3. APPLICATION OF GIBBS-DUHEM EQUATION

Gibbs-Duhem Equation

When extensive property of a solution is given by;

\[ Q' = Q'(T,P,n_1,n_2 ...) \]

The change in extensive property with composition was;

\[ dQ' = \frac{\partial Q'}{\partial n_1} T,P,n_2...n_j \ dn_1 + \frac{\partial Q'}{\partial n_2} T,P,n_1...n_j \ dn_2 + \ldots \]  
\( (1) \)

Partial molar value of an extensive property of component “i” was defined as;

\[ \bar{Q}_i = \frac{\partial Q'}{\partial n_i} T,P,n_j \neq i \]  
\( (2) \)

Combination of equations (1) and (2) yields;

\[ dQ' = \bar{Q}_1 \ dn_1 + \bar{Q}_2 \ dn_2 + \ldots \]  
\( (3) \)

But, \( Q' = n_1 \bar{Q}_1 + n_2 \bar{Q}_2 + \ldots \)  
\( (4) \)

Differentiation of equation (4) gives

\[ dQ' = \bar{Q}_1 \ dn_1 + \bar{Q}_2 \ dn_2 + \ldots + n_1 d\bar{Q}_1 + n_2 d\bar{Q}_2 + \ldots \]  
\( (5) \)

Subtraction of equation (3) from equation (5) yields

\[ n_1 d\bar{Q}_1 + n_2 d\bar{Q}_2 + \ldots = 0 \]

In general,

\[ \sum n_i d\bar{Q}_i = 0 \]  
\( (6) \)

Dividing by \( n \), total number of moles of all the components, gives

\[ \sum X_i d\bar{Q}_i = 0 \]  
\( (7) \)

Equations (6) and (7) are equivalent expressions of the Gibbs-Duhem equation.
3.1. Integration of Gibbs-Duhem Equation

It is performed to calculate partial properties from each other. Consider a 2 component system, say $\bar{Q}_1$ is given. $\bar{Q}_2$ is asked.

Gibbs-Duhem equation: $X_1 \, d\bar{Q}_1 + X_2 \, d\bar{Q}_2 = 0$

equivalents can be written for mixing (relative molar) and excess properties. Rearrangement of Gibbs-Duhem equation yields:

$$d\bar{Q}_2 = -\frac{X_1}{X_2} \, d\bar{Q}_1$$

Integration of both sides

$$\int_{\bar{Q}_2(at \, X_2')} \bar{Q}_2(at \, X_2'') \, d\bar{Q}_2 = \int_{\bar{Q}_1(at \, X_2')} \frac{X_1}{X_2} \, d\bar{Q}_1$$

Integration yields:

$$\bar{Q}_2(at \, X_2'') - \bar{Q}_2(at \, X_2') = \int_{\bar{Q}_1(at \, X_2')} \frac{X_1}{X_2} \, d\bar{Q}_1$$

The value of $\bar{Q}_2$ must be known as boundary condition to integrate this function. Usually properties of pure substances are easier to find. Say property at $X_2 = 1$ is known. Then let $X_2'$ as $X_2=1$ and $X_2''$ to any $X_2$;

$$\bar{Q}_2(at \, X_2) - Q_o'' = \int_{\bar{Q}_1(X_2=1)} \frac{X_1}{X_2} \, d\bar{Q}_1$$

The value of integral may be determined graphically or analytically (if analytical dependence of $\bar{Q}_1$ to composition is given).

Analytical determination involves the following steps:

i. Organize $\bar{Q}_1$ as a function of only one composition variable ($X_1$ or $X_2$).

ii. Take the derervative of $\bar{Q}_1$ and replace it into the integral.

iii. Organize the function inside the integral in such a way to leave only one variable. At the same time, change, if and when necessary,
the limits of the integral to make it in accord with the derivative of the integral. Use the relationship $dX_1 = -dX_2$ when necessary.

iv. Integrate the function, replace the limits to determine the value of the integral.

Analytical integration with relative partial and partial excess properties are also possible. The same steps can be used, by replacing $\bar{Q}_1$ with $\Delta\bar{Q}_1^M$ and/or $\bar{Q}_1^{xs}$ in the case of relative partial molar properties and partial excess properties respectively.

Graphical determination requires plot of $X_1/X_2$ vs. $\bar{Q}_1$. The value of the integral is the area under the curve between the specified limits. However there are some problems with this integration:

i. the value of $\bar{Q}_1$ becomes plus or $-\infty$, if $\bar{Q}_1$ has logarithmic composition terms.

ii. $X_1/X_2$ becomes $\infty$, when $X_2$ becomes zero.

Therefore, the area under the curve may not be bounded well with the given limits. To determine the area under the curve properly; either alternative limits may be given or ways to resolve the problems of tails to infinity should be found. Furthermore, Gibbs-Duhem integration with partial molar properties can only be used for entropy and volume. For other properties Gibbs-Duhem integrations involving relative partial and/or excess properties have to be used. Then with relative partial molar properties, Gibbs-Duhem integration is (in general form):

$$
\Delta\bar{Q}_2^M(atX_2') - \Delta\bar{Q}_2^M(atX_2') = \int_{\Delta\bar{Q}_1^M(atX_2')}^{\Delta\bar{Q}_1^M(atX_2'')} \frac{X_1}{X_2} d\Delta\bar{Q}_1^M
$$

By setting the lower limit $X_2'$ as $X_2=1$ and $X_2''$ to any $X_2$, $\Delta\bar{Q}_2^M(atX_2=1)$ is zero, then

$$
\Delta\bar{Q}_2^M(atX_2) = \int_{\Delta\bar{Q}_1^M(atX_2=1)}^{\Delta\bar{Q}_1^M(atX_2)} \frac{X_1}{X_2} d\Delta\bar{Q}_1^M
$$
Therefore, area under $X_1/X_2$ vs. $\Delta Q_i^M$ curve gives the value of integral. Two of the above problems are still valid in this case (for some properties), but this form of the integral may be used with any thermodynamic property. To illustrate the problem, consider the following data for Fe-Ni alloys at 1600°C.

<table>
<thead>
<tr>
<th>$X_{Ni}$</th>
<th>1 0.9 0.8 0.7 0.6 0.5 0.4 0.3 0.2 0.1 0</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_{Ni}$</td>
<td>1 0.89 0.766 0.62 0.485 0.374 0.283 0.207 0.136 0.067 0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$\Delta G_{Ni}^M$</th>
<th>0 -432 -989 -1773 -2684 -3647 -4681 -5841 -7399 -10024 -\infty</th>
</tr>
</thead>
</table>

| $X_{Ni}/X_{Fe}$ | $\infty$ 9 4 2.33 1.5 1 0.67 0.43 0.25 0.11 0 |

The value of $\Delta G_{Ni}^M$ at lower limit (i.e. $X_{Fe}=1$) is $-\infty$, results in an unbounded area under the curve. Therefore, to get precise value for $\Delta G_{Fe}^M$ (at $X_{Fe}$); either $\Delta G_{Fe}^M$ at a composition other than $X_{Fe}=1$ should be given (known) or other alternatives should be considered.

Use of excess properties: (in general form) Gibbs-Duhem integration with excess properties are:

$$\bar{Q}_{2}^{xs}(at\ X_2'') - \bar{Q}_{2}^{xs}(at\ X_2') = \int_{\bar{Q}_{1}^{xs}(at\ X_2')}^{\bar{Q}_{1}^{xs}(at\ X_2'')} \frac{X_1}{X_2} d\bar{Q}_{1}^{xs}$$

By setting the lower limit $X_2'$ as $X_2=1$ and $X_2''$ to any $X_2$, $\bar{Q}_{2}^{xs}$ (at $X_2=1$) is zero, then
\[ \bar{Q}^{xs}(at \ X_2) = \int_{\bar{Q}^{xs}(at \ X_2=1)}^{\bar{Q}^{xs}(at \ X_2)} \frac{X_1}{X_2} d\bar{Q}^{xs} \]

Area under \( X_1/X_2 \) vs. \( \bar{Q}^{xs} \) curve gives the value of integral. One of the above problems is solved; by using excess properties, a finite value is assigned to the value of \( \bar{Q}^{xs}(at \ X_2=1) \). Therefore the area is bounded from the lower end of the integral. The problem of tail to infinity for \( X_1/X_2 \) at \( X_2=0 \) is still valid in this case.

Then, previous problem for Fe-Ni alloys at 1600°C requires integration of:

\[ G^{xs}_{Ni} = \int_{G^{xs}_{Ni}(at \ X_Fe)}^{G^{xs}_{Ni}(at \ X_Fe=1)} \frac{X_{Ni}}{X_{Fe}} dG^{xs}_{Ni} \]

This is good for values \( X_{Fe}=1 \) to \( X_{Fe} > 0 \). As \( X_{Fe} \to 0; X_{Ni}/X_{Fe} \to \infty \). Therefore, \( G^{xs}_{Fe}(at \ X_{Fe} \to 0) \) is mathematically indeterminate with excess properties.
The use of $\alpha$-Function:

Problems arising from $X_1/X_2 \to \infty$ as $X_2 \to 0$ may be resolved using this function. For any component $i$, $\alpha_i$ is defined as:

$$\alpha_i = \frac{Q_i^{xs}}{(1 - X_i)^2}$$

For 1-2 binary solution from previous relationships

$$\overline{Q}_2^{xs}(at \ X_2) = -\int_{\alpha_1^{xs}(at \ X_2 = 1)}^{\alpha_1^{xs}(at \ X_2)} \frac{X_1}{X_2} d\overline{Q}_1^{xs}$$

From above relationship $\overline{Q}_1^{xs} = \alpha_1 X_2^2$

Then $d\overline{Q}_1^{xs} = d\alpha_1 X_2^2 + 2\alpha_1 X_2 dX_2$

Replacing into the integral yields

$$\overline{Q}_2^{xs}(at \ X_2) = -\int_{\alpha_1^{xs}(at \ X_2 = 1)}^{\alpha_1^{xs}(at \ X_2)} X_1 X_2 d\alpha_1 - \int_{X_2 = 1}^{X_2} \frac{X_1}{X_2} 2\alpha_1 X_2 dX_2$$

By virtue of identity $\int d(xy) = \int y dx + \int x dy$, the first integral

$$\int_{\alpha_1^{xs}(at \ X_2 = 1)}^{\alpha_1^{xs}(at \ X_2)} X_1 X_2 d\alpha_1 = \int d(X_1 X_2 \alpha_1) - \int \alpha_1 d(X_1 X_2)$$

Then,

$$\overline{Q}_2^{xs}(at \ X_2) = -\int d(X_1 X_2 \alpha_1) + \int \alpha_1 d(X_1 X_2) - 2\alpha_1 X_2 dX_2$$

$$= -X_1 X_2 \alpha_1 + \int \alpha_1 X_2 dX_2 + \int \alpha_1 X_2 dX_1 - 2\alpha_1 X_1 dX_2$$

$$= -X_1 X_2 \alpha_1 - \int_{X_2 = 1}^{X_2} \alpha_1 (2X_1 - X_1 + X_2) dX_2$$

$$= -X_1 X_2 \alpha_1 - \int_{X_2 = 1}^{X_2} \alpha_1 dX_2$$
Numerical value for \(-X_1X_2\alpha_1\) can be determined, then the value of the integral can be determined graphically or analytically (if an analytical expression for the composition dependence of \(\alpha_1\) or other properties that leads to determine \(\alpha_1\) given). Analytical integration with \(\alpha\)-function can be done by replacing \(\alpha_1\) into the equation and integrating it between the given limits. Graphical determination can be done from the area under \(X_2\) vs. \(\alpha_1\) graph.

Then, previous problem for Fe-Ni alloys at 1600°C requires determination of:

\[
\overline{G}_{Fe}^{xs}(at \ X_{Fe}) = -X_{Ni} \ X_{Fe} \ \alpha_{Ni} - \int_{X_{Fe}=1}^{X_{Fe}} \alpha_{Ni} \ dX_{Fe}
\]

<table>
<thead>
<tr>
<th>(X_{Ni})</th>
<th>1</th>
<th>0.9</th>
<th>0.8</th>
<th>0.7</th>
<th>0.6</th>
<th>0.5</th>
<th>0.4</th>
<th>0.3</th>
<th>0.2</th>
<th>0.1</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\alpha_{Ni})</td>
<td>0/0</td>
<td>-1</td>
<td>-1.07</td>
<td>-1.3</td>
<td>-1.33</td>
<td>-1.16</td>
<td>-.96</td>
<td>-.76</td>
<td>-.62</td>
<td>-.49</td>
<td>ln (\gamma^{o}_{Ni})</td>
</tr>
<tr>
<td>(\overline{G}_{Ni}^{xs})</td>
<td>0</td>
<td>-41.4</td>
<td>-161</td>
<td>-450</td>
<td>-789</td>
<td>-1077</td>
<td>-1283</td>
<td>-1376</td>
<td>-1430</td>
<td>-1485</td>
<td>RT ln (\gamma^{o}_{Ni})</td>
</tr>
<tr>
<td>cal/mol</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(X_{Ni}/X_{Fe})</td>
<td>(\infty)</td>
<td>9</td>
<td>4</td>
<td>2.33</td>
<td>1.5</td>
<td>1</td>
<td>0.67</td>
<td>0.43</td>
<td>0.25</td>
<td>0.11</td>
<td>0</td>
</tr>
<tr>
<td>log (\gamma_{Ni})</td>
<td>0</td>
<td>-.005</td>
<td>-.019</td>
<td>-.053</td>
<td>-.092</td>
<td>-.126</td>
<td>-.15</td>
<td>-.161</td>
<td>-.167</td>
<td>-.174</td>
<td>log (\gamma^{o}_{Ni})</td>
</tr>
</tbody>
</table>

| \(\alpha_{Ni}\) | \(X_{Fe}\) |
For $X_{Fe} = 0.7$
\[
\ln \gamma_{Fe} = -0.3 \times 0.7 \times (-0.76) - (0.3 \times 0.4 + 0.36 \times 0.3 \times 0.5) = 0.1596 - 0.174
\]
\[
\ln \gamma_{Fe} = -0.0144; \quad \gamma_{Fe} = 0.985; \quad a_{Fe} = 0.6895
\]

**Direct Calculation of the Integral Property**

Consider a 2 component system, say $\bar{Q}_1$ is given. $Q$ is asked. Indirect method involves determination of $\bar{Q}_2$ by Gibbs-Duhem integration, then computation of the integral property from

\[
Q = X_1 \bar{Q}_1 + X_2 \bar{Q}_2
\]

but

\[
\bar{Q}_1 = Q + (1 - X_1) \frac{dQ}{dX_1}
\]

multiply both sides by $dX_1$ and divide by $X_2^2$, then

\[
\frac{\bar{Q}_1 dX_1}{X_2^2} = \frac{Q dX_1 + (1 - X_1) dQ}{X_2^2}
\]

Replacing $(1 - X_1) = X_2$ and $dX_1 = -dX_2$

\[
\frac{\bar{Q}_1 dX_1}{X_2^2} = \frac{-Q dX_2 + X_2 dQ}{X_2^2} = d\left(\frac{Q}{X_2}\right)
\]

Integration of both sides
\[
\int \frac{Q}{X^2} \ d\left(\frac{Q}{X^2}\right) = \int_{X_1=0}^{X_1=1} \frac{\bar{Q}_1}{X^2} \ dX
\]

\[
\frac{Q}{X^2} - Q^o_2 = \int_{X_1=0}^{X_1=1} \frac{\bar{Q}_1}{X^2} \ dX
\]

Using relative partial molar properties and setting \( \Delta Q^M \) at \( X_2=1 \) to zero;

\[
\frac{\Delta Q^M}{X^2} = \int_{X_1=0}^{X_1=1} \frac{\Delta \bar{Q}_1^M}{X^2} \ dX
\]

or \( \Delta Q^M = X_2 \int_{X_1=0}^{X_1=1} \frac{\Delta \bar{Q}_1^M}{X^2} \ dX \)

Equivalent relationship from partial excess properties and setting \( Q^{xs} \) at \( X_2=1 \) to zero;

\[
Q^{xs} = X_2 \int_{X_1=0}^{X_1=1} \frac{\bar{Q}_1^{xs}}{X^2} \ dX
\]

Values of integrals can be obtained either analytically (if analytical dependence of \( \bar{Q}_1 \) or \( \Delta \bar{Q}_1^M \) or \( \bar{Q}_1^{xs} \) to composition is given) or graphically. Analytical integration involves the following steps:

i. The replacement of the property (\( \bar{Q}_1 \) or \( \Delta \bar{Q}_1^M \) or \( \bar{Q}_1^{xs} \)) into the integral.

ii. Organization of the function inside the integral in such a way to leave only one variable.

iii. Integration and replacement of the limits.

Graphical integration involves the determination of the area under the curve (\( \bar{Q}_1/X^2 \) or \( \Delta \bar{Q}_1^M/X^2 \) or \( \bar{Q}_1^{xs}/X^2 \) vs. \( X_1 \) between the limits.

\[
\begin{array}{cccccccccc}
X_1 & 0 & .1 & .2 & .3 & .4 & .5 & .6 & .7 & .8 & .9 & 1 \\
\end{array}
\]
$\widetilde{G}_1^{xs} \quad \text{RT ln} \gamma_1 \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots$

$\widetilde{G}_1^{xs} / X_2^2 \quad \text{RT ln} \gamma_1 \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots$

$\widetilde{G}_1^{xs} / X_2^2$
11.4. The vapor pressure exerted by the A-B system at 1000 K are

<table>
<thead>
<tr>
<th>X_A</th>
<th>1</th>
<th>9</th>
<th>.8</th>
<th>.7</th>
<th>6</th>
<th>.5</th>
<th>4</th>
<th>3</th>
<th>.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>P_A x 10^6</td>
<td>5</td>
<td>4.4</td>
<td>3.75</td>
<td>2.9</td>
<td>1.8</td>
<td>1.1</td>
<td>0.8</td>
<td>0.6</td>
<td>0.4</td>
</tr>
<tr>
<td>P_A x 10^6</td>
<td>5</td>
<td>4.89</td>
<td>4.688</td>
<td>4.14</td>
<td>3</td>
<td>2.2</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
</tbody>
</table>

a) Henry's law obeyed by the solute A (Composition range)?

\[ a_A = \frac{P_A}{P^0} \quad a_A = \gamma_A^0 x_A \]

Henry's activity coefficient (constant)

\[ \gamma_A^0 x_A = \frac{P_A}{P^0} \quad \Rightarrow \quad \gamma_A^0 = \frac{P_A}{P^0 \cdot x_A} \quad \text{or} \quad \gamma_A^0 = \frac{P_A}{x_A \cdot \text{const}} (T \text{ constant}) \]

\[ \gamma_A^0 = 2 \quad \text{for Henry's law range,} \quad x_A < 0.4 \]

b) Henry's law constant at 1000 K? |

\[ \log \gamma_A^0 = -\frac{109.3}{T} - 0.2886 \quad \Rightarrow \quad \gamma_A^0(1000K) = 0.4 \]

c) \( \Delta H_A^M \) in Henry's law range? |

\[ RT \ln \gamma_A^0 = G_A^0 = 2.303 \times RT \cdot \log \gamma_A^0 \]

\[ \Delta H_A^M = \frac{\partial (\gamma_A^0)}{\partial (1/T)} \quad \Rightarrow \quad \Delta H_A^M = \frac{\partial (2.303 \times R \cdot \log \gamma_A^0)}{\partial (1/T)} \]

\[ \Delta H_A^M = \frac{\partial (2.303 \times R \times \frac{109.3}{T} - 2.303 \times R 	imes 0.2886)}{\partial (1/T)} \quad \Rightarrow \quad \Delta H_A^M = 2.303 \times R \times 109.3 \]

\[ \Delta H_A^M = -209.3 \text{ J/mole} \]

d) \( \Delta H^M = X_A \Delta H_A^M + X_B \Delta H_B^M \)

\[ \Delta H^M = -209.3 X_A \]
\( T = 473°C \)

\[ \log Y_{Pb} = -0.32 \left( 1 - X_{Pb} \right)^2 \]

Gibbs-Duhem Ind.

\[ \frac{\partial \rho}{\partial X_{Bi}} = -\int \frac{X_{Pb}}{X_{Bi}} dG_{Pb} \]

\[ \int \frac{X_{Pb}}{X_{Bi}} \left( -0.32 \right) \rho_{Bi} = \int \frac{X_{Pb}}{X_{Bi}} \left[ 2 \left( -0.32 \right) X_{Bi} \cdot dX_{Bi} \right] \]

\( \log Y_{Bi} (at X_{Bi}) = \frac{X_{Pb}}{X_{Bi}} \frac{dX_{Bi}}{dX_{Pb}} \]

\( \log Y_{Pb} (at X_{Bi}) = -0.32 X_{Pb}^2 \)

\[ \log Y_{Bi} = -0.32 X_{Pb}^2 \] at 473°C
1 mole Pb added at 25°C to large quantity liq. alloy

\[ X_{Pb} = 0.5 \text{ at } 473°C \]

a) Heat flow into liq. Alloy

\[
\Delta H = \Delta H_B + \Delta H_M
\]

\[
\Delta H_B = \int \frac{C_p(Pb(s))dT}{298} + \Delta H_m + \int \frac{C_p(Pb(l))dT}{600}
\]

\[
= \left(\frac{244.36 + 7.96 \times 10^3 T}{298}\right) + 5128 + \left(\frac{28.46dT}{600}\right)
\]

\[
= \frac{244.36 (600 - 298) + 7.96 \times 10^3 (600^2 - 298^2)}{298} + 5128 + 28.46 \cdot (746 - 600)
\]

\[
= 18798 \text{ J/mole}
\]

\[
\Delta H_M = \Delta H_{Pb} - \Delta H_{Pb}^m = \alpha X_{Pb} X_{Bi} \quad \Delta H_{Pb}^m = \alpha \Delta H_{Pb}^E
\]

\[
\Delta H_{Pb}^E = \frac{\Delta H_{Pb}}{X_{Pb}} = \Delta H_{Pb} = \frac{RT \ln Y_{Pb}}{X_{Pb}} \quad \text{at } X_{Pb} = 0.5 \quad \ln Y_{Pb} = -0.08
\]

\[
\bar{Y}_{Pb} = 0.83176
\]

\[
\Delta H_{Pb}^m = 8.314 \times 746 \times \ln 0.83176 = -1142.5 \text{ J/mole} \quad \alpha X_{Bi} = -4570 X_{Bi}
\]

\[
\Delta H = 18798 \text{ J/mole} - 1142.5 \text{ J/mole} = 17655.5 \text{ J/mole}
\]

b) \[
\Delta S_{sat} = -\frac{\Delta H}{T} = \frac{-17655.5}{746} = -23.67 \text{ J/mole.K}
\]

c) \[
\alpha_{Pb} = Y_{Pb} \times X_{Pb} = 0.83176 \times 0.5 = 0.4159 \text{ at } 476\text{K}
\]

\[
\text{at } 1000\text{K} \quad \bar{C}^E_{Pb} = \frac{\Delta H_{Pb}}{T} = -1142.5 = RT \ln Y_{Pb} \implies Y_{Pb} = 0.8716
\]

\[
\alpha_{Pb} = Y_{Pb} \times X_{Pb} = 0.4358 \text{ at } 1000\text{K}
\]

\[
\ln Y_{Pb} = -0.13742
\]