EPFL

Thermodynamics of Earth systems

Lecture 7:
Gibbs Free Energy, Chemical Potential and their applications

Material covered in Lecture

Part 2: Framework

Phase Equilibria

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

Physical chemistry of water solutions – solution thermodynamics

- Activity and chemical potential
- Ideal solutions – Real solutions
- Equilibrium constants
- Some examples from aerosols (deliquescence and water update).

From Lecture 6

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

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

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

$G = \sum \mu_i n_i$ cost T, P.

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.***

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

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

per mol

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

$$\mu(P,T) - \mu^* = -\int_{298.15}^{T} sdT + \int_{1atm}^{P} vdP$$

$\mu\,(P,T)$ 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, $v_i = RT/P_i$

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

Partial pressure of gas "i"

Mol fraction of "i" in gas phase

In ideal solutions, μ for each component j:

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

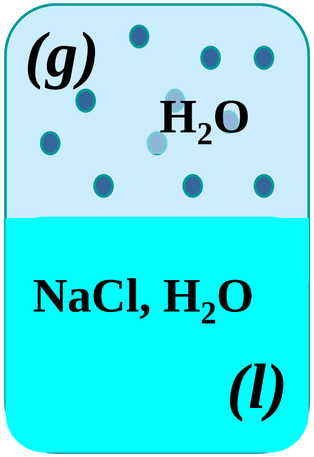
Mol fraction of "j" in solution

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.

Chemical Potential: ideal solutions

What is μ^* for each component in ideal solutions?

Ideal solution of NaCl in $H_2O_{(l)}$ in equilibrium with $H_2O_{(g)}$



$$\mu_{H_2O_{(l)}}(P, 298.15K) - \mu^*_{H_2O_{(l)}} = RT \ln x_{H_2O_{(l)}}$$

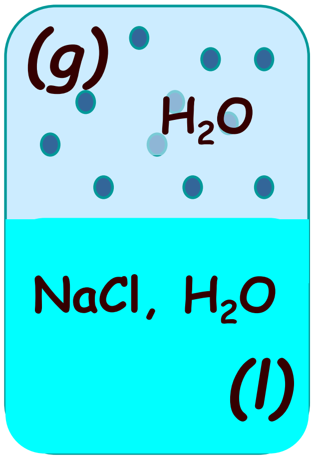
when $x_{H2O} \rightarrow 1$, you approach pure water, so

$$\mu_{H_2O_{(l)}}(P, 298.15K) = \mu^*_{H_2O_{(l)}}$$

So the *reference chemical potential* is the chemical potential of **pure liquid water**.

Chemical Potential: Raoults Law

Ideal solution in $H_2O_{(l)}$ in equilibrium with $H_2O_{(g)}$



Looking at water vapor in the gas phase

$$\mu_{H_2O_{(g)}}(P, 298.15K) - \mu^*_{H_2O_{(g)}} = RT \ln P_{H_2O_{(g)}}$$

when $x_{H2O} \rightarrow 1$, you approach pure water,

$$\mu^*_{H_2O_{(l)}} = \mu^*_{H_2O_{(g)}} + RT \ln P_{sat}(T)$$

Saturation Vapor pressure

At equilibrium $\mu_{H_2O_{(g)}} = \mu_{H_2O_{(l)}}$ which with the above leads to

$$P_{H_2O_{(g)}} = P_{sat}(T) x_{H_2O_{(l)}}$$

Raoult's Law for ideal solutions

Raoult's Law: non-electrolytes

How about non-ideal (e.g.,almost all) solutions?

Replace mol fraction with ***activitity*** of j in the expression of chemical potential

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

← Activity of "j" in solution

Where $a_j = \gamma_j x_j$ with γ_j known as the "activity coefficient"

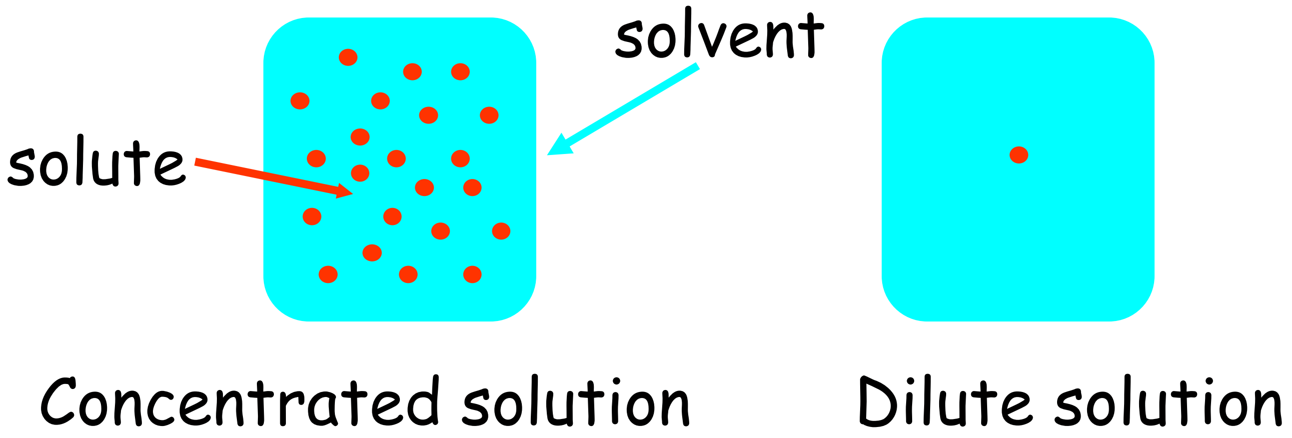
At equilibrium $\mu_{H_2O_{(g)}} = \mu_{H_2O_{(l)}}$ which with the above leads to

$$P_{H_2O_{(g)}} = P_{sat}(T)\gamma_{H_2O_{(l)}} x_{H_2O_{(l)}}$$

Modified Raoult's Law

Activity coefficients: properties

As a solution becomes more dilute in solute, the solvent molecules "feel" less and less of their presence.



Solution tends to ideal behavior at "infinite" dilution, so:

$$\gamma_{H_2O_{(l)}} x_{H_2O_{(l)}} \rightarrow x_{H_2O_{(l)}} \quad \text{as} \quad x_{H_2O_{(l)}} \rightarrow 1 \quad \text{or}$$

$$\gamma_{H_2O_{(l)}} \rightarrow 1 \quad \text{as} \quad x_{H_2O_{(l)}} \rightarrow 1$$

Activity: electrolytes

Activitity of electrolyte i that dissociates in an aqueous solution producing ν_+ cations and ν_- anions can be written in terms of a mean activity coefficient γ_i

$$a_i = \gamma_i^{(\nu_+ + \nu_-)} m_+^{\nu_+} m_-^{\nu_-}$$

m_+, m_- are the molality of the cation and anion, respectively.

Example: activity of $(NH_4)_2SO_4$ in solution

$$a_{(NH_4)_2SO_4} = \gamma^3_{(NH_4)_2SO_4} m^2_{NH_4^+} m_{SO_4^{2-}}$$

Formulating the Equilibrium Constant

Start from "generic" chemical reaction

$$aA + bB \longleftrightarrow cC + dD$$

Statement of chemical equilibrium

$$\sum_i \nu_i \mu_i = 0 \qquad \text{where} \qquad \mu_i = \mu_i^0(T) + RT\ln a_i$$

Expanding chemical potentials gives $\sum_i \nu_i \mu_i^0 + RT \sum_i \nu_i \ln a_i = 0$

After some rearrangement:

$$\frac{a_D^d a_C^c}{a_A^a a_B^b} = \exp\left(-\frac{d\nu_D + c\nu_C - a\nu_A - b\nu_B}{RT} \right)$$

Equilibrium constant $K(T)$

Equilibrium Constant — Example

Dissolving $(NH_4)_2SO_4$ in water until saturation

$$2NH^{+}_{4(aq)} + SO^{2-}_{4(aq)} \longleftrightarrow (NH_4)_2SO_{4(s)}$$

Formulation of equilibrium constant

$$\frac{a^2_{NH_4^+} a_{SO_4^{2-}}}{a_{(NH_4)_2SO_4}} = \exp\left(\frac{\mu^0_{(NH_4)_2SO_4} - 2\mu^0_{NH_4^+} - \mu^0_{SO_4^{2-}}}{RT}\right) = K(T)$$

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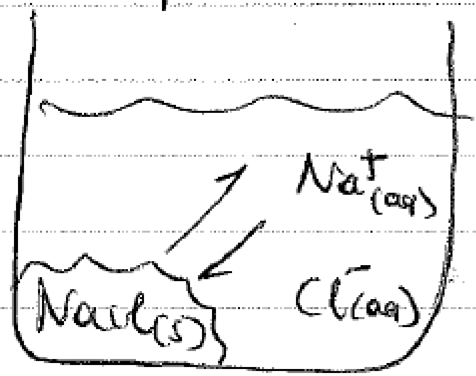
Final form $\gamma^3_{(NH_4)_2SO_4} m^2_{NH_4^+} m_{SO_4^{2-}} = K(T)$

Applications to real problems

Example

Sea salt in solution being in equilibrium with a solid precipitate. Calulate relationship at equilibrium.



$$NaCl_{(s)} \rightleftharpoons Na^{+}_{(aq)} + Cl^{-}_{(aq)}$$

See "LectureNotes05.pdf"

Applications to real problems

Another example

$$2NH_{3(g)} + H_2SO_{4(s)} \rightleftarrows (NH_4)_2SO_{4(s)}$$

Recap:

$$\mu_{gas} = \mu^0_{gas}(T) + RT \ln p_i$$

See "LectureNotes05.pdf"