MAXWELL RELATIONS

7-1 THE MAXWELL RELATIONS

In Section 3.6 we observed that quantities such as the isothermal compressibility, the coefficient of thermal expansion, and the molar heat capacities describe properties of physical interest. Each of these is essentially a derivative \((\partial X/\partial Y)_{z,w,...}\) in which the variables are either extensive or intensive thermodynamic parameters. With a wide range of extensive and intensive parameters from which to choose, in general systems, the number of such possible derivatives is immense. But there are relations among such derivatives, so that a relatively small number of them can be considered as independent; all others can be expressed in terms of these few. Needless to say such relationships enormously simplify thermodynamic analyses. Nevertheless the relationships need not be memorized. There is a simple, straightforward procedure for producing the appropriate relationships as needed in the course of a thermodynamic calculation. That procedure is the subject of this chapter.

As an illustration of the existence of such relationships we recall equations 3.70 to 3.71

\[
\frac{\partial^2 U}{\partial S \partial V} = \frac{\partial^2 U}{\partial V \partial S}
\]  

(7.1)

or

\[-(\frac{\partial P}{\partial S})_{v,N_1,N_2,...} = (\frac{\partial T}{\partial V})_{s,N_1,N_2,...}\]

(7.2)

This relation is the prototype of a whole class of similar equalities known as the Maxwell relations. These relations arise from the equality of the mixed partial derivatives of the fundamental relation expressed in any of the various possible alternative representations.