

2.F.2. Enthalpy

Combining the results of §2.F.0-1, we see that under the Legendre transform (2.66f)

$$L \equiv U - \frac{\partial U}{\partial \mathcal{X}_i} \mathcal{X}_i = U - \mathcal{Y}_i \mathcal{X}_i \quad (2.83a)$$

we have

$$\begin{aligned} dL &= dU - \mathcal{Y}_i d\mathcal{X}_i - \mathcal{X}_i d\mathcal{Y}_i \\ &= -\mathcal{X}_i d\mathcal{Y}_i + \sum_{k \neq i} \mathcal{Y}_k d\mathcal{X}_k - \bar{d}W_{\text{free}} \end{aligned} \quad (2.83b)$$

so that

$$L = L(\mathcal{Y}_i, \{\mathcal{X}_{k \neq i}\}) = L(\xi_L)$$

where

$$\xi_L = (\mathcal{Y}_i, \{\mathcal{X}_{k \neq i}\}) \quad (2.83c)$$

is the set of independent variables for L . Note that $\xi_U = \mathcal{X}$.

From (2.63b), we have

$$dL = -\bar{d}W_{\text{free}} \Big|_{\xi_L = \text{const}} \rightarrow \Delta L = -W_{\text{free}} \Big|_{\xi_L = \text{const}} \quad (2.83d)$$

so that at constant ξ_L , the reversible work $-W_{\text{free}}$ done on the system is converted entirely to ΔL by imposing constraints on some internal degrees of freedom of the system [see discussion of fig.2.7]. If we remove these constraints, the system will evolve spontaneously back to the former state. Hence [c.f. (2.82)],

$$\Delta L < 0 \quad \text{for all spontaneous processes at constant } \xi_L \quad (2.83e)$$

When all spontaneous processes have stopped, an equilibrium state is reached. (2.83e) then implies L must be a minimum for processes at constant ξ_L .

Thus, L serves as the potential, or **free energy**, for processes at constant ξ_L . In this sense, ξ_L will be called the **natural variables** of L .

For example, consider the case

$$(\mathcal{X}, \mathcal{Y}) = (S, \mathbf{X}, \{N_j\}; T, \mathbf{Y}, \{\mu_j'\})$$

with the fundamental equation

$$U = ST + \mathbf{X} \cdot \mathbf{Y} + \sum_j \mu_j' dN_j \quad (2.83f)$$

and the 1st law for reversible process

$$dU = TdS + \mathbf{Y} \cdot d\mathbf{X} + \sum_j \mu_j' dN_j \quad (2.83g)$$

The Legendre transform

$$\begin{aligned} H &= U - \mathbf{X} \cdot \mathbf{Y} \\ &= ST + \sum_j \mu_j' dN_j \quad [(2.83f) \text{ used. }] \end{aligned} \quad (2.83)$$

then gives

$$dH = TdS - \mathbf{X} \cdot d\mathbf{Y} + \sum_j \mu_j' dN_j \quad (2.84)$$

where the **enthalpy** H is the thermodynamic potential with natural variables

$$\xi_H = (S, \mathbf{Y}, \{N_j\}) \quad (2.84a)$$

Obviously, one can also transform only a few components of \mathbf{X} and leave the rest untouched. However, the resultant potentials are not deemed important enough to warrant a special name.

Comparing (2.84) with

$$\begin{aligned} dH &= \left(\frac{\partial H}{\partial S} \right)_{\mathbf{Y}, \{N_j\}} dS + \left(\frac{\partial H}{\partial \mathbf{Y}} \right)_{S, \{N_j\}} \cdot d\mathbf{Y} + \sum_j \left(\frac{\partial H}{\partial N_j} \right)_{S, \mathbf{Y}, \{N_{k \neq j}\}} dN_j \\ &= \frac{\partial H}{\partial \xi_H} \cdot d\xi_H \end{aligned}$$

gives

$$T = \left(\frac{\partial H}{\partial S} \right)_{\mathbf{Y}, \{N_j\}} \quad (2.85)$$

$$\mathbf{X} = - \left(\frac{\partial H}{\partial \mathbf{Y}} \right)_{S, \{N_j\}} \quad \text{or} \quad X_k = - \left(\frac{\partial H}{\partial Y_k} \right)_{S, \{Y_{i \neq k}\}, \{N_j\}} \quad (2.86)$$

$$\mu_j' = \left(\frac{\partial H}{\partial N_j} \right)_{S, \mathbf{Y}, \{N_{k \neq j}\}} \quad (2.87)$$

or

$$\Psi_H \equiv (T, -\mathbf{X}, \{N_j\}) = \frac{\partial H}{\partial \xi_H} \quad (2.87a)$$

From the necessary condition (2.4) of an exact differential, we have

$$\frac{\partial}{\partial \xi_{Hj}} \left(\frac{\partial H}{\partial \xi_{Hk}} \right) = \frac{\partial}{\partial \xi_{Hk}} \left(\frac{\partial H}{\partial \xi_{Hj}} \right)$$

which gives a new set of Maxwell relations

$$\frac{\partial \Psi_{Hk}}{\partial \xi_{Hj}} = \frac{\partial \Psi_{Hj}}{\partial \xi_{Hk}} \quad (2.87b)$$

Specifically,

$$\begin{aligned} \frac{\partial}{\partial \mathbf{Y}} \left(\frac{\partial H}{\partial S} \right) &= \frac{\partial}{\partial S} \left(\frac{\partial H}{\partial \mathbf{Y}} \right) \\ \rightarrow \left(\frac{\partial T}{\partial \mathbf{Y}} \right)_{S, \{N_j\}} &= - \left(\frac{\partial \mathbf{X}}{\partial S} \right)_{\mathbf{Y}, \{N_j\}} \quad \text{or} \quad \left(\frac{\partial T}{\partial Y_k} \right)_{S, \{Y_{i \neq k}\}, \{N_j\}} = - \left(\frac{\partial X_k}{\partial S} \right)_{\mathbf{Y}, \{N_j\}} \end{aligned} \quad (2.88)$$

$$\begin{aligned} \frac{\partial}{\partial N_k} \left(\frac{\partial H}{\partial S} \right) &= \frac{\partial}{\partial S} \left(\frac{\partial H}{\partial N_k} \right) \\ \rightarrow \left(\frac{\partial T}{\partial N_k} \right)_{S, \mathbf{Y}, \{N_{j \neq k}\}} &= \left(\frac{\partial \mu_k'}{\partial S} \right)_{\mathbf{Y}, \{N_j\}} \end{aligned} \quad (2.89)$$

$$\begin{aligned} \frac{\partial}{\partial N_k} \left(\frac{\partial H}{\partial \mathbf{Y}} \right) &= \frac{\partial}{\partial \mathbf{Y}} \left(\frac{\partial H}{\partial N_k} \right) \\ \rightarrow - \left(\frac{\partial \mathbf{X}}{\partial N_k} \right)_{S, \mathbf{Y}, \{N_{j \neq k}\}} &= \left(\frac{\partial \mu_k'}{\partial \mathbf{Y}} \right)_{S, \{N_j\}} \\ \text{or} \quad - \left(\frac{\partial X_m}{\partial N_k} \right)_{S, \mathbf{Y}, \{N_{j \neq k}\}} &= \left(\frac{\partial \mu_k'}{\partial Y_m} \right)_{S, \{Y_{i \neq m}\}, \{N_j\}} \end{aligned} \quad (2.90)$$

$$\begin{aligned} & \frac{\partial}{\partial N_k} \left(\frac{\partial H}{\partial N_i} \right) = \frac{\partial}{\partial N_i} \left(\frac{\partial H}{\partial N_k} \right) \\ \rightarrow & \left(\frac{\partial \mu_i'}{\partial N_k} \right)_{S, Y, \{N_{j \neq k}\}} = \left(\frac{\partial \mu_k'}{\partial N_i} \right)_{S, Y, \{N_{j \neq i}\}} \end{aligned} \quad (2.91)$$

(2.83d) becomes

$$dH = -\bar{d}W_{\text{free}} \Big|_{(S, Y, \{N_j\}) = \text{const}} \rightarrow \Delta H = -W_{\text{free}} \Big|_{(S, Y, \{N_j\}) = \text{const}} \quad (2.93)$$

so that at constant $(S, Y, \{N_j\})$, the reversible work $-W_{\text{free}}$ done on the system is converted entirely to ΔH . Hence [c.f. (2.83e)],

$$\Delta H < 0 \quad \text{for all spontaneous processes at constant } (S, Y, \{N_j\}) \quad (2.94)$$

which means the equilibrium state for processes at constant $(S, Y, \{N_j\})$ has the minimal enthalpy.

We now proceed to find the equations for a monatomic substance in terms of molar quantities using the notation

$$x = \frac{X}{n} \quad \text{for any extensive variable } X. \quad (2.91a)$$

To begin, (2.83)/ n gives

$$h = u - \mathbf{x} \cdot \mathbf{Y} = sT + \mu \quad (2.91b)$$

where

$$\mu = \frac{\mu' N}{n} = \text{molar chemical potential} \quad (2.91c)$$

Next, (2.84) gives

$$\begin{aligned} & d(nh) = Td(ns) - n\mathbf{x} \cdot d\mathbf{Y} + \mu dn \\ \rightarrow & n(dh - Tds + \mathbf{x} \cdot d\mathbf{Y}) + (h - Ts - \mu)dn = 0 \\ \therefore & dh = Tds - \mathbf{x} \cdot d\mathbf{Y} \quad [(2.91b) \text{ used. }] \end{aligned} \quad (2.91d)$$

(2.89-90) become

$$T = \left(\frac{\partial h}{\partial s} \right)_Y \quad \mathbf{x} = - \left(\frac{\partial h}{\partial \mathbf{Y}} \right)_s \quad (2.91e)$$

There is only one Maxwell relation, namely [see (2.88)]

$$\left(\frac{\partial T}{\partial \mathbf{Y}} \right)_s = - \left(\frac{\partial \mathbf{x}}{\partial s} \right)_Y \quad (2.91f)$$

Ex.2.4.

Compute the enthalpy for n moles of a monatomic ideal gas and express it in terms of its natural variables. The mechanical equation of state is

$$PV = nRT \quad (1a)$$

and the entropy is [see (3) of Ex.2.3]

$$S = \frac{5}{2}nR + nR \ln \left[\frac{V}{V_0} \frac{n_0}{n} \left(\frac{T}{T_0} \right)^{3/2} \right] \quad (1b)$$

Answer

(2.91d) gives

$$dh = T ds + v dP \quad (1c)$$

which can be integrated to give h if T & v are given in term of s & P .

(1b)/ n gives the molar entropy as

$$s = \frac{5}{2}R + R \ln \left[\frac{V}{V_0} \frac{n_0}{n} \left(\frac{T}{T_0} \right)^{3/2} \right] \quad (1d)$$

From (1a), we have

$$\frac{V}{n} = \frac{RT}{P} \quad \& \quad \frac{V_0}{n_0} = \frac{RT_0}{P_0}$$

so that (1d) can be written as

$$\begin{aligned} s &= \frac{5}{2}R + R \ln \left[\frac{RT}{P} \frac{P_0}{RT_0} \left(\frac{T}{T_0} \right)^{3/2} \right] \\ &= \frac{5}{2}R + R \ln \left[\frac{P_0}{P} \left(\frac{T}{T_0} \right)^{5/2} \right] \end{aligned} \quad (1e)$$

with

$$s_0 = s \Big|_{(P,V,T)=(P_0,V_0,T_0)} = \frac{5}{2}R \quad (1f)$$

(1e) & (1a) give

$$\frac{P_0}{P} \left(\frac{T}{T_0} \right)^{5/2} = e^{(s-s_0)/R} \quad \rightarrow \quad \frac{T}{T_0} = \left(\frac{P}{P_0} \right)^{2/5} e^{(s-s_0)/s_0} \quad (1g)$$

$$v = \frac{RT}{P} = \frac{R}{P} T_0 \left(\frac{P}{P_0} \right)^{2/5} e^{(s-s_0)/s_0} \quad (1h)$$

Using

$$\begin{aligned} h &= \int \left(\frac{\partial h}{\partial s} \right)_P ds + c_1(P) \quad [c_1(P) = \text{arbitrary function of } P.] \\ &= \int T ds + c_1(P) \\ &= T_0 \left(\frac{P}{P_0} \right)^{2/5} \int e^{(s-s_0)/s_0} ds + c_1(P) \\ &= T_0 \left(\frac{P}{P_0} \right)^{2/5} s_0 e^{(s-s_0)/s_0} + c_1(P) \end{aligned} \quad (2a)$$

and

$$\begin{aligned} h &= \int \left(\frac{\partial h}{\partial P} \right)_s dP + c_2(s) \quad [c_2(s) = \text{arbitrary function of } s.] \\ &= \frac{RT_0}{P_0^{2/5}} e^{(s-s_0)/s_0} \int P^{-3/5} dP + c_2(s) \\ &= \frac{5}{2} \frac{RT_0}{P_0^{2/5}} e^{(s-s_0)/s_0} P^{2/5} + c_2(s) \\ &= T_0 \left(\frac{P}{P_0} \right)^{2/5} s_0 e^{(s-s_0)/s_0} + c_2(s) \end{aligned} \quad (2b)$$

Combining (2a) & (2b) gives

$$c_1(P) = c_2(s) = 0$$

and

$$h = T_0 \left(\frac{P}{P_0} \right)^{2/5} s_0 e^{(s-s_0)/s_0}$$

$$\rightarrow h_0 = T_0 s_0 = \frac{5}{2} R T_0 \quad [(1f) \text{ used. }]$$

so that

$$h = h_0 \left(\frac{P}{P_0} \right)^{2/5} e^{(s-s_0)/s_0}$$

$$= \frac{5}{2} R T_0 \left(\frac{P}{P_0} \right)^{2/5} e^{(s-s_0)/s_0}$$

$$= \frac{5}{2} R T \quad [(1g) \text{ used. }] \quad (3)$$

Alternatively, using [see Ex.2.3]

$$u = \frac{3}{2} R T$$

(2.91b) gives

$$h = u + vP$$

$$= \frac{3}{2} R T + R T \quad [(1h) \text{ used. }]$$

$$= \frac{5}{2} R T$$

$$= \frac{5}{3} u$$