**Topic 10 – Mixtures I**

**Content & Objectives:** This and the following topic concerns the thermodynamics of multi-component systems, primarily liquid solutions. We begin with a general discussion of how the thermodynamics of such mixtures are described in terms of partial molar properties. We discuss some of the general characteristics of partial molar quantities and the inter-relations existing among them, especially in the case of binary mixtures. We then introduce two reference systems, the ideal gas mixture and the ideal solution. These idealized models are such that the properties of the components in the mixture are simply related to pure-component properties. The more complicated behavior of real solutions is most conveniently described in terms of departure from these ideal models. We will employ two “logarithmic” representations the departure of the chemical potential from ideal behavior -- the fugacity, already discussed in Topic 8 with respect to pure gases, and a new quantity, the activity, which provides the simplest description of chemical equilibria. Use of these quantities will require the specification of standard states, which vary depending on the type of solution considered. The present topic concerns mainly liquid-liquid mixtures. Topic 11 will cover solid-liquid solutions, especially solutions of electrolytes.

**Reading:** M&S Chapter 10; Pitzer Ch. 7,10-12 excerpts.

**Other Sources:**
- general description of multi-component systems: Sandler Ch. 6; Callen Ch. 3
- ideal mixtures: Sandler Ch. 7
- fugacities, activities, etc.: Rock Ch. 10, Sandler Ch. 7
- binary phase diagrams: Sandler Ch. 8

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**The General Description of Multi-Component Systems**

- Complete specification of the state of a single-phase mixture of \( c \) components can be made using the set of variables \( \{T, P, n_1, n_2, \ldots, n_c\} \equiv \{T, P, \tilde{n}\} \), where \( n_i \) is the number of moles of chemical species \( i \). The intensive state of a system (i.e. the state independent of its overall size) is often more conveniently specified in terms of the mole fractions \( \frac{n_i}{n} \), i.e. using the independent set of variables \( \{T, P, x_1, x_2, \ldots, x_{c-1}\} \equiv \{T, P, \tilde{x}\} \). (Only \( c-1 \) mole fractions are independent since \( \sum_i x_i = 1 \).)

- Equations of state describing any extensive property of a binary mixture, “\( Y \)”, or its molar equivalent, “\( \bar{Y} \)”, are therefore of the general form:
  \[
  Y = Y(T, P, \tilde{n}) \quad \text{and} \quad \bar{Y} = \frac{Y}{n} = \bar{Y}(T, P, \tilde{x})
  \]

- The differential of \( Y \) is:
  \[
  dY = \left( \frac{\partial Y}{\partial T} \right)_{P, \tilde{n}} dT + \left( \frac{\partial Y}{\partial P} \right)_{T, \tilde{n}} dP + \sum_{i=1}^{c-1} \left( \frac{\partial Y}{\partial n_i} \right)_{T, P, \tilde{n}, x_j} dn_i
  \]
  (The subscript \( \tilde{n} \) indicates that all mole numbers are fixed, whereas \( n_{j \neq i} \) indicates all mole numbers but that of component \( i \) are fixed.)
The derivatives with respect to mole numbers at fixed $T$ and $P$ play a central role in the
thermodynamics of mixtures. These derivatives are termed \textbf{partial molar quantities}, $\bar{Y}_i$

\[
\bar{Y}_i = \bar{Y}_i(T, P, \bar{x}) \equiv \left( \frac{\partial Y}{\partial n_i} \right)_{T, P, n_{\text{p.j}}} \quad \text{in general } \bar{Y}_i(T, P, \bar{x}) \neq \bar{Y}_i^*(T, P)!
\]

Examples of partial molar quantities are $\bar{V}_i$, $\bar{S}_i$, $\bar{U}_i$, $\bar{H}_i$, $\bar{A}_i$, and $\bar{G}_i$, termed the partial molar volume, partial molar entropy, etc. It is important to note that these partial molar quantities
are distinct from the molar quantities associated with the pure constituents. We will use the notation $\bar{Y}_i = \bar{Y}_i(T, P, \bar{x})$ to denote a partial molar (i.e. mixture) quantity and $\bar{Y}_i^* = \bar{Y}_i^*(T, P)$ to
denote a molar property of a pure substance $i$.

The homogeneous nature of extensive properties, i.e. the mathematical property
$Y(T, P, \lambda n_1, \lambda n_2, ..., \lambda n_c) = \lambda Y(T, P, n_1, n_2, ..., n_c)$ leads to the following important characteristic
of partial molar quantities:

\[
Y(T, P, \bar{n}) = n_1 \bar{Y}_1 + n_2 \bar{Y}_2 + ... + n_c \bar{Y}_c \quad \text{or} \quad \bar{Y}(T, P, \bar{x}) = x_1 \bar{Y}_1 + x_2 \bar{Y}_2 + ... + x_c \bar{Y}_c
\]

Differentiating this expression and comparing it to the differential that defines the $\bar{Y}_i$, one also
finds the following relations,

\[
n_1 d\bar{Y}_1 + n_2 d\bar{Y}_2 + ... + n_c d\bar{Y}_c = 0 \quad \text{or} \quad x_1 d\bar{Y}_1 + x_2 d\bar{Y}_2 + ... + x_c d\bar{Y}_c = 0
\]

which indicate that the partial molar quantities are not all independent. (These relationships
are particularly useful in binary systems, as will be discussed below.)

The most important partial molar quantity for considering phase and chemical equilibria is the
\textbf{partial molar Gibbs energy}, otherwise known as the \textbf{chemical potential}:

\[
\mu_i(T, P, \bar{x}) \equiv \bar{G}_i \equiv \left( \frac{\partial G}{\partial n_i} \right)_{T, P, n_{\text{p.j}}} = \left( \frac{\partial U}{\partial n_i} \right)_{S, V, n_{\text{p.j}}} = \left( \frac{\partial H}{\partial n_i} \right)_{S, P, n_{\text{p.j}}} = \left( \frac{\partial A}{\partial n_i} \right)_{T, S, n_{\text{p.j}}}
\]

This definition of the chemical potential is a straightforward generalization of the definition
introduced for single-component systems.

The requirement that the total Gibbs energy be a minimum at equilibrium for constant $T$ and $P$
leads to the following conditions for phase equilibrium among mixed phases (I and II):

\[
T^I = T^\Pi \quad P^I = P^\Pi \quad \mu_i^I(T, P, \bar{x}^I) = \mu_i^\Pi(T, P, \bar{x}^\Pi) \quad \text{for } i = 1, 2, ..., c
\]

For each relationship among the thermodynamic variables of a pure substance, an
identical relationship holds for the partial molar quantities in a mixture.

For example, $G = H - TS$ becomes $\bar{G}_i = \bar{H}_i - T\bar{S}_i$, $(\partial \bar{G} / \partial T)_P = -\bar{S}$ becomes
$(\partial \bar{G} / \partial T)_{P, n_j} = (\partial \mu_i / \partial T)_{P, n_j} = -\bar{S}_i$, etc.
Relations for Binary Mixtures

• In the case of binary mixtures, the interdependence of the $d\bar{Y}_i$ discussed above leads to simple methods for determining partial molar quantities from experimental data. For example, from the relation $x_1d\bar{Y}_1 + x_2d\bar{Y}_2 = 0$ one obtains: $d\bar{Y}_i = -\frac{x_2}{1-x_2}d\bar{Y}_2$. Thus, if the dependence $\bar{Y}_2(x_2)$ is known one can obtain $\bar{Y}_1(x_2)$ by integration.

• More commonly, one measures an extensive property (or an excess property, see below) of the mixture as a whole, $\bar{Y}(x_2)$.

• Differentiating $\bar{Y}(x_2)$ one finds:

$$\bar{Y}_1 = \bar{Y} - x_2 \left( \frac{\partial \bar{Y}}{\partial x_2} \right)_{T,P} \quad \text{and} \quad \bar{Y}_2 = \bar{Y} + (1-x_2) \left( \frac{\partial \bar{Y}}{\partial x_2} \right)_{T,P}$$

• This expression has the simple graphical interpretation illustrated at the right. The values of $\bar{Y}_1$ and $\bar{Y}_2$ at a given composition $x_2$ are equal to the intersections of the line tangent to $\bar{Y}(x_2)$ and the $x_2 = 0$ and $x_1 = 1$ axes.

• Two quantities easy to measure experimentally, which also serve to characterize the ideality of a mixture, are its total volume $\bar{V} = \bar{V}$ and the enthalpy of mixing. The latter quantity is measured by the heat absorbed $q_{mix}$ upon mixing $n_1$ moles of component 1 and $n_2$ moles of component 2 (at constant $T$ and $P$):

$$q_{mix} = \Delta_{mix} H = H - \{n_1\tilde{H}_1^* + n_2\tilde{H}_2^*\}$$

$\Delta_{mix} \tilde{H}$ is one of a general class of mixing quantities all defined by:

$$\Delta_{mix} \bar{Y}(T,P,\tilde{x}) \equiv \bar{Y}(T,P,\tilde{x}) - \sum_{i=1}^{c} x_i\bar{Y}_i^*(T,P)$$

$$= \sum_{i=1}^{c} x_i[\bar{Y}_i(T,P,\tilde{x}) - \bar{Y}_i^*(T,P)]$$

(Recall that the superscript “*” denotes a property of a pure component.)

• Some representative mixing data are illustrated below.
\( \Delta_{\text{mix}} H \) for the mixtures methyl formate + ethanol (top) and methyl formate + methanol (bottom).

\( \Delta_{\text{mix}} H \) observed in mixtures of benzene and fluorinated benzenes \( C_6F_5Y \).


- A similar construction to the one described above for determining \( Y_1 \) and \( Y_2 \) also holds for mixing properties in a binary system, namely:

\[
\left( Y_1 - Y_1^* \right) = \Delta_{\text{mix}} H - x_2 \left( \frac{\partial \Delta_{\text{mix}} H}{\partial x_2} \right)_{T,P} \quad \text{and} \quad \left( Y_2 - Y_2^* \right) = \Delta_{\text{mix}} H + (1 - x_2) \left( \frac{\partial \Delta_{\text{mix}} H}{\partial x_2} \right)_{T,P}
\]

- Mixing data is often summarized by fits to a \textbf{Redlich-Kister polynomial}:

\[
\Delta_{\text{mix}} Y = x_1 x_2 \sum_{i=0}^{n} a_i (x_1 - x_2)^i = x_1 (1 - x_1) \sum_{i=0}^{n} a_i (2x_1 - 1)^i
\]

This flexible fitting function constrains \( \Delta_{\text{mix}} Y \) to be zero at both \( x_1 = 0 \) and \( x_2 = 0 \), as required by the definition of \( \Delta_{\text{mix}} Y \).

\begin{center}
\textbf{Ideal Gas Mixtures}
\end{center}

- The \textit{ideal gas mixture} ("IGM") provides a theoretically important reference for describing the behavior of real mixtures. It is characterized by the two equations of state:

\[
P^\text{IGM}(T,V,\bar{n}) = \left( \sum_{i=1}^{C} n_i \right) \frac{RT}{V} = n \frac{RT}{V} \quad \text{and} \quad U^\text{IGM}(T,V,\bar{n}) = \sum_{i=1}^{C} n_i \bar{U}_i^\text{IG}(T)
\]

where \( \bar{U}_i^\text{IG}(T) = \bar{U}_i^*(T,P) \) denotes the energy of the pure ideal gas \( i \).
• The partial pressure $P_i$ of a component $i$ in any gas mixture (real or ideal) is defined by $P_i = x_i P$, where $x_i$ is the mole fraction of $i$ and $P$ is the total pressure. In an ideal gas mixture the partial pressure of a component $i$ is equal to the pressure that it would exert if it were alone under the same $T, V$ conditions as the mixture, i.e. $P_i^{IGM} = P_i^{IG}(T,V,n_i)$.

• Either thermodynamic arguments (“Gibbs’ theorem”) or statistical mechanics show that the entropy of a mixture of ideal gases is the sum of the entropies that each of the individual (ideal) gases would have if it occupied the same volume as the mixture. Thus the partial molar entropy of a component differs from the entropy of the pure ideal gas by an amount:

$$\Delta_{mix} S_i^{IG}(T, P, \bar{x}) = S_i^{IG}(T, P, \bar{x}) - \sum_{i=1}^{c} x_i S_i^{IG}(T, P) = -R \sum_{i=1}^{c} x_i \ln x_i$$

• The dependence of the chemical potential (or Gibbs energy) on composition and pressure in fluid mixtures is conveniently expressed in terms of the species fugacities $f_i$, which are defined in terms of deviations from ideal gas mixture behavior via:

$$f_i(T, P, \bar{x}) \equiv x_i P \exp \left\{ \frac{\left( \mu_i^{IGM} - \mu_i^{IG} \right)_{T,P,\bar{x}}}{RT} \right\} = x_i P \exp \left\{ \frac{1}{RT} \int_0^P \left( \frac{\mu_i^{IGM} - \mu_i^{IG}}{RT} \right) dP' \right\}$$

Note that this definition of fugacities in a mixture corresponds to our previous definition of the fugacity of a pure gas of $i$ for $x_i=1$, i.e. $f_i(x_i=1) = f_i^{*} \equiv P \exp \left\{ \left( \mu_i^{IG} \right) / RT \right\}$.
• Species fugacities have units of pressure. In the limit $P \to 0$ and the fluid mixture approaches ideal gas behavior, $f_i \to x_i P = P_i$, the fugacity becomes the partial pressure of gas $i$.

• Fugacities provide an alternative to the use of chemical potentials. For example, the requirements for coexistence of two phases, I and II, can either be expressed as $\mu_i(T,P,\bar{x}) = \mu_i^\text{II}(T,P,\bar{x})$ or as $f_i^\text{I}(T,P,\bar{x}) = f_i^\text{II}(T,P,\bar{x})$. Fugacities are often preferred because they eliminate the divergence associated with $\mu_i$ as $x_i \to 0$ and because they are more directly connected with the observable pressure (or partial pressure).

• The **fugacities of liquids and solids** are defined with respect to the IGM in the same manner just described. However, the fugacities of such phases are usually determined from the properties of the vapor with which they coexist. In particular, the fugacity of a pure condensed phase can be expressed:

$$f^{L,S}_i(T,P) = f^V(T,P)\exp\left(\frac{1}{RT} \int_{P_v}^P V^{L,S} dP'\right)$$

where $f^V(T,P_v)$ is the fugacity of the vapor that would be in equilibrium with the condensed phase at the temperature $T$ and some equilibrium vapor pressure $P_v(T)$. The exponential term, called the “**Poynting correction**”, accounts for the change in fugacity caused by the pressure difference $P - P_v(T)$. In most cases of interest the equilibrium vapor pressures of liquids and especially solids is small enough so that the vapor behaves ideally and $f^V(T,P_v) \approx P_v(T)$. In addition, except at high (kbar) pressures the Poynting correction is usually negligible, so that one can often use the simple approximation:

$$f^{L,S}_i(T,P) \approx P_v(T)$$

In the case of liquid-liquid mixtures (well below $T_c$ of either component), the fugacity of species $i$ in solution is also similarly well approximated by the partial pressure of $i$ in the coexisting vapor phase:

$$f^L_i(T,P,\bar{x}) = f^V_i(T,P,\bar{y}) \equiv P_v \equiv y_i P$$

($\bar{y}$ denotes the vapor mole fractions)

M&S use these last two equations throughout their discussion. But it is important that you recognize them for what they are -- only convenient approximations to the exact relations.

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### Ideal Solutions and Excess Properties

• The **ideal solution** (“IS”) is a generalization of the ideal gas mixture. It provides a useful reference for describing the behavior of condensed-phase mixtures. We define an ideal solution as one in which species fugacities are simply proportional to mole fractions over the entire range of composition:

$$f_i^{IS}(T,P,\bar{x}) = x_i f_i^*(T,P)$$

where $f_i^*(T,P)$ is the fugacity of pure component $i$ at the same temperature and pressure as the mixture. You may be more familiar with the definition in terms of chemical potentials:

$$\mu_i^{IS}(T,P,\bar{x}) = \mu_i^*(T,P) + RT \ln x_i,$$
which is entirely equivalent. (We will generalize these definitions later to include any standard state fugacity \( f_i^* \) or chemical potential \( \mu_i^* \), not necessarily pure component \( i \)).

- An equivalent definition of an ideal mixture is one in which \( \bar{H}_{\text{mix}}^\circ (T, P, \bar{x}) = \bar{H}_i^* (T, P) \) and \( \bar{V}_{\text{mix}}^\circ (T, P, \bar{x}) = \bar{V}_i^* (T, P) \) at all temperatures, pressures, and compositions.

- **Excess properties** of mixtures are defined relative to those of an ideal mixture by:

\[
\bar{Y}_{\text{ex}}^i \equiv \Delta_{\text{mix}} \bar{Y}(T, P, \bar{x}) - \Delta_{\text{mix}} \bar{Y}_{\text{IS}}^\circ (T, P, \bar{x}) = \sum_{i=1}^{c} x_i (\bar{Y}_i - \bar{Y}_i^\circ) = \sum_{i=1}^{c} x_i \bar{Y}_{\text{ex}}^i
\]

where \( \bar{Y}_{\text{ex}}^i \) represents a molar excess quantity and \( \bar{Y}_{\text{ex}}^i \) a partial molar excess quantity.

- Using these excess properties, the behavior of ideal and real mixtures can be summarized:

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Ideal Solutions</th>
<th>Real Solutions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume</td>
<td>( \Delta_{\text{mix}} \bar{V}<em>{\text{IS}}^\circ = 0 ), ( \bar{V}</em>{\text{IS}}^\circ = \bar{V}_i^* )</td>
<td>( \bar{V}<em>{\text{ex}}^i = \Delta</em>{\text{mix}} \bar{V}<em>i^*, \bar{V}</em>{\text{ex}}^\circ = \bar{V}_i^* - \bar{V}_i^* )</td>
</tr>
<tr>
<td>Internal Energy</td>
<td>( \Delta_{\text{mix}} \bar{U}<em>{\text{IS}}^\circ = 0 ), ( \bar{U}</em>{\text{IS}}^\circ = \bar{U}_i^* )</td>
<td>( \bar{U}<em>{\text{ex}}^i = \Delta</em>{\text{mix}} \bar{U}<em>i^*, \bar{U}</em>{\text{ex}}^\circ = \bar{U}_i^* - \bar{U}_i^* )</td>
</tr>
<tr>
<td>Enthalpy</td>
<td>( \Delta_{\text{mix}} \bar{H}<em>{\text{IS}}^\circ = 0 ), ( \bar{H}</em>{\text{IS}}^\circ = \bar{H}_i^* )</td>
<td>( \bar{H}<em>{\text{ex}}^i = \Delta</em>{\text{mix}} \bar{H}<em>i^*, \bar{H}</em>{\text{ex}}^\circ = \bar{H}_i^* - \bar{H}_i^* )</td>
</tr>
<tr>
<td>Entropy</td>
<td>( \Delta_{\text{mix}} \bar{S}<em>{\text{IS}}^\circ = -RT \sum</em>{i=1}^{c} x_i \ln x_i ), ( \bar{S}_{\text{IS}}^\circ = \bar{S}_i^* - RT \ln x_i )</td>
<td>( \bar{S}<em>{\text{ex}}^i = \Delta</em>{\text{mix}} \bar{S} + RT \sum_{i=1}^{c} x_i \ln x_i ), ( \bar{S}_{\text{ex}}^i = \bar{S}_i^* - \bar{S}_i^* + RT \ln x_i )</td>
</tr>
<tr>
<td>Helmholtz Energy</td>
<td>( \Delta_{\text{mix}} \bar{A}<em>{\text{IS}}^\circ = +RT \sum</em>{i=1}^{c} x_i \ln x_i ), ( \bar{A}_{\text{IS}}^\circ = \bar{A}_i^* + RT \ln x_i )</td>
<td>( \bar{A}<em>{\text{ex}}^i = \Delta</em>{\text{mix}} \bar{A} - RT \sum_{i=1}^{c} x_i \ln x_i ), ( \bar{A}_{\text{ex}}^i = \bar{A}_i^* - \bar{A}_i^* - RT \ln x_i )</td>
</tr>
<tr>
<td>Gibbs Energy or</td>
<td>( \Delta_{\text{mix}} \bar{G}<em>{\text{IS}}^\circ = +RT \sum</em>{i=1}^{c} x_i \ln x_i ), ( \bar{G}_{\text{IS}}^\circ = \bar{G}_i^* + RT \ln x_i )</td>
<td>( \bar{G}<em>{\text{ex}}^i = \Delta</em>{\text{mix}} \bar{G} - RT \sum_{i=1}^{c} x_i \ln x_i ), ( \bar{G}_{\text{ex}}^i = \bar{G}_i^* - \bar{G}_i^* - RT \ln x_i )</td>
</tr>
<tr>
<td>Chemical Potential</td>
<td>( \mu_{\text{IS}}^i = \mu_i^* + RT \ln x_i )</td>
<td>( \mu_{\text{ex}}^i = \mu_i - \mu_i^* - RT \ln x_i )</td>
</tr>
</tbody>
</table>

where \( \bar{Y}_i^* \) refers to the molar property \( Y \) in the pure component \( i \).

- Two examples of the behavior of binary liquid solutions are provided at the right. The ordinate on these plots is the partial pressure of each component in the vapor phase. In these examples the partial pressure of each component provides an excellent approximation for the fugacity of the component in the vapor phase and thus therefore also in solution, i.e. \( f_i^* \approx P_i^V \), as discussed above.

• The benzene + toluene ("methylbenzene") mixture shown at the left provides an example of ideal solution behavior. The linear vapor pressure curves here signal the proportionality between the fugacity of each component of the solution and its mole fraction – the defining characteristic of ideality. The behavior $P_i = x_i P^*_i$ is known as "Raoult's Law". The acetone – CS$_2$ system shown at the right represents a case of a non-ideal mixture. Liquids that are miscible in all proportions usually display behavior somewhere between the extremes represented by these two examples.

• Ideal solutions lead to the simplest type of liquid-vapor coexistence behavior. Example data for the coexistence of a nearly ideal mixture of 1- and 2-propanol are shown at the right.

• The top figure shows the composition dependence of the total pressure for a fixed temperature (25°C). Decreasing the pressure beginning at the point labeled $P_a$ (liquid mixture) one first hits the "liquidus" or "bubble point curve" at the point A, which is the point where vapor first begins to form. At point C the system is a mixture of liquid and vapor, whose relative amounts can be determined using the lever rule on the "tie line" indicated. At point B, on the vapor or "dew-point curve", the last bit of liquid disappears. For all lower pressures the system is a single-phase vapor. The bottom figure is a temperature-composition diagram (for $P = 1$ atm), which illustrates the idea behind fractional distillation. (Figures from M&S.)

• The phase rule for multi-component systems can be written:

$$f = c - \pi + 2$$

where $c$ represents the number of components and $\pi$ the number of phases. Applied to 2-component systems, this rule shows that a 1-d coexistence curve in a 1-component system becomes a 2-d surface in a binary mixture. An illustration of such a surface for an ideal mixture is shown at the right. (The system is hexane–triethylamine). Note that the coexistence regions in the two previous figures represent 2-d slices of this 3-d coexistence surface.

Figure from S. I. Sandler, Chemical and Engineering Thermodynamics, 3rd edition (Wiley, 1999), Chapter 8.
In the case of non-ideal binary mixtures, much more complex liquid-vapor coexistence behavior is possible, as illustrated by the phase diagram of methanol-hexane (P=0.133 bar) shown at the right. In this highly non-ideal mixture an azeotrope (constant boiling mixture) is formed. In addition, the two liquids are immiscible over a wide composition range and phase separate into two distinct liquid mixtures L₁ and L₂. (At the particular pressure shown the L-V coexistence curve intersects the L₁-L₂ coexistence curve so that the azeotrope is also a triple point.)

For characterizing non-ideal mixtures, the primary quantities of interest are the Gibbs excess 
\( G^e(T,P,\vec{x}) \) of the mixture as a whole and the component excess chemical potentials, \( \mu^e_i(T,P,\vec{x}) \). Since \( G = G(T,P,\vec{x}) \) is a fundamental relation, all other thermodynamic quantities follow from \( G(T,P,\vec{x}) \) or equivalently the \( \bar{\mu}_i(T,P,\vec{x}) \) for all components \( i \). For example:

\[
\n\begin{align*}
\bar{V}_i &= \left( \frac{\partial \mu_i}{\partial P} \right)_{T,\vec{x}} \\
\bar{S}_i &= \left( \frac{\partial \mu_i}{\partial T} \right)_{P,\vec{x}} \\
\bar{H}_i &= -T^2 \left( \frac{\partial (\mu_i / T)}{\partial T} \right)_{P,\vec{x}} = \left( \frac{\partial (\mu_i / T)}{\partial (1/T)} \right)_{P,\vec{x}}
\end{align*}
\]

Note that the same relations hold for these excess quantities as for the partial molar quantities themselves.

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**Characterizing Nonideality: Activities, and Activity Coefficients**

The departure of real solutions from ideal behavior is most easily described using two quantities suggested by the following expression for the excess chemical potential:

\[
\mu^e_i(T,P,\vec{x}) = RT \ln \frac{f_i(T,P,\vec{x})}{x_i f_i^*(T,P)} = \int \left( \bar{V}_i - \bar{V}_i^* \right) dP'
\]

The activity \( a_i(T,P,\vec{x}) \) and activity coefficient \( \gamma_i(T,P,\vec{x}) \) of a species \( i \) are defined* by:

\[
\begin{align*}
a_i(T,P,\vec{x}) &= \frac{f_i(T,P,\vec{x})}{f_i^*(T,P)} \\
\gamma_i(T,P,\vec{x}) &= \frac{a_i(T,P,\vec{x})}{x_i}
\end{align*}
\]

(*In these expressions \( f_i^*(T,P) \) denotes the fugacity of the pure substance \( i \). We will revise this definition later by replacing \( f_i(T,P) \) with \( f_i^*(T) \) -- the fugacity of species \( i \) in its standard state at a temperature \( T \).)

**The activity coefficient (as defined above**) is a direct measure of the excess chemical potential:**

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Figure adapted from S. I. Sandler, Chemical and Engineering Thermodynamics, 3rd edition (Wiley, 1999), Chapter 8.
Activity coefficients (as defined above**) are typically strong functions of composition. Because they describe the excess upon mixing, activities have the property that \( \gamma_i \to 1 \) as \( x_i \to 1 \) and they tend to differ most from unity as \( x_i \to 0 \).

The activity coefficients in binary mixtures are linked by a **Gibbs-Duhem relation**: 

\[
\frac{x_1}{\ln \gamma_i} = \frac{x_2}{\ln \gamma_2} = \frac{x_1}{\ln \gamma_1} = \frac{x_2}{\ln \gamma_2}
\]

**Aside**: This relationship comes from the inter-dependence of partial molar quantities \( x_i dY_i + x_2 dY_2 = 0 \) when applied to chemical potentials. Equivalent statements of the above relationship can be written:

\[
x_1 \left( \frac{\partial f_i}{\partial x_1} \right)_{T,P} = x_2 \left( \frac{\partial f_2}{\partial x_2} \right)_{T,P}
\]

**Aside**: The temperature and pressure dependence of \( \gamma_i \) can be described by**:

\[
\gamma_i(T, P, \bar{x}) = \gamma_i(T, P, \bar{x}) \exp \left[ \int_{P_i}^{P_1} \frac{f_i^{ex}}{RT} dP \right] \quad \text{and} \quad \gamma_i(T, P, \bar{x}) = \gamma_i(T, P, \bar{x}) \exp \left[ \int_{T_i}^{T_1} \frac{H_i^{ex}}{RT^2} dT \right]
\]

** (These statements may not hold when the reference value \( f_i(T_0) \) used to define the activity is not \( f_i(T, P) \). For example, some “solute” reference states are defined in the limit of \( x_i \to 0 \) rather than \( x_i = 1 \) so that in fact \( \gamma_i \to 1 \) as \( x_i \to 0 \).)

**Characterizing Liquid Mixtures using Empirical Equations**

The most useful way to characterize the behavior of binary mixtures is through analytic equations for the excess Gibbs energy. A general expression which captures the behavior of many binary liquid mixtures is the **Redlich-Kister expansion**, already mentioned wrt \( \Delta_{mix} \bar{Y} \)

\[
\frac{G^{ex}}{RT} = x_1 x_2 \left[ A + B(x_1 - x_2) + C(x_1 - x_2)^2 + \ldots \right]
\]

where the coefficients will in general be temperature dependent. (Since \( G^{ex} = G^{ex}(T, P, \bar{x}) \), the coefficients will also be pressure dependent but in most practical cases involving liquids the pressure dependence is inconsequential.)

The simplest type of non-ideal solution behavior occurs when only the \( A \) term is non-zero, \( G^{ex}(T, P, \bar{x}) \equiv A(T, P)x_1x_2 \). For solutions conforming to this equation (often called the **Margules equation**), all of the excess functions are symmetric about the point \( x_1 = x_2 = \frac{1}{2} \), and the species activities and the other excess quantities can be expressed in the simple forms:
**An example of a system displaying this type of behavior is provided by the benzene – cyclohexane data (1 bar, 20°C) shown at the right.**

• An example of a system displaying this type of behavior is provided by the benzene – cyclohexane data (1 bar, 20°C) shown at the right.

• Note that the activity coefficients in such a system follow the relation \( \gamma_1(x_2) = \gamma_2(x_1) \).

• In the limit of almost pure component 1 (i.e. \( x_1 \to 1, x_2 \to 0 \)) the activity coefficient of component 1 varies as \( \gamma_1 \to 1 + A x_2^2 + ... \) and its fugacity as \( f_1 \to x_1 f_1^* (1 + A x_2^2 + ...) \). In this limit the abundant component (the “solvent”) only deviates from ideal or **Raoult’s Law behavior**

\[
f_1 = x_1 f_1^* \quad \text{(or} \quad P_1 = x_1 P_1^* \text{)} \quad \text{as} \quad x_1 \to 1
\]

by terms of order \( x_2^2 \) and higher. In this same limit, the activity coefficient of component 2 varies as \( \gamma_2 \to e^4 (1 - 2A x_2 + ...) \) and its fugacity as \( f_2 \to x_2 f_2^* e^4 (1 - 2A x_2 + ...) \). Thus, at sufficient dilution, the minority component (the “solute”) behaves “ideally”, but in a different sense. At sufficient dilution the solute’s fugacity is also proportional to its mole fraction. But, instead of Raoult’s Law, it obeys what is known as **Henry’s Law**, (or 1,222 \( H_2 = \ln \gamma_2 \)

The proportionality constant, \( H_{2,1} = e^4 f_2^* \) is termed **Henry’s constant**. (The subscript “2,1” is a reminder that this constant is characteristic of both components 2 and 1.) Note that because the departure from Henry’s Law is linear in \( x_2 \), departure from this limiting behavior is expected to be more rapid than departure from Raoult’s Law.

• Many mixtures display complicated behavior than that described by the Margules equation. In such cases further terms in the Redlich-Kister expansion are required. The activity coefficients are then determined by:

\[
\ln \gamma_1 = (A + 3B + 5C + ...) x_2^2 - 4(B + 4C + ...) x_2^3 + (12C + ...) x_2^4 + ...
\]

\[
\ln \gamma_2 = (A - 3B + 5C + ...) x_2^2 + 4(B - 4C + ...) x_2^3 + (12C + ...) x_2^4 + ...
\]

• Examples of Redlich-Kister coefficients and the behavior observed in more complex mixtures are provided on the following page.
Parameters Derived Empirical Fits of $\bar{G}^{ex}$ to the Redlich-Kister Equation

<table>
<thead>
<tr>
<th>Components 1–2</th>
<th>$T$/K</th>
<th>$A$</th>
<th>$B$</th>
<th>$C$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Ethanol–methylcyclohexane</td>
<td>305</td>
<td>2.118</td>
<td>−0.239</td>
<td>0.375a</td>
</tr>
<tr>
<td>2. Methylcyclohexane–acetone</td>
<td>318</td>
<td>1.6907</td>
<td>−0.0001</td>
<td>0.1832</td>
</tr>
<tr>
<td>3. Toluene–nitroethane</td>
<td>318</td>
<td>0.7637</td>
<td>0.0703</td>
<td>0.0619</td>
</tr>
<tr>
<td>4. Toluene–acetone</td>
<td>318</td>
<td>0.6637</td>
<td>−0.0048</td>
<td>0.0023</td>
</tr>
<tr>
<td>5. Benzene–cyclopentane</td>
<td>298</td>
<td>0.4560</td>
<td>−0.0182</td>
<td>−</td>
</tr>
<tr>
<td>6. Pyridine–acetone</td>
<td>303</td>
<td>0.1919</td>
<td>0.0050</td>
<td>0.0075</td>
</tr>
<tr>
<td>7. Chloroform–furan</td>
<td>303</td>
<td>−0.1083</td>
<td>−0.0177</td>
<td>0.0071</td>
</tr>
<tr>
<td>8. Dichloromethane–acetone</td>
<td>303</td>
<td>−0.6479</td>
<td>−0.0887</td>
<td>−0.0299</td>
</tr>
<tr>
<td>9. Pyridine–chloroform</td>
<td>303</td>
<td>−1.0271</td>
<td>0.2270</td>
<td>0.0930</td>
</tr>
<tr>
<td>10. Chloroform–1,4-dioxane</td>
<td>303</td>
<td>−1.2006</td>
<td>−0.4131</td>
<td>0.0318</td>
</tr>
<tr>
<td>11. Pyridine–dichloromethane</td>
<td>303</td>
<td>−0.5140</td>
<td>0.0652</td>
<td>0.0088</td>
</tr>
</tbody>
</table>

Table from Pitzer, Thermodynamics 3rd Ed. (McGraw-Hill, 1995)

Ethanol(1)+Methylcyclohexane(2) $A = +2.1$

$G^{ex}/RT, \mu_{i}^{ex}/RT$

Fugacity $f$/kPa

Activity Coeff. $\gamma_{i}$

Above: $\bar{G}^{ex}/RTx_{1}x_{2}$ for all of the mixtures tabulated.

Right: Various quantities for two selected mixtures.
• The Margules equation or the Redlich-Kister expansion are most useful for components of similar size. For mixtures consisting of molecules of different size, simpler results are often obtained when free energies are expressed in terms of volume fractions rather than mole fractions. The most important example of this type of approach is due to van Laar (1906), who expressed, $\bar{G}^{ex}$ in the form

$$\frac{G^{ex}}{RT} = a_{12}z_1z_2$$

where $z_1 \equiv \frac{n_1b_1}{n_1b_1 + n_2b_2}$ and $z_2 \equiv \frac{n_2b_2}{n_1b_1 + n_2b_2}$

and $n_i$ are mole numbers. This expression leads to activity coefficients:

$$\ln \gamma_1 = \frac{a_{12}}{RT} b_1 z_1^2 \quad \text{and} \quad \ln \gamma_2 = \frac{a_{12}}{RT} b_2 z_2^2$$

When van Laar (a student of van der Waals) originally proposed this equation, $b_1$ and $b_2$ were defined to be the van der Waals volume parameters of the two components. Subsequently, the equation has most often been used for deriving a 2-parameter fits to activity coefficient data in the form:

$$\ln \gamma_1 = \frac{\alpha}{\left[1 + \alpha x_1 \beta x_2 \right]^2} \quad \text{ln} \gamma_2 = \frac{\beta}{\left[1 + \beta x_1 \alpha x_2 \right]^2}$$

where $\alpha = a_{12}b_1$ and $\beta = a_{12}b_2$. An example of a fit of experimental data using these equations is provided at the right. (In this example $\alpha = 0.419$, $\beta = .745$).

• Alternatively, one can reinterpret the $b$’s in the original equation as molar volumes and thereby obtain a (less accurate) 1-parameter ($a_{12}$) fitting function of the form:

$$\frac{G^{ex}}{RT} = a_{12}V^* \varphi \varphi^*$$

where $\varphi_i = \frac{n_i \bar{V}^*_i}{n_i \bar{V}^*_1 + n_2 \bar{V}^*_2}$

and $\bar{V}^* = x_1 \bar{V}^*_1 + x_2 \bar{V}^*_2$.

### Statistical Models of Liquid Mixtures

• Theoretical models for liquids and liquid mixtures are not capable of quantitatively predicting the behavior observed in experimental systems, except perhaps in the simplest of cases. (Computer simulation methods are, however, rapidly approaching quantitative accuracy.) Nevertheless, simple analytical models provide useful insights into observed behavior and also offer useful frameworks for correlating experimental data.

• The Margules equation can be derived on the basis of a random mixing lattice model, as discussed in M&S and the Pitzer reading. The key ideas are that molecules are of equal size (so that molecules can be freely exchanged on a “lattice”) and are randomly distributed.
Considering only pair-wise interactions between nearest neighbors on the lattice, the constant $A$ appearing in the equation for $G^{ex}$ can be interpreted as:

$$A = \frac{ZN \Delta}{2RT} (\varepsilon_{11} + \varepsilon_{22} - 2\varepsilon_{12})$$

where $Z$ is the coordination number of the lattice and $\varepsilon_{ij}$ is the energy of interaction of a pair of $i$-$j$ neighbors. In this model one has $V^E = 0$, $S^E = 0$, and $G^E = \Delta_{\text{mix}} \overline{U}$, with $\Delta_{\text{mix}} \overline{U}$ being described by the above energy expression. Pitzer shows how these nearest-neighbor energies can be approximately related to observable energies of vaporization via:

$$A \cong \left( \frac{\Delta_{\text{vap}} U_1^* - \Delta_{\text{vap}} U_2^*}{RT} \right)^2 / RT$$

- A more useful model for liquid mixtures, developed independently by Scatchard and Hildebrand, can be used to interpret and or predict the parameters in the van Laar equations. The theory treats what are termed “regular solutions” – ones in which components mix with no excess entropy provided that there is no volume change upon mixing. This theory provides the regular solution equations:

$$\ln \gamma_1 = \frac{\overline{V}_i^* \phi_i^2}{RT} (\delta_1 - \delta_2)^2$$

$$\ln \gamma_2 = \frac{\overline{V}_2^* \phi_2^2}{RT} (\delta_1 - \delta_2)^2$$

where $\delta_i$ is termed the “(Hildebrand) solubility parameter” of species $i$, defined by:

$$\delta_i \equiv \left( \frac{\Delta_{\text{vap}} U_i^*}{\overline{V}_i^*} \right)^{1/2}$$

(The designation solubility parameter results from the fact that if the $\delta_i$ values of two liquids are significantly different, activities calculated in this manner are high, and the liquids are likely to be relatively insoluble in one another.)

Regular solution theory provides a method for estimating the activities and mixing properties of two liquids using only the properties of the pure components. Its predictions are of quantitative value only for nonpolar fluids. The relationship between the predictions of regular solution theory and the empirical van Laar constants is:

$$\alpha = \frac{\overline{V}_1^*}{RT} (\delta_1 - \delta_2)^2 \quad \text{and} \quad \beta = \frac{\overline{V}_2^*}{RT} (\delta_1 - \delta_2)^2$$
## Summary of Terminology: Chemical Potential, Fugacity, and Activity

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Definition &amp; Relation to $\mu$</th>
<th>Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>chemical potential</td>
<td>$\mu_i(T, P, \bar{x}) \equiv \bar{G}<em>i(T, P, \bar{x}) \equiv \left( \frac{\partial G}{\partial n_i} \right)</em>{T,P,n_{i,ref}}$</td>
<td>• fundamental quantity governing matter flow</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• units of energy</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• no absolute zero</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• $\mu_i \to -\infty$ as $x_i \to 0$</td>
</tr>
<tr>
<td>fugacity</td>
<td>$f_i(T, P, \bar{x}) \equiv x_i P \exp \left{ \frac{(\mu_i - \mu_i^{IGM})_{T,P,\bar{x}}}{RT} \right}$</td>
<td>• log rep. of $\mu_i$; ref. IGM</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• units of pressure</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• “effective pressure” or escaping potential</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• most useful in gases</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• $f_i \to x_i P$ as $P \to 0$</td>
</tr>
<tr>
<td>activity</td>
<td></td>
<td>• alternative log. rep. of $\mu_i$; ref. standard state (“°”) or “*”</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• equivalent of effective concentration, but unitless</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• most useful measure of $\mu$ for general reaction equilibria</td>
</tr>
<tr>
<td>activity coefficient</td>
<td>$\gamma_i(T, P, \bar{x}) \equiv \frac{a_i(T, P, \bar{x})}{x_i}$</td>
<td>• direct measure of non-ideality</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• $\gamma_i = 1$ defines ideal (either wrt standard state or IS)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• main object of solution theories and measurements</td>
</tr>
</tbody>
</table>