

## 2.F.4. Gibbs Free Energy

The Gibbs free energy  $G$  is defined by the double Legendre transform

$$\begin{aligned} G &= U - ST - \mathbf{X} \cdot \mathbf{Y} \\ &= H - ST = A - \mathbf{X} \cdot \mathbf{Y} \\ &= \sum_j \mu_j' N_j \quad \text{[ (2.61) used. ]} \end{aligned} \quad (2.107)$$

so that

$$G = G(\xi_G) \quad \text{with} \quad \xi_G = (T, \mathbf{Y}, \{N_j\}) \quad (2.107a)$$

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

$$\begin{aligned} dG &= -SdT - \mathbf{X} \cdot d\mathbf{Y} + \sum_j \mu_j' dN_j \quad (2.108) \\ &= \Psi_G \cdot d\xi_G \quad \text{with} \quad \Psi_G = (-S, -\mathbf{X}, \{\mu_j'\}) \\ &= \frac{\partial G}{\partial \xi_G} \cdot d\xi_G \end{aligned}$$

Thus,

$$\Psi_G = \frac{\partial G}{\partial \xi_G} \quad (2.108a)$$

or, more specifically,

$$-S = \left( \frac{\partial G}{\partial T} \right)_{\mathbf{Y}, \{N_j\}} \quad (2.109)$$

$$-\mathbf{X} = \left( \frac{\partial G}{\partial \mathbf{Y}} \right)_{T, \{N_j\}} \quad \text{or} \quad -X_k = \left( \frac{\partial G}{\partial Y_k} \right)_{T, \{Y_{i \neq k}\}, \{N_j\}} \quad (2.110)$$

$$\mu_j' = \left( \frac{\partial G}{\partial N_j} \right)_{T, \mathbf{Y}, \{N_{k \neq j}\}} \quad (2.111)$$

The Maxwell equations are

$$\frac{\partial \Psi_{Gk}}{\partial \xi_{Gj}} = \frac{\partial \Psi_{Gj}}{\partial \xi_{Gk}} \quad (2.111a)$$

or

$$\begin{aligned} \frac{\partial}{\partial \mathbf{Y}} \left( \frac{\partial G}{\partial T} \right) &= \frac{\partial}{\partial T} \left( \frac{\partial G}{\partial \mathbf{Y}} \right) \\ \rightarrow \left( \frac{\partial S}{\partial Y_k} \right)_{T, \{Y_{i \neq k}\}, \{N_j\}} &= - \left( \frac{\partial X_k}{\partial T} \right)_{\mathbf{Y}, \{N_j\}} \end{aligned} \quad (2.112)$$

$$\begin{aligned} \frac{\partial}{\partial N_k} \left( \frac{\partial G}{\partial T} \right) &= \frac{\partial}{\partial T} \left( \frac{\partial G}{\partial N_k} \right) \\ \rightarrow - \left( \frac{\partial S}{\partial N_k} \right)_{T, \mathbf{Y}, \{N_{j \neq k}\}} &= \left( \frac{\partial \mu_k'}{\partial T} \right)_{\mathbf{Y}, \{N_j\}} \end{aligned} \quad (2.113)$$

$$\begin{aligned} \frac{\partial}{\partial N_k} \left( \frac{\partial G}{\partial Y_i} \right) &= \frac{\partial}{\partial Y_i} \left( \frac{\partial G}{\partial N_k} \right) \\ \rightarrow - \left( \frac{\partial X_i}{\partial N_k} \right)_{T, \mathbf{Y}, \{N_{j \neq k}\}} &= \left( \frac{\partial \mu_k'}{\partial Y_i} \right)_{T, \{Y_{n \neq i}\}, \{N_j\}} \end{aligned} \quad (2.114)$$

$$\begin{aligned} \frac{\partial}{\partial N_k} \left( \frac{\partial G}{\partial N_i} \right) &= \frac{\partial}{\partial N_i} \left( \frac{\partial G}{\partial N_k} \right) \\ \rightarrow \left( \frac{\partial \mu_i'}{\partial N_k} \right)_{T, Y, \{N_{j \neq k}\}} &= \left( \frac{\partial \mu_k'}{\partial N_i} \right)_{T, Y, \{N_{j \neq i}\}} \end{aligned} \quad (2.115)$$

(2.83d) becomes

$$dG = -\bar{d}W_{\text{free}} \Big|_{(T, Y, \{N_j\}) = \text{const}} \rightarrow \Delta G = -W_{\text{free}} \Big|_{(T, Y, \{N_j\}) = \text{const}} \quad (2.117)$$

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

$$\Delta G < 0 \quad \text{for all spontaneous processes at constant } (T, Y, \{N_j\}) \quad (2.118)$$

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

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

$$x = \frac{X}{n} \quad \text{for any extensive variable } X. \quad (2.118a)$$

To begin, (2.107)/ $n$  gives

$$g = u - sT - xY = \mu \quad (2.118b)$$

where

$$\mu = \frac{\mu' N}{n} = \text{molar chemical potential} \quad (2.118c)$$

Next, (2.108) gives

$$\begin{aligned} d(n g) &= -n s dT - n x dY + \mu dn \\ \rightarrow n(dg + s dT + x dY) + (g - \mu) dn &= 0 \\ \therefore dg &= -s dT - x dY \quad [ (2.118b) \text{ used. } ] \end{aligned} \quad (2.118d)$$

(2.109-10) become

$$-s = \left( \frac{\partial g}{\partial T} \right)_Y \quad -x = \left( \frac{\partial g}{\partial Y} \right)_T \quad (2.118e)$$

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

$$-\left( \frac{\partial s}{\partial Y} \right)_T = -\left( \frac{\partial x}{\partial T} \right)_Y \quad (2.118f)$$

### Ex.2.5.

Consider a system that can do work

$$\bar{d}W = -Y dX + \bar{d}W' \quad (1a)$$

Assume the processes take place spontaneously so that

$$dS = \frac{\bar{d}Q}{T} + dS_i \quad (1b)$$

where  $d_i S$  is the excess entropy. Given the definition

$$G = U - XY - TS \quad (1c)$$

show that

$$-(dG)_{Y,T} = \bar{d}W' + T dS_i \quad (1d)$$

Therefore, at fixed  $Y$  &  $T$ , all of  $G$  is available to do work for reversible processes. However, for spontaneous processes, the amount of work that can be done is diminished because part of  $G$  is used to produce entropy. This result is the starting point for non-equilibrium thermodynamics.

## Answer

(1c) gives

$$dG = dU - X dY - Y dX - T dS - S dT \quad (1e)$$

Using the 1st law

$$\begin{aligned} dU &= \bar{d}Q - \bar{d}W \\ &= \bar{d}Q + Y dX - \bar{d}W' \quad [ (1a) \text{ used. } ] \end{aligned} \quad (1f)$$

(1e) becomes

$$dG = \bar{d}Q - \bar{d}W' - X dY - T dS - S dT$$

$$\begin{aligned} \rightarrow (dG)_{Y,T} &= \bar{d}Q - \bar{d}W' - T dS \\ &= -\bar{d}W' - T dS_i \quad [ (1b) \text{ used. } ] \end{aligned}$$

QED.

----- End of Ex.2.6. -----

For a system of mixtures, it is convenient to introduce partial quantities that can be attributed to each type of molecules. For example, the **partial pressure**  $P_j$  of type  $j$  molecules is related to the total pressure  $P$  by

$$P = \sum_j P_j$$

For an extensive quantity  $X$ , one can also introduce the partial molar quantities  $x_j$  through

$$X = \sum_j X_j = \sum_j n_j x_j$$

which also shows that  $X$  is a 1st order homogeneous function of  $n_j$ , i.e.,

$$X(\{\lambda n_j\}) = \lambda X(\{n_j\})$$

Consider now a  $PVT$  system of mixtures. (2.107) then gives

$$G = \sum_j \mu_j' N_j = \sum_j \mu_j n_j \quad (2.119)$$

$$= \sum_j \left( \frac{\partial G}{\partial n_j} \right)_{T,P,\{n_{k \neq j}\}} n_j \quad [ (2.111) \text{ used. } ] \quad (2.119a)$$

so that the molar chemical potential  $\mu_j$  is also the **partial molar Gibbs free energy** for type  $j$  molecules..

The **partial molar volume**  $v_j$  is given by

$$V = \sum_j n_j v_j = \sum_j \left( \frac{\partial V}{\partial n_j} \right)_{T,P,\{n_{k \neq j}\}} n_j \quad (2.120)$$

The **partial molar entropy**  $s_j$  is given by

$$S = \sum_j n_j s_j = \sum_j \left( \frac{\partial S}{\partial n_j} \right)_{T, P, \{n_{k \neq j}\}} n_j \quad (2.121)$$

The **partial molar enthalpy**  $h_j$  is given by

$$\begin{aligned} H &= \sum_j n_j h_j = \sum_j n_j (\mu_j + T s_j) \quad [ (2.91b) \text{ of } \S 2.F.2 \text{ used. } ] \\ &= \sum_j \left( \frac{\partial H}{\partial n_j} \right)_{S, P, \{n_{k \neq j}\}} n_j \end{aligned} \quad (2.121a)$$

### Ex.2.7.

Consider a fluid of  $m$  different types of particles subject to an electric potential  $\phi$ . Thus,

$$dU = T dS - P dV + \phi de + \sum_{j=1}^m \mu_j dn_j \quad (1a)$$

Find  $dG$  needed to bring  $dn_j$  moles of particles into the system by a reversible process at fixed  $(T, P, \{n_{k \neq j}\})$ . Assume that a type  $j$  particle has valence  $z_j$ .

### Answer

The charge of  $dn_j$  moles of particles is given by

$$de = \sum_{j=1}^m z_j F dn_j \quad (1b)$$

where

$F$  = Faraday = amount of charge in 1 mole of protons.

(1a) thus becomes

$$dU = T dS - P dV + \sum_{j=1}^m (\mu_j + z_j F \phi) dn_j$$

so that

$$\begin{aligned} dG &= dU - T dS - S dT + P dV + V dP \\ &= -S dT + V dP + \sum_{j=1}^m (\mu_j + z_j F \phi) dn_j \end{aligned}$$

Thus,  $dG$  needed to bring  $dn_j$  moles of particles into the system by a reversible process at fixed  $(T, P, \{n_{k \neq j}\})$  is

$$(dG)_{T, P, \{n_{k \neq j}\}} = (\mu_j + z_j F \phi) dn_j \quad (2)$$

The quantity

$$\tilde{\mu}_j = \mu_j + z_j F \phi \quad (3)$$

is called the **electrochemical potential**.