# MSE-204 Thermodynamics for Materials Science

## L3. MOLAR & PARTIAL MOLAR QUANTITIES

HOMOGENEOUS FUNCTIONS | EXTENSIVE & INTENSIVE VARIABLES | EXPLICIT EXPRESSIONS FOR U, H, A, G | GIBBS-DUHEM EQUATION | PARTIAL MOLAR QUANTITIES | MEASUREMENT OF PARTIAL MOLAR QUANTITIES

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# REMINDER FROM LAST WEEK

# THE FUNDAMENTAL EQUATIONS IN TERMS OF U, H, A, AND G & THE NATURAL VARIABLES OF EACH FUNCTION

$$dU = TdS - pdV \qquad dH = TdS + Vdp \qquad dA = -SdT - pdV \qquad dG = -SdT + Vdp$$

If you know the natural variables of a state function, you can define the derivative of this function by its partial derivative expression. Let's look at the partial derivatives of U, H, A, G with respect to their natural variables.

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

$$dH = \left(\frac{\partial H}{\partial S}\right)_{p,n_i} dS + \underset{V}{\overset{T}{\left(\frac{\partial H}{\partial p}\right)_{S,n_i}}} dp + \sum_i \overset{-p}{\boxed{\left(\frac{\partial H}{\partial n_i}\right)_{p,S} dn_i}}$$

$$dA = \overset{T}{\left(\frac{\partial A}{\partial T}\right)_{V,n_i}} dT + \left(\frac{\partial A}{\partial V}\right)_{T,n_i} dV + \sum_i \boxed{\left(\frac{\partial A}{\partial n_i}\right)_{V,T} dn_i}$$

$$dG = \underset{-S}{\overset{-S}{\left(\frac{\partial G}{\partial T}\right)_{p,n_i}}} dT + \underset{V}{\overset{-p}{\left(\frac{\partial G}{\partial p}\right)_{T,n_i}}} dp + \sum_i \boxed{\left(\frac{\partial G}{\partial n_i}\right)_{p,T} dn_i}$$

# THE CHEMICAL POTENTIAL

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

The chemical potential was introduced by J. Willard Gibbs and it is defined as:

$$\mu_i = \left(\frac{\partial \boldsymbol{U}}{\partial n_i}\right)_{\mathbf{S},\,\mathbf{V},\,nj\neq ni} = \left(\frac{\partial \boldsymbol{H}}{\partial n_i}\right)_{\boldsymbol{S},\,\boldsymbol{p},\,nj\neq ni} = \left(\frac{\partial \boldsymbol{A}}{\partial n_i}\right)_{\boldsymbol{T},\,\boldsymbol{V},\,nj\neq ni} = \left(\frac{\partial \boldsymbol{G}}{\partial n_i}\right)_{\boldsymbol{T},\,\mathbf{p},\,nj\neq ni}$$

$=$

The chemical potential has an important function, analogous to temperature and pressure. A difference in chemical potential may be regarded as the cause of a chemical reaction or a tendency of a substance to diffuse from one phase into another. The chemical potential is a kind of ”chemical pressure” and it is an intensive property of the system.

# SUMMARY: FUNDAMENTAL EQUATIONS OF STATE FOR OPEN SYSTEMS

The basic equations are:

$$dU = TdS - pdV + \sum_i \mu_i \, dn_i$$

$$dH = TdS + Vdp + \sum_i \mu_i \, dn_i$$

$$dA = -SdT - pdV + \sum_i \mu_i \, dn_i$$

$$dG = -SdT + Vdp + \sum_i \mu_i \, dn_i$$

From these, the following equations can be extracted:

$$T = \left(\frac{\partial U}{\partial S}\right)_{V,n_i} = \left(\frac{\partial H}{\partial S}\right)_{p,n_i}$$

$$p = -\left(\frac{\partial U}{\partial V}\right)_{S,n_i} = -\left(\frac{\partial A}{\partial V}\right)_{T,n_i}$$

$$S = -\left(\frac{\partial G}{\partial T}\right)_{p,n_i} = -\left(\frac{\partial A}{\partial T}\right)_{V,n_i}$$

$$V = \left(\frac{\partial G}{\partial p}\right)_{T,n_i} = \left(\frac{\partial H}{\partial p}\right)_{S,n_i}$$

# GIBBS-HELMHOLTZ EQUATIONS

By combining the previous identities with defining equations for A and G, further expressions can be obtained. Specifically, we will look into how the free energy of a system depends on temperature.

$$S = -\left(\frac{\partial G}{\partial T}\right)_{p,n_i} = -\left(\frac{\partial A}{\partial T}\right)_{V,n_i}$$

# CHANGE OF CHARACTERISTIC VARIABLES

One can change the characteristic variables of $U$, $H$, $A$, and $G$, according to what fits best the experiment. Below, we will change the characteristic variables of internal energy from $U=U(S, V, n_i)$ to variables that we can measure easier $U=U(T, V, n_i)$. We will do the transformation in a closed system.

$$dU = TdS - pdV$$

# MATHEMATICAL RELATIONS BETWEEN THE VARIOUS FUNCTIONS OF STATE: MAXWELL'S RELATIONS

An additional number of useful identities, know as Maxwell's relations, can be obtained by applying a theorem of the calculus concerning exact differentials (Euler's reciprocal relation). Maxwell's relations are relationships between partial derivatives.

$$\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x} = \frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right) = \frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right)$$

For example, let consider the internal energy:

# SUMMARY: IMPORTANT MAXWELL'S RELATIONS

$$\left(\frac{\partial T}{\partial V}\right)_{S,n_i} = -\left(\frac{\partial p}{\partial S}\right)_{V,n_i}$$

$$\left(\frac{\partial T}{\partial p}\right)_{S,n_i} = \left(\frac{\partial V}{\partial S}\right)_{p,n_i}$$

$$\left(\frac{\partial S}{\partial V}\right)_{T,n_i} = \left(\frac{\partial p}{\partial T}\right)_{V,n_i}$$

$$-\left(\frac{\partial S}{\partial p}\right)_{T,n_i} = \left(\frac{\partial V}{\partial T}\right)_{p,n_i}$$

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

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

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

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

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

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

$$\left(\frac{\partial \mu_i}{\partial n_j}\right)_{V,S,n_{k\neq j}} = \left(\frac{\partial \mu_j}{\partial n_i}\right)_{V,S,n_{k\neq i}}$$

# METHOD FOR CHOICE OF MAXWELL'S RELATIONS

Suppose you want to understand how the entropies of materials change as you squeeze them: $\left(\frac{\partial S}{\partial p}\right)_{T,n_i}$

First, identify what independent variables are needed.

Second, find the natural function of these variables.

Third, express the total deferential of the natural function.

Fourth, based on Euler's reciprocal relation, set equal the two cross derivatives you want.

The Maxwell's relation gives you a quantity you cannot measure $\left(\frac{\partial S}{\partial p}\right)_{T,n_i}$ from a quantity that is easy to measure $\left(\frac{\partial V}{\partial T}\right)_{p,n_i}$

# EXAMPLE: INTERNAL ENERGY (& ENTHALPY) OF IDEAL GAS

Earlier, we expressed the internal energy of a closed system using V and T as the characteristic variables:

$$dU = \left\{-p + T\left(\frac{\partial S}{\partial V}\right)_T\right\} dV + T\left(\frac{\partial S}{\partial T}\right)_V dT$$

Through Maxwell's relations we know that:

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$$

Therefore, for an ideal gas the variation of internal energy with respect to volume is:

## PURE SUBSTANCES

## MULTICOMPONENT (PRIOR)

## MULTICOMPONENT SYSTEMS AFTER MIXING

# DEFINITION OF HOMOGENEOUS FUNCTION

To proceed further with the analytical study of open systems, it is helpful to recall the mathematical properties of Euler's homogeneous functions.

A function F of the variables, $x_1, x_2, \ldots x_i$ is said to be a **homogeneous function of degree *n*** if:

A key property of a homogeneous function results if I take the derivative of lamda times $x_1$ over $x_1$

**The partial derivatives of a homogenous functions of degree n with respect to one of the variables are homogenous function of degree *n-1*.**

# ANOTHER IMPORTANT PROPERTY OF HOMOGENEOUS FUNCTION

Another interesting property of a homogeneous function is obtained by taking the derivative of both sides of the main equation with respect to lamda, then give lamda the value of 1:

This result shows that a homogeneous function of degree n can be expressed simply in terms of its partial derivatives with respect to its variables. This last relation is known as **Euler's identity.**

# EXTENSIVE THERMODYNAMIC FUNCTIONS ARE HOMOGENEOUS FUNCTIONS OF DEGREE 1

We consider a system where only one single homogeneous phase is present and that contains several species, with $n_i$ moles of species i. Any extensive variable X of such a system can be considered as a function of a number of other extensive and intensive properties. For example, the internal energy U can be considered as a function of V, S, the number of moles of each species, pressure, temperature and chemical potential.

*Experimental evidence teaches us that any extensive variable is a homogeneous function of degree 1 of other extensive variables of the system.*

# INTENSIVE THERMODYNAMIC FUNCTIONS ARE HOMOGENEOUS FUNCTIONS OF DEGREE 0

A direct consequence of the previous property is that any partial derivative of any extensive variable with respect to another extensive variable are intensive variables. We will indicate with a ***** superscript the variables relative to the system obtained after multiplying the extensive variables by a factor of lamda. Let’s see what this means. To do this we will evaluate the partial derivatives of **internal energy with respect to entropy**.

# INTENSIVE THERMODYNAMIC FUNCTIONS ARE HOMOGENEOUS FUNCTIONS OF DEGREE 0 (EXAMPLES)

We can perform a similar derivation of internal energy with respect to number of moles. We will then get:

Therefore, the chemical potentials of all components in a system are intensive variables:

Also, mole fractions are intensive variables:

# EXPLICIT RELATIONSHIP FOR U

In view of the mathematical properties of extensive variables, we can now obtain explicit expressions for some of the extensive thermodynamic functions. We will start by calculating the **partial derivatives with respect to lamda**.

# EXPLICIT RELATIONSHIPS FOR U, H, A, AND G

$$U = TS - pV + \sum_i \mu_i n_i$$

$$H = TS + \sum_i \mu_i n_i$$

$$A = -pV + \sum_i \mu_i n_i$$

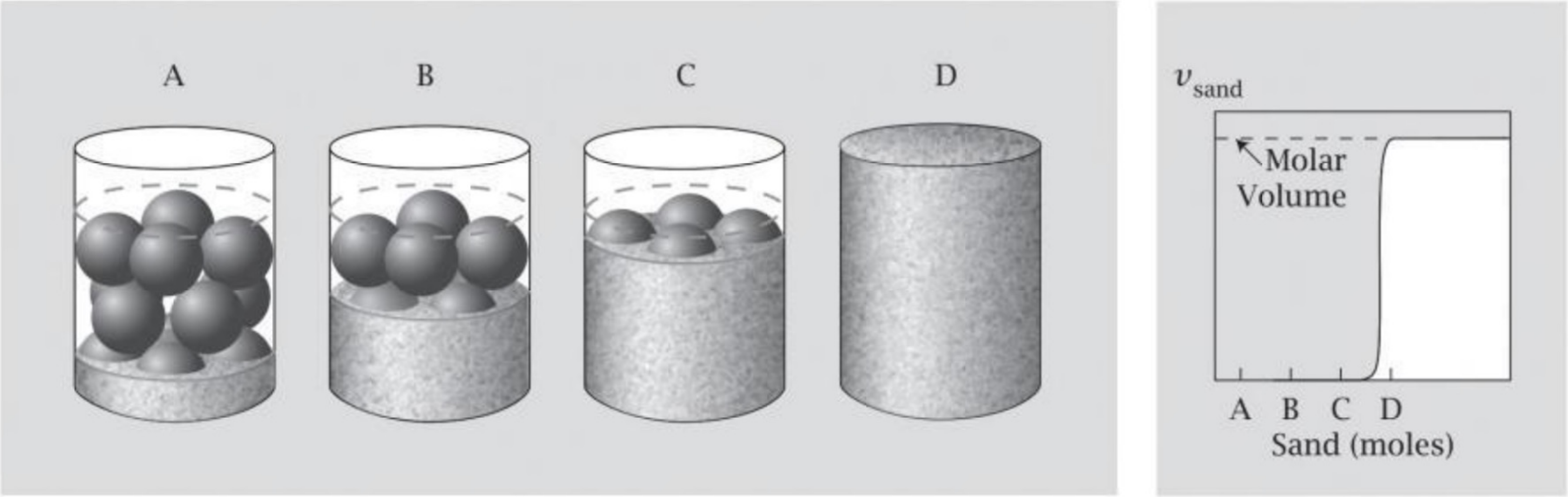
$$G = \sum_i \mu_i n_i$$

All of these derivations are significant because they really allow us to understand the meaning of U, H, A, and G.

# GIBBS-DUHEM EQUATION

If we now look at the two possible differential forms of G we get:

# MULTICOMPONENT SYSTEMS HAVE PARTIAL MOLAR QUANTITIES



Adding sand to a barrel of bowling balls indicates the idea of partial molar quantities. At first, the sand is at low "concentration", adding sand just fills in the holes between the bowling balls and does not increase the barrel volume that is needed to contain the bowling balls and sand. However, when all the space between the bowling balls is filled, adding sand does add volume. At the point D, the partial molar volume of the sand equals the molar volume.

# PARTIAL MOLAR QUANTITIES

It is of particular interest to consider extensive variables as functions of temperature and pressure, since then the only extensive variable needed to define the state of the system are the number of moles of the various components. We will consider X to be an extensive variable and take the derivative with respect to lamda:

# PARTIAL MOLAR QUANTITIES – EXAMPLES

$$U = \sum_i n_i \overline{U_i}$$

$$V = \sum_i n_i \overline{V_i}$$

$$S = \sum_i n_i \overline{S_i}$$

$$H = \sum_i n_i \overline{H_i}$$

$$A = \sum_i n_i \overline{A_i}$$

$$G = \sum_i n_i \overline{G_i}$$

$$C_p = \sum_i n_i \overline{C_{p,i}}$$

# RELATIONSHIP BETWEEN PARTIAL MOLAR QUANTITIES

The differentials of partial molar quantities are exact differentials. We will now write two expressions for the differential of X:

We can see that if G is selected as X, this gives us the Gibbs-Duhem equation. Importantly, for isothermal and isobaric conditions, we get:

# EXAMPLE | MIXTURE OF WATER & ETHANOL

Calculate the total volume before and after mixing of 1 mol of water with 100 mol of ethanol.

Data: molar volumes of pure water and ethanol are 18.00 and 58.00 cm$^3$/mol, respectively; the partial molar volume of water in a dilute solution of water in ethanol is 14.00 cm$^3$/mol.

# EXAMPLE | GRAPHICAL EXTRACTION OF PARTIAL MOLAR QUANTITIES

We will now determine the partial molar volumes in a water-ethanol mixture at 20°C and at a pressure of 1 atm.

# EXAMPLE | GRAPHICAL EXTRACTION OF PARTIAL MOLAR QUANTITIES

$$\frac{\Delta_{mix}V}{\sum n} = (1 - x_e)(\bar{V}_w - v_w) + x_e(\bar{V}_e - v_e)$$