Thermodynamics of Earth systems

Lecture 6:

Entropy, the Second Law of Thermodynamics (continued)

Material covered in Lecture

Part 2: Framework

Entropy and the 2nd law

- Entropy: reversible and irreversible processes; Clausius inequality; Boltzmann-Gibbs statistical picture of entropy
- Heat engines, Carnot Cycle and the maximum efficiency
- Applications of heat engines and Carnot Efficiency to atmosphere, ocean and deep earth
- 2nd Law of thermodynamics
- First and second laws combined; Energy functions (Gibbs and Helmholz)

Other

- Energy functions; Maxwell Equations
- Definition of Thermodynamic Equilibrium (single component system, multicomponent system).

Phase Equilibria

- Gibbs phase rule: thermodynamic degrees of freedom, phases and components
- Energy in phase changes and chemical reactions

Thermodynamic relationships

Euler's relationship : $du = M\,dx + N\,dy$
and du is an exact differential, Then

$$\frac{\partial M}{\partial y} = \frac{\partial N}{\partial x}$$

Maxwell's relations

So: $du = -p\,dv + T\,ds \Rightarrow \frac{\partial(-p)}{\partial s} = \left(\frac{\partial T}{\partial v}\right)$

$dh = v\,dp + T\,ds \Rightarrow \left(\frac{\partial T}{\partial p}\right) = \left(\frac{\partial v}{\partial s}\right)$

$da = -p\,dv - s\,dT \Rightarrow \frac{\partial(-s)}{\partial v} = \frac{\partial(-p)}{\partial T}$

$dg = v\,dp - s\,dT \Rightarrow \frac{\partial(-s)}{\partial p} = \frac{\partial v}{\partial T}$

Thermodynamic relationships

Also, from the definition of equilibrium:

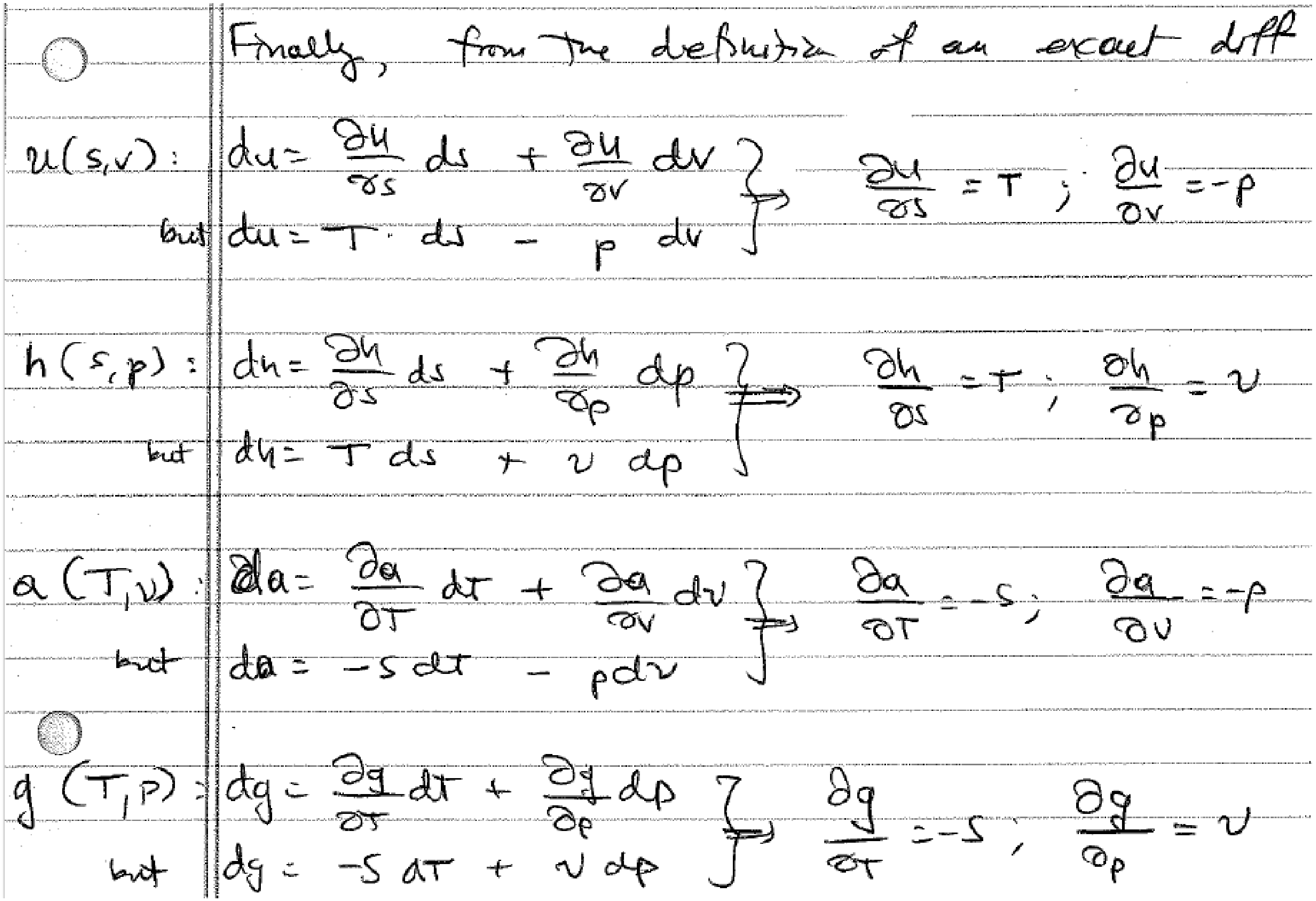
$$du = 0 = T\,ds - p\,dv \Rightarrow \left(\frac{\partial s}{\partial v}\right)_{u=\text{const}} = \frac{p}{T}$$

$$dh = 0 = T\,ds + v\,dp \Rightarrow \left(\frac{\partial s}{\partial p}\right)_{h=\text{const}} = -\frac{v}{T}$$

$$da = 0 = -s\,dT - p\,dv \Rightarrow \left(\frac{\partial v}{\partial T}\right)_{a=\text{const}} = -\frac{s}{p}$$

$$dg = 0 = -s\,dT + v\,dp \Rightarrow \left(\frac{\partial p}{\partial T}\right)_{g=\text{const}} = -\frac{s}{v}$$

Thermodynamic relationships



Finally, from the definition of an exact diff

$$u(s,v):\quad \left.\begin{aligned} du &= \frac{\partial u}{\partial s}\,ds + \frac{\partial u}{\partial v}\,dv \\ \text{but}\quad du &= T\,ds - p\,dv \end{aligned}\right\} \Rightarrow \frac{\partial u}{\partial s} = T\;;\quad \frac{\partial u}{\partial v} = -p$$

$$h(s,p):\quad \left.\begin{aligned} dh &= \frac{\partial h}{\partial s}\,ds + \frac{\partial h}{\partial p}\,dp \\ \text{but}\quad dh &= T\,ds + v\,dp \end{aligned}\right\} \Rightarrow \frac{\partial h}{\partial s} = T\;;\quad \frac{\partial h}{\partial p} = v$$

$$a(T,v):\quad \left.\begin{aligned} da &= \frac{\partial a}{\partial T}\,dT + \frac{\partial a}{\partial v}\,dv \\ \text{but}\quad da &= -s\,dT - p\,dv \end{aligned}\right\} \Rightarrow \frac{\partial a}{\partial T} = -s\;;\quad \frac{\partial a}{\partial v} = -p$$

$$g(T,p):\quad \left.\begin{aligned} dg &= \frac{\partial g}{\partial T}\,dT + \frac{\partial g}{\partial p}\,dp \\ \text{but}\quad dg &= -s\,dT + v\,dp \end{aligned}\right\} \Rightarrow \frac{\partial g}{\partial T} = -s\;,\quad \frac{\partial g}{\partial p} = v$$

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

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

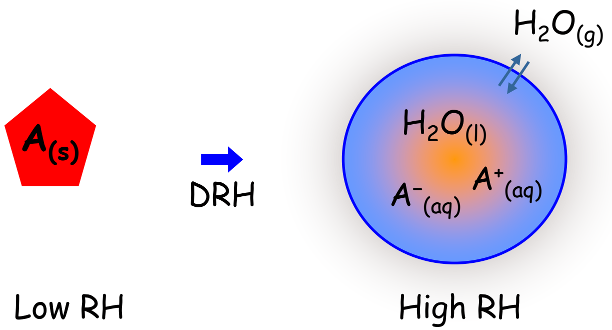
Changes in G are then expressed as:

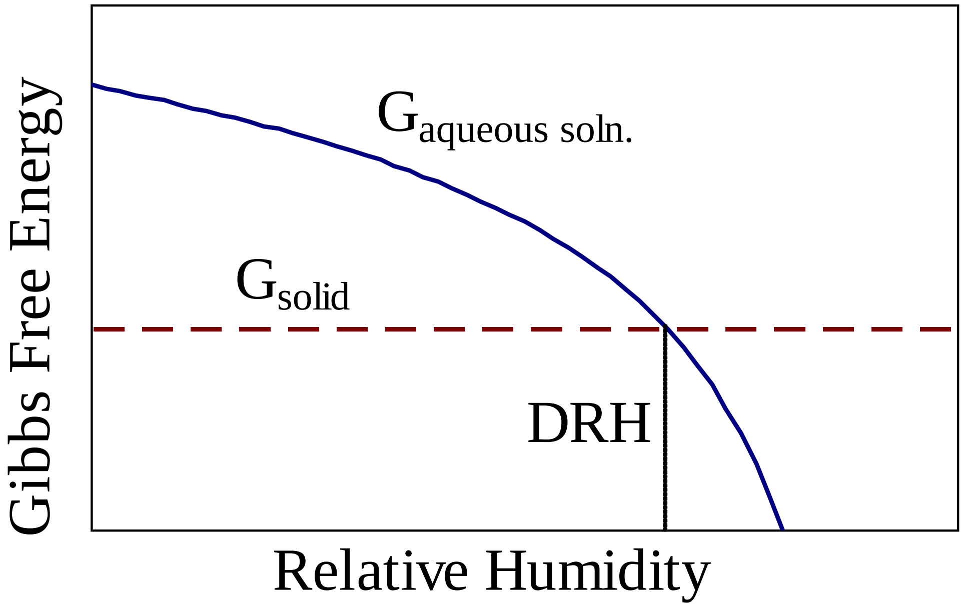
$$dG = \boxed{dU + PdV - TdS} + VdP - SdT$$

Zero from combined First & Second Law

How useful is this criterion? Very!

Deliquescence Relative Humidity (DRH): RH at which an aerosol transitions from a solid to an aqueous solution





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**

How useful is this relationship?

Formulating Thermodynamic Equilibrium

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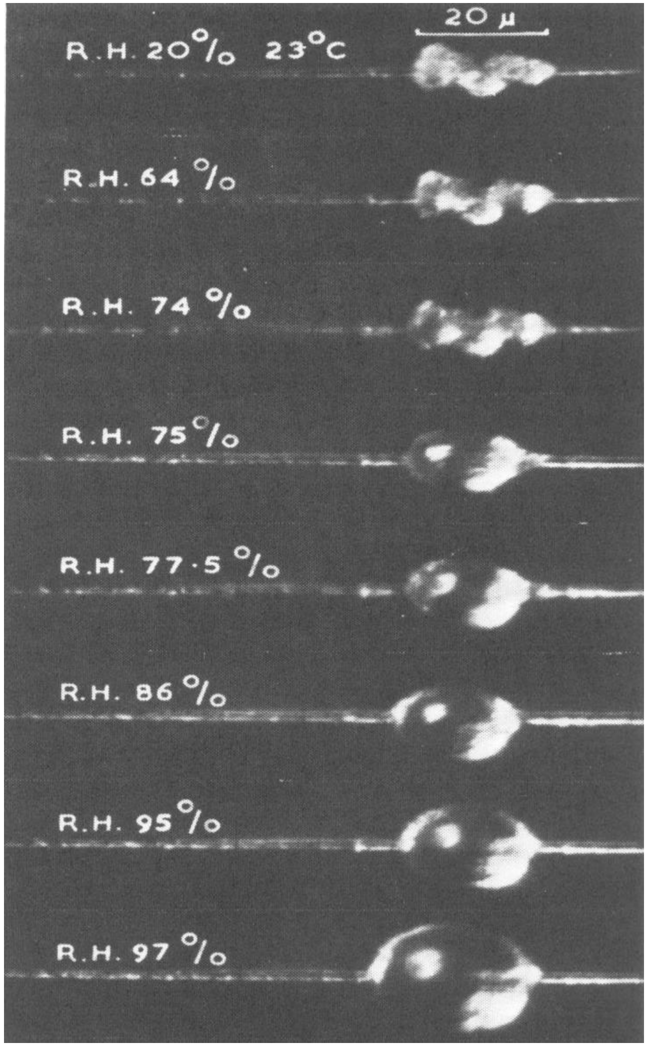
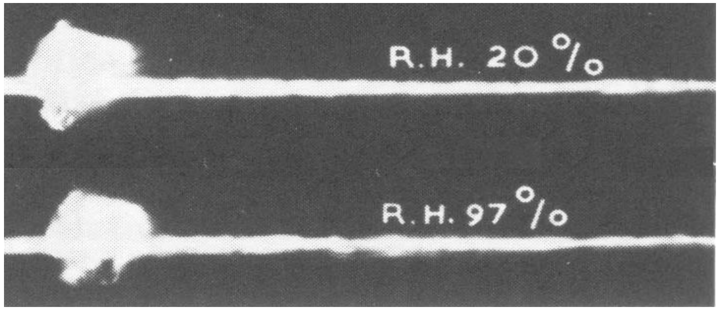
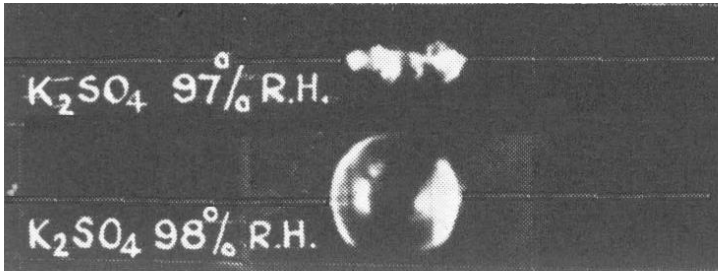
Deliquescence: Some examples



Sea Salt Particle: DRH ~ 75%



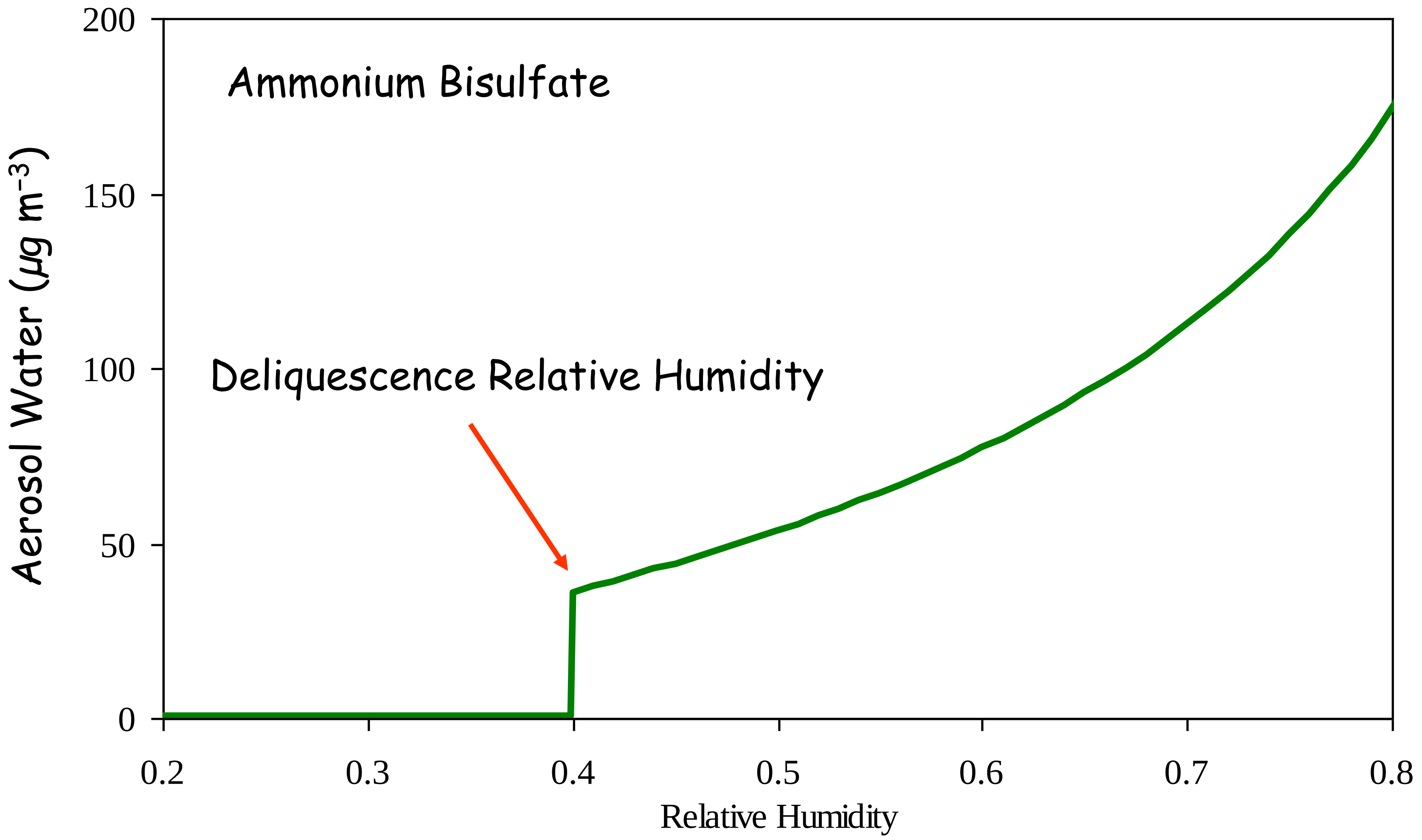
Dust Particle: no DRH



K_2SO_4 particle: DRH = 98%

Source: Twomey (1977)

Aerosol water uptake: deliquescence



Formulating Thermodynamic Equilibrium

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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:

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

$$\left(\frac{\partial G}{\partial n_1}\right),\ldots,\left(\frac{\partial G}{\partial n_n}\right)$$

are the **chemical potentials** $\mu_1, \ldots, \mu_n$

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 aerosols: Dissolution of ammonium sulfate in water.

Chemical Equilibrium: Example

$$2NH_{4(aq)}^{+} + SO_{4(aq)}^{2-} \longleftrightarrow (NH_4)_2SO_{4(s)}$$

At equilibrium (P,T=const):

$$\mu_{NH_4^+}dn_{NH_4^+} + \mu_{SO_4^{2-}}dn_{SO_4^{2-}} + \mu_{(NH_4)_2SO_4}dn_{(NH_4)_2SO_4} = 0$$

From stoichiometry: $dn_{NH_4^+} = 2dn_{SO_4^{2-}} = -2dn_{(NH_4)_2SO_4}$

So: $(-2\mu_{NH_4^+} - \mu_{SO_4^{2-}} + \mu_{(NH_4)_2SO_4})dn_{(NH_4)_2SO_4} = 0$

Or simply: $-2\mu_{NH_4^+} - \mu_{SO_4^{2-}} + \mu_{(NH_4)_2SO_4} = 0$

Chemical Equilibrium: General Reaction

$$a\mathrm{A} + b\mathrm{B} \longleftrightarrow c\mathrm{C} + d\mathrm{D}$$

At equilibrium, *and* constant P, T :

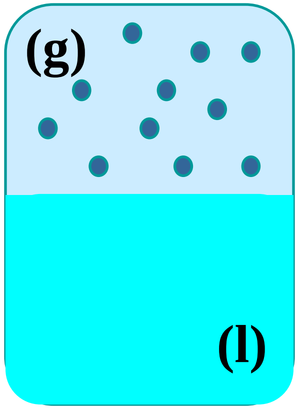
$$d\mu_D + c\mu_C - a\mu_A - b\mu_B = 0$$

$$\sum_i v_i \mu_i = 0$$

i.e., chemical potential of the reactants equals chemical potential of the products

Chemical Equilibrium: Phase Equilibria

Even 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

What is Thermodynamic Equilibrium?

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

This state is characterized by:

- **Thermal** equilibrium

  dT=0, T=constant everywhere

- **Mechanical** equilibrium

  dP=0, P=constant everywhere

- **Diffusional** equilibrium

  $\mu_i^g = \mu_i^l$ ***a compound i between phases shares the same chemical potential.***

Some things more about G

G however is also the sum of its partial constituents. For constant T, P:

$G = \sum g_i n_i$ ← # of moles of substance "i".

↑ GFE per unit mol of substance "i"

and, since we showed already that $\mu_i = g_i$

$$\boxed{G = \sum \mu_i n_i \qquad \text{const } T, P.}$$

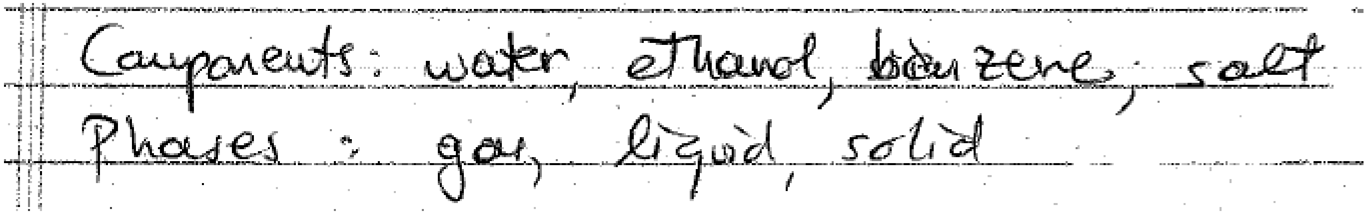
Total GFE of the system is given by the sum of the chemical potentials × # of moles of each constituent.

Is the number of species limited?

Yes. It's given by the Gibbs Phase Rule

$$F = C - P + 2$$

- F: number of independent variables
- P: number of phases
- C: Number of compounds



Components: water, ethanol, benzene, salt

Phases: gas, liquid, solid

e.g., pure water in equilibrium with its vapor:
$C=1$, $P=2$ so $F=1$ (one independent variable, e.g. T)

e.g., a water/salt mixture in equilibrium with its vapor:
$C=2$, $P=2$ so $F=2$ (two independent variables, e.g. $T + n_{NaCl}$)