I.G   Approach to Equilibrium and Thermodynamic Potentials

Evolution of non-equilibrium systems towards equilibrium is governed by the second law of thermodynamics. For example, in the previous section we showed that for an adiabatically isolated system entropy must increase in any spontaneous change and reaches a maximum in equilibrium. What about out of equilibrium systems that are not adiabatically isolated and which may also be subject to external mechanical work? It is usually possible to define other thermodynamic potentials that are extremized when the system is in equilibrium.

Enthalpy is the appropriate function when there is no heat exchange ($đQ = 0$), and the system comes to mechanical equilibrium with a *constant external force*. The minimum enthalpy principle merely formulates the observation that stable mechanical equilibrium is obtained by minimizing the net potential energy of the system plus the external agent. For example, consider a spring of natural extension L_0 and spring constant K, subject to the force exerted by a particle of mass m. For an extension $x = L - L_0$, the internal energy of the spring is $Kx^2/2$, while there is a change of $-mgx$ in the potential energy of the particle. Mechanical equilibrium is obtained by minimizing $Kx^2/2 - mgx$ at an extension $x_{\text{eq}} = mg/K$. The spring at any other value of the displacement initially oscillates before coming to rest at x_{eq} due to friction. For general displacements $\mathbf{x}$, at constant generalized forces $\mathbf{J}$, the work input to the system is $đW \leq \mathbf{J} \cdot \delta \mathbf{x}$. (Equality is achieved for a reversible change, but there is generally some loss of the external work into friction.) Since $đQ = 0$, using the first law, $\delta E \leq \mathbf{J} \cdot \delta \mathbf{x}$, and

$$\delta H \leq 0, \quad \text{where} \quad H = E - \mathbf{J} \cdot \mathbf{x} \tag{I.30}$$

is the enthalpy. The variations of H *in equilibrium* are given by

$$dH = dE - d(\mathbf{J} \cdot \mathbf{x}) = TdS + \mathbf{J} \cdot d\mathbf{x} - \mathbf{x} \cdot d\mathbf{J} - \mathbf{J} \cdot d\mathbf{x} = TdS - \mathbf{x} \cdot d\mathbf{J} \quad . \tag{I.31}$$

The equality in eq.(I.31), and the inequality in eq.(I.30), are a possible source of confusion. Note that eq.(I.30) refers to variations of H on approaching equilibrium as some parameter that is not a function of state is varied (e.g. the velocity of the particle joined to the spring in the above example). By contrast eq.(I.31) describes a relation between equilibrium coordinates. To differentiate the two cases, I will denoted the former non-equilibrium variations by δ.

The coordinate set $(S, \mathbf{J})$ is the natural choice for describing the enthalpy, and it follows from eq.(I.31) that

$$x_i = -\left.\frac{\partial H}{\partial J_i}\right|_{S, J_{j \neq i}}. \tag{I.32}$$

Variations of the enthalpy with temperature are related to heat capacities at constant force, for example

$$C_P = \left.\frac{dQ}{dT}\right|_P = \left.\frac{dE + PdV}{dT}\right|_P = \left.\frac{d(E + PV)}{dT}\right|_P = \left.\frac{dH}{dT}\right|_P. \tag{I.33}$$

Note, however, that a change of variables is necessary to express H in terms of T, rather than the more natural variable S.

Helmholtz Free energy is useful for isothermal transformations in the absence of mechanical work ($dW = 0$). From Clausius's theorem, the heat intake of a system at a constant temperature T satisfies $dQ \leq T\delta S$. Hence $\delta E = dQ + dW \leq T\delta S$, and

$$\delta F \leq 0, \quad \text{where} \quad F = E - TS \tag{I.34}$$

is the Helmholtz free energy. Since

$$dF = dE - d(TS) = TdS + \mathbf{J} \cdot d\mathbf{x} - SdT - TdS = -SdT + \mathbf{J} \cdot d\mathbf{x}, \tag{I.35}$$

the coordinate set $(T, \mathbf{x})$ (the quantities kept constant during an isothermal transformation with no work) is most suitable for describing the free energy. The equilibrium forces and entropy can be obtained from

$$J_i = \left.\frac{\partial F}{\partial x_i}\right|_{T, x_{j \neq i}} \quad , \quad S = -\left.\frac{\partial F}{\partial T}\right|_{\mathbf{x}}. \tag{I.36}$$

The internal energy can also be calculated from F using

$$E = F + TS = F - T\left.\frac{\partial F}{\partial T}\right|_{\mathbf{x}} = -T^2\left.\frac{\partial(F/T)}{\partial T}\right|_{\mathbf{x}}. \tag{I.37}$$

Gibbs Free Energy applies to isothermal transformations involving mechanical work at constant external force. The natural inequalities for work and heat input into the system are given by $dW \leq \mathbf{J} \cdot \delta\mathbf{x}$ and $dQ \leq T\delta S$. Hence $\delta E \leq T\delta S + \mathbf{J} \cdot \delta\mathbf{x}$ leading to

$$\delta G \leq 0, \quad \text{where} \quad G = E - TS - \mathbf{J} \cdot \mathbf{x} \tag{I.38}$$

is the Gibbs free energy. Variations of G are given by

$$dG = dE - d(TS) - d(\mathbf{J} \cdot \mathbf{x}) = TdS + \mathbf{J} \cdot d\mathbf{x} - SdT - TdS - \mathbf{x} \cdot d\mathbf{J} - \mathbf{J} \cdot d\mathbf{x} = -SdT - \mathbf{x} \cdot d\mathbf{J}, \quad \text{(I.39)}$$

and most easily expressed in terms of $(T, \mathbf{J})$.

(handwritten: ✱ Examples of energies that are defined as a function of T not S (like E))

	$dQ = 0$	Constant T
$dW = 0$	$\delta S \geq 0$	$\delta F \leq 0$
Constant $\mathbf{J}$	$\delta H \leq 0$	$\delta G \leq 0$

Table 2: Inequalities satisfied by thermodynamic potentials.

(handwritten: ✱ each being constant ∂F, ∂G, $\partial H = 0$ means that the equilibrium is achieved under different conditions)

Table (2) summarizes the above results on thermodynamic functions. Eqs.(I.30), (I.34), and (I.38) are examples of Legendre transformations, used to change variables to the most natural set of coordinates for describing a particular situation. So far, we implicitly assumed a constant number of particles in the system. In chemical reactions, and in equilibrium between two phases, the number of particles in a given constituent may change. The change in the number of particles necessarily involves changes in the internal energy, which is expressed in terms of a *chemical work* $dW = \mu \cdot d\mathbf{N}$. Here $\mathbf{N} = \{N_1, N_2, \cdots\}$ lists the number of particles of each species, and $\mu = \{\mu_1, \mu_2, \cdots\}$ the associated *chemical potentials* which measure the work necessary to add additional particles to the system. Traditionally, chemical work is treated differently from mechanical work and is not subtracted from E in the Gibbs free energy of eq.(I.38). For chemical equilibrium in circumstances that involve no mechanical work, the appropriate state function is the **Grand Potential** given by

(handwritten left: $dE = TdS + \sum_i J_i d^i x_i + \sum_\alpha \mu_\alpha dN_\alpha$)

$$\mathcal{G} = E - TS - \mu \cdot \mathbf{N} \quad . \quad \text{(I.40)}$$

(handwritten right: if both mechanical & chemical work were to be considered $\mathcal{G} = E - TS - \mu \cdot N - J \cdot x$; $d\mathcal{G} = -TdS - SdT - \mu dN - Nd\mu - Jdx - x dJ$ (T, μ, J) all intensive)

$\mathcal{G}(T, \mu, \mathbf{x})$ is minimized in chemical equilibrium, and its variations in general satisfy

$$d\mathcal{G} = -SdT - \mathbf{J} \cdot d\mathbf{x} - \mathbf{N} \cdot d\mu \quad . \quad \text{(I.41)}$$

Example: To illustrate the concepts of this section, consider N particles of supersaturated steam in a container of volume V at a temperature T. How can we describe the approach of steam to an equilibrium mixture with N_w particles in the liquid and N_s particles in the gas phase? The fixed coordinates describing this system are V, T, and N. The appropriate

15

thermodynamic function from Table (2) is the Helmholtz free energy $F(V, T, N)$, whose variations satisfy

$$dF = d(E - TS) = -SdT - PdV + \mu dN. \tag{I.42}$$

Before the system reaches equilibrium at a particular value of N_w, it goes through a series of non-equilibrium states with smaller amounts of water. If the process is sufficiently slow, we can construct an out of equilibrium value for F as

$$F(V, T, N|N_w) = F_w(T, N_w) + F_s(V, T, N - N_w), \tag{I.43}$$

which depends on an additional variable N_w. (It is assumed that the volume occupied by water is small and irrelevant.) According to eq.(I.34), the equilibrium point is obtained by minimizing F with respect to this variable. Since

$$\delta F = \left.\frac{\partial F_w}{\partial N_w}\right|_{T,V} \delta N_w - \left.\frac{\partial F_s}{\partial N_s}\right|_{T,V} \delta N_w, \tag{I.44}$$

and $\partial F/\partial N|_{T,V} = \mu$ from eq.(I.42), the equilibrium condition can be obtained by equating the chemical potentials, i.e. from $\mu_w(V, T) = \mu_s(V, T)$. The identity of chemical potentials is the condition for chemical equilibrium. Naturally, to proceed further we need expressions for μ_w and μ_s.

I.H   Useful Mathematical Results

(1) Extensivity: Including chemical work, variations of the *extensive* coordinates of the system are related by (generalizing eq.(I.28))

*[handwritten: * for I.46 to apply, the intensives must be fixed.]*

$$dE = TdS + \mathbf{J} \cdot d\mathbf{x} + \mu \cdot d\mathbf{N}. \tag{I.45}$$

For fixed intensive coordinates, the extensive quantities are simply proportional to size or to the number of particles. This proportionality is expressed mathematically by

[handwritten: This is only valid for extensive systems ←]

$$E(\lambda S, \lambda \mathbf{x}, \lambda \mathbf{N}) = \lambda E(S, \mathbf{x}, \mathbf{N}). \tag{I.46}$$

[handwritten: → how is this relation justified (?) is it based on observation(?)]

Evaluating the derivative of the above equation with respect to λ at $\lambda = 1$, results in

$$\left.\frac{\partial E}{\partial S}\right|_{\mathbf{x},\mathbf{N}} S + \sum_i \left.\frac{\partial E}{\partial x_i}\right|_{S,x_{j\neq i},\mathbf{N}} x_i + \sum_\alpha \left.\frac{\partial E}{\partial N_\alpha}\right|_{S,\mathbf{x},N_{\beta\neq\alpha}} N_\alpha = E(S, \mathbf{x}, \mathbf{N}). \tag{I.47}$$

[handwritten: $\frac{\partial E(\lambda S, \lambda x, \lambda N)}{\partial \lambda} = \frac{\partial E}{\partial (\lambda S)} \frac{\partial (\lambda S)}{\partial \lambda}$]

16

The partial derivatives in the above equation can be identified from eq.(I.45) as T, J_i, and μ_α respectively. Substituting these values into eq.(I.47) leads to the so called fundamental equation of thermodynamics

(handwritten: not so fundamental since it is a special case for extensive systems.)

$$E = TS + \mathbf{J} \cdot \mathbf{x} + \mu \cdot \mathbf{N}. \qquad (\text{I.48})$$

Combining the variations of eq.(I.48) with eq.(I.45) leads to a constraint between the variations of intensive coordinates

(handwritten: holds for extensive systems)

$$SdT + \mathbf{x} \cdot d\mathbf{J} + \mathbf{N} \cdot d\mu = 0, \qquad (\text{I.49})$$

known as the *Gibbs–Duhem* relation. *(handwritten: → describes the constraint between intensive variables — this relation is the reason we cannot have all-intensive variables.)*

Example: For a fixed amount of gas ($dN = 0$), variations of the chemical potential along an isotherm can be calculated as follows. Since $dT = 0$, the Gibbs-Duhem relation gives $-VdP + Nd\mu = 0$, and

$$d\mu = \frac{V}{N}dP = k_B T \frac{dP}{P}, \qquad (\text{I.50})$$

(handwritten: $\left.\frac{\partial V}{\partial N}\right)_{T,P} = \frac{V}{N}$; $\left.\frac{\partial V}{\partial N}\right)_{T,S} \neq \frac{V}{N}$; only for fixed intensives)

where we have used the ideal gas equation of state $PV = Nk_B T$. Integrating the above equation gives

$$\mu = \mu_0 + k_B T \ln \frac{P}{P_0} = \mu_0 - k_B T \ln \frac{V}{V_0}, \qquad (\text{I.51})$$

where (P_0, V_0, μ_0) refer to the coordinates of a reference point.

(2) Maxwell's Relations: Combining the mathematical rules of differentiation with thermodynamic relationships leads to several useful results. The most important of these are Maxwell's relations which follow from the commutative property $[\partial_x \partial_y f(x, y) = \partial_y \partial_x f(x, y)]$ of derivatives. For example, it follows from eq.(I.45) that

$$\left.\frac{\partial E}{\partial S}\right|_{\mathbf{x},\mathbf{N}} = T, \quad \text{and} \quad \left.\frac{\partial E}{\partial x_i}\right|_{S, x_{j\neq i}, \mathbf{N}} = J_i. \qquad (\text{I.52})$$

The joint second derivative of E is then given by

$$\frac{\partial^2 E}{\partial S \partial x_i} = \frac{\partial^2 E}{\partial x_i \partial S} = \left.\frac{\partial T}{\partial x_i}\right|_S = \left.\frac{\partial J_i}{\partial S}\right|_{x_i}. \qquad (\text{I.53})$$

Since $(\partial y/\partial x) = (\partial x/\partial y)^{-1}$, the above equation can be inverted to give

$$\left.\frac{\partial S}{\partial J_i}\right|_{x_i} = \left.\frac{\partial x_i}{\partial T}\right|_S. \qquad (\text{I.54})$$

17

Similar identities can be obtained from the variations of other state functions. Supposing that we are interested in finding an identity involving $\partial S/\partial x|_T$. We would like to find a state function whose variations include SdT and Jdx. The correct choice is $dF = d(E - TS) = -SdT + Jdx$. Looking at the second derivative of F yields the Maxwell relation

$$- \left. \frac{\partial S}{\partial x} \right|_T = \left. \frac{\partial J}{\partial T} \right|_x .$$ (I.55)

To calculate $\partial S/\partial J|_T$, consider $d(E - TS - Jx) = -SdT - xdJ$, which leads to the identity

$$\left. \frac{\partial S}{\partial J} \right|_T = \left. \frac{\partial x}{\partial T} \right|_J .$$ (I.56)

There are a variety of mnemonics which are supposed to help you remember and construct Maxwell's equations, such as Magic Squares, Jacobians, etc. I personally don't find any of these methods worth learning. The most logical approach is to remember the laws of thermodynamics and hence eq.(I.28), and to then manipulate it so as to find the appropriate derivative using the rules of differentiation.

Example: To obtain $\partial \mu/\partial P|_{N,T}$ for an ideal gas, start with $d(E - TS + PV) = -SdT + VdP + \mu dN$. Clearly

$$\left. \frac{\partial \mu}{\partial P} \right|_{N,T} = \left. \frac{\partial V}{\partial N} \right|_{T,P} = \frac{V}{N} = \frac{k_B T}{P},$$ (I.57)

as in eq.(I.50). From eq.(I.28) it also follows that

$$\left. \frac{\partial S}{\partial V} \right|_{E,N} = \frac{P}{T} = - \frac{\partial E/\partial V|_{S,N}}{\partial E/\partial S|_{V,N}},$$ (I.58)

where we have used eq.(I.45) for the final identity. The above equation can be rearranged into

$$\left. \frac{\partial S}{\partial V} \right|_{E,N} \left. \frac{\partial E}{\partial S} \right|_{V,N} \left. \frac{\partial V}{\partial E} \right|_{S,N} = -1,$$ (I.59)

which is an illustration of the *chain rule* of differentiation.

8.333 Statistical Mechanics I: Statistical Mechanics of Particles
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