4.6 THE FUNDAMENTAL THERMODYNAMIC IDENTITY

The definition of entropy in terms of heat involved in a reversible process allows us to rewrite the first law of thermodynamics in terms of entropy by replacing heat by the product of temperature at which the process occurs and the change in entropy. Consider, an infinitesimal reversible process with internal energy change dU, work dW and heat dQ:

$$dU = dQ - dW. \tag{4.21}$$

For the reversible process, dQ can also be written in terms of entropy.

$$\boxed{dQ = TdS \quad \text{(reversible)}} \tag{4.22}$$

Therefore, the first law of thermodynamics for a reversible infinitesimal process has another form:

$$dU = TdS - dW \quad \text{(reversible)} \tag{4.23}$$

Additionally, for hydrostatic systems, the work by the system is given by pdV.

$$\boxed{dU = TdS - pdV \quad \text{(reversible)}} \tag{4.24}$$

This equation is called the **fundamental thermodynamic relation** or **thermodynamic identity**. This equation allows one to develop more powerful tools for thermodynamics. For instance, according to Eq. 4.24, internal energy U can be treated as a function of S and V, that is $U(S, V)$. Using partial derivatives, a change in U can be expressed in terms of the changes in S and V as follows.

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV \tag{4.25}$$

Comparing this equation with the equation for the first law of thermodynamics in the form given in Eq. 4.24 we find that the temperature and pressure are related to the partial derivatives of U with respect to entropy and volume respectively.

$$T = \left(\frac{\partial U}{\partial S}\right)_V \tag{4.26}$$

$$-p = \left(\frac{\partial U}{\partial V}\right)_S \tag{4.27}$$

These relations can be used as defining temperature and pressure respectively and are helpful in developing a more abstract treatment of thermodynamics. We will not pursue these more mathematical aspects of thermodynamics in this book.