sw}\alpha_v = R_v T$ [Ideal gas law for the water vapor]

We get:

$$\frac{de_{sw}}{e_{sw}} = \frac{l_v}{R_v}\frac{dT}{T^2}$$

If we integrate this from some reference point (e.g. the triple point: e_{s0}, T_0) to some arbitrary point (e_{sw}, T) along the curve assuming l_v is constant:

$$\int_{e_{s0}}^{e_{sw}} \frac{de_{sw}}{e_{sw}} = \frac{l_v}{R_v}\int_{T_0}^{T} \frac{dT}{T^2}$$

Clausius-Clapeyron Equation

Application: Saturation vapor pressure for a given temperature

$$\int_{e_{s0}}^{e_{sw}} \frac{de_{sw}}{e_{sw}} = \frac{l_v}{R_v}\int_{T_0}^{T} \frac{dT}{T^2}$$

After integration we obtain:

$$\ln\frac{e_{sw}}{e_{s0}} = \frac{l_v}{R_v}\left(\frac{1}{T_0} - \frac{1}{T}\right)$$

After some algebra and substitution for e_{s0} = 6.11 mb and T_0 = 273.15 K we get:

$$e_{sw}(\text{mb}) = 6.11\exp\left[\frac{l_v}{R_v}\left(\frac{1}{273.15} - \frac{1}{T(K)}\right)\right]$$

Clausius-Clapeyron Equation

Application: Saturation vapor pressure for a given temperature

$$e_{sw}(\text{mb}) = 6.11 \exp\left[\frac{l_v}{R_v}\left(\frac{1}{273.15} - \frac{1}{T(K)}\right)\right]$$

A more accurate form of the above equation can be obtained when we do not assume l_v is constant (recall l_v is a function of temperature). See your book for the derivation of this more accurate form:

$$e_{sw}(\text{mb}) = 6.11 \exp\left[53.49 - \frac{6808}{T(K)} - 5.09 \ln[T(K)]\right]$$

Clausius-Clapeyron Equation

Application: **Saturation vapor pressure for a given temperature**

$$e_{sw}\,(\mathrm{mb}) = 6.11 \exp\left[53.49 - \frac{6808}{T(K)} - 5.09 \ln\left[T(K)\right]\right]$$

- What is the saturation vapor pressure with respect to water at 25ºC?

  T = 298.15 K

  e_{sw} = 32 mb

- What is the saturation vapor pressure with respect to water at 100ºC?

  T = 373.15 K   Boiling point

  e_{sw} = 1005 mb

Clausius-Clapeyron Equation

Application: Boiling Point of Water

$$\frac{de_{sw}}{dT} = \frac{l_v}{T(\alpha_v - \alpha_w)}$$

- At typical atmospheric conditions near the boiling point:

$T = 100^oC = 373\ K$
$l_v = 2.26 \times 10^6\ J\ kg^{-1}$
$\alpha_v = 1.673\ m^3\ kg^{-1}$
$\alpha_w = 0.00104\ m^3\ kg^{-1}$

$$\frac{de_{sw}}{dT} = 36.21\ \ mb\ K^{-1}$$

- This equation describes the change in boiling point temperature (T) as a function of atmospheric pressure when the saturated with respect to water (e_{sw})

Clausius-Clapeyron Equation

Application: Boiling Point of Water

- What would the boiling point temperature be on the top of Mount Mitchell if the air pressure was 750mb?

  - From the previous slide we know the boiling point at ~1005 mb is 100ºC

$$\frac{de_{sw}}{dT} = 36.21 \text{ mb K}^{-1}$$

  - Let this be our reference point:

    T_{ref} = 100ºC = 373.15 K
    $e_{sw\text{-}ref}$ = 1005 mb

$$\frac{e_{sw} - e_{sw-ref}}{T - T_{ref}} = 36.21 \text{ mb K}^{-1}$$

  - Let e_{sw} and T represent the values on Mt. Mitchell:

    e_{sw} = 750 mb

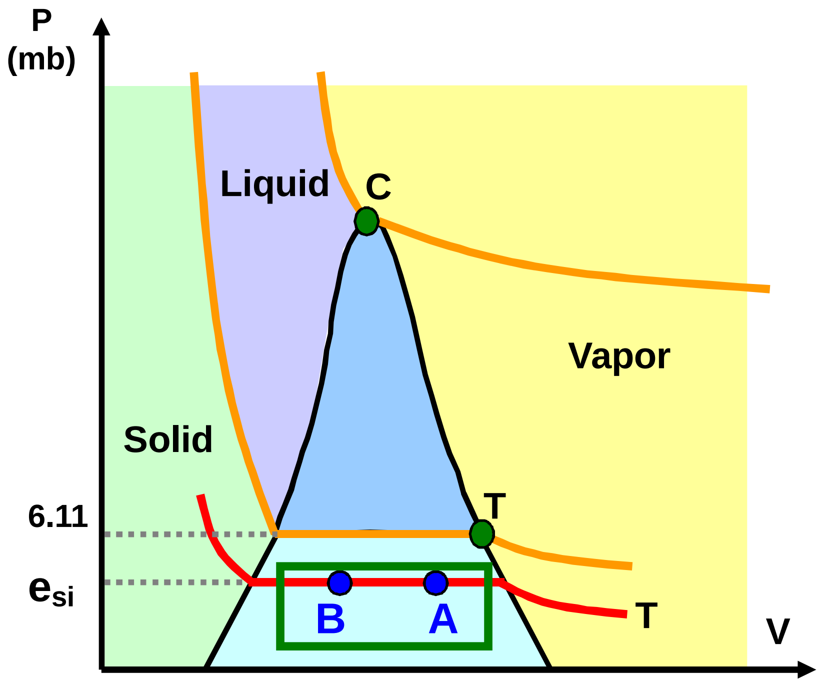
$$T = \frac{e_{sw} - e_{sw-ref}}{36.21} + T_{ref}$$

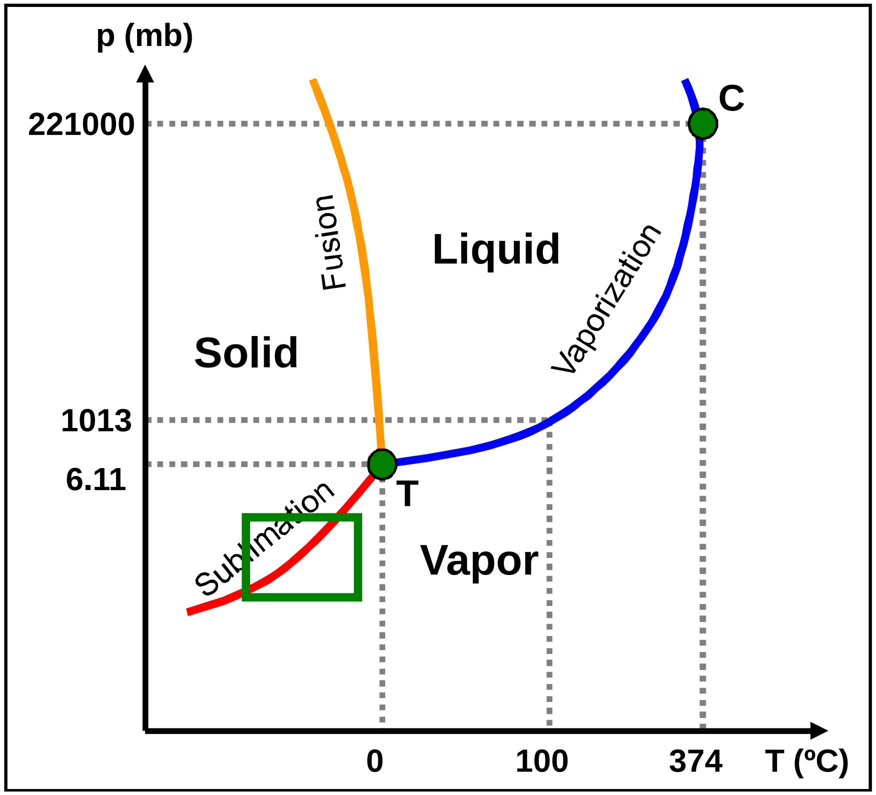
T = 366.11 K
T = 93ºC (boiling point temperature on Mt. Mitchell)

Clausius-Clapeyron Equation

Equilibrium with respect to Ice:

- We will know examine the equilibrium vapor pressure for a heterogeneous system containing vapor and ice





Clausius-Clapeyron Equation

Equilibrium with respect to Ice:

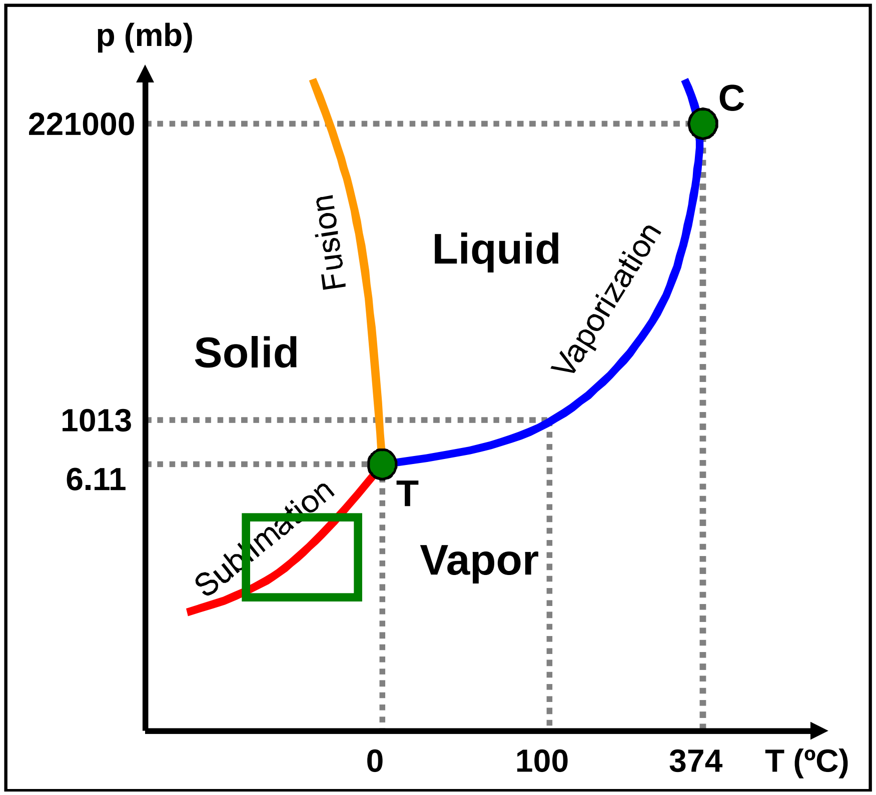
- Return to our "general form" of the Clausius-Clapeyron equation

$$\frac{de_s}{dT} = \frac{l}{T\Delta\alpha}$$

- Make the appropriate substitution for the two phases (vapor and ice)

$$\frac{de_{si}}{dT} = \frac{l_s}{T(\alpha_v - \alpha_i)}$$

Clausius-Clapeyron Equation for the equilibrium vapor pressure with respect to ice



Clausius-Clapeyron Equation

Application: Saturation vapor pressure of ice for a given temperature

Following the same logic as before, we can derive the following equation for **saturation with respect to ice**

$$e_{si}(\text{mb}) = 6.11 \exp\left[\frac{l_s}{R_v}\left(\frac{1}{273.15} - \frac{1}{T(K)}\right)\right]$$

A more accurate form of the above equation can be obtained when we do not assume l_s is constant (recall l_s is a function of temperature). See your book for the derivation of this more accurate form:

$$e_{si}(\text{mb}) = 6.11 \exp\left[26.16 - \frac{6293}{T(K)} - 0.555 \ln[T(K)]\right]$$

Clausius-Clapeyron Equation

Application: Melting Point of Water

- Return to the "general form" of the Clausius-Clapeyron equation and make the appropriate substitutions for our two phases (liquid water and ice)

$$\frac{dp_{wi}}{dT} = \frac{l_f}{T(\alpha_w - \alpha_i)}$$

- At typical atmospheric conditions near the melting point:

$T = 0^oC = 273\ K$
$l_s = 0.334 \times 10^6\ J\ kg^{-1}$
$\alpha_w = 1.00013 \times 10^{-3}\ m^3\ kg^{-1}$
$\alpha_i = 1.0907 \times 10^{-3}\ m^3\ kg^{-1}$

$$\frac{dp_{wi}}{dT} = -135{,}038\ \text{mb K}^{-1}$$

- This equation describes the change in melting point temperature (T) as a function of pressure when liquid water is saturated with respect to ice (p_{wi})