

Lecture 10: 10.14.05 Chemical potentials and the Gibbs free energy

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Reading: Engel and Reid, Ch. 6.4.

Supplementary Reading: -

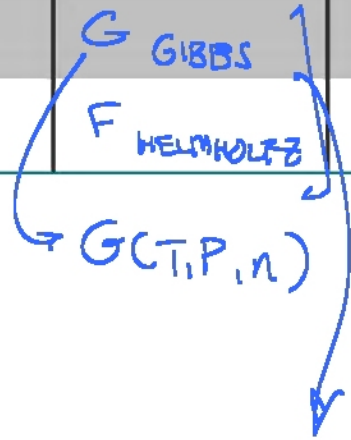
ANNOUNCEMENTS: - QUIZ 1 WILL BE RETURNED ON MONDAY
- PROBLEM SET 4 WILL BE POSTED ON MONDAY

 Last time

A summary of fundamental equations:

Experimental conditions	Key Fundamental Equation	At equilibrium, this function is...	Mathematical criterion for possible processes	Mathematical criterion for equilibrium
ISOLATED SYSTEMS	S	MAXIMIZED	$\Delta S \geq 0$	$dS = 0$
CONSTANT S	U	MINIMIZED	$\Delta U \leq 0$	$dU = 0$
CONSTANT T, P	G GIBBS	MINIMIZED	$\Delta G \leq 0$	$dG = 0$
CONSTANT T, V	F HELMHOLTZ	"	$\Delta F \leq 0$	$dF = 0$

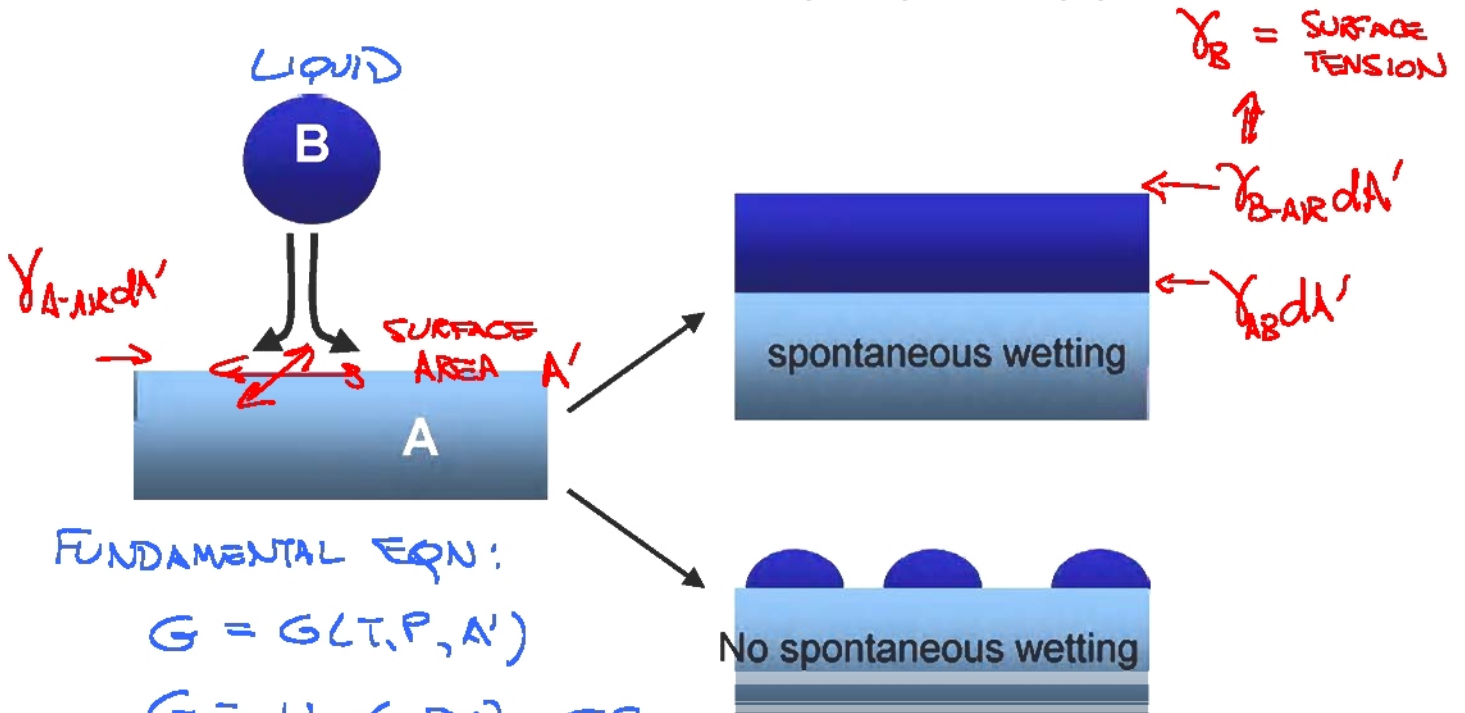
$$\Delta S = 0$$



THESE ARE EXAMINING SYSTEM ONLY!

Application Example: Predicting spontaneous wetting

CONSTANT TEMPERATURE, PRESSURE: Will liquid B spontaneously spread on solid A?



FUNDAMENTAL EQN:

$$G = G(T, P, A')$$

$$G \equiv U - (-PV) - TS$$

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

$$= \underbrace{\cancel{TdS} - \cancel{PdV} + \sum_{i \in I} \gamma_i dA'}_{dW_{OTHER}} + \cancel{PdV} + \cancel{VdP} - \cancel{TdS} - \cancel{SdT}$$

ALL INTERFACES

CONST T, P

$$dG = (\gamma_{AB}dA' + \gamma_{B-AIR}dA' - \gamma_{A-AIR}dA') < 0$$

$$(\gamma_{AB} + \gamma_B - \gamma_A)dA' < 0$$

FOR SPONTANEITY

$$\gamma_{AB} + \gamma_B - \gamma_A < 0$$

FOR SPONTANEITY

SPONTANEOUS B SPREADING

- Implications for:
 - Mixing of liquids
 - Formation of stable coatings
 - Designing biocompatible materials

Describing multi-phase/multi-component systems

- Before discussing chemical equilibrium in multi-phase/multi-component systems, we need to introduce some nomenclature used to describe such systems

Molar and Partial molar quantities

Molar quantities

- Rather than calculating total amounts for extensive quantities like internal energy and entropy, it is often convenient to define molar quantities for single-component systems- the amount of Y per mole of material. The molar value of some extensive quantity Y is defined as:

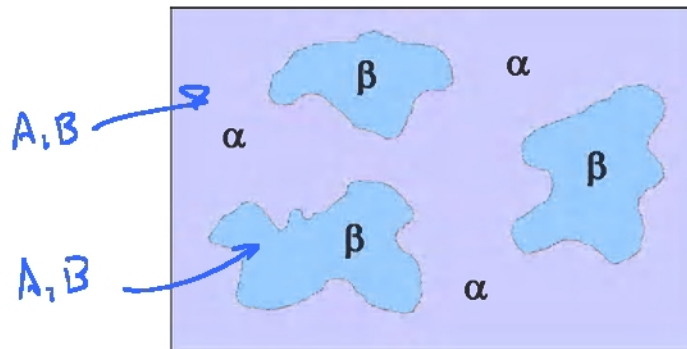
$$Y \rightarrow \text{MOLAR: } \bar{Y} = \frac{Y}{n_{\text{TOTAL}}} \quad \text{SINGLE COMPONENT SYSTEM}$$

$$\text{e.g. } \rightarrow S \rightarrow \bar{S} = \frac{S}{n_{\text{TOTAL}}} = \frac{J}{\text{K}\cdot\text{mole}}$$

- The units of molar quantities are thus the same as the parent variable *per mole*- internal energy is J/mole, entropy is J/mole·K.

Molar quantities for composition

- consider a two-component system (A and B atoms) that has 2 phases present, α and β :



- The composition of each phase is:

α phase: total moles of atoms in α phase:

$$n_{\text{TOTAL}}^{\alpha} = n_A^{\alpha} + n_B^{\alpha}$$

moles of A atoms in α phase:

$$n_A^{\alpha}$$

mole fraction of A atoms in α phase:

$$X_A^{\alpha} = \frac{n_A^{\alpha}}{n_{\text{TOTAL}}^{\alpha}} = \frac{n_A^{\alpha}}{n_A^{\alpha} + n_B^{\alpha}}$$

moles of B atoms in α phase:

$$n_B^{\alpha}$$

mole fraction of B atoms in α phase:

$$X_B^{\alpha} = \frac{n_B^{\alpha}}{n_{\text{TOTAL}}^{\alpha}}$$

$$\beta \text{ phase: } \begin{cases} X_A^\beta \equiv \frac{n_A^\beta}{n_{\text{TOTAL}}^\beta} = \frac{n_A^\beta}{n_A^\beta + n_B^\beta} \\ X_B^\beta \equiv \frac{n_B^\beta}{n_{\text{TOTAL}}^\beta} \end{cases}$$

- How do we describe the composition of the system as a whole? The convention is to use the average composition: The average composition is expressed as total mole fractions of A and B in the system.

AVE MOLE FRACTION OF A: $X_A \equiv \frac{n_{A, \text{TOTAL}}}{n_{\text{TOTAL}}} = \frac{n_A^\alpha + n_A^\beta}{n_A^\alpha + n_B^\alpha + n_A^\beta + n_B^\beta}$

$$X_B \equiv \frac{n_{B, \text{TOTAL}}}{n_{\text{TOTAL}}} = 1 - X_A$$

- The phase fractions f^α and f^β are the mole fraction of total atoms residing in each phase:

$$f^\alpha = \frac{n_{\text{TOTAL}}^\alpha}{n_{\text{TOTAL}}} = \frac{n_A^\alpha + n_B^\alpha}{n_A^\alpha + n_B^\alpha + n_A^\beta + n_B^\beta}$$

$$f^\beta = \frac{n_{\text{TOTAL}}^\beta}{n_{\text{TOTAL}}} = 1 - f^\alpha$$

- The last relationship is required since the sum of the phase fractions must be 1.

Partial molar quantities in multi-component systems

- Molar quantities are more complicated for a multi-component system. When multiple components are present, the question becomes, Y per mole of *what*? To handle this situation, we define partial molar quantities that define extensive variables per mole of each component. A general partial molar quantity is defined as:

$Y \rightarrow$ TOTAL VALUE \Rightarrow PARTIAL MOLAR VALUE

$$\bar{V}_i \equiv \left(\frac{\partial Y}{\partial n_i} \right)_{T, P, \text{OTHER } n}$$

COMPONENT

- Because Y depends on the amount n_A, n_B, n_C, \dots of moles of each component present, we define it as a partial derivative with respect to one of the components, while the numbers of all other

components are kept constant. The partial molar quantity is thus, in words, 'the amount Y changes upon addition of a mole of component i , while all other components are kept constant (and at constant temperature and pressure).' Note this last phrase that is part of the definition of partial molar quantities- the derivative is taken at *constant temperature and pressure*.

- Partial molar quantities \bar{Y}_i are related to the total quantity Y by:

$$Y = \sum_{i=1}^C n_i \bar{Y}_i = \sum_{i=1}^C n_i \left(\frac{\partial Y}{\partial n_i} \right)_{T, P, \text{OTHER } n}$$

- The usefulness of partial molar quantities can be seen if we consider the example of determining the partial molar volume of a multi-component system. If we have a single-component system, the molar volume is just:

Ⓐ $\bar{V} = \frac{V}{n_A} = \frac{V}{n_{\text{TOTAL}}}$
A MOLECULES

- But suppose we have a two-component system (with components A and B). A and B may have very different molecular volumes- thus addition of a mole of A to the system may have a very different effect on the total volume than addition of a mole of B . The partial molar volumes allow us to quantify these differences:

Ⓑ $\bar{V}_A = \left(\frac{\partial V}{\partial n_A} \right)_{T, P, n_B}$ $\bar{V}_B = \left(\frac{\partial V}{\partial n_B} \right)_{T, P, n_A}$

- This can be of course generalized to any number of components.

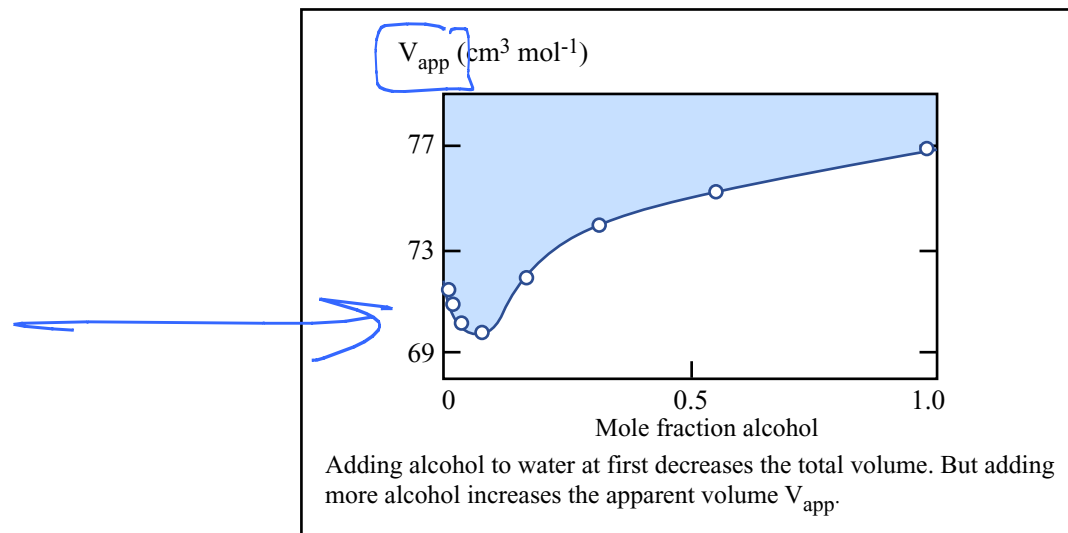


Figure by MIT OCW.

The partial molar free energy

- A very useful partial molar quantity is the partial molar free energy:

$$\rightarrow \bar{G}_i \equiv \left(\frac{\partial G}{\partial n_i} \right)_{T,P,n_{j \neq i}}$$

$$dG = -SdT + vdp + \underbrace{\sum_{i=1}^C N_i dn_i}_{\text{CHEMICAL WORK!}} = dG(T,P,n_i)$$

$$dG = \left(\frac{\partial G}{\partial T} \right)_{P,n} dT + \left(\frac{\partial G}{\partial P} \right)_{T,n} dP + \sum_{i=1}^C \left(\frac{\partial G}{\partial n_i} \right)_{T,P, \text{OTHER } n} dn_i$$

$$N_i = \left(\frac{\partial G}{\partial n_i} \right)_{T,P, \text{OTHER } n}$$

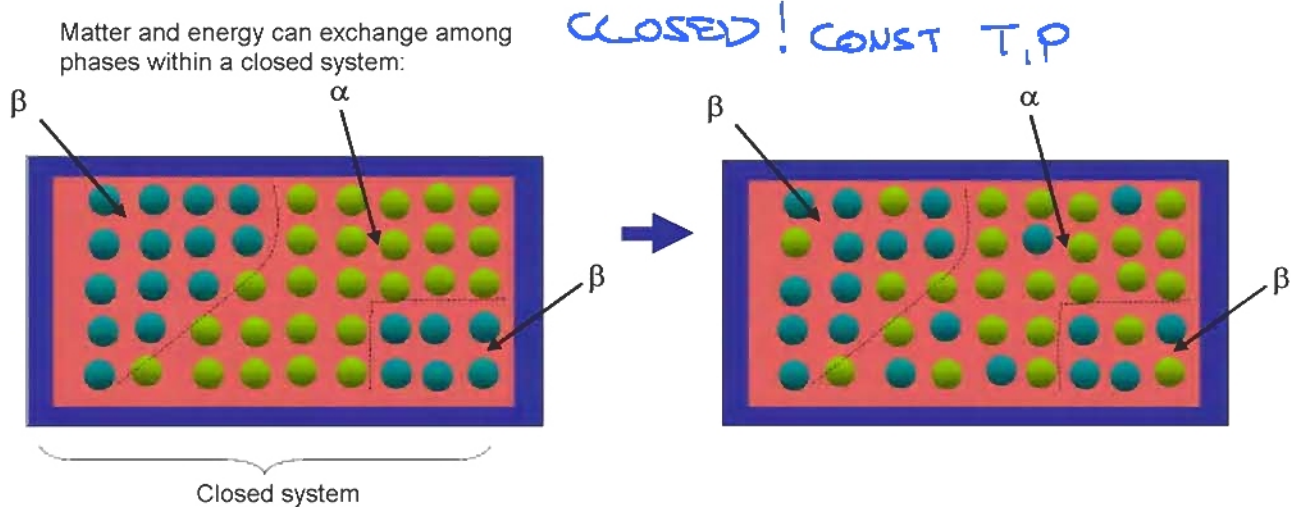
- Thus, the partial molar free energy is equal to the chemical potential. In words, the partial molar free energy is the change in total free energy that occurs per mole of component i added, with all other components constant (at constant T and P). The chemical potential of i measures the change in free energy caused by adding more of species i to the system.

$$\Rightarrow G = H - TS$$

Chemical Potentials in Multi-phase materials at equilibrium

Materials that rearrange their components to reach equilibrium

- We briefly discussed chemical work in Lecture 7- and how a multi-phase material that cannot exchange molecules with its surroundings can still alter its internal energy (or free energy) by rearranging the molecules within its phases, creating new phases, or eliminating phases that were present initially.



- These rearrangements are driven by the chemical potential, but we haven't yet examined what happens to the chemical potentials of different components at equilibrium, and we haven't yet shown how the value of the chemical potential dictates motion of molecules. Do molecules move from high chemical potential to low chemical potential, or vice versa? When is there no driving force for molecules to exchange between phases?
- In lectures 8 and 9 we saw how one can use the second law to predict the equilibrium values for temperature and pressure. **We can now perform a similar analysis to determine what the chemical potential should be in a closed multiphase system at equilibrium under conditions of constant temperature and pressure. We do this by applying the equilibrium condition $dG = 0$ under the constraint of conservation of matter:**

CONSTRAINTS: CLOSED

$$n_{A, TOTAL} = \text{CONSTANT}$$

$$n_A^\alpha + n_A^\beta = \text{CONSTANT}$$

$$dn_A^\alpha + dn_A^\beta = 0 \rightarrow dn_A^\alpha = -dn_A^\beta$$

$$n_{B, TOTAL} = \text{CONSTANT}$$

$$dn_B^\alpha = -dn_B^\beta$$

- Our equilibrium condition at constant T and P is $dG = 0$. If we combine this equilibrium criterion with the conservation of matter equations above, we can write the following:

EQUILIBRIUM: $dG = 0$

CONST T, P

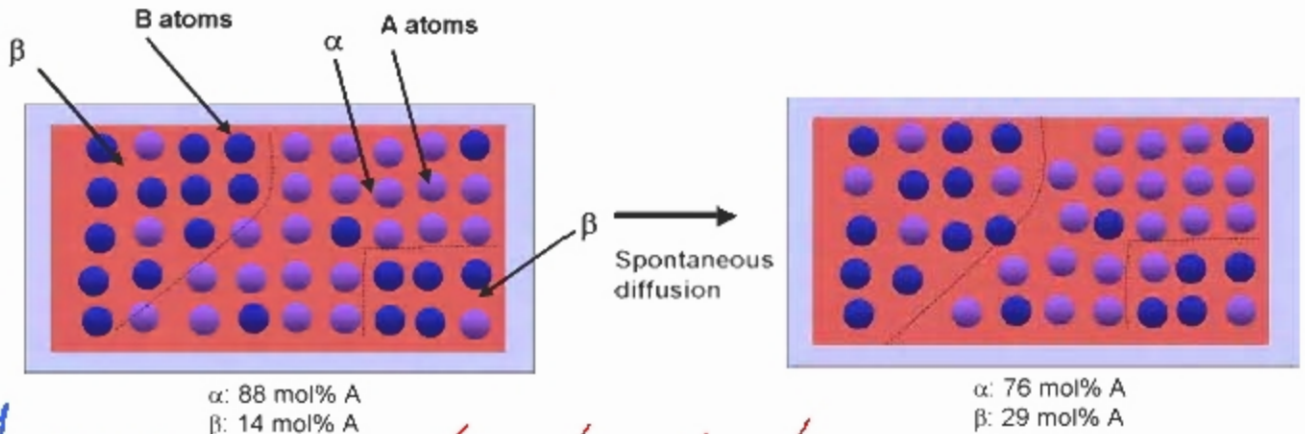
$$dG = -SdT + VdP + \sum_{i=1}^C \sum_{j=1}^P N_i^j dn_i^j$$

0 0

$$dG = \sum_{i=1}^C \sum_{j=1}^P N_i^j dn_i^j = 0 \text{ FOR EQUILIBRIUM}$$

- This expression expanded for the case illustrated above, of a two-component, two-phase system would be:

$$N_A^\alpha dn_A^\alpha + N_A^\beta dn_A^\beta + N_B^\alpha dn_B^\alpha + N_B^\beta dn_B^\beta = 0$$



APPLY CONSTRAINTS:

$$(N_A^\alpha - N_A^\beta) dn_A^\alpha + (N_B^\alpha - N_B^\beta) dn_B^\alpha = 0$$

BOTH TERMS MUST GO TO ZERO INDEPENDENTLY!

... REGARDLESS OF dn_A^α AND dn_B^α !

$$(N_A^\alpha - N_A^\beta) = 0 \quad (N_B^\alpha - N_B^\beta) = 0$$

AT EQUILIBRIUM:

$$\begin{aligned} N_A^\alpha &= N_A^\beta \\ N_B^\alpha &= N_B^\beta \end{aligned}$$

EQUALITY OF
CHEMICAL
POTENTIALS

MOLECULES MOVE TOWARD PHASE OF LOWEST CHEMICAL POTENTIAL!

- *At equilibrium, the chemical potential of a given component in the system must be equal in every phase. The chemical potential of one component does NOT necessarily equal that of another, different component.*

References

1. Dill, K. & Bromberg, S. *Molecular Driving Forces* (New York, 2003) 704 pp, QC311.5.D55 2003.