

5.3: Enthalpy, Helmholtz Energy, and Gibbs Energy

For the moment we shall confine our attention to closed systems with one component in one phase. The total differential of the internal energy in such a system is given by Eq. 5.2.2: $dU = T dS - p dV$. The independent variables in this equation, S and V , are called the *natural variables* of U .

In the laboratory, entropy and volume may not be the most convenient variables to measure and control. Entropy is especially inconvenient, as its value cannot be measured directly. The way to change the independent variables is to make Legendre transforms, as explained in Sec. F.4 in Appendix F.

A Legendre transform of a dependent variable is made by subtracting one or more products of *conjugate variables*. In the total differential $dU = T dS - p dV$, T and S are conjugates (that is, they comprise a *conjugate pair*), and $-p$ and V are conjugates. Thus the products that can be subtracted from U are either TS or $-pV$, or both. Three Legendre transforms of the internal energy are possible, defined as follows:

$$\text{Enthalpy} \quad H \stackrel{\text{def}}{=} U + pV \quad (5.3.1)$$

$$\text{Helmholtz energy} \quad A \stackrel{\text{def}}{=} U - TS \quad (5.3.2)$$

$$\text{Gibbs energy} \quad G \stackrel{\text{def}}{=} U - TS + pV = H - TS \quad (5.3.3)$$

These definitions are used whether or not the system has only two independent variables.

The enthalpy, Helmholtz energy, and Gibbs energy are important functions used extensively in thermodynamics. They are state functions (because the quantities used to define them are state functions) and are extensive (because U , S , and V are extensive). If temperature or pressure are not uniform in the system, we can apply the definitions to constituent phases, or to subsystems small enough to be essentially uniform, and sum over the phases or subsystems.

Alternative names for the Helmholtz energy are Helmholtz function, Helmholtz free energy, and work function. Alternative names for the Gibbs energy are Gibbs function and Gibbs free energy. Both the Helmholtz energy and Gibbs energy have been called simply free energy, and the symbol F has been used for both. The nomenclature in this e-book follows the recommendations of the IUPAC Green Book (E. Richard Cohen et al, *Quantities, Units and Symbols in Physical Chemistry*, 3rd edition, RSC Publishing, Cambridge, 2007).

Expressions for infinitesimal changes of H , A , and G are obtained by applying the rules of differentiation to their defining equations:

$$dH = dU + p dV + V dp \quad (5.3.4)$$

$$dA = dU - T dS - S dT \quad (5.3.5)$$

$$dG = dU - T dS - S dT + p dV + V dp \quad (5.3.6)$$

These expressions for dH , dA , and dG are general expressions for any system or phase with uniform T and p . They are *not* total differentials of H , A , and G , as the variables in the differentials in each expression are not independent.

A useful property of the enthalpy in a closed system can be found by replacing dU in Eq. 5.3.4 by the first law expression $\delta q - p dV + \delta w'$, to obtain $dH = \delta q + V dp + \delta w'$. Thus, in a process at constant pressure ($dp = 0$) with expansion work only ($\delta w' = 0$), we have

$$dH = \delta q \quad (5.3.7)$$

(closed system, constant p ,
 $\delta w' = 0$)

The enthalpy change under these conditions is equal to the heat. The integrated form of this relation is $\int dH = \int \delta q$, or

$$\Delta H = q \quad (5.3.8)$$

(closed system, constant p ,
 $w' = 0$)

Equation 5.3.7 is analogous to the following relation involving the internal energy, obtained from the first law:

$$dU = dq \quad (5.3.9)$$

(closed system, constant V ,
 $\dot{w}'=0$)

That is, in a process at constant volume with expansion work only, the internal energy change is equal to the heat.

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