

## Lecture 2 - ENV 407

### Review of Atmospheric Thermodynamics

Clausius Clapeyron, Phase  
diagram, Humidity variables

## Next topics that will be covered:

- Review of (Atmospheric) Thermodynamics
- Chemical Potential and importance for phase equilibria

# What is Thermodynamic Equilibrium?

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It is the state a given system tends to reach (given enough time).

This state is characterized by:

- **Thermal** equilibrium

*No net heat flux between components of the system*

- **Mechanical** equilibrium

*Pressure tends to become uniform*

- **Diffusional** equilibrium

*No net mass flux between components of a system*

# Formulating Thermodynamic Equilibrium

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In other words,

$$dG = VdP - SdT$$

If  $P$  and  $T$  are kept constant,  $dG=0$ , with  $d^2G > 0$

So  $G$  of a **closed** system at constant  $P, T$  is  
**minimum at equilibrium**

What happens if the system is open or it has  
multiple phases and components?

We need to consider mass in the Gibbs Energy  
formulation

# Formulating Thermodynamic Equilibrium

In other words,

$$G(P, T, \underbrace{n_1, \dots, n_n}_{\text{mass of components } 1, 2, \dots, n})$$

Chain rule:

$$dG = \left( \frac{\partial G}{\partial T} \right) dT + \left( \frac{\partial G}{\partial P} \right) dP + \left( \frac{\partial G}{\partial n_1} \right) dn_1 + \dots + \left( \frac{\partial G}{\partial n_n} \right) dn_n$$

$\uparrow$   
 $-S$

$\uparrow$   
 $V$

$\underbrace{\hspace{10em}}$   
Contribution of each  
component to the free  
energy

$\left( \frac{\partial G}{\partial n_1} \right), \dots, \left( \frac{\partial G}{\partial n_n} \right)$  are the **chemical potentials**  $\mu_1, \dots, \mu_n$

# Formulating Thermodynamic Equilibrium

$\mu$  is Gibbs free energy per mol of substance

important  $\rightarrow$  energy content of a substance

$\rightarrow$  determines how

substance changes equilibrium.

Equilibrium:

$$\mu_{(H_2O(l))} = \mu_{(H_2O(g))}$$

how to use  $\mu$ ?

$$\mu = \left(\frac{G}{n}\right)_{\text{substance}}$$

$$d\mu = d\left(\frac{G}{n}\right) = \left(\frac{-SdT + VdP}{n}\right)$$

entropy of substance  
V of substance

$$d\mu = -sdT + vdp \quad (3)$$

entropy/mol      volume/mol

$f$  pure substance.

calculating values of  $\mu$ :  
apply equation 3

$$\int_{\text{ref state}}^{P,T} d\mu = \int_{T_{\text{ref}}}^T -sdT + \int_{P_{\text{ref}}}^P vdp \Rightarrow \mu(P,T) - \mu^*(\text{reference}) = -\int_{T_{\text{ref}}}^T sdT + \int_{P_{\text{ref}}}^P vdp$$

Liquid

$$G(P,T)$$

$$dG = \left(\frac{\partial G}{\partial P}\right)_T dP + \left(\frac{\partial G}{\partial T}\right)_P dT$$

$$+ \left(\frac{\partial G}{\partial n}\right)_T, P d n$$

$$\left(\frac{\partial G}{\partial n}\right)_T, P = \mu$$

# Formulating Thermodynamic Equilibrium

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So:  $dG = -SdT + VdP + \mu_1 dn_1 + \dots + \mu_n dn_n$

At thermodynamic equilibrium,  $dG = 0$

For constant  $P, T$  this means:  $\mu_1 dn_1 + \dots + \mu_n dn_n = 0$

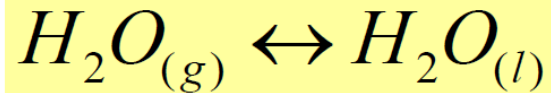
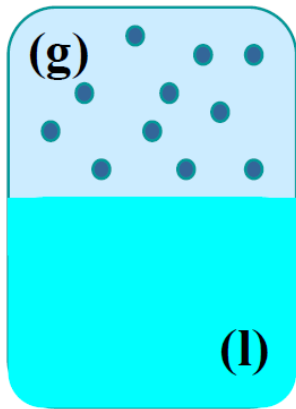
This statement is known as "chemical equilibrium" and is the basis of any aerosol thermodynamic model

Let's apply this to a chemical reaction found in clouds:  
Water partitioning between phases.

# Chemical Equilibrium: Phase Equilibria

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Phase equilibria is (for thermo) a reaction:



$$\mu_{H_2O_{(g)}} - \mu_{H_2O_{(l)}} = 0$$

or

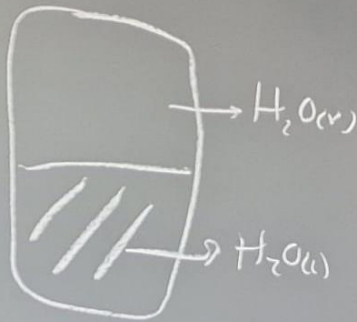
$$\mu_{H_2O_{(g)}} = \mu_{H_2O_{(l)}}$$

when two phases are in equilibrium with each other, they share the same chemical potential

# Chemical Equilibrium: Phase Equilibria

Chemical Equilibrium condition explained in more detail.

$$\mu_{\text{H}_2\text{O}(l)} dn_{\text{H}_2\text{O}(l)} + \mu_{\text{H}_2\text{O}(g)} dn_{\text{H}_2\text{O}(g)} = 0 \quad (1)$$



mass balance

$$n_{\text{H}_2\text{O}} = n_{\text{H}_2\text{O}(g)} + n_{\text{H}_2\text{O}(l)} = \text{const.}$$

$$dn_{\text{H}_2\text{O}} = 0 \Rightarrow dn_{\text{H}_2\text{O}(g)} = -dn_{\text{H}_2\text{O}(l)} \quad (2)$$

$$(1) \stackrel{(2)}{\Rightarrow} -\mu_{\text{H}_2\text{O}(l)} dn_{\text{H}_2\text{O}(l)} + \mu_{\text{H}_2\text{O}(g)} dn_{\text{H}_2\text{O}(l)} = 0$$

$$\Rightarrow dn_{\text{H}_2\text{O}(l)} \left[ \mu_{\text{H}_2\text{O}(g)} - \mu_{\text{H}_2\text{O}(l)} \right] = 0 \Rightarrow \boxed{\mu_{\text{H}_2\text{O}(l)} = \mu_{\text{H}_2\text{O}(g)}}$$

# A little more on Chemical Potential

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For pure substances:

$\mu(P, T)$  - because it is derived from  $G(P, T)$

$\mu$  is the Gibbs free energy per mol substance

$$d\mu = d\left(\frac{G}{n}\right) = -\left(\frac{S}{n}\right)dT + \left(\frac{V}{n}\right)dP = -s dT + v dP$$

per mol

Calculation of  $\mu(P, T)$  is done with respect to a **reference state**,  $\mu^*$  ( $P=1\text{atm}$  and  $T=298.15\text{K}$ )

$$\mu(P, T) - \mu^* = - \int_{298.15}^T s dT + \int_{1\text{atm}}^P v dP$$

$\mu(P, T)$  depends on the phase state of compound

# Chemical Potential: pure substances

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For pure ideal gases,  $v = RT/P$

$$\mu(P, 298.15K) - \mu^* = RT \ln\left(\frac{P}{1}\right) = RT \ln P$$

Pure fluids and solids are effectively incompressible (for atmospheric conditions),  
 $v = 1/\rho \sim \text{constant}$

$$\mu(P, 298.15K) - \mu^* = \frac{1}{\rho}(P - 1)$$

RHS is negligible, so  $\mu(P, 298.15K) \approx \mu^* = \text{const.}$

# Chemical Potential: ideal solutions

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In a mixture of ideal gases,  $v_i = RT/P_i$

$$\mu_i(P, 298.15K) - \mu^* = RT \ln P_i = RT \ln P y_i$$

Partial pressure  
of gas "i"

Mol fraction of  
"i" in gas phase

In ideal solutions,  $\mu$  for each component  $j$ :

$$\mu_j(P, 298.15K) - \mu^* = RT \ln x_j$$

Mol fraction of "j" in solution

**Ideal solutions** are those for which each molecule interacts the same with all molecules in solution. They are the "analog" of ideal gases for solutions.

# Thermodynamics Applications:

- Clausius-Clapeyron Equation
  - Humidity Variables
- See lecture notes (posted on Moodle)

# Applications of $\mu$ to water

Some terms and concepts we will use a lot.

→ Vapor pressure of  $H_2O$ ?

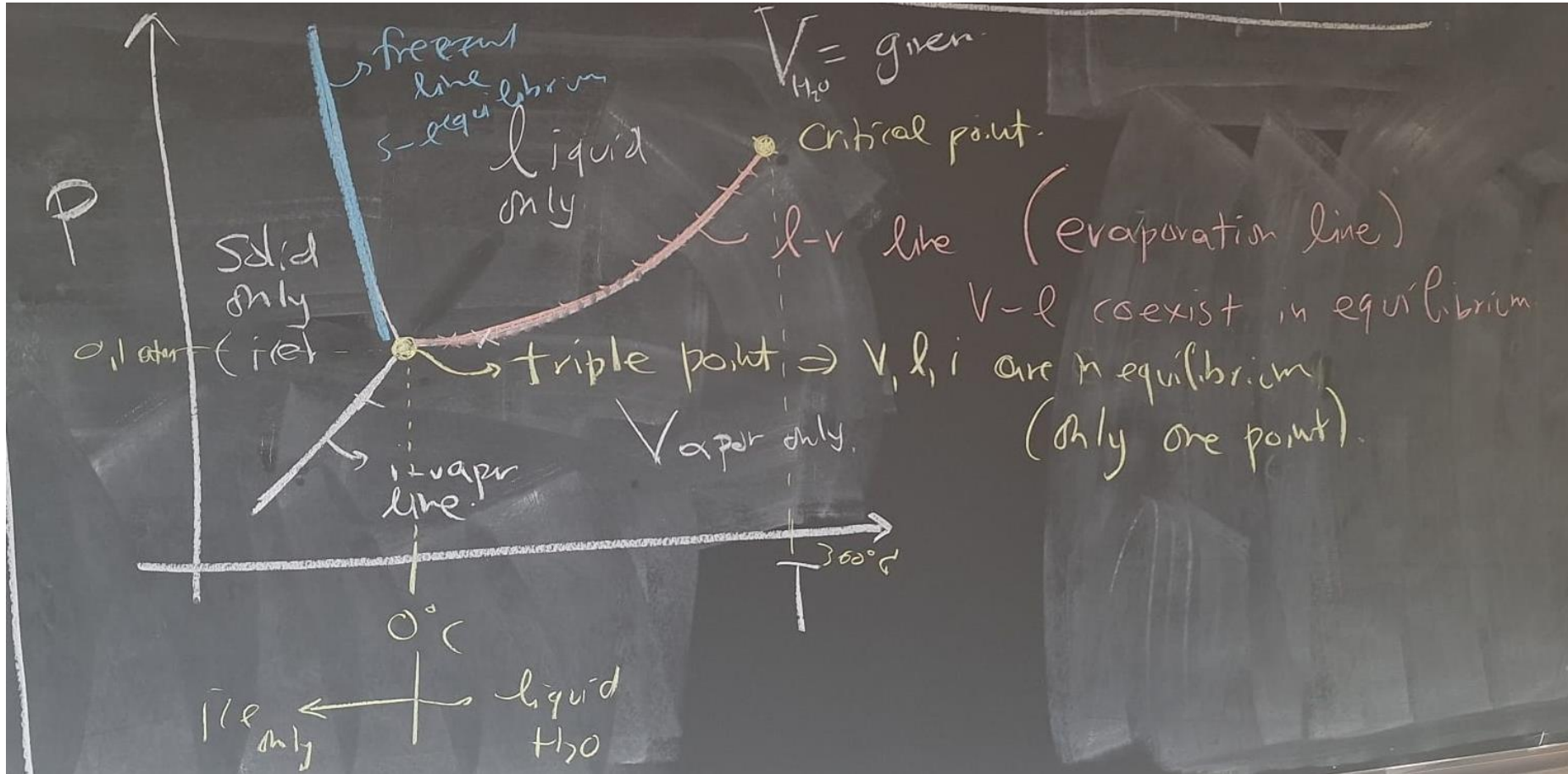
$P_{H_2O}$  (partial pressure)  $H_2O$  in gas phase

→ Equilibrium vapor pressure of  $H_2O$   
(Saturation)



# Phase diagram of water

Tells you what phases are possible for a given P,T

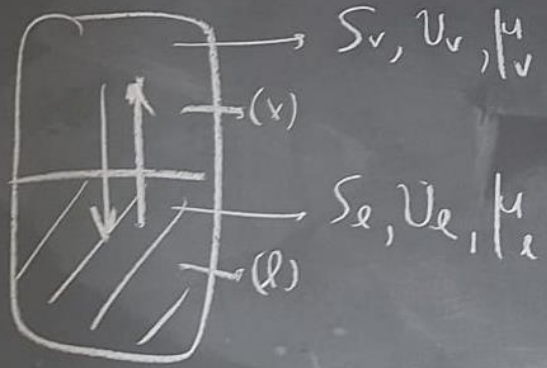


# Clausius Clapeyron Equation - part 1

How to get values of saturation vapor pressure?

- get them from tables (observedly accurate)
- fits to the data
- Clausius-Clapeyron equation.

→ V-l equilibrium.



both phases in equilibrium.

$$\mu_v = \mu_l \Rightarrow d\mu_v = d\mu_l \Rightarrow$$
$$\Rightarrow \underbrace{-S_v dT + U_v dP}_{d\mu_v} = \underbrace{-S_l dT + U_l dP}_{d\mu_l} \Rightarrow$$

# Clausius Clapeyron Equation - part 2

... continued

$$dP (v_v - v_l) = dT (s_v - s_l) \Rightarrow \boxed{\frac{dP}{dT} = \left( \frac{s_v - s_l}{v_v - v_l} \right)}$$

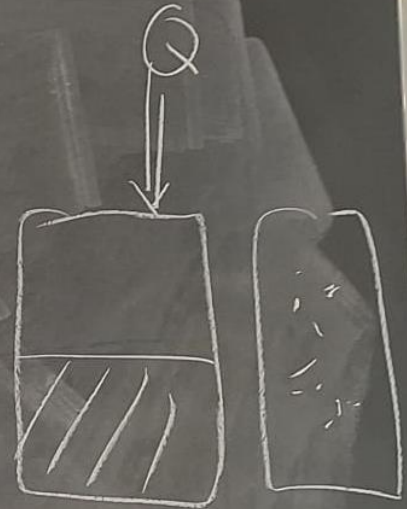
Start expressing things

$$s_v - s_l = \frac{L_{ve}}{T}$$

← latent heat of vaporization  
← temperature

$$ds = \frac{dq_r}{T}$$

$$\Delta s = \frac{\Delta q_r}{T}$$



$$\boxed{\frac{dP}{dT} = \frac{L_{ve}}{T} \left( \frac{1}{v_v - v_l} \right)}$$

Clapeyron Equation.  
no simplifications.

# Humidity Variables - part 1

## Vapor pressure, relative humidity

Other variables,

other variables,

$H$  relative humidity  $(0-1) \times 100$  (%)

$H = \frac{P_{H_2O}}{P_{sat}}$

$H = 1$  saturated ← cloudy conditions

$H < 1$  undersaturated

$H > 1$  (supersaturated) Unstable condition

liquid water

relative humidity over ice

$H_i = \frac{P_{H_2O}}{P_{sat,i}}$

$P_{H_2O} < H P_{sat}(T)$

$P_{H_2O} = H_i P_{sat,i}(T)$

vapor pressures  
equilibrium (sat)  
- data, cont  
- Clausius Clapeyron

Not saturated (i.e. only vapor?)  
Humidity variables to quantify.  
(water vapor)

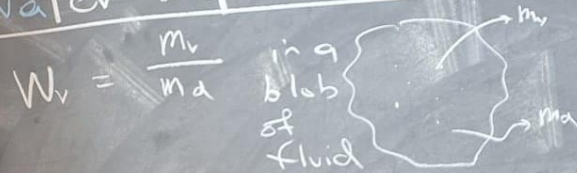
vapor pressure  $P_{H_2O}$ ,  $e$   
partial pressure of  $H_2O$  vapor.

$P_{H_2O}$  saturated →  $P_{sat}$ ,  $e_{sat}$

# Humidity Variables - part 2

## Water vapor mixing ratio

Water vapor mixing ratio  $\left(\frac{\text{kg H}_2\text{O}}{\text{kg air}}\right)$



$$W_v = \frac{m_v}{m_a}$$

$$W_v = \frac{\frac{P_{H_2O} V}{\left(\frac{R}{M_{H_2O}}\right) T}}{\frac{(P - P_{H_2O}) V}{\left(\frac{R}{M_{air}}\right) T}}$$

$$= \frac{P_{H_2O}}{P - P_{H_2O}} \left(\frac{M_{H_2O}}{M_{air}}\right) \approx 0.62$$

$$W_v = \frac{P_v}{P - P_v} \approx 0.62$$

ideal gas law  
water:  $P_{H_2O} V = \frac{m_v}{M_{H_2O}} RT \Rightarrow m_v = \frac{P_{H_2O} V}{\left(\frac{R}{M_{H_2O}}\right) T}$


Similarly for dry air  
 $m_d = \frac{(P - P_{H_2O}) V}{\left(\frac{R}{M_{air}}\right) T}$

$$\text{Saturation } W_v = \frac{P_{sat}}{(P - P_{sat})} \approx 0.62$$

Express  $H$  in terms of  $W_v$ .  
 $P_v, P_{sat} \ll P$   
 $W_v \approx \frac{P_v}{P}$   
 $W_{v,sat} \approx \frac{P_{sat}}{P}$   
 $H \approx \frac{W_v}{W_{v,sat}}$

# A nice video on boiling and vapor pressure

YouTube CH clausius clapeyron × Q



**Boiling, Atmospheric Pressure, and Vapor Pressure**

Wayne Breslyn (Dr. B.) 824K subscribers Join Subscribe

259K views · 8 years ago  
A video about the phenomenon of boiling for the Khan Academy talent search contest, July 2016.  
[Images: ...more](#)

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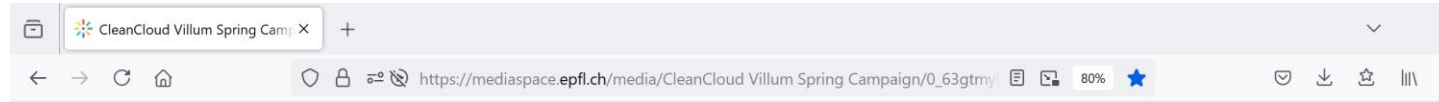
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S @syedaairfan · 3 years ago  
No jargon, no BS intro; cuts straight to the point with clear animation/demonstration and simple explanation. We need more such videos!

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IET Institute for Energy Technology

<https://www.youtube.com/watch?v=Ag4ILUXKuSM>

# Let's take a short break to stretch... and watch some aerosol-cloud study in action



## CleanCloud Villum Spring Campaign

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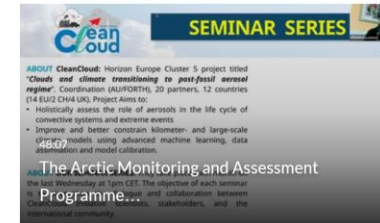
From Athanasios Nenes May 31st, 2024

Details Share Q

A short video documentary with scenes and pictures from the CleanCloud Spring 2024 campaign at Villum, Greenland.

Campaign PIs: Henrik Skov (Aarhus U), Andreas Massling (Aarhus U), Athanasios Nenes (FORTH/EPFL),

### Related Media



[https://mediaspace.epfl.ch/media/CleanCloud%20Villum%20Spring%20Campaign/0\\_63gtmyl6](https://mediaspace.epfl.ch/media/CleanCloud%20Villum%20Spring%20Campaign/0_63gtmyl6)