MSE-204 Thermodynamics for Materials Science

L3.PART 1 | MOLAR & PARTIAL MOLAR QUANTITIES

HOMOGENEOUS FUNCTIONS | EXTENSIVE & INTENSIVE VARIABLES | EXPLICIT EXPRESSIONS FOR U, H, A, G | GIBBS-DUHEM EQUATION

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Define the annotations, FOR ALL EXTENSIVE VARIABLES

PURE SUBSTANCES

$$v = \frac{V}{n}$$

↳ small v is the molar volume

$cm^3/mole$

$$V = \frac{m\ (kg)}{\rho\ (kg/cm^3)}$$ volume cm^3

MULTICOMPONENT (PRIOR)

n_i = # of moles of components $i = 1, 2, \ldots, k$

$$v_i = \frac{V}{n_i}$$ molar volume of component i

MULTICOMPONENT SYSTEMS AFTER MIXING

partial molar quantity : (if for volume, $\bar{V}_i = ?$

FOR THE GENERAL CASE OF X ENTENSIVE VARIABLE

$\bar{X}$: partial molar quantity of X

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:

$$F(\lambda x_1, \lambda x_2, \ldots, \lambda x_i) = \lambda^n F(x_1, x_2, \ldots, x_i)$$

where λ is an arbitrary number

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

$$\frac{\partial F(\lambda x_1, \lambda x_2, \ldots, \lambda x_i)}{\partial x_i} = \frac{\partial \lambda^n F(x_1, x_2, \ldots x_i)}{\partial x_i} = \frac{\lambda^n F(x_1, x_2, \ldots, x_i)}{\partial x_i}$$

$$\frac{\partial F(\lambda x_1, \lambda x_2, \ldots \lambda x_i)}{\partial x_i} = \frac{\partial F(\lambda x_1, \lambda x_2, \ldots \lambda x_i)}{\partial \lambda x_i} \cdot \boxed{\frac{\partial \lambda x_i}{\partial x_i}} = \lambda$$

$$\frac{\partial F(\lambda x_1, \lambda x_2, \ldots \lambda x_i)}{\partial \lambda x_i} = \lambda^{n-1} \frac{\partial F(x_1, x_2, \ldots x_i)}{\partial x_i}$$

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:

$$\frac{\partial F(\lambda x_1, \lambda x_2, \dots, \lambda x_i)}{\partial \lambda} = \frac{\partial \lambda^n F(x_1, x_2, \dots, x_i)}{\partial \lambda} = n\lambda^{n-1} F(x_1, x_2, \dots, x_i)$$

$$\frac{\partial F(\lambda x_1, \lambda x_2, \dots, \lambda x_i)}{\partial \lambda} = \sum_i \frac{\partial F(\lambda x_1, \lambda x_2, \dots, \lambda x_i)}{\partial \lambda x_i} \cdot \boxed{\frac{\partial \lambda x_i}{\partial \lambda}} = x_i$$

$$\sum_i x_i \cdot \frac{\partial F(\lambda x_1, \lambda x_2, \dots, \lambda x_i)}{\partial \lambda x_i} = n\lambda^{n-1} F(x_1, x_2, \dots, x_i)$$

$$\boxed{\lambda = 1}$$

$$\sum_i x_i \frac{\partial F(x_1, x_2, \dots, x_i)}{\partial x_i} = n F(x_1, x_2, \dots, x_i)$$

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

$$\text{Pt-Au alloy} \left| \begin{matrix} 1\,\text{mm}^3 \\ n_{Pt},\ n_{Au} \\ U_{Pt-Au}(1\,\text{mm}^3) \end{matrix} \right\} T, p \left\{ \begin{matrix} \lambda \cdot 1\,\text{mm}^3 \\ \lambda \cdot n_{Pt},\ \lambda \cdot n_{Au} \\ \lambda \cdot U_{PtAu}(1\,\text{mm}^3) \end{matrix} \right.$$

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.

$$U(S, V, n_i, T, p, \mu_i, \ldots)$$

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

$$U(\lambda S, \lambda V, \lambda n_i, T, p, \mu_i, \ldots) = \lambda^{n=1}\, U(S, V, n_i, T, p, \mu_i)$$

$$G(T, p, \lambda n_i, \ldots) = \lambda\, G(T, p, n_i, \ldots)$$

If I have a system where T, p remain constant & the number of mole changes by a value of λ, then all other extensive variables of the system will change by this value λ : ASSUMPTIONS : 1) the composition is the same

2) surfaces do not affect the properties

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**. S $S^* = S(\lambda x_1, \ldots \lambda x_i)$

$$V^* = \lambda V, \quad S^* = \lambda S, \quad n_i^* = \lambda n_i \Rightarrow \frac{\partial V^*}{\partial V} = \frac{\partial S^*}{\partial S} = \frac{\partial n_i^*}{\partial n_i} = \lambda$$

$$\partial U^*(\lambda S, \lambda V, \lambda n_i) = \partial U^*(S^*, V^*, n_i^*)$$

$$\left(\frac{\partial U^*(S^*, V^*, n_i^*)}{\partial S}\right)_{V^*, n_i^*} = \lambda\left(\frac{\partial U(S, V, n_i)}{\partial S}\right)_{V, n_i} = \lambda\left(\frac{\partial U}{\partial S}\right)_{V, n_i}$$

$$\left(\left(\frac{\partial U^*(S^*, V^*, n_i^*)}{\partial S^*}\right)_{V^*, n_i^*} \cdot \frac{\partial S^*}{\partial S}\right.$$

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

$$\left(\frac{\partial U^*}{\partial V^*}\right)_{S^*, n_i^*} = \left(\frac{\partial U}{\partial V}\right)_{S, n_i} = -P$$

The partial derivative of a homogeneous function of degree 1 with respect to ther extensive variables is a homogeneous function of degree 0 $\Rightarrow$ intensive variables

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:

$$\left(\frac{\partial U^*}{\partial n_i^*}\right)_{S^*, V^*, n_{j\neq i}} = \left(\frac{\partial U}{\partial n_i}\right)_{S, V, n_{j\neq i}} = \mu_i \rightarrow \text{intensive property}$$

$$\mu_i(T, p, \lambda n_i, \ldots) = \lambda^{0}\, \mu_i(T, p, n_i, \ldots)$$

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

Euler's identity

$$\sum_j n_j \frac{\partial \mu_i}{\partial n_j} = 0$$

Also, mole fractions are intensive variables:

$$x_i = \frac{n_i}{\sum_i n_i}$$