1.4 Gibbs–Duhem and Maxwell Relations

The internal energy E has as its natural independent variables the entropy S, the volume V, and other generalized displacements which are all extensive variables. If these quantities are rescaled by a factor λ, the internal energy must itself change by the same factor:

$$E(\lambda S, \{\lambda x_i\}, \{\lambda N_j\}) = \lambda E(S, \{x_i\}, \{N_j\}) \ . \tag{1.41}$$

Differentiating both sides with respect to λ using (1.25) on the right-hand side, we obtain the *Gibbs–Duhem equation*:

$$E(S, \{x_i\}, \{N_j\}) = TS + \sum_i X_i x_i + \sum_j \mu_j N_j \ . \tag{1.42}$$

For a single-component PVT system, (1.42) reduces to

$$E = TS - PV + \mu N \tag{1.43}$$

or

$$G(P, T, N) = \mu N \ . \tag{1.44}$$

Taking the differential of (1.42) and using (1.25), we find that

$$0 = SdT + \sum_i x_i dX_i + \sum_j N_j d\mu_j \tag{1.45}$$

which illustrates the fact that the intensive variables T, $\{X_i\}$, $\{\mu_j\}$ are not all independent. An r-component PVT system thus has $r+1$ independent intensive thermodynamic variables. Another consequence is that at least one extensive variable is needed to specify completely the state of the system.

It follows from the differential form (1.27) for a single-component PVT system that

$$\begin{aligned} \left(\frac{\partial A}{\partial T}\right)_{N,V} &= -S \\ \left(\frac{\partial A}{\partial V}\right)_{T,N} &= -P \\ \left(\frac{\partial A}{\partial N}\right)_{T,V} &= \mu \ . \end{aligned} \tag{1.46}$$

It is a well-known result from the theory of partial differentiation that higher order derivatives are independent of the order in which the differentiation is carried out; that is, if ϕ is a single-valued function of the independent variables $x_1, x_2, ..., x_n$, then

$$\frac{\partial}{\partial x_i}\left(\frac{\partial \phi}{\partial x_j}\right) = \frac{\partial}{\partial x_j}\left(\frac{\partial \phi}{\partial x_i}\right) . \tag{1.47}$$

By applying this result to (1.46) we immediately obtain the *Maxwell relations*:

$$\begin{aligned}
\left(\frac{\partial S}{\partial V}\right)_{T,N} &= \left(\frac{\partial P}{\partial T}\right)_{V,N} \\
\left(\frac{\partial S}{\partial N}\right)_{V,T} &= -\left(\frac{\partial \mu}{\partial T}\right)_{V,N} \\
\left(\frac{\partial P}{\partial N}\right)_{V,T} &= -\left(\frac{\partial \mu}{\partial V}\right)_{T,N} .
\end{aligned} \tag{1.48}$$

Similarly, in the case of the Gibbs potential we find from (1.32)

$$\begin{aligned}
\left(\frac{\partial G}{\partial T}\right)_{N,P} &= -S \\
\left(\frac{\partial G}{\partial P}\right)_{T,N} &= V \\
\left(\frac{\partial G}{\partial N}\right)_{T,P} &= \mu
\end{aligned} \tag{1.49}$$

from which we have the additional Maxwell relations:

$$\begin{aligned}
\left(\frac{\partial S}{\partial P}\right)_{T,N} &= -\left(\frac{\partial V}{\partial T}\right)_{P,N} \\
\left(\frac{\partial V}{\partial N}\right)_{P,T} &= \left(\frac{\partial \mu}{\partial P}\right)_{T,N} \\
\left(\frac{\partial S}{\partial N}\right)_{P,T} &= -\left(\frac{\partial \mu}{\partial T}\right)_{P,N}
\end{aligned} \tag{1.50}$$

Further equations of this type can be found for magnetic systems, using (1.37), or, in the case of PVT systems, by using the internal energy or the grand potential. The usefulness of these relations is demonstrated in the next section, in which we derive relations between some of the most commonly measured response functions.