

8.1: Fundamental Equation of Thermodynamics

Let's summarize some of the results from the first and second law of thermodynamics that we have seen so far. For reversible processes in closed systems:

$$\begin{aligned} \text{From 1}^{\text{st}} \text{ Law:} \quad & dU = dQ_{\text{REV}} - PdV \\ \text{From The Definition of Entropy:} \quad & dS = \frac{dQ_{\text{REV}}}{T} \rightarrow dQ_{\text{REV}} = TdS \\ \Rightarrow & dU = TdS - PdV. \end{aligned} \tag{8.1.1}$$

Equation 8.1.1 is called the **fundamental equation of thermodynamics** since it combines the first and the second laws. Even though we started the derivation above by restricting to reversible transformations only, if we look carefully at Equation 8.1.1, we notice that it exclusively involves state functions. As such, it applies to both reversible and irreversible processes. The fundamental equation, however, remains constrained to closed systems. This fact restricts its utility for chemistry, since when a chemical reaction happens, the mass in the system will change, and the system is no longer closed.

At the end of the 19th century, Josiah Willard Gibbs (1839–1903) proposed an important addition to the fundamental equation to account for chemical reactions. Gibbs was able to do so by introducing a new quantity that he called the chemical potential:

Definition: Chemical Potential

The chemical potential is the amount of energy absorbed or released due to a change of the particle number of a given chemical species.

The chemical potential of species i is usually abbreviated as μ_i , and it enters the fundamental equation of thermodynamics as:

$$dU = TdS - PdV + \sum_i \mu_i dn_i,$$

where dn_i is the differential change in the number of moles of substance i , and the summation extends over all chemical species in the system.

According to the fundamental equation, the internal energy of a system is a function of the three variables entropy, S , volume, V , and the numbers of moles $\{n_i\}$.¹ Because of their importance in determining the internal energy, these three variables are crucial in thermodynamics. Under several circumstances, however, they might not be the most convenient variables to use.² To emphasize the important connections given by the fundamental equation, we can use the notation $U(S, V, \{n_i\})$ and we can term S , V , and $\{n_i\}$ **natural variables** of the energy.

1. In the case of the numbers of moles we include them in curly brackets to indicate that there might be more than one, depending on how many species undergo chemical reactions.
2. For example, we don't always have a simple way to calculate or to measure the entropy.

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