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?

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

Combination of the first and second laws give:

$$dU = -PdV + TdS$$

P: pressure, V: system volume, T: temperature, S: entropy and U: internal energy

During a process:

- if V and S are kept constant, $dU=0$
  it can be shown that $d^2U > 0$, or U is **minimum**
- if V and U are kept constant, $dS=0$
  it can be shown that $d^2S < 0$, or S is **maximum**

So, if U is **minimum** and S is **maximum**, then $dV=0$ too
This means that the system is in equilibrium.

Formulating Thermodynamic Equilibrium

A criterion for equilibrium in terms of measurable quantities would be very useful (hard to measure S).

Gibbs Free Energy "G" is perfectly suited for this.

$$G(T,P) = U + PV - TS$$

P: pressure, V: system volume, T: temperature, S: entropy and U: internal energy

Changes in G are then expressed as:

$$dG = \boxed{dU + PdV - TdS} + VdP - SdT$$

Zero from combined First & Second Law

Formulating Thermodynamic Equilibrium

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,

$$G(P, T, \underbrace{n_1, \ldots n_n})$$

mass of components
1, 2, ..., n

Chain rule:

$$dG = \underbrace{\left(\frac{\partial G}{\partial T}\right)}_{-S} dT + \underbrace{\left(\frac{\partial G}{\partial P}\right)}_{V} dP + \underbrace{\left(\frac{\partial G}{\partial n_1}\right) dn_1 + \ldots + \left(\frac{\partial G}{\partial n_n}\right) dn_n}_{\text{Contribution of each component to the free energy}}$$

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

Formulating Thermodynamic Equilibrium

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

At thermodynamic equilibrium, $\mathrm{d}G = 0$

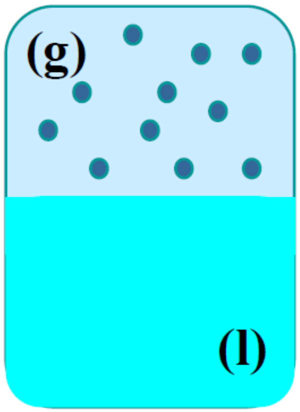
For constant P,T this means: $\mu_1 dn_1 + \ldots + \mu_n dn_n = 0$

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

Phase equilibria is (for thermo) a reaction:



$$H_2O_{(g)} \leftrightarrow H_2O_{(l)}$$

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

or

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

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

A little more on Chemical Potential

For pure substances:

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

μ 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,** μ^* (P=1atm and T=298.15K)

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

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

Chemical Potential: pure substances

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), $v = 1/\rho$ ~ constant

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

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

Chemical Potential: ideal solutions

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

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

Partial pressure of gas "i"

Mol fraction of "i" in gas phase

In ideal solutions, μ for each component j:

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

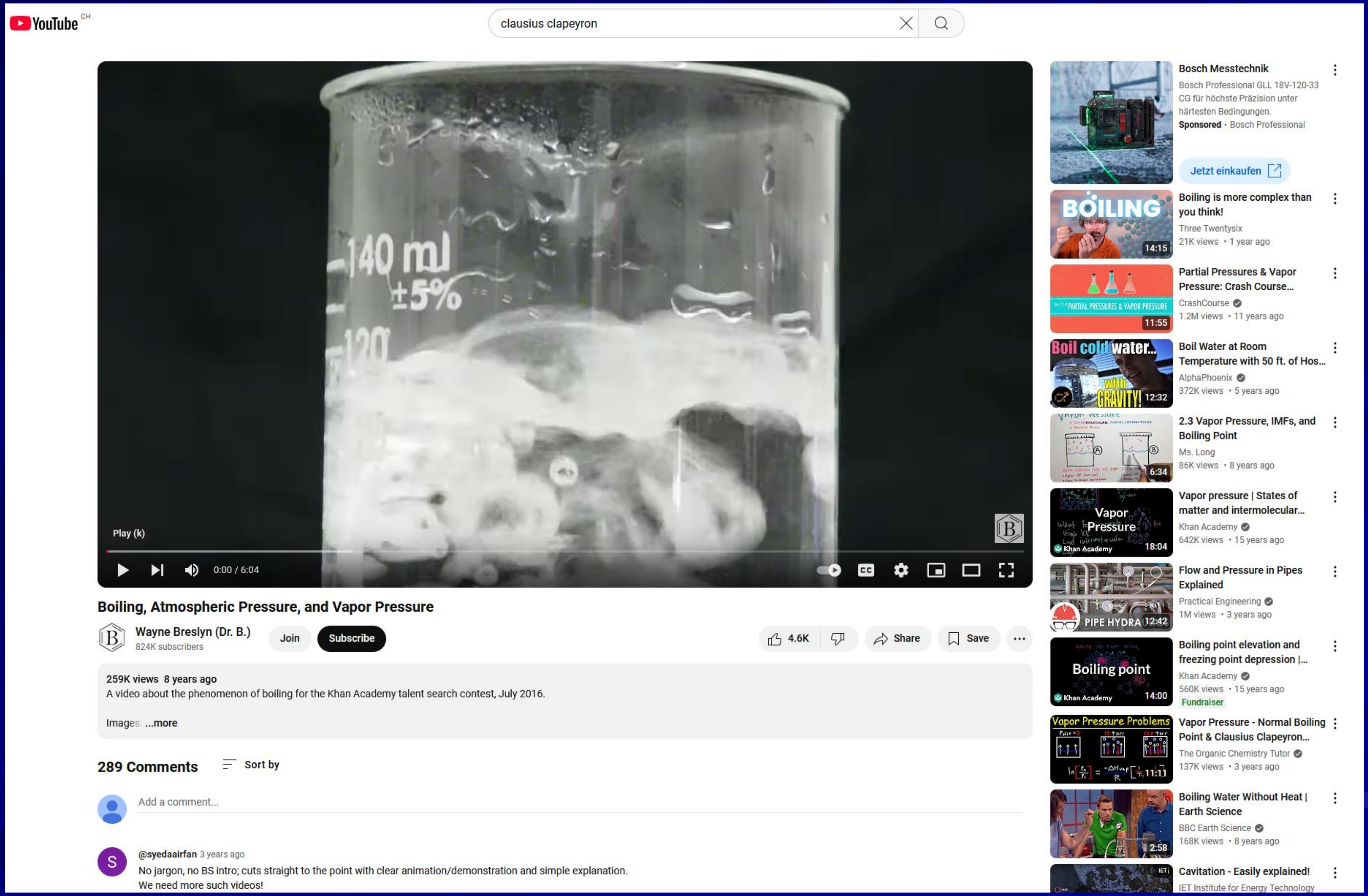
Mol fraction of "j" in solution

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.

Thermondyamics Applications:

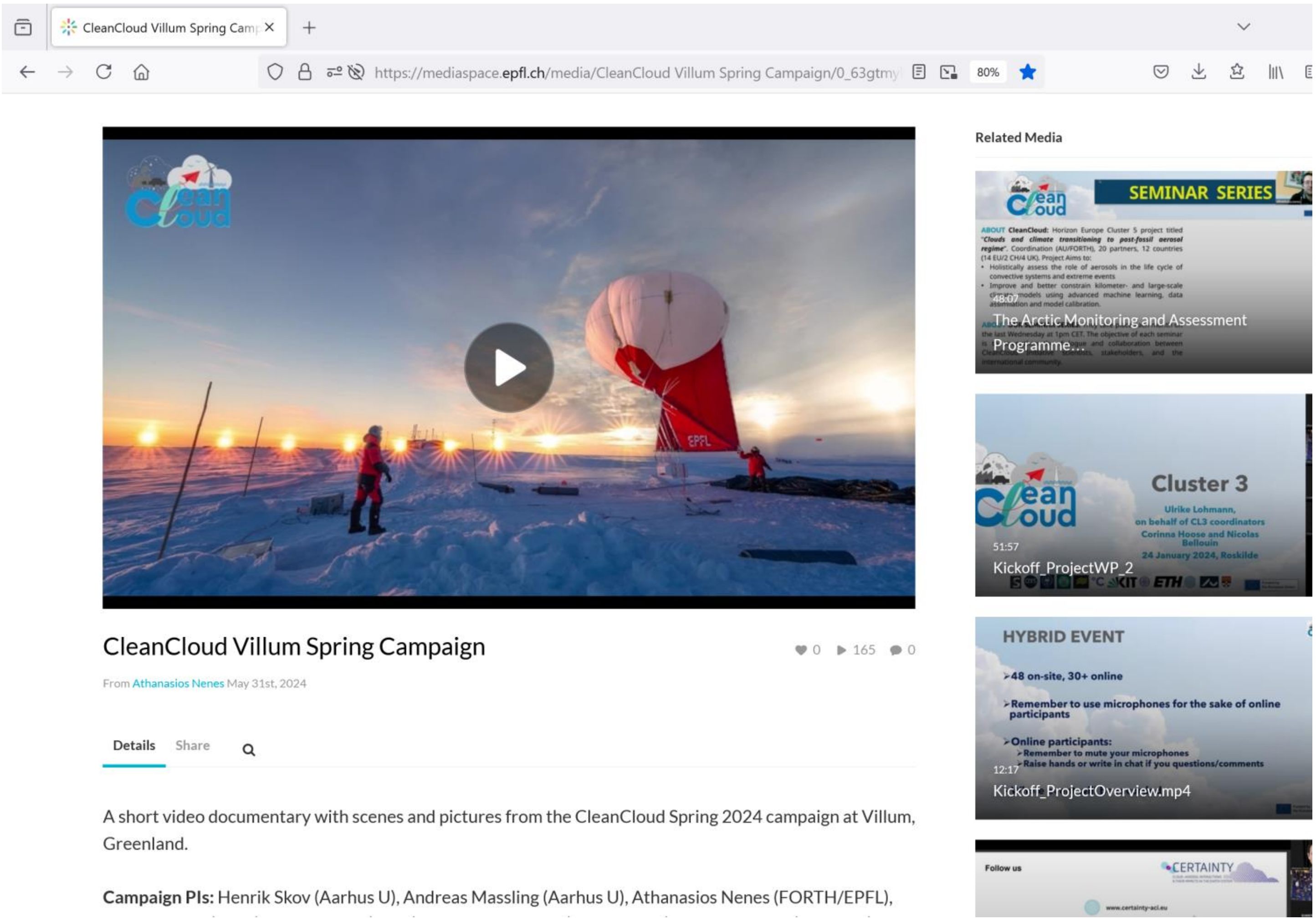
- Clausius-Clapeyron Equation
- Humidity Variables

A nice video on boling and vapor pressure



https://www.youtube.com/watch?v=Ag4lLUXKuSM

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



https://mediaspace.epfl.ch/media/CleanCloud%20Villum%20Spring%20Campaign/0_63gtmyl6