Chapter 8
Multicomponent Homogeneous Nonreacting Systems: Solutions

Notes on
Thermodynamics in Materials Science
by
Robert T. DeHoff
Extensive Quantities of the State Functions: $F'$, $G'$, $H'$, $S'$, $U'$, $V'$

Using $G'$ as example:

$$G' = G'(T, P, n_1, n_2 \ldots n_k \ldots n_c)$$

A differential form of $G'$:

$$dG' = \left(\frac{\partial G'}{\partial T}\right)_{P,n_k} dT + \left(\frac{\partial G'}{\partial P}\right)_{T,n_k} dP + \sum_{k=1}^{c} \left(\frac{\partial G'}{\partial n_k}\right)_{T,P,n_{j\neq k}} dn_k$$

and at constant $T$ & $P$:

$$\left(dG'\right)_{T,P} = \sum_{k=1}^{c} \left(\frac{\partial G'}{\partial n_k}\right)_{T,P,n_{j\neq k}} dn_k$$
Partial Molal Quantities of the State Functions: $\overline{F}_k, \overline{G}_k, \overline{H}_k, \overline{S}_k, \overline{U}_k, \overline{V}_k$.

Using $\overline{G}_k$ as example:

$$\overline{G}_k = \left( \frac{\partial G'}{\partial n_k} \right)_{T,P,n_j \neq n_k}$$

A differential form of $G'$ (use definition of $\overline{G}_k$):

$$dG' = \left( \frac{\partial G'}{\partial T} \right)_{P,n_k} dT + \left( \frac{\partial G'}{\partial P} \right)_{T,n_k} dP + \sum_{k=1}^{c} \overline{G}_k dn_k$$

and at constant $T$ & $P$:

$$\left( dG' \right)_{T,P} = \sum_{k=1}^{c} \overline{G}_k dn_k$$
Gibbs-Duhem Equation

The contributions of the components sum to the whole:

\[ G' = \sum_{k=1}^{c} G_k n_k \]

Differentiating the products on the right yields:

\[ dG' = \sum_{k=1}^{c} G_k d n_k + \sum_{k=1}^{c} n_k dG_k \]

Inspection yields the Gibbs-Duhem equation:

\[ \sum_{k=1}^{c} n_k dG_k = 0 \]

For a binary system:

\[ dG_2 = -\frac{n_1}{n_2} dG_1 \]
Reference States:
\[ F^O, G^O, H^O, S^O, U^O, V^O \]

- T, S, V, P have absolute values.
- F, G, H, U have relative values.
- The difference in values between states is unique.
- To compare values, use the same reference state.
- Superscript \(^O\) refers to the reference state.

**Rule of mixtures.**

\[
G^O = \sum_{k=1}^{c} G_k^O n_k
\]

- Preferably, for a solution use the pure components in the same phase as the solution as the reference state.
Rule of Mixtures

For binary

Extensive $G^{/o} = \sum_{k=1}^{2} G_k^o n_k = G_1^o n_1 + G_2^o n_2$

Molar

$G^o = G_1^o X_1 + G_2^o X_2$

Rule of mixtures

$\frac{G^{/o}}{n_1 + n_2} = \frac{G_1^o}{n_1 + n_2} \frac{n_1}{n_1 + n_2} + \frac{G_2^o}{n_1 + n_2} \frac{n_2}{n_1 + n_2}$
Mixing Values for Solutions
\( \Delta F'_\text{mix}, \Delta G'_\text{mix}, \Delta H'_\text{mix}, \Delta S'_\text{mix}, \Delta U'_\text{mix}, \Delta V'_\text{mix} \)

For solution: Gibbs free energy of mixing.
\[
\Delta G'_\text{mix} = G'_\text{so ln} - G'^O
\]

For component \( k \): Change experienced when 1 mole of \( k \) is transferred from its reference state to the given solution.
\[
\Delta \overline{G}_k = \overline{G}_k - G^O_k
\]

Contributions of the components add to the whole:
\[
\Delta G'_\text{mix} = \sum_{k=1}^{c} \overline{G}_k n_k - \sum_{k=1}^{c} G^O_k n_k
\]

and
\[
\Delta G'_\text{mix} = \sum_{k=1}^{c} \Delta \overline{G}_k n_k
\]
Mixing Values

\[ \Delta G_{\text{mix}}' \equiv G_{so \ln}' - G'^{\circ} \]
Mixing values for Solutions
\[ \Delta F'_{\text{mix}}, \Delta G'_{\text{mix}}, \Delta H'_{\text{mix}}, \Delta S'_{\text{mix}}, \Delta U'_{\text{mix}}, \Delta V'_{\text{mix}} \]

Differential form:
\[
d\Delta G'_{\text{mix}} = \sum_{k=1}^{c} \left[ \overline{G}_k \, dn_k + n_k \, d\overline{G}_k - G^0_k \, dn_k - n_k \, dG^0_k \right]
\]

Total derivative:
\[
d\Delta G'_{\text{mix}} = \sum_{k=1}^{c} \left[ \Delta \overline{G}_k \, dn_k + n_k \, d\Delta \overline{G}_k \right]
\]

Gibbs-Duhem for mixing:
\[
\sum_{k=1}^{c} n_k \, d\Delta \overline{G}_k = 0
\]
Graphical Evaluation of Partial Molal Values

Consider a binary system (alloy):

$$\Delta G_{mix} = \Delta \bar{G}_1 X_1 + \Delta \bar{G}_2 X_2$$

$$d\Delta G_{mix} = \Delta \bar{G}_1 dX_1 + \Delta \bar{G}_2 dX_2$$

Note:

$$X_1 + X_2 = 1 \quad dX_1 = -dX_2$$

Substitute & rearrange:

$$\Delta \bar{G}_2 = \Delta G_{mix} + (1 - X_2) \frac{d\Delta G_{mix}}{dX_2}$$

$$\Delta \bar{G}_1 = \Delta G_{mix} + (1 - X_1) \frac{d\Delta G_{mix}}{dX_1}$$

and

$$\frac{d\Delta G_{mix}}{dX_2} = -\frac{d\Delta G_{mix}}{dX_1} = -(\Delta \bar{G}_2 - \Delta \bar{G}_1)$$
Derivation: Graphical Evaluation of Partial Molal Values

\[
\Delta G_{\text{mix}} = \Delta G_1 X_1 + \Delta G_2 X_2 \tag{1}
\]

\[
d\Delta G_{\text{mix}} = \Delta G_1 dX_1 + \Delta G_2 dX_2 \tag{2}
\]

\[
X_1 + X_2 = 1 \quad \text{(3a)} \quad \quad \quad \quad dX_1 = -dX_2 \quad \text{(3b)}
\]

Rearrange (2) \[\Delta \overline{G}_2 = +\Delta \overline{G}_1 + \frac{d\Delta G_{\text{mix}}}{dX_2} \tag{4}\]

Rearrange (1) \[\Delta \overline{G}_1 = \frac{\Delta G_{\text{mix}}}{X_1} - \Delta \overline{G}_2 \frac{X_2}{X_1} \tag{5}\]

Insert (5) in (4) \[\Delta \overline{G}_2 \left( \frac{X_1 + X_2}{X_1} \right) = \frac{\Delta G_{\text{mix}}}{X_1} + \frac{d\Delta G_{\text{mix}}}{dX_2} \tag{6}\]

Yielding \[\Delta \overline{G}_2 = \Delta G_{\text{mix}} + \left(1 - X_2 \right) \frac{d\Delta G_{\text{mix}}}{dX_2} \]
Integration of the Gibbs-Duhem Equation(s)

For a binary system (alloy):

\[ X_1 d\Delta \overline{G}_1 + X_2 d\Delta \overline{G}_2 = 0 \]

and

\[ d\Delta \overline{G}_1 = -\frac{X_2}{X_1} d\Delta \overline{G}_2 \]

Integrating the left side from \( X_2 = 0 \) to \( X_2 \):

\[ \int_{X_2=0}^{X_2} d\Delta \overline{G}_1 = \Delta \overline{G}_1(X_2) - \Delta \overline{G}_1(X_1 = 1) = \Delta \overline{G}_1(X_2) \]

Now integrate right side:

\[ \Delta \overline{G}_1 = - \int_{X_2=0}^{X_2} \frac{X_2}{X_1} \frac{d \Delta \overline{G}_2}{dX_2} dX_2 \]
Molar Values of the State Functions

Note:

Then,

\[ X_k = \frac{n_k}{\sum_{k=1}^{c} n_k} \]

\[ dG = \sum_{k=1}^{c} \bar{G}_k dX_k \]

\[ G = \sum_{k=1}^{c} \bar{G}_k X_k \]

\[ \sum_{k=1}^{c} X_k d\bar{G}_k = 0 \]

\[ d\Delta G_{mix} = \sum_{k=1}^{c} \Delta \bar{G}_k dX_k \]

\[ \Delta G_{mix} = \sum_{k=1}^{c} \Delta \bar{G}_k X_k \]

\[ \sum_{k=1}^{c} X_k d\Delta \bar{G}_k = 0 \]
Chemical Potential of (Open) Multicomponent Systems

\[ U' = U'(T, P, n_1, n_2 \ldots n_k \ldots n_c) \]

\[ dU' = T dS' - P dV' + \sum_{k=1}^{c} \mu_k d n_k \quad (c+2 \text{term}) \]

\[ \mu_k = \left( \frac{\partial U'}{\partial n_k} \right)_{S',V',n_j \neq n_k} \]

\[ \delta W' = \sum_{k=1}^{c} \mu_k d n_k \]

\[ \mu_k = \left( \frac{\partial U'}{\partial n_k} \right)_{S',V',n_j} = \left( \frac{\partial H'}{\partial n_k} \right)_{S',P,n_j} = \left( \frac{\partial F'}{\partial n_k} \right)_{T,V',n_j} = \left( \frac{\partial G'}{\partial n_k} \right)_{T,P,n_j} \]
Chemical Potential of (Open) Multicomponent Systems

\[ \mu_k = \bar{G}_k = \left( \frac{\partial G'}{\partial n_k} \right)_{T,P,n_j \neq n_k} \]

\[ \bar{S}_k = -\left( \frac{\partial \bar{G}_k}{\partial T} \right)_{P,n_k} = -\left( \frac{\partial \mu_k}{\partial T} \right)_{P,n_k} \]

\[ \bar{V}_k = \left( \frac{\partial \bar{G}_k}{\partial P} \right)_{T,n_k} = \left( \frac{\partial \mu_k}{\partial P} \right)_{T,n_k} \]

\[ \bar{H}_k = \bar{G}_k + T\bar{S}_k = \mu_k - T\left( \frac{\partial \mu_k}{\partial T} \right)_{P,n_k} \]

\[ \bar{F}_k = \bar{U}_k - T\bar{S}_k = \mu_k - P\left( \frac{\partial \mu_k}{\partial P} \right)_{T,n_k} \]

\[ \bar{U}_k = \bar{H}_k - P\bar{V}_k = \mu_k - P\left( \frac{\partial \mu_k}{\partial P} \right)_{T,n_k} - T\left( \frac{\partial \mu_k}{\partial T} \right)_{P,n_k} \]
Activities and Activity Coefficients

Definition of activity, $a_k$ (dimensionless):

$$
\mu_k - \mu_k^0 = \Delta \mu_k = RT \ln a_k
$$

Definition of activity coefficient, $\gamma_k$ (dimensionless):

$$
a_k = \gamma_k X_k \quad \mu_k - \mu_k^0 = \Delta \mu_k = RT \ln \gamma_k X_k
$$

If

- $\gamma_k < 1 \quad a_k < X_k$  $k$ is less apparent than its mole fraction.
- $\gamma_k = 1 \quad a_k = X_k$  $k$ is as apparent as its mole fraction.
- $\gamma_k > 1 \quad a_k > X_k$  $k$ is more apparent than its mole fraction.
Ideal Solution

No heat of mixing.  \[ \Delta H_k = 0 \quad \Delta H_{mix} = 0 \]

No volume change.  \[ \Delta V_k = 0 \quad \Delta V_{mix} = 0 \]

No change in internal energy.  \[ \Delta U_k = 0 \quad \Delta U_{mix} = 0 \]

Entropy increases.  \[ \Delta S_k = -R \ln X_k \]

\[ \Delta S_{mix} = -R \sum_{k=1}^{c} X_k \ln X_k \]

Helmholtz free energy decreases.  \[ \Delta F_k = RT \ln X_k \]

\[ \Delta F_{mix} = RT \sum_{k=1}^{c} X_k \ln X_k \]

Gibbs free energy decreases.  \[ \Delta G_k = RT \ln X_k \]

\[ \Delta G_{mix} = RT \sum_{k=1}^{c} X_k \ln X_k \]
Ideal Solution

\[ \Delta S_{\text{mix}} \]

\[ \Delta H_{\text{mix}} \]

0

\[ X_2 \]

\[ \Delta G_{\text{mix}} \]

0

\[ T \]

\[ X_2 \]
Ideal Solution

• All plots (e.g. $\Delta G_{\text{mix}}$ vs. $X_k$) are symmetrical with composition.

• Slopes of plots of $\Delta S_{\text{mix}}$, $\Delta F_{\text{mix}}$, $\Delta G_{\text{mix}}$ are infinite at $X_k = 0$ & $X_k = 1$.

• Entropy of mixing is independent of temperature.
Ideal Solution

Activity is the same as mole fraction.
Activity coefficient is one.

\[ a_k = X_k \]

\[ \gamma_k = 1 \]

Slope = 1
Dilute Solutions: Raoult & Henry’s Laws

Raoult’s Law for the solvent in dilute solutions:

\[ \lim_{X_1 \to 1} a_1 = X_1 \]

Henry’s Law for the solute in dilute solutions:

\[ \lim_{X_2 \to 0} a_2 = \gamma^0 X_2 \]

\( \gamma^0 \neq 0 \) for small \( X_2 \)
Real Solutions: Relation of Activity Coefficient to Free Energy

\[ a_k \equiv \gamma_k X_k \]

\[ \Delta \mu_k = \Delta \bar{G}_k = RT \ln \gamma_k X_k = RT \ln \gamma_k + RT \ln X_k \]

\[ \Delta \mu_k = \Delta \bar{G}_k = \Delta \bar{G}_k^{XS} + \Delta \bar{G}_k^{ID} \]

Ideal partial molal free energy of mixing:

\[ \Delta \bar{G}_k^{ID} = RT \ln X_k \]

Excess partial molal free energy of mixing:

\[ \Delta \bar{G}_k^{XS} = RT \ln \gamma_k \]
Regular Solution

Heat of mixing is a function of composition, only.

\[ \Delta H_{\text{mix}} = \Delta H_{\text{mix}}(X_1, X_2, \ldots X_k, \ldots X_c) \]

\[ \Delta H_{\text{mix}} \neq \Delta H_{\text{mix}}(T, P) \]

Entropy is the same as for ideal solution.

\[ \Delta S_k = -R \ln X_k \quad \Delta S_{\text{mix}} = -R \sum_{k=1}^{c} X_k \ln X_k \]

Helmholtz free energy decreases.

\[ \Delta F_k = \Delta U_k + RT \ln X_k \quad \Delta F_{\text{mix}} = \Delta U_{\text{mix}} + RT \sum_{k=1}^{c} X_k \ln X_k \]

Gibbs free energy decreases.

\[ \Delta G_k = \Delta H_k + RT \ln X_k \quad \Delta G_{\text{mix}} = \Delta H_{\text{mix}} + RT \sum_{k=1}^{c} X_k \ln X_k \]
Regular Solution

\[ \Delta S_{\text{mix}} \]

\[ \Delta H_{\text{mix}} \]

\[ X_2 \]

\[ \Delta G_{\text{mix}} \]

\[ X_2 \]

09/19/2001 Notes from R.T. DeHoff, Thermodynamics in Materials Science (McGraw-Hill, 1993)
Regular Solution

\[ \Delta H_{\text{mix}} \]

\[ \Delta S_{\text{mix}} \]

\[ 0 \]

\[ X_2 \]

\[ \Delta G_{\text{mix}} \]

\[ 0 \]

\[ X_2 \]

\[ T \]
Regular Solution

$\Delta H_{\text{mix}}$

$\Delta S_{\text{mix}}$

$0$

$X_2$

$\Delta G_{\text{mix}}$

$X_2$

$0$

Regular Solution

\[ \Delta H_{\text{mix}} \]
\[ \Delta S_{\text{mix}} \]

\[ X_2 \]

\[ \Delta G_{\text{mix}} \]

Problem 8.6 DeHoff

Find: $\Delta H_{\text{mix}} = f(X)$

Given: $\Delta H_{pn} = 12500X_{pn}^2 X_{cn} \text{ J/mol}$

Rewrite in general form:

$$\Delta H_2 = aX_2^2 X_1$$

Differentiate:

$$d\Delta H_2 = aX_2^2 dX_1 + 2aX_1X_2 dX_2$$

Substitute $dX_1 = -dX_2$:

$$\frac{d\Delta H_2}{dX_1} = -aX_2^2 + 2aX_1X_2$$

Substitute $X_1 + X_2 = 1$:

$$\frac{d\Delta H_2}{dX_2} = -aX_2(X_2 - 2X_1) = -aX_2(1 - 3X_1)$$

Gibbs-Duhem:

$$\Delta H_1 = \int_{X_2=0}^{X_2} \frac{X_2}{X_1} \frac{d\Delta H_2}{dX_2} dX_2$$

$$\Delta H_1 = \int_{X_2=0}^{X_2} \frac{X_2}{X_1} \left[-aX_2(1 - 3X_1)\right] dX_2$$