5.2: Total Differential of the Internal Energy

For a closed system undergoing processes in which the only kind of work is expansion work, the first law becomes $dU = đq + đw = đq − p_b\,dV$. Since it will often be useful to make a distinction between expansion work and other kinds of work, this e-book will sometimes write the first law in the form

$$dU = đq − p_b\,dV + đw'$$

$$\text{(5.2.1)}$$
$$\text{(closed system)}$$

where $đw'$ is **nonexpansion work**—that is, any thermodynamic work that is not expansion work.

Consider a closed system of one chemical component (e.g., a pure substance) in a single homogeneous phase. The only kind of work is expansion work, with V as the work variable. This kind of system has *two* independent variables (Sec. 2.4.3). During a *reversible* process in this system, the heat is $đq = T\,dS$, the work is $đw = −p\,dV$, and an infinitesimal internal energy change is given by

$$dU = T\,dS − p\,dV$$

$$\text{(5.2.2)}$$
$$\text{(closed system, } C{=}1,$$
$$P{=}1,\ đw'{=}0)$$

In the conditions of validity shown next to this equation, $C{=}1$ means there is one component (C is the number of components) and $P{=}1$ means there is one phase (P is the number of phases).

The appearance of the intensive variables T and p in Eq. 5.2.2 implies, of course, that the temperature and pressure are uniform throughout the system during the process. If they were not uniform, the phase would not be homogeneous and there would be more than two independent variables. The temperature and pressure are strictly uniform only if the process is reversible; it is not necessary to include "reversible" as one of the conditions of validity.

A real process approaches a reversible process in the limit of infinite slowness. For all practical purposes, therefore, we may apply Eq. 5.2.2 to a process obeying the conditions of validity and taking place so slowly that the temperature and pressure remain essentially uniform—that is, for a process in which the system stays very close to thermal and mechanical equilibrium.

Because the system under consideration has two independent variables, Eq. 5.2.2 is an expression for the total differential of U with S and V as the independent variables. In general, an expression for the differential dX of a state function X is a total differential if

1. Note that the work coordinate of any kind of dissipative work—work without a reversible limit—cannot appear in the expression for a total differential, because it is not a state function (Sec. 3.10).

   As explained in Appendix F, we may identify the coefficient of each term in an expression for the total differential of a state function as a partial derivative of the function. We identify the coefficients on the right side of Eq. 5.2.2 as follows:

$$T = \left(\frac{\partial U}{\partial S}\right)_V \qquad −p = \left(\frac{\partial U}{\partial V}\right)_S$$

$$\text{(5.2.3)}$$

   The quantity given by the third partial derivative, $(\partial U/\partial n)_{S,V}$, is represented by the symbol μ (mu). This quantity is an intensive state function called the **chemical potential**.

   With these substitutions, Eq. 5.2.4 becomes

$$dU = T\,dS − p\,dV + \mu\,dn$$

$$\text{(5.2.5)}$$
$$\text{(pure substance,}$$
$$P{=}1,\ đw'{=}0)$$

   and this is a valid expression for the total differential of U under the given conditions.

   If a system contains a mixture of s different substances in a single phase, and the system is open so that the amount of each substance can vary independently, there are $2 + s$ independent variables and the total differential of U can be written

$$dU = T\,dS − p\,dV + \sum_{i=1}^{s} \mu_i\,dn_i$$

$$\text{(5.2.6)}$$
$$\text{(open system,}$$
$$P{=}1,\ đw'{=}0)$$

The coefficient μ_i is the chemical potential of substance i. We identify it as the partial derivative $(\partial U/\partial n_i)_{S,V,n_{j\neq i}}$.

> The term $-p\,\mathrm{d}V$ on the right side of Eq. 5.2.6 is the reversible work. However, the term $T\,\mathrm{d}S$ does not equal the reversible heat as it would if the system were closed. This is because the entropy change $\mathrm{d}S$ is partly due to the entropy of the matter transferred across the boundary. It follows that the remaining term, $\sum_i \mu_i\,\mathrm{d}n_i$ (sometimes called the "chemical work"), should not be interpreted as the energy brought into the system by the transfer of matter.

Suppose that in addition to expansion work, other kinds of reversible work are possible. Each work coordinate adds an additional independent variable. Thus, for a closed system of one component in one phase, with reversible nonexpansion work given by $đw' = Y\,\mathrm{d}X$, the total differential of U becomes

$$\mathrm{d}U = T\,\mathrm{d}S - p\,\mathrm{d}V + Y\,\mathrm{d}X \qquad\qquad (5.2.7)$$
$$\text{(closed system,}$$
$$C{=}1,\ P{=}1)$$