

2.F.3. Helmholtz Free Energy

The Helmholtz free energy, usually denoted by A or F , is defined by the Legendre transform

$$\begin{aligned} A &= U - ST \\ &= \mathbf{X} \cdot \mathbf{Y} + \sum_j \mu_j' N_j \quad [(2.61) \text{ used. }] \end{aligned} \quad (2.95)$$

so that

$$A = A(\xi_A) \quad \text{with} \quad \xi_A = (T, \mathbf{X}, \{N_j\}) \quad (2.96a)$$

Following closely the procedure described in §2.F.2, we have

$$\begin{aligned} dA &= -SdT + \mathbf{Y} \cdot d\mathbf{X} + \sum_j \mu_j' dN_j \\ &= \Psi_A \cdot d\xi_A \quad \text{with} \quad \Psi_A = (-S, \mathbf{Y}, \{\mu_j'\}) \\ &= \frac{\partial A}{\partial \xi_A} \cdot d\xi_A \end{aligned} \quad (2.96)$$

Thus,

$$\Psi_A = \frac{\partial A}{\partial \xi_A} \quad (2.96b)$$

or, more specifically,

$$-S = \left(\frac{\partial A}{\partial T} \right)_{\mathbf{X}, \{N_j\}} \quad (2.97)$$

$$\mathbf{Y} = \left(\frac{\partial A}{\partial \mathbf{X}} \right)_{T, \{N_j\}} \quad \text{or} \quad Y_k = \left(\frac{\partial A}{\partial X_k} \right)_{T, \{X_{i \neq k}\}, \{N_j\}} \quad (2.98)$$

$$\mu_j' = \left(\frac{\partial A}{\partial N_j} \right)_{T, \mathbf{X}, \{N_{k \neq j}\}} \quad (2.99)$$

The Maxwell equations are

$$\frac{\partial \Psi_{Ak}}{\partial \xi_{Aj}} = \frac{\partial \Psi_{Aj}}{\partial \xi_{Ak}} \quad (2.99a)$$

or

$$\begin{aligned} \frac{\partial}{\partial \mathbf{X}} \left(\frac{\partial A}{\partial T} \right) &= \frac{\partial}{\partial T} \left(\frac{\partial A}{\partial \mathbf{X}} \right) \\ \rightarrow - \left(\frac{\partial S}{\partial X_k} \right)_{T, \{X_{i \neq k}\}, \{N_j\}} &= \left(\frac{\partial Y_k}{\partial T} \right)_{\mathbf{X}, \{N_j\}} \end{aligned} \quad (2.100)$$

$$\begin{aligned} \frac{\partial}{\partial N_k} \left(\frac{\partial A}{\partial T} \right) &= \frac{\partial}{\partial T} \left(\frac{\partial A}{\partial N_k} \right) \\ \rightarrow - \left(\frac{\partial S}{\partial N_k} \right)_{T, \mathbf{X}, \{N_{j \neq k}\}} &= \left(\frac{\partial \mu_k'}{\partial T} \right)_{\mathbf{X}, \{N_j\}} \end{aligned} \quad (2.101)$$

$$\begin{aligned} \frac{\partial}{\partial N_k} \left(\frac{\partial A}{\partial X_i} \right) &= \frac{\partial}{\partial X_i} \left(\frac{\partial A}{\partial N_k} \right) \\ \rightarrow \left(\frac{\partial Y_i}{\partial N_k} \right)_{T, \mathbf{X}, \{N_{j \neq k}\}} &= \left(\frac{\partial \mu_k'}{\partial X_i} \right)_{T, \{X_{i \neq i}\}, \{N_j\}} \end{aligned} \quad (2.102)$$

$$\begin{aligned} & \frac{\partial}{\partial N_k} \left(\frac{\partial A}{\partial N_i} \right) = \frac{\partial}{\partial N_i} \left(\frac{\partial A}{\partial N_k} \right) \\ \rightarrow & \left(\frac{\partial \mu_i'}{\partial N_k} \right)_{T, X, \{N_j \neq k\}} = \left(\frac{\partial \mu_k'}{\partial N_i} \right)_{T, X, \{N_j \neq i\}} \end{aligned} \quad (2.103)$$

(2.83d) becomes

$$dA = -\bar{d}W_{\text{free}} \Big|_{(T, X, \{N_j\}) = \text{const}} \rightarrow \Delta A = -W_{\text{free}} \Big|_{(T, X, \{N_j\}) = \text{const}} \quad (2.105)$$

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

$$\Delta A < 0 \quad \text{for all spontaneous processes at constant } (T, X, \{N_j\}) \quad (2.106)$$

which means the equilibrium state for processes at constant $(T, X, \{N_j\})$ has the minimal Helmholtz free energy.

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

$$x = \frac{X}{n} \quad \text{for any extensive variable } X. \quad (2.106a)$$

To begin, (2.95)/ n gives

$$a = u - sT = xY + \mu \quad (2.106b)$$

where

$$\mu = \frac{\mu' N}{n} = \text{molar chemical potential} \quad (2.106c)$$

Next, (2.96) gives

$$\begin{aligned} & d(na) = -nsdT + Yd(nx) + \mu dn \\ \rightarrow & n(da + sdT - Ydx) + (a - xY - \mu)dn = 0 \\ \therefore & da = -sdT + Ydx \quad [(2.106b) \text{ used. }] \end{aligned} \quad (2.106d)$$

(2.97-98) become

$$-s = \left(\frac{\partial a}{\partial T} \right)_x \quad Y = \left(\frac{\partial a}{\partial x} \right)_T \quad (2.106e)$$

There is only one Maxwell relation, namely [see (2.100)]

$$-\left(\frac{\partial s}{\partial x} \right)_T = \left(\frac{\partial Y}{\partial T} \right)_x \quad (2.106f)$$

Ex.2.5.

Compute the Helmholtz free energy 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

(2.106d) gives

$$da = -s dT - P dv \quad (1c)$$

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

(1b)/ n gives the molar entropy as

$$s = \frac{5}{2}R + R \ln \left[\frac{v}{v_0} \left(\frac{T}{T_0} \right)^{3/2} \right] \quad (1d)$$

with

$$s_0 = s \Big|_{(P, v, T) = (P_0, v_0, T_0)} = \frac{5}{2}R \quad (1e)$$

(1a) gives

$$P = \frac{RT}{v} \quad (1f)$$

Using

$$\begin{aligned} a &= \int \left(\frac{\partial a}{\partial T} \right)_v dT + c_1(v) \quad [c_1(v) = \text{arbitrary function of } v.] \\ &= - \int s dT + c_1(v) \\ &= - \int \left\{ \frac{5}{2}R + R \ln \left[\frac{v}{v_0} \left(\frac{T}{T_0} \right)^{3/2} \right] \right\} dT + c_1(v) \quad [(1d) \text{ used.}] \\ &= - \left\{ \frac{5}{2}R + R \ln \left[\frac{v}{v_0} \left(\frac{1}{T_0} \right)^{3/2} \right] \right\} T - \frac{3}{2}R(-T + T \ln T) + c_1(v) \\ &= -RT \left\{ 1 + \ln \left[\frac{v}{v_0} \left(\frac{T}{T_0} \right)^{3/2} \right] \right\} + c_1(v) \quad (2a) \end{aligned}$$

and

$$\begin{aligned} h &= \int \left(\frac{\partial a}{\partial v} \right)_T dv + c_2(T) \quad [c_2(T) = \text{arbitrary function of } T.] \\ &= - \int P dv + c_2(T) \\ &= -RT \int \frac{1}{v} dv + c_2(T) \quad [(1f) \text{ used.}] \\ &= -RT \ln v + c_2(T) \quad (2b) \end{aligned}$$

Combining (2a) & (2b) gives

$$\begin{aligned} c_1(v) &= 0 \\ c_2(T) &= -RT \left\{ 1 + \ln \left[\frac{1}{v_0} \left(\frac{T}{T_0} \right)^{3/2} \right] \right\} \end{aligned}$$

and

$$a = -RT \left\{ 1 + \ln \left[\frac{v}{v_0} \left(\frac{T}{T_0} \right)^{3/2} \right] \right\}$$

Alternatively, using [see Ex.2.3]

$$u = \frac{3}{2}RT$$

(2.106b) gives

$$\begin{aligned} a &= u - sT \\ &= \frac{3}{2}RT - \left\{ \frac{5}{2}R + R \ln \left[\frac{v}{v_0} \left(\frac{T}{T_0} \right)^{3/2} \right] \right\} T && \text{[(1d) used.]} \\ &= -RT \left\{ 1 + \ln \left[\frac{v}{v_0} \left(\frac{T}{T_0} \right)^{3/2} \right] \right\} \end{aligned}$$