Given a particular thermodynamic potential, expressed in terms of its \((t + 1)\) natural variables, there are \(t(t + 1)/2\) separate pairs of mixed second derivatives. Thus each potential yields \(t(t + 1)/2\) Maxwell relations.

For a single-component simple system the internal energy is a function of three variables \(t = 2\), and the three \([=(2 \cdot 3)/2]\) pairs of mixed second derivatives are \(\partial^2 U/\partial S \partial V = \partial^2 U/\partial V \partial S\), \(\partial^2 U/\partial S \partial N = \partial^2 U/\partial N \partial S\), and \(\partial^2 U/\partial V \partial N = \partial^2 U/\partial N \partial V\). The complete set of Maxwell relations for a single-component simple system is given in the following listing, in which the first column states the potential from which the relation derives, the second column states the pair of independent variables with respect to which the mixed partial derivatives are taken, and the last column states the Maxwell relations themselves. A mnemonic diagram to be described in Section 7.2 provides a mental device for recalling relations of this form. In Section 7.3 we present a procedure for utilizing these relations in the solution of thermodynamic problems.

\[
U \\
S, V \\
\left( \frac{\partial U}{\partial V} \right)_S = -\left( \frac{\partial P}{\partial S} \right)_V \tag{7.3}
\]

\[
dU = TdS - PdV + \mu dN \\
S, N \\
\left( \frac{\partial dU}{\partial N} \right)_S = \left( \frac{\partial P}{\partial S} \right)_V \tag{7.4}
\]

\[
V, N \\
-\left( \frac{\partial P}{\partial N} \right)_S = \left( \frac{\partial \mu}{\partial S} \right)_V \tag{7.5}
\]

\[
U[T] = F \\
T, V \\
\left( \frac{\partial U}{\partial V} \right)_T = \left( \frac{\partial P}{\partial S} \right)_V \tag{7.6}
\]

\[
dF = -SdT + VdP + \mu dN \\
T, N \\
\left( \frac{\partial F}{\partial N} \right)_T = \left( \frac{\partial \mu}{\partial T} \right)_V \tag{7.7}
\]

\[
V, N \\
-\left( \frac{\partial \mu}{\partial N} \right)_T = \left( \frac{\partial \mu}{\partial T} \right)_V \tag{7.8}
\]

\[
U[P] = H \\
S, P \\
\left( \frac{\partial U}{\partial P} \right)_S = \left( \frac{\partial F}{\partial S} \right)_P \tag{7.9}
\]

\[
dH = TdS + VdP + \mu dN \\
S, N \\
\left( \frac{\partial H}{\partial N} \right)_S = \left( \frac{\partial \mu}{\partial S} \right)_P \tag{7.10}
\]

\[
P, N \\
\left( \frac{\partial H}{\partial P} \right)_S = \left( \frac{\partial \mu}{\partial P} \right)_S \tag{7.11}
\]

\[
U[\mu] \\
S, V \\
\left( \frac{\partial U}{\partial V} \right)_S = -\left( \frac{\partial P}{\partial S} \right)_V \tag{7.12}
\]

\[
dU[\mu] = TdS - PdV - N \mu \phi \\
S, \mu \\
\left( \frac{\partial U}{\partial \mu} \right)_S = -\left( \frac{\partial N}{\partial S} \right)_V \tag{7.13}
\]

\[
V, \mu \\
\left( \frac{\partial U}{\partial \mu} \right)_S = -\left( \frac{\partial N}{\partial V} \right)_S \tag{7.14}
\]

7.2 A THERMODYNAMIC MNEMONIC DIAGRAM

A number of the most useful Maxwell relations can be remembered conveniently in terms of a simple mnemonic diagram. This diagram, given in Fig. 7.1, consists of a square with arrows pointing upward along the two diagonals. The sides are labeled with the four common thermodynamic potentials, \(F, G, H,\) and \(U\), in alphabetical order clockwise around the diagram, the Helmholtz potential \(F\) at the top. The two corners at the left are labeled with the extensive parameters \(S\) and \(V\), and the two corners at the right are labeled with the intensive parameters \(T\) and \(P\). ("Valid Facts and Theoretical Understanding Generate Solutions to Hard Problems" suggests the sequence of the labels.)

Each of the four thermodynamic potentials appearing on the square is flanked by its natural independent variables. Thus \(U\) is a natural function of \(V\) and \(S\); \(F\) is a natural function of \(V\) and \(T\); and \(G\) is a natural function of \(T\) and \(P\). Each of the potentials also depends on the mole numbers, which are not indicated explicitly on the diagram.

\(^{1}\text{This diagram was presented by Professor Max Born in 1929 in a lecture heard by Professor Tisza. It appeared in the literature in a paper by F. O. Koenig, J. Chem. Phys. 3, 29 (1935), and 56, 4556 (1972). See also L. T. Klauder, Am. Journ. Phys. 36, 556 (1968), and a number of other variants presented by a succession of authors in this journal.}\)