

Expression for Maximum Non Expansion Work as a Function of Gibbs Free (Available) Energy

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December 10, 2021

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1 Pre-requisites

- Elementary Thermodynamics including definition of First Law and Enthalpy
- Understanding the derivation of Gibbs Free (Available) Energy. Readers are directed to [Gibbs Free Energy Fundamentals](#) for a short description and derivation.

2 Discussion

The first law of thermodynamics for the change of state of a system takes the form;

$$dU = \pm\delta Q \pm \delta W$$

- dU is the change in internal energy
- δQ is the heat transfer across the system boundary
- δW is the work transfer across the system boundary

Considering the process to involve heat transfer to the system and work done by the system, the equation takes the form;

$$dU = \delta Q - \delta W$$

Note that in the above equation, on the right hand side, the quantity that contributes to internal energy increase is taken as positive (δQ) and the quantity that results in the reduction of internal energy is taken as negative (δW). Rearranging the equation;

$$\delta Q = \delta W + dU \tag{1}$$

Equation 1 is the standard form of first law of thermodynamics for a change of state of a system. In equation 1, δW basically constitutes two types of work terms;

- a) Expansion work δW_{exp} , associated with a change in the volume of the system under the influence of some pressure. This expansion work is classically represented as PdV where P is the resisting force and dV is the change in volume. Thus;

$$\delta W_{exp} = PdV$$

b) Non expansion work δW_{nexp} associated with all forms of work excluding the expansion work. The classic example would be electrical work.

Thus;

$$\delta Q = \delta W_{exp} + \delta W_{nexp} + dU$$

Replacing δW_{exp} with PdV in the above expression, equation 1 can be represented as;

$$\delta Q = PdV + \delta W_{nexp} + dU \quad (2)$$

Invoking the definition of enthalpy as $H = U + PV$ and considering its differential form of

$$dH = dU + PdV + VdP \quad \text{Rearranging} \quad dU = dH - PdV - VdP$$

Substituting the expression for change in internal energy dU in equation 2 and rearranging;

$$\delta Q = PdV + \delta W_{nexp} + dH - PdV - VdP$$

$$\delta Q = \cancel{PdV} + \delta W_{nexp} + dH - \cancel{PdV} - VdP$$

$$\delta Q = \delta W_{nexp} + dH - Vdp \quad (3)$$

Rearranging,

$$\delta W_{nexp} = \delta Q - dH + VdP \quad (4)$$

For reversible heat transfer, $dS = \frac{\delta Q}{T}$ and hence $\delta Q = TdS$. Substituting in equation 4;

$$\delta W_{nexp} = TdS - dH + VdP \quad (5)$$

Invoking the definition of Gibbs Free (Available) Energy change, $G = H - TS$ and as specifically applicable to a constant pressure and temperature process, $dG = dH - TdS$, equation 5 is modified to;

$$\delta W_{nexp} = TdS - dH = -[dH - TdS] = -dG$$

Thus,

$$\delta W_{nexp} = -dG \tag{6}$$

The maximum non expansion work for a system at constant T and P can thus be estimated from the change in Gibbs Available Energy as established in equation 6.