

Thermodynamics

Thermodynamic variables are classified as *extensive* if they scale as the volume of the system, V . Thus U , the internal energy, N , the number of particles, and S , the entropy, are extensive variables. (Here attention is restricted to a system in which there is only one kind of particle.) Variables that do not scale as the size of the system are called *intensive*. The internal energy of the system may be expressed as a function of the extensive variables [i.e., $U = U(V, N, S)$]. Thus

$$\begin{aligned} dU &= \left(\frac{\partial U}{\partial V}\right)_{N,S} dV + \left(\frac{\partial U}{\partial N}\right)_{V,S} dN + \left(\frac{\partial U}{\partial S}\right)_{N,V} dS \\ &= -P dV + \mu dN + T dS. \end{aligned} \quad (\text{WA.1})$$

One sees by comparing the coefficients of dV , dN , and dS that P , the pressure, T , the temperature, and μ , the chemical potential, are intensive variables. Equation (WA.1) is known as the *first law of thermodynamics*. It recognizes that energy is conserved and that heat is a form of energy. The differential quantity TdS represents the heat input to a system, PdV is the work done by the system, $-\mu dN$ the energy transported by particles leaving the system, and dU the increase of internal energy of the system.

Since one often has control over variables other than (V, N, S) it is convenient to introduce thermodynamic potentials. The Helmholtz free energy, F , is defined as

$$F = U - TS. \quad (\text{WA.2})$$

Forming the differential and combining the result with Eq. (WA.1) leads to

$$dF = -P dV + \mu dN - S dT. \quad (\text{WA.3})$$

The Helmholtz free energy is useful in problems in which one controls the variables (V, N, T) . If (V, N, T) are constant, $dF = 0$ at equilibrium.

The enthalpy, H , is defined by

$$H = U + PV. \quad (\text{WA.4})$$

Its differential leads to the formula

$$dH = T dS + \mu dN + V dP. \quad (\text{WA.5})$$

The enthalpy is used when one controls (S, N, P) . If (S, N, P) are held constant, $dH = 0$ at equilibrium.

The *Gibbs free energy* is defined by

$$G = U - TS + PV = F + PV = H - TS. \quad (\text{WA.6})$$

Its differential results in

$$dG = \mu dN - S dT + V dP. \quad (\text{WA.7})$$

The Gibbs free energy is of use in problems where one controls (N, T, P) . If (N, T, P) are held constant, $dG = 0$ at equilibrium.

From Eqs. (WA.2), (WA.4), and (WA.6), one sees that F , H , and G are all extensive variables. One may integrate Eq. (WA.1) to obtain the Euler relation

$$U = -PV + \mu N + TS, \quad (\text{WA.8})$$

from which it is seen that

$$G = N\mu. \quad (\text{WA.9})$$

The chemical potential for a one-component system is thus the Gibbs free energy per particle. From Eqs. (WA.1) and (WA.8) one obtains the *Gibbs–Duhem formula*:

$$N d\mu = V dP - S dT. \quad (\text{WA.10})$$

A number of thermodynamic relations follow from expressing Eqs. (WA.1), (WA.3), (WA.5), and (WA.7) as partial derivatives. They are

$$T = \left(\frac{\partial U}{\partial S} \right)_{N,V}, \quad P = - \left(\frac{\partial U}{\partial V} \right)_{N,S}, \quad \mu = \left(\frac{\partial U}{\partial N} \right)_{V,S}, \quad (\text{WA.11a})$$

$$P = - \left(\frac{\partial F}{\partial V} \right)_{N,T}, \quad S = - \left(\frac{\partial F}{\partial T} \right)_{N,V}, \quad \mu = \left(\frac{\partial F}{\partial N} \right)_{V,T}, \quad (\text{WA.11b})$$

$$T = \left(\frac{\partial H}{\partial S} \right)_{N,P}, \quad \mu = \left(\frac{\partial H}{\partial N} \right)_{P,S}, \quad V = \left(\frac{\partial H}{\partial P} \right)_{N,S}, \quad (\text{WA.11c})$$

$$\mu = \left(\frac{\partial G}{\partial N} \right)_{T,P}, \quad S = - \left(\frac{\partial G}{\partial T} \right)_{N,P}, \quad V = \left(\frac{\partial G}{\partial P} \right)_{N,T}. \quad (\text{WA.11d})$$

A pair of useful mathematical identities follow from forming the differential of a function $z(u, v)$:

$$dz = \left(\frac{\partial z}{\partial u} \right)_v du + \left(\frac{\partial z}{\partial v} \right)_u dv, \quad (\text{WA.12})$$

and then forming $u(z, v)$,

$$dz = \left(\frac{\partial z}{\partial u} \right)_v \left(\left(\frac{\partial u}{\partial z} \right)_v dz + \left(\frac{\partial u}{\partial v} \right)_z dv \right) + \left(\frac{\partial z}{\partial v} \right)_u dv, \quad (\text{WA.13})$$

Matching coefficients of like differentials leads to

$$1 = \left(\frac{\partial z}{\partial u} \right)_v \left(\frac{\partial u}{\partial z} \right)_v, \quad (\text{WA.14})$$

$$0 = \left(\frac{\partial z}{\partial u} \right)_v \left(\frac{\partial u}{\partial v} \right)_z + \left(\frac{\partial z}{\partial v} \right)_u. \quad (\text{WA.15})$$

The Maxwell relations are a set of formulas that state that the order of differentiation does not matter when a second derivative is formed. Thus, for $z(u,v)$,

$$dz = \left(\frac{\partial z}{\partial u} \right)_v du + \left(\frac{\partial z}{\partial v} \right)_u dv \equiv \xi du + \eta dv, \quad (\text{WA.12}')$$

the Maxwell relation is

$$\left(\frac{\partial \xi}{\partial v} \right)_u = \left(\frac{\partial \eta}{\partial u} \right)_v. \quad (\text{WA.16})$$

Applying this to Eqs. (WA.1), (WA.3), (WA.5), and (WA.7) gives

$$-\left(\frac{\partial P}{\partial N} \right)_{V,T} = \left(\frac{\partial \mu}{\partial V} \right)_{N,T}, \quad \left(\frac{\partial P}{\partial T} \right)_{V,N} = \left(\frac{\partial S}{\partial V} \right)_{N,T}, \quad \left(\frac{\partial \mu}{\partial T} \right)_{V,N} = -\left(\frac{\partial S}{\partial N} \right)_{V,T} \quad (\text{WA.17})$$

$$-\left(\frac{\partial P}{\partial N} \right)_{V,S} = \left(\frac{\partial \mu}{\partial V} \right)_{N,S}, \quad -\left(\frac{\partial P}{\partial S} \right)_{V,N} = \left(\frac{\partial T}{\partial V} \right)_{N,S}, \quad \left(\frac{\partial \mu}{\partial S} \right)_{V,N} = \left(\frac{\partial T}{\partial N} \right)_{V,S} \quad (\text{WA.18})$$

$$\left(\frac{\partial T}{\partial N} \right)_{S,P} = \left(\frac{\partial \mu}{\partial S} \right)_{N,P}, \quad \left(\frac{\partial T}{\partial P} \right)_{S,N} = \left(\frac{\partial V}{\partial S} \right)_{N,P}, \quad \left(\frac{\partial \mu}{\partial P} \right)_{S,N} = \left(\frac{\partial V}{\partial N} \right)_{S,P} \quad (\text{WA.19})$$

$$\left(\frac{\partial \mu}{\partial T} \right)_{N,P} = -\left(\frac{\partial S}{\partial N} \right)_{T,P}, \quad \left(\frac{\partial \mu}{\partial P} \right)_{T,N} = \left(\frac{\partial V}{\partial N} \right)_{T,P}, \quad -\left(\frac{\partial S}{\partial P} \right)_{T,N} = \left(\frac{\partial V}{\partial T} \right)_{N,P}. \quad (\text{WA.20})$$

The heat capacity at constant pressure and constant number of particles is

$$C_{P,N} = T \left(\frac{\partial S}{\partial T} \right)_{P,N} = \left(\frac{\partial H}{\partial T} \right)_{P,N}. \quad (\text{WA.21a})$$

The heat capacity at constant volume and constant number is

$$C_{V,N} = T \left(\frac{\partial S}{\partial T} \right)_{V,N} = \left(\frac{\partial U}{\partial T} \right)_{V,N}. \quad (\text{WA.21b})$$

The *second law of thermodynamics* states that the entropy of the universe (system plus environment) never decreases [i.e., $\Delta S \geq 0$]. Of course, S can decrease locally, as when a system orders, but this decrease must be matched by at least as large an increase in the entropy of the environment. An idealized process in which $\Delta S = 0$ is called a *reversible process*.

The *third law of thermodynamics* states that the entropy of a pure crystalline material is zero at $T = 0$ K. At $T = 0$ K the system finds itself in the ground state. If g is the

degeneracy of that state, $g/N \rightarrow 0$ as $N \rightarrow \infty$. The third law implies that is impossible for the system to attain the temperature $T = 0$ K.

For a multicomponent system, one generalizes Eq. (WA.1) to

$$dU = -P dV + \sum_i \mu_i dN_i + T dS. \quad (\text{WA.1a})$$

One may simply regard the quantities μ_i and N_i as elements of vectors and interpret terms like μdN in the previous formulas as being scalar products between these vectors.

One may apply thermodynamics to a chemically reacting system. For such a system, the set $\{N_j\}$ denotes the reactants or products. In a chemical reaction

$$\sum_j \nu_j A[j] = 0, \quad (\text{WA.22})$$

where $A[j]$ is the symbol for chemical j (e.g., $A = \text{Cu}$ or $A = \text{SiO}_2$). The stoichiometric coefficients ν_j are positive integers for the reactants and negative integers for the products. If dM is the number of times that this reaction occurs, $dN_j = \nu_j dM$. Inserting this into Eq. (WA.7) gives, for equilibrium at constant P and T ,

$$\frac{dG}{dM} = \sum_j \nu_j \mu_j = 0. \quad (\text{WA.23})$$

This is called the *equation of reaction equilibrium* and relates the different chemical potentials of the products and reactants.

At equilibrium some extremal principles apply: For fixed (N, V, U) , S will be maximized; for fixed (N, V, T) , F will be minimized; for fixed (S, N, P) , H will be minimized; for fixed (N, T, P) , G will be minimized.