

8.2: Thermodynamic Potentials

Starting from the fundamental equation, we can define new thermodynamic state functions that are more convenient to use under certain specific conditions. The new functions are determined by using a mathematical procedure called the Legendre transformation. A Legendre transformation is a linear change in variables that brings from an initial mathematical function to a new function obtained by subtracting one or more products of conjugate variables.¹

Taking the internal energy as defined in Equation 8.1.1, we can perform such procedure by subtracting products of the following conjugate variables pairs: T and S or $-P$ and V . This procedure aims to define new state functions that depend on more convenient natural variables.² The new functions are called “thermodynamic potential energies,” or simply **thermodynamic potentials**.³ An example of this procedure is given by the definition of enthalpy that we have already seen in section 3.1.4. If we take the internal energy and subtract the product of two conjugate variables ($-P$ and V), we obtain a new state function called **enthalpy**, as we did in Equation 3.1.9). Taking the differential of this definition, we obtain:

$$dH = dU + VdP + PdV, \quad (8.2.1)$$

and using the fundamental equation, Equation 8.1.2, to replace dU , we obtain:

$$\begin{aligned} dH &= TdS - PdV + \sum_i \mu_i dn_i + VdP + PdV \\ &= TdS + VdP + \sum_i \mu_i dn_i. \end{aligned} \quad (8.2.2)$$

which is the fundamental equation for enthalpy. The natural variables of the enthalpy are S , P , and $\{n_i\}$. The Legendre transformation has allowed us to go from $U(S, V, \{n_i\})$ to $H(S, P, \{n_i\})$ by replacing the dependence on the extensive variable, V , with an intensive one, P .

Following the same procedure, we can perform another Legendre transformation to replace the entropy with a more convenient intensive variable such as the temperature. This can be done by defining a new function called the **Helmholtz free energy**, A , as:

$$A = U - TS \quad (8.2.3)$$

which, taking the differential and using the fundamental equation (Equation ???) becomes:

$$\begin{aligned} dA &= dU - SdT - TdS = TdS - PdV + \sum_i \mu_i dn_i - SdT - TdS \\ &= -SdT - PdV + \sum_i \mu_i dn_i. \end{aligned} \quad (8.2.4)$$

The Helmholtz free energy is named after Hermann Ludwig Ferdinand von Helmholtz (1821—1894), and its natural variables are temperature, volume, and the number of moles.

Finally, suppose we perform a Legendre transformation on the internal energy to replace both the entropy and the volume with intensive variables. In that case, we can define a new function called the **Gibbs free energy**, G , as:

$$G = U - TS + PV \quad (8.2.5)$$

which, taking again the differential and using Equation ??? becomes:

$$\begin{aligned} dG &= dU - SdT - TdS + VdP + PdV \\ &= TdS - PdV + \sum_i \mu_i dn_i - SdT - TdS + VdP + PdV \\ &= VdP - SdT + \sum_i \mu_i dn_i. \end{aligned}$$

The Gibbs free energy is named after Willard Gibbs himself, and its natural variables are temperature, pressure, and number of moles.

A summary of the four thermodynamic potentials is given in the following table.

Table 8.2.1

Name	Symbol	Fundamental Equation	Natural Variables
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Name	Symbol	Fundamental Equation	Natural Variables
Energy	U	$dU = TdS - PdV + \sum_i \mu_i dn_i$	$S, V, \{n_i\}$
Enthalpy	H	$dH = TdS + VdP + \sum_i \mu_i dn_i$	$S, P, \{n_i\}$
Helmholtz Free Energy	A	$dA = -SdT - PdV + \sum_i \mu_i dn_i$	$T, V, \{n_i\}$
Gibbs Free Energy	G	$dG = VdP - SdT + \sum_i \mu_i dn_i$	$T, P, \{n_i\}$

The thermodynamic potentials are the analog of the potential energy in classical mechanics. Since the potential energy is interpreted as the capacity to do work, the thermodynamic potentials assume the following interpretations:

- Internal energy (U) is the capacity to do work plus the capacity to release heat.
- Enthalpy (H) is the capacity to do non-mechanical work plus the capacity to release heat.
- Gibbs free energy (G) is the capacity to do non-mechanical work.
- Helmholtz free energy (A) is the capacity to do mechanical plus non-mechanical work.⁴

Where non-mechanical work is defined as any type of work that is not expansion or compression (PV -work). A typical example of non-mechanical work is electrical work.

1. The mathematical condition that is fulfilled when performing a Legendre transformation is that the first derivatives of the original function and its transformation are inverse functions of each other.
2. The rigorous mathematical definition of conjugate variables is unimportant at this stage. However, we can relate the variables in a pair with basic physics by noticing how the first variable in a pair is always intensive (T and $-P$), while the second one is always extensive (S and V). The intensive variables represent thermodynamic driving forces (as compared with mechanical forces in classical mechanics), while the extensive ones are the thermodynamic displacements (as compared with spatial displacements in classical mechanics). Similarly to classical mechanics, the product of two conjugate variables in a pair yields an energy. The minus sign in front of P is explained by the fact that an increase in the force should always correspond to an increase in the displacement (while P and V are inversely related).
3. Even if we introduced both concepts in the same chapter, it is important to never confuse the *thermodynamic potentials*—which are potential energy functions—with the *chemical potential*—which have been introduced by Gibbs to study heat in chemical reactions.
4. For the mathematically inclined, an entertaining method to summarize the same thermodynamic potentials is the [thermodynamic square](#).

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