

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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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, \dots, x_j 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 λF times x_1 over x_1

The partial derivatives of a homogeneous functions of degree n with respect to one of the variables are homogeneous 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 λ , then give λ 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 λ . 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: