

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).

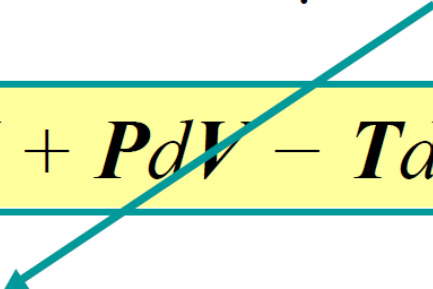
Gibbs Free Energy " G " is perfectly suited for this.

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

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

Changes in G are then expressed as:

$$dG = dU + PdV - TdS + VdP - SdT$$



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,

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

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

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

At thermodynamic equilibrium, $dG = 0$

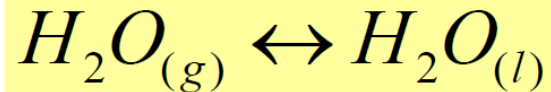
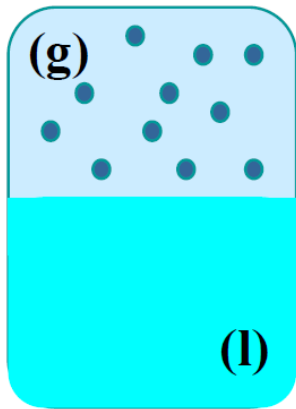
For constant P, T this means: $\mu_1 dn_1 + \dots + \mu_n dn_n = 0$

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

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

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^* ($P=1\text{atm}$ 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

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

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, 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.

Thermodynamics Applications:

- Clausius-Clapeyron Equation
 - Humidity Variables

A nice video on boiling and vapor pressure

YouTube CH

clausius clapeyron

Play (k)

0:00 / 6:04

Boiling, Atmospheric Pressure, and Vapor Pressure

 Wayne Breslyn (Dr. B.)
824K subscribers

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259K views · 8 years ago
A video about the phenomenon of boiling for the Khan Academy talent search contest, July 2016.

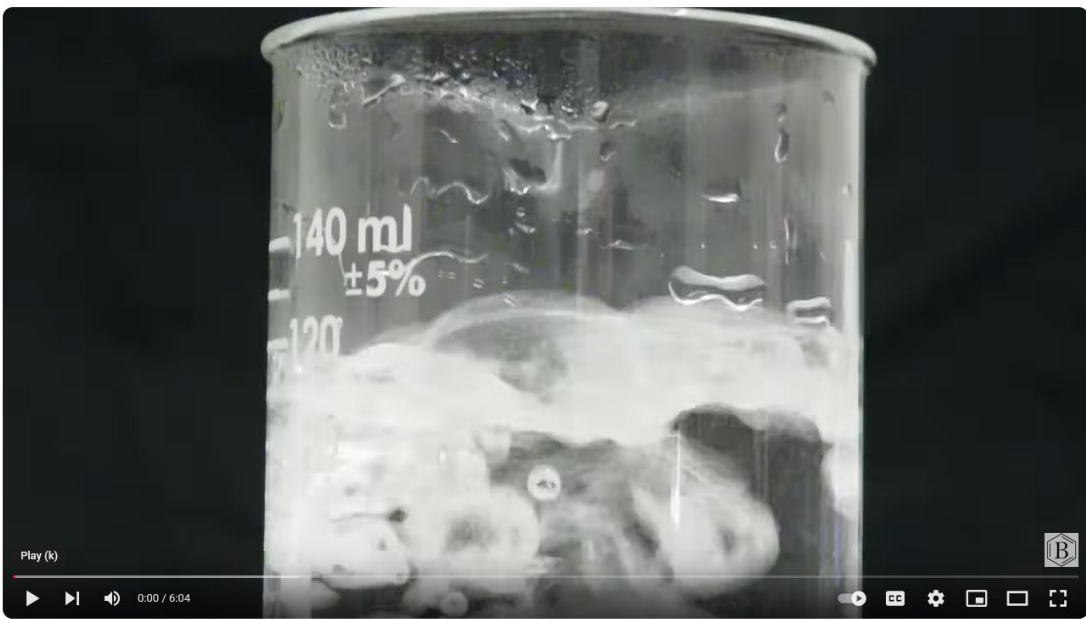
Images ...more

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 @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!

Boiling, Atmospheric Pressure, and Vapor Pressure



Boiling, Atmospheric Pressure, and Vapor Pressure

 Bosch Messtechnik
Bosch Professional GLL 18V-120-33
CG für höchste Präzision unter härtesten Bedingungen.
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 Boiling is more complex than you think!
Three TwentySix
21K views · 1 year ago

 Partial Pressures & Vapor Pressure: Crash Course...
CrashCourse
1.2M views · 11 years ago

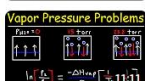
 Boil cold water...
AlphaPhoenix
372K views · 5 years ago

 2.3 Vapor Pressure, IMFs, and Boiling Point
Ms. Long
86K views · 8 years ago

 Vapor Pressure | States of matter and intermolecular...
Khan Academy
642K views · 15 years ago

 Flow and Pressure in Pipes Explained
Practical Engineering
1M views · 3 years ago

 Boiling point elevation and freezing point depression...
Khan Academy
560K views · 15 years ago

 Vapor Pressure Problems
The Organic Chemistry Tutor
137K views · 3 years ago

 Boiling Water Without Heat | Earth Science
BBC Earth Science
168K views · 8 years ago

 Cavitation - Easily explained!
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 Camp

https://mediaspace.epfl.ch/media/CleanCloud Villum Spring Campaign/0_63gtmyl6 80%



CleanCloud Villum Spring Campaign 0 165 0

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

CleanCloud SEMINAR SERIES

ABOUT CleanCloud: Horizon Europe Cluster 3 project titled "Clouds and climate: transitioning to post-fossil aerosol regime". Coordination (AUFORTH), 20 partners, 12 countries (14 EU2 CH4 UK). Project Aims to:

- Historically assess the role of aerosols in the life cycle of convective systems and extreme events
- Improve and better constrain kilometer- and large-scale models using advanced machine learning, data assimilation and model calibration.

The Arctic Monitoring and Assessment Programme...

Cluster 3

Ulrike Lohmann,
on behalf of CL3 coordinators
Corinna Hoppe and Nicolas Bellouin

51:57
Kickoff_ProjectWP_2

HYBRID EVENT

- > 48 on-site, 30+ online
- > Remember to use microphones for the sake of online participants
- > Online participants:
 - > Remember to mute your microphones
 - > Raise hands or write in chat if you questions/comments

12:17
Kickoff_ProjectOverview.mp4

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www.certainty-ec.eu

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