

STATISTICAL MOLECULAR THERMODYNAMICS

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Video 10.1

Euler's Theorem and Thermodynamics

A LITTLE FORMAL MATHEMATICS

EULER'S THEOREM

A **homogeneous** function of **degree** m exhibits the following behavior upon **scaling** of its arguments:

$$f(\lambda x_1, \lambda x_2, \dots, \lambda x_n) = \lambda^m f(x_1, x_2, \dots, x_n) \quad (1)$$

Euler's theorem asserts that for homogeneous functions:

$$mf(x_1, x_2, \dots, x_n) = \sum_{i=1}^n x_i \frac{\partial f}{\partial x_i} \quad (2)$$

Proof proceeds by first differentiating both sides of eq. (1) by λ

PROOF OF EULER'S THEOREM

$$\frac{\partial}{\partial \lambda} [f(\lambda x_1, \lambda x_2, \dots, \lambda x_n)] = \frac{\partial}{\partial \lambda} [\lambda^m f(x_1, x_2, \dots, x_n)]$$

$$\sum_{i=1}^n \frac{\partial f}{\partial \lambda x_i} \frac{\partial \lambda x_i}{\partial \lambda} = m \lambda^{m-1} f(x_1, x_2, \dots, x_n)$$

$$\sum_{i=1}^n x_i \frac{\partial f}{\partial \lambda x_i} = m \lambda^{m-1} f(x_1, x_2, \dots, x_n)$$

Homogeneity holds for all values of λ so we may set

$\lambda = 1$, yielding

$$\sum_{i=1}^n x_i \frac{\partial f}{\partial x_i} = m f(x_1, x_2, \dots, x_n)$$

Q.E.D.

RELEVANCE TO THERMODYNAMICS

$$f(\lambda x_1, \lambda x_2, \dots, \lambda x_n) = \lambda^m f(x_1, x_2, \dots, x_n)$$

Now, a homogeneous function of degree $m = 1$ implies

$$f(\lambda x_1, \lambda x_2, \dots, \lambda x_n) = \lambda f(x_1, x_2, \dots, x_n)$$

Expressed in words, we might say, “double (or triple, or quadruple, etc.) your system size, and you double (or etc.) the value of your function.” *And, that’s exactly how extensive thermodynamic properties, that are themselves functions of only extensive variables, behave!*

RELEVANCE TO THERMODYNAMICS

We may thus exploit Euler's Theorem with $m = 1$

$$mf(x_1, x_2, \dots, x_n) = \sum_{i=1}^n x_i \frac{\partial f}{\partial x_i}$$

to determine:

$$f(x_1, x_2, \dots, x_n) = \sum_{i=1}^n x_i \frac{\partial f}{\partial x_i}$$

Consider the particular example of Gibbs free energy at constant temperature and pressure for a two-component system, i.e.,

$$G(n_1, n_2) = n_1 \frac{\partial G}{\partial n_1} + n_2 \frac{\partial G}{\partial n_2}$$

FREE ENERGY IS THE SUM OF CHEMICAL POTENTIALS

$$G(n_1, n_2) = n_1 \frac{\partial G}{\partial n_1} + n_2 \frac{\partial G}{\partial n_2}$$

We already have a definition for those derivatives, they are the chemical potentials (which *do* depend on P and T)

$$G(n_1, n_2; P, T) = n_1 \mu_1(P, T) + n_2 \mu_2(P, T)$$

The notation emphasizes that we get to use Euler's theorem for a *fixed* P and T , but the chemical potentials *will* themselves change at *different values* of P and T . A cleaner notation is:

$$G(n_1, n_2) = n_1 \mu_1 + n_2 \mu_2$$

AN ALTERNATIVE DERIVATION

From simply the total differential we already know:

$$dG(n_1, n_2, P, T) = \left(\frac{\partial G}{\partial n_1} \right)_{P, T, n_2} dn_1 + \left(\frac{\partial G}{\partial n_2} \right)_{P, n_1, T} dn_2 + \left(\frac{\partial G}{\partial P} \right)_{T, n_1, n_2} dP + \left(\frac{\partial G}{\partial T} \right)_{P, n_1, n_2} dT$$

which at constant P and T yields:

$$dG(n_1, n_2; P, T) = \mu_1 dn_1 + \mu_2 dn_2$$

Consideration of appropriate boundary conditions and definite integration can then *also* yield

$$G(n_1, n_2) = n_1 \mu_1 + n_2 \mu_2$$

but Euler's theorem is general for all extensive thermodynamic functions without the need to argue boundary conditions for each one separately

$$dU = \delta q + \delta w$$



Next: Partial Molar Quantities and the Gibbs-Duhem Equation