

C8863 Free Energy Calculations

Lesson 2 Chemical Potential

JS/2022 Present Form of Teaching: Rev1

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Overview

macroworld

states

(thermodynamic properties, G, T,...)

phenomenological thermodynamics

equilibrium (equilibrium constant)

kinetics (rate constant)

free energy

(Gibbs/Heimholtz)

partition function

statistical thermodynamics

microstates

(mechanical properties, E)

microstate \neq microworld

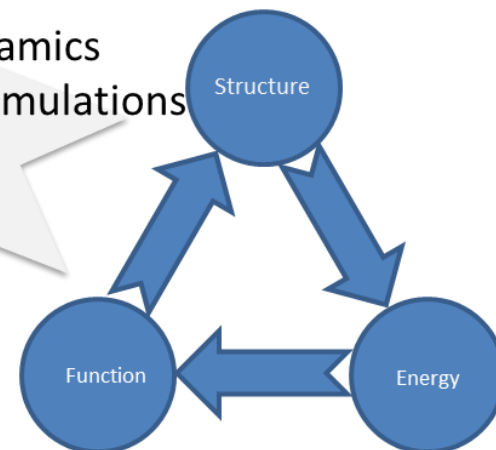
microworld

Description levels (model chemistry):

- quantum mechanics
 - semiempirical methods
 - ab initio methods
 - post-HF methods
 - DFT methods
- molecular mechanics
- coarse-grained mechanics

Simulations:

- molecular dynamics
- Monte Carlo simulations
- docking
- ...



Chemical Mixture

The internal energy of closed system **without change in chemical composition** (recapitulation):

$$U(S, V) \quad dU = \left(\frac{\partial U}{\partial S} \right)_V dS + \left(\frac{\partial U}{\partial V} \right)_S dV \quad dU = TdS - pdV$$

state variables total differential fundamental thermodynamic relation

The internal energy of closed system **with change in chemical composition** needs an extension:

$$U(S, V, n_i) \quad dU = \left(\frac{\partial U}{\partial S} \right)_{V, n_i} dS + \left(\frac{\partial U}{\partial V} \right)_{S, n_i} dV + \sum_i \left(\frac{\partial U}{\partial n_i} \right)_{S, V, n_j \neq n_i} dn_i$$

composition of chemical mixture, molar amounts total differential

$$\left(\frac{\partial U}{\partial n_i} \right)_{S, V, n_j \neq n_i} = \mu_i$$

chemical potential

Chemical Mixture, cont.

fundamental thermodynamic relations (total) chemical potential

$$dU = TdS - pdV + \sum_i \mu_i dn_i \qquad \left(\frac{\partial U}{\partial n_i} \right)_{S,V,n_{j \neq i}} = \mu_i$$

The Legendre transform provides other fundamental relations:

$$dH = TdS + Vdp + \sum_i \mu_i dn_i \qquad \left(\frac{\partial H}{\partial n_i} \right)_{S,p,n_{j \neq i}} = \mu_i$$

$$dA = -SdT - pdV + \sum_i \mu_i dn_i \qquad \left(\frac{\partial A}{\partial n_i} \right)_{T,V,n_{j \neq i}} = \mu_i$$

$$dG = -SdT + Vdp + \sum_i \mu_i dn_i \qquad \left(\frac{\partial G}{\partial n_i} \right)_{T,p,n_{j \neq i}} = \mu_i$$

not convenient
definition due to
constant entropy
condition

equivalent definitions of (total) chemical potential

Total Chemical Potential

The abstract definition of chemical potential given previously, total change in free energy per extra mole of substance, is more specifically called **total chemical potential**.

If two locations have different total chemical potentials for a species, some of it may be due to potentials associated with "**external**" force fields (electric potential energy, gravitational potential energy, etc.), while the rest would be due to "**internal**" factors (density, temperature, etc.).

Therefore, the total chemical potential can be split into **internal chemical potential** and **external chemical potential**:

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{T,p,n_j \neq n_i} = \mu_{i,int} + \mu_{i,ext}$$

the external potential is the sum of electric potential, gravitational potential, etc.

In this course, we will consider only internal chemical potential.

https://en.wikipedia.org/wiki/Chemical_potential

Chemical Potential

In thermodynamics, the **chemical potential** of a species is the energy that can be absorbed or released due to a change of the particle number of the given species, *e.g.*, in a chemical reaction or phase transition.

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{T,p,n_j \neq n_i}$$

Chemical potential expresses the effort of the substance:

- to react with another substance
- to change its status
- to change its spatial distribution

Value of chemical potential:

- is related to the very nature of the substance
- is related to the environment (temperature, pressure, concentration, ...)
- **however, it is not related** to the nature of the substances with which it reacts or is transformed to

Chemical Potential of Ideal Gas

Consider the closed system with one component behaving as an ideal gas:

$$dG = -SdT + Vdp$$

$$pV = nRT$$

At constant temperature, the Gibbs energy change is:

$$dG = Vdp$$

Consider the pressure change ($p^0 \rightarrow p$), then the Gibbs energy change is:

$$G = G^0 + \int_{p^0}^p Vdp = G^0 + \int_{p^0}^p \frac{nRT}{p} dp = G^0 + nRT \ln \frac{p}{p^0}$$

Finally, differentiating with respect to molar amount, the following expression for the chemical potential is obtained:

$$\mu = \left(\frac{\partial G}{\partial n} \right)_{T,p} = \frac{\partial G^0}{\partial n} + RT \ln \frac{p}{p^0} = \mu^0 + RT \ln \frac{p}{p^0}$$

Ideal and Real Gas Mixtures

Ideal gas:

$$\mu_i = \mu_i^0 + RT \ln \frac{p_i}{p^0}$$

Real gas:

$$\mu_i = \mu_i^0 + RT \ln \frac{f_i}{p^0}$$

f - fugacity - effective pressure of the gas substance

Unification of two situations:

$$\mu_i = \mu_i^0 + RT \ln(a_i)$$

a - activity of substance

In chemical thermodynamics, an **activity** is a measure of the "effective concentration/pressure" of a species in a mixture, in the sense that the species' chemical potential depends on the activity of a real solution in the same way that it would depend on concentration for an ideal solution.

$$a_i = e^{\frac{\mu_i - \mu_i^0}{RT}}$$

$$a_i = \frac{f_i}{p^0} \approx \frac{p_i}{p^0}$$

https://en.wikipedia.org/wiki/Thermodynamic_activity

Ideal and Real Solutions

The chemical potential for a substance in ideal and real solutions can be described similarly as gas mixtures:

$$\mu_i = \mu_i^0 + RT \ln(a_i)$$

However, the activity is now expressed by concentrations:

$$a_i = \gamma_i \frac{c_i}{c^0} \approx \frac{c_i}{c^0}$$

activity coefficient

An **activity coefficient** is a factor used in thermodynamics to account for deviations from ideal behavior in a mixture of chemical substances.

https://en.wikipedia.org/wiki/Activity_coefficient

Pure Liquids and Solids

The pure liquids and solids have the chemical potential, which is a constant at constant temperature and pressure:

$$\mu_i = \mu_i^0$$

Then, the activity of pure solids and liquids is one.

$$a_i = 1 \quad \ln(1) = 0$$

$$\mu_i = \mu_i^0 + RT \ln(a_i)$$

$$\mu_i = \mu_i^0 + 0$$

Solvent in an ideal diluted solution can be approximated as a pure liquid. Thus, the solvent has activity one.

Reference State

- To work with the chemical potential, we need to define the **reference state**.
- The **choice** of the reference state is **arbitrary**.
- But once selected, it must be **the same for all compounds** considered in the reaction mixture or phase transition.

IUPAC recommends a conventional set of reference states, which are called **standard states** for general use.

$$\mu_i = \mu_i^0 + RT \ln \frac{f_i}{p^0}$$

↓

?

$$\mu_i = \mu_i^0 + RT \ln \frac{\gamma_i c_i}{c^0}$$

↓

?

Standard state (IUPAC):

$$p^0 = 100 \text{ kPa}$$

$$c^0 = 1 \text{ mol dm}^{-3} = 1 \text{ M}$$

we need some suitable choice of zero to properly reference all compounds.

Standard Chemical Potential

Standard chemical potential is the change in Gibbs energy that is associated with the formation of one mole of compound in the standard state.

The change of the Gibbs energy is most often expressed in the form of the **standard formation Gibbs energies**.

$$\mu_i^0 = \Delta G_{f,i}^0$$

Standard formation Gibbs energy is the change of Gibbs energy that corresponds to the formation of one mole of matter from **chemical elements in the standard state**.

Chemical elements in the standard state have zero formation Gibbs energy (this is the definition of the reference state).

Standard state (IUPAC):

$$p^0 = 100 \text{ kPa}$$

$$c^0 = 1 \text{ mol dm}^{-3} = 1 \text{ M}$$

https://en.wikipedia.org/wiki/Standard_state

Summary

- The chemical potential is the property of the compound.
- It express the ability of the compound to react with another substance, to change its status, or to change its spatial distribution.
- The standard chemical potential is the change in the Gibbs energy that is associated with the formation of one mole of compound in the standard state.
- At different conditions, the chemical potential is proportional to the standard chemical potential and the activity of the compound.
- The activity then express an effective amount in comparison to the standard state.

$$\mu_i = \mu_i^0 + RT \ln(a_i)$$

Recommended Literature

- Atkins, P. W. *Physical Chemistry*, 5. ed., repr. (with correct.); Oxford Univ. Press: Oxford, 1994.
- Bokshteĭn, B. S.; Mendeleev, M. I.; Srolovitz, D. J. *Thermodynamics and Kinetics in Materials Science: A Short Course*; Oxford University Press: New York, 2005.
- Dill, K. A.; Bromberg, S. *Molecular Driving Forces: Statistical Thermodynamics in Biology, Chemistry, Physics, and Nanoscience*, 2nd ed.; Garland Science: London ; New York, 2011.