Fundamental equation of thermodynamics [tln16]

The first and second laws of thermodynamics imply that

$$dU = TdS + YdX + \mu dN \tag{1}$$

with

$$\left(\frac{\partial U}{\partial S}\right)_{X,N} = T, \quad \left(\frac{\partial U}{\partial X}\right)_{S,N} = Y, \quad \left(\frac{\partial U}{\partial N}\right)_{S,X} = \mu$$

is the exact differential of a function $U(S, X, N)$.

Here X stands for $V, M, \ldots$ and Y stands for $-p, H, \ldots$.

Note: for irreversible processes $dU < TdS + YdX + \mu dN$ holds.

U, S, X, N are extensive state variables.

$U(S, X, N)$ is a 1st order homogeneous function: $U(\lambda S, \lambda X, \lambda N) = \lambda U(S, X, N)$.

$$U[(1+\epsilon)S, (1+\epsilon)X, (1+\epsilon)N] = U + \frac{\partial U}{\partial S}\epsilon S + \frac{\partial U}{\partial X}\epsilon X + \frac{\partial U}{\partial N}\epsilon N = (1+\epsilon)U.$$

Euler equation:

$$U = TS + YX + \mu N. \tag{2}$$

Total differential of (2):

$$dU = TdS + SdT + YdX + XdY + \mu dN + Nd\mu \tag{3}$$

Subtract (1) from (3):

Gibbs-Duhem equation: $SdT + XdY + Nd\mu = 0$.

The Gibbs-Duhem equation expresses a relationship between the intensive variables T, Y, μ. It can be integrated, for example, into a function $\mu(T, Y)$.

Note: a system specified by m independent extensive variables possesses $m - 1$ independent intensive variables.

Example for $m = 3$: S, V, N (extensive); $S/N, V/N$ or p, T (intensive).

Complete specification of a thermodynamic system must involve at least one extensive variable.