OUTLINE OF CHAPTER 9

IDEAL GAS MIXTURES

$$PV = NRT \quad \text{or} \quad P\underline{V} = RT$$

We expect no interaction between molecules. Then

$$PV^{\text{IGM}} = (N_1 + N_2 + \cdots)RT = \left(\sum_{j=1}^{C} N_j\right) RT = NRT$$

$$U^{\text{IGM}}(T, N) = \sum_{j=1}^{C} N_j \underline{U}_j^{\text{IG}}(T)$$

and therefore

$$\bar{U}_i^{\text{IGM}}(T, \underline{x}) = \left.\frac{\partial U^{\text{IGM}}(T, N)}{\partial N_i}\right|_{T,P,N_{j\neq i}} = \left.\frac{\partial}{\partial N_i}\right|_{T,P,N_{j\neq i}} \sum_{j=1}^{C} N_j \underline{U}_j^{\text{IG}}(T) = \underline{U}_i^{\text{IG}}(T)$$

$$\bar{V}_i^{\text{IGM}}(T, P, \underline{x}) = \left.\frac{\partial V^{\text{IGM}}(T, P, N)}{\partial N_i}\right|_{T,P,N_{j\neq i}} = \left.\frac{\partial}{\partial N_i}\right|_{T,P,N_{j\neq i}} \sum_{j}^{C} N_j \frac{RT}{P} = \frac{RT}{P} = \underline{V}_i^{\text{IG}}(T, P)$$

$$P_i = x_i P$$

$$P_i^{IGM}(N, V, T, \underline{x}) = \frac{N_i}{\sum_{j=i}^{C} N_j} P = \frac{N_i}{\sum_{j=i}^{C} N_j} \left\{ \sum_{j=1}^{C} N_j \frac{RT}{V} \right\} = \frac{N_i RT}{V} = P^{IG}(N_i, V, T)$$

Since there is no energy of interaction in an ideal gas mixture, the effect on each species of forming an ideal gas mixture at constant temperature and total pressure is equivalent to reducing the pressure from P to its partial pressure in the mixture P_i. Alternatively, the effect is equivalent to expanding each gas from its initial volume $V_i = N_i RT/P$ to the volume of the mixture $V = \sum_i N_i RT/P$. Thus, from Eqs. 6.4-2 and 6.4-3, we have

$$\bar{S}_i^{IGM}(T, P, \underline{x}) - \underline{S}_i^{IG}(T, P) = -R \ln \frac{P_i}{P} = -R \ln x_i$$

or

$$\bar{S}_i^{IGM}(T, V, \underline{x}) - \underline{S}_i^{IG}(T, V_i) = R \ln \frac{V}{V_i} = R \ln \frac{\sum N_j RT/P}{N_i RT/P} = -R \ln x_i$$

Consequently,

$$\Delta_{mix} S^{IGM} = \sum_{i=1}^{C} N_i [\bar{S}_i^{IGM}(T, P, \underline{x}) - \underline{S}_i^{IG}(T, P)] = -R \sum_{i=1}^{C} N_i \ln x_i$$

and

$$\Delta_{mix} \underline{S}^{IGM} = \frac{\Delta_{mix} S^{IGM}}{N} = -R \sum_{i=1}^{C} x_i \ln x_i$$

$\bar{G}_i^{IGM}(T, P, \underline{x})$ and $\Delta_{mix} \underline{G}^{IGM}$:

$$\begin{aligned} \bar{G}_i^{IGM}(T, P, \underline{x}) &= \bar{H}_i^{IGM}(T, P, \underline{x}) - T\bar{S}_i^{IGM}(T, P, \underline{x}) \\ &= \underline{H}_i^{IG}(T, P) - T(\underline{S}_i^{IG}(T, P) - R \ln x_i) \\ &= \underline{G}_i^{IG}(T, P) + RT \ln x_i \end{aligned}$$

$$\begin{aligned} \Delta_{mix} \underline{G}^{IGM} &= \sum_{i=1}^{C} x_i \{\bar{G}_i^{IGM}(T, P, \underline{x}) - \underline{G}_i^{IG}(T, P)\} \\ &= RT \sum x_i \ln x_i \end{aligned}$$

COMPONENT CHEMICAL POTENTIAL AND FUGACITY CALCULATION

We start with

$$dG = -S\,dT + V\,dP + \sum_{i=1}^{C} \bar{G}_i\,dN_i$$

Commutative property tells

$$\left.\frac{\partial}{\partial N_i}\right|_{T,P,N_{j\neq i}} \left(\frac{\partial G}{\partial T}\right)_{P,N_j} = \left.\frac{\partial}{\partial T}\right|_{P,N_j} \left(\frac{\partial G}{\partial N_i}\right)_{T,P,N_{j\neq i}}$$

$$\left.\frac{\partial}{\partial N_i}\right|_{T,P,N_{j\neq i}} \left(\frac{\partial G}{\partial P}\right)_{T,N_j} = \left.\frac{\partial}{\partial P}\right|_{T,N_j} \left(\frac{\partial G}{\partial N_i}\right)_{T,P,N_{j\neq i}}$$

So that

$$\bar{S}_i = -\left(\frac{\partial \bar{G}_i}{\partial T}\right)_{P,N_j}$$

$$\bar{V}_i = \left(\frac{\partial \bar{G}_i}{\partial P}\right)_{T,N_j}$$

The second leads to

$$\bar{G}_i(T_1, P_2, \underline{x}) - \bar{G}_i(T_1, P_1, \underline{x}) = \int_{P_1}^{P_2} \bar{V}_i\,dP$$

Thus, we define fugacity of a component in a mixture

$$\bar{f}_i(T,P,\underline{x}) = x_i P \exp\left\{\frac{\bar{G}_i(T,P,\underline{x}) - \bar{G}_i^{IGM}(T,P,\underline{x})}{RT}\right\}$$

$$= x_i P \exp\left\{\frac{1}{RT}\int_0^P (\bar{V}_i - \bar{V}_i^{IG})\,dP\right\}$$

$$= P \exp\left\{\frac{\bar{G}_i(T,P,\underline{x}) - \underline{G}_i^{IG}(T,P)}{RT}\right\}$$

And the fugacity coefficient

$$\bar{\phi}_i = \frac{\bar{f}_i}{x_i P} = \exp\left\{\frac{\bar{G}_i(T,P,\underline{x}) - \bar{G}_i^{IGM}(T,P,\underline{x})}{RT}\right\}$$

$$= \exp\left\{\frac{1}{RT}\int_0^P (\bar{V}_i - \bar{V}_i^{IGM})\,dP\right\}$$

and therefore

$$RT\left(\frac{\partial \ln \bar{f}_i}{\partial P}\right)_{T,\underline{x}} = \left(\frac{\partial \bar{G}_i}{\partial P}\right)_{T,\underline{x}} = \bar{V}_i$$

$$RT\ln\left\{\frac{\bar{f}_i(T,P,\underline{x})}{\bar{f}_i(T,P\to 0,\underline{x})}\right\} - RT\ln\left\{\frac{f_i(T,P)}{f_i(T,P\to 0)}\right\} = \int_{P\to 0}^{P}(\bar{V}_i - \underline{V}_i)\,dP$$

We now use the fact that as $P \to 0$, $\bar{f}_i \to x_i P$ and $f_i \to P$, to obtain

$$RT\ln\left\{\frac{\bar{f}_i(T,P,\underline{x})}{x_i f_i(T,P)}\right\} = \int_0^P (\bar{V}_i - \underline{V}_i)\,dP$$

Therefore, for a mixture in which the pure component and partial molar volumes are identical [i.e., $\bar{V}_i(T, P, \underline{x}) = x_i V_i(T, P)$ *at all conditions*], the fugacity of each species in the mixture is equal to its mole fraction times its pure-component fugacity evaluated at the same temperature and pressure as the mixture $\bar{f}_i(T, P, \underline{x}) = x_i f_i(T, P)$. However, if, as is generally the case, $\bar{V}_i \neq \underline{V}_i$, then $\bar{f}_i$ and f_i are related through the integral over all pressures of the difference between the species partial molar and pure-component molar volumes.

Dependence with T

$$\left[\frac{\partial \ln(\bar{f}_i/x_i P)}{\partial T}\right]_{P,\underline{x}} = -\frac{(\bar{G}_i - \bar{G}_i^{IG})}{RT^2} + \frac{1}{RT}\left[\frac{\partial(\bar{G}_i - \bar{G}_i^{IGM})}{\partial T}\right]_{P,\underline{x}}$$

and then using $d\underline{G} = \underline{V}\,dP - \underline{S}\,dT$ and $\underline{G} = \underline{H} - T\underline{S}$, to obtain

$$\left[\frac{\partial \ln(\bar{f}_i/x_i P)}{\partial T}\right]_{P,\underline{x}} = \left[\frac{\partial \ln \bar{\phi}_i}{\partial T}\right]_{P,\underline{x}} = -\frac{(\bar{H}_i - \bar{H}_i^{IGM})}{RT^2}$$

Change of Chemical potential with composition at constant T and P

We start with:

$$\bar{G}_i(T, P, \underline{x}) = \bar{G}_i^{IGM}(T, P, \underline{x}) + RT \ln\left(\frac{\bar{f}_i(T, P, \underline{x})}{x_i P}\right)$$

$$= \bar{G}_i^{IGM}(T, P, \underline{x}) + RT \ln \bar{\phi}_i(T, P, \underline{x})$$

But recall

$$\begin{aligned}\bar{G}_i^{IGM}(T, P, \underline{x}) &= \bar{H}_i^{IGM}(T, P, \underline{x}) - T\bar{S}_i^{IGM}(T, P, \underline{x}) \\ &= \underline{H}_i^{IG}(T, P) - T(\underline{S}_i^{IG}(T, P) - R \ln x_i) \\ &= \underline{G}_i^{IG}(T, P) + RT \ln x_i\end{aligned}$$

Then:

$$\bar{G}_i^{IGM}(T, P, \underline{x}) = \underline{G}_i^{IG}(T, P) + RT \ln x_i$$

So we get

$$\bar{G}_i(T,P,\underline{x}^{II}) - \bar{G}_i(T,P,\underline{x}^{I}) = \bar{G}_i^{IGM}(T,P,\underline{x}^{II}) + RT\ln\left\{\frac{\bar{f}_i(T,P,\underline{x}^{II})}{x_i^{II}P}\right\} - \bar{G}_i^{IGM}(T,P,\underline{x}^{I}) - RT\ln\left\{\frac{\bar{f}_i(T,P,\underline{x}^{I})}{x_i^{I}P}\right\}$$

$$= \underline{G}_i^{IG}(T,P) + RT\ln x_i^{II} + RT\ln\left\{\frac{\bar{f}_i(T,P,\underline{x}^{II})}{x_i^{II}P}\right\} - \underline{G}_i^{IG}(T,P) - RT\ln x_i^{I} - RT\ln\left\{\frac{\bar{f}_i(T,P,\underline{x}^{I})}{x_i^{I}P}\right\}$$

Or

$$\bar{G}_i(T,P,\underline{x}^{II}) - \bar{G}_i(T,P,\underline{x}^{I}) = RT\ln\left\{\frac{\bar{f}_i(T,P,\underline{x}^{II})}{\bar{f}_i(T,P,\underline{x}^{I})}\right\} = RT\ln\left\{\frac{x_i^{II}\bar{\phi}_i(T,P,\underline{x}^{II})}{x_i^{I}\bar{\phi}_i(T,P,\underline{x}^{I})}\right\}$$

Phase equilibrium says $\bar{G}_i^{I} = \bar{G}_i^{II}$ *. Then*

$$\bar{f}_i^{I} = \bar{f}_i(T,P,\underline{x}^{I}) = \bar{f}_i(T,P,\underline{x}^{II}) = \bar{f}_i^{II}$$

In analogy to pure component, we define fugacity of the mixture as follows:

$$\bar{f} = P\exp\left\{\frac{\underline{G}(T,P,\underline{x}) - \underline{G}^{IGM}(T,P,\underline{x})}{RT}\right\}$$

Not a partial molar fugacity!!!!!! $\bar{f}_i \neq \left(\frac{\partial(N\bar{f})}{\partial N_i}\right)_{T,P,N_{j\neq i}}$

Computing fugacity.

Start with

$$dP = \frac{1}{\underline{V}}\,d(P\underline{V}) - \frac{P}{\underline{V}}\,d\underline{V} = \frac{P}{Z}\,dZ - \frac{P}{\underline{V}}\,d\underline{V}$$

Use triple product

$$\left(\frac{\partial V}{\partial N_i}\right)_{T,P,N_{j\neq i}} \left(\frac{\partial P}{\partial V}\right)_{T,N_j} \left(\frac{\partial N_i}{\partial P}\right)_{T,V,N_{j\neq i}} = -1$$

In the following form

$$\left(\frac{\partial V}{\partial N_i}\right)_{T,P,N_{j\neq i}} dP = -\left(\frac{\partial P}{\partial N_i}\right)_{T,V,N_{j\neq i}} dV$$

Then substitute in

$$\bar{\phi}_i = \frac{\bar{f}_i}{x_i P} = \exp\left\{\frac{\bar{G}_i(T,P,\underline{x}) - \bar{G}_i^{\mathrm{IGM}}(T,P,\underline{x})}{RT}\right\} = \exp\left\{\frac{1}{RT}\int_0^P (\bar{V}_i - \bar{V}_i^{\mathrm{IGM}})\,dP\right\}$$

to get

$$\ln\bar{\phi}_i = \ln\frac{\bar{f}_i(T,P,\underline{x})}{x_i P} = \frac{1}{RT}\int_{\underline{V}=\infty}^{\underline{V}=ZRT/P}\left[\frac{RT}{\underline{V}} - N\left(\frac{\partial P}{\partial N_i}\right)_{T,V,N_{j\neq i}}\right] d\underline{V} - \ln Z$$

which is similar to that of a pure fluid.

EXCESS PROPERTIES

Ideal Mixture…

$$\overline{H}_i^{IM}(T, P, \underline{x}) = \underline{H}_i(T, P)$$

$$\overline{V}_i^{IM}(T, P, \underline{x}) = \underline{V}_i(T, P)$$

It is easy to check (Chapter 8):

$$\Delta_{mix} V^{IM}(T, P, \underline{x}) = \sum_{i=1}^{C} N_i[\overline{V}_i^{IM}(T, P, \underline{x}) - \underline{V}_i(T, P)] = 0$$

$$\Delta_{mix} H^{IM}(T, P, \underline{x}) = \sum_{i=1}^{C} N_i[\overline{H}_i^{IM}(T, P, \underline{x}) - \underline{H}_i(T, P)] = 0$$

Since $\overline{V}_i^{IM} = \underline{V}_i$ ***we have***

$$\overline{f}_i^{IM}(T, P, \underline{x}) = x_i f_i(T, P)$$

$$\overline{U}_i^{IM}(T, P, \underline{x}) = \underline{U}_i(T, P)$$

$$\bar{G}_i^{IM}(T,P,\underline{x}) - \underline{G}_i(T,P) = RT \ln\left\{\frac{\bar{f}_i^{IM}(T,P,\underline{x})}{f_i(T,P)}\right\}$$
$$= RT \ln\left\{\frac{x_i f_i(T,P)}{f_i(T,P)}\right\} = RT \ln x_i$$

Thus, we have

$$\bar{G}_i^{IM}(T,P,\underline{x}) = \underline{G}_i(T,P) + RT \ln x_i$$
$$\bar{A}_i^{IM}(T,P,\underline{x}) = \underline{A}_i(T,P) + RT \ln x_i$$
$$\bar{S}_i^{IM}(T,P,\underline{x}) = \underline{S}_i(T,P) - R \ln x_i$$

and

$$\underline{U}^{IM}(T,P,\underline{x}) = \sum x_i \underline{U}_i(T,P)$$
$$\underline{V}^{IM}(T,P,\underline{x}) = \sum x_i \underline{V}_i(T,P)$$
$$\underline{H}^{IM}(T,P,\underline{x}) = \sum x_i \underline{H}_i(T,P)$$
$$\underline{S}^{IM}(T,P,\underline{x}) = \sum x_i \underline{S}_i(T,P) - R \sum x_i \ln x_i$$
$$\underline{G}^{IM}(T,P,\underline{x}) = \sum x_i \underline{G}_i(T,P) + RT \sum x_i \ln x_i$$
$$\underline{A}^{IM}(T,P,\underline{x}) = \sum x_i \underline{A}_i(T,P) + RT \sum x_i \ln x_i$$

Although all the above equations resemble a lot those of the ideal gas mixtures, these are properties of real gases, then all the techniques from Chapter 6 apply.

Thus molar volume is not equal to RT/P and fugacity is not equal to pressure…

Also from $\bar{f}_i^{IM}(T,P,\underline{x}) = x_i f_i(T,P)$ ***, we have***

$$\bar{\phi}_i^{IM}(T, P, \underline{x}) = \phi_i(T, P)$$

And since all derivatives w.r.t. composition need to be equal

$$\left[\frac{\partial \ln(\bar{f}_i^{IM}/x_i P)}{\partial T}\right]_{P,\underline{x}} = \left[\frac{\partial \ln(f_i/P)}{\partial T}\right]_P$$

Also, an ideal mixture satisfies the Gibbs-duhem equation

$$\begin{aligned} \underline{S}^{IM}\, dT - \underline{V}^{IM}\, dP + \sum x_i\, d\bar{G}_i^{IM} &= \sum x_i \bar{S}_i^{IM}\, dT - \sum x_i \bar{V}_i^{IM}\, dP + \sum x_i\, d(\underline{G}_i + RT \ln x_i) \\ &= \sum x_i \underline{S}_i\, dT - R \sum x_i \ln x_i\, dT - \sum x_i \underline{V}_i\, dP + \sum x_i\, d\underline{G}_i \\ &\quad + R \sum x_i \ln x_i\, dT + RT \sum x_i\, d \ln x_i \\ &= \sum x_i (\underline{S}_i\, dT - \underline{V}_i\, dP + d\underline{G}_i) + RT \sum dx_i \\ &\equiv 0 \end{aligned}$$

since $d\underline{G} = \underline{V}\, dP - \underline{S}\, dT$ for a pure component, and $\sum x_i = 1$, so that $d \sum x_i = \sum dx_i = d(1) = 0$.

We define Excess Property the departure from IDEAL mixtures

$$\Delta_{mix}\underline{\theta}(T,P,\underline{x}) = \Delta_{mix}\underline{\theta}^{IM}(T,P,\underline{x}) + [\Delta_{mix}\underline{\theta}(T,P,\underline{x}) - \Delta_{mix}\underline{\theta}^{IM}(T,P,\underline{x})]$$
$$= \Delta_{mix}\underline{\theta}^{IM} + \underline{\theta}^{ex}$$

where

$$\underline{\theta}^{ex} = \Delta_{mix}\underline{\theta}(T,P,\underline{x}) - \Delta_{mix}\underline{\theta}^{IM}(T,P,\underline{x}) = \sum_i x_i\bar{\theta}_i - \sum_i x_i\bar{\theta}_i^{IM} = \sum_i x_i(\bar{\theta}_i - \bar{\theta}_i^{IM})$$

Finally we define the corresponding partial molar property

$$\bar{\theta}_i^{ex} = \left.\frac{\partial(N\underline{\theta}^{ex})}{\partial N_i}\right|_{T,P,N_{j\neq i}} = \left.\frac{\partial}{\partial N_i}\right|_{T,P,N_{j\neq i}} \sum_k N_k(\bar{\theta}_k - \bar{\theta}_k^{IM})$$

But

$$\sum_k N_k \frac{\partial}{\partial N_i}(\bar{\theta}_k - \bar{\theta}_k^{IM})|_{T,P,N_{j\neq i}} = 0$$

Then

$$\bar{\theta}_i^{ex} = \bar{\theta}_i - \bar{\theta}_i^{IM}$$

For chemical potential, we have

$$\begin{aligned}
\bar{G}_i^{ex} &= (\bar{G}_i - \bar{G}_i^{IM}) = (\bar{G}_i - \bar{G}_i^{IG}) + (\bar{G}_i^{IG} - \bar{G}_i^{IM}) \\
&= (\bar{G}_i - \bar{G}_i^{IG}) + (\underline{G}_i^{IG} + RT\ln x_i - \underline{G}_i - RT\ln x_i) \\
&= (\bar{G}_i - \bar{G}_i^{IG}) + (\underline{G}_i^{IG} - \underline{G}_i) \\
&= RT\ln\frac{\bar{f}_i}{x_i P} - RT\ln\frac{f_i}{P} \\
&= RT\ln\left(\frac{\bar{f}_i}{x_i f_i}\right) = RT\ln\left(\frac{\bar{\phi}_i}{\phi_i}\right) = \int_0^P [\bar{V}_i - \underline{V}_i]\,dP
\end{aligned}$$

But for liquids, we usually do not have an equation of state. Then we define liquid activity coefficients

$$\bar{f}_i^L(T, P, \underset{\sim}{x}) = x_i \gamma_i(T, P, \underset{\sim}{x}) f_i^L(T, P)$$

Or, alternatively

$$RT \ln \gamma_i(T, P, \underset{\sim}{x}) = \bar{G}_i^{ex} = \left(\frac{\partial N \underset{\sim}{G}^{ex}}{\partial N_i}\right)_{T,P,N_{j \neq i}}$$

Illustration 9.3-2

Analyzing the Gibbs Energy of a Mixture to Determine Whether It Is an Ideal Mixture

Experimentally (as will be described in Sec. 10.2) it has been found that the Gibbs energy for certain binary mixture has the form

$$\underline{G}_{mix}(T, P, \underline{x}) = \sum_{i=1}^{2} x_i \underline{G}_i(T, P) + RT \sum_{i=1}^{2} x_i \ln x_i + a x_1 x_2 \qquad ($$

where a is a constant. Determine whether this mixture is an ideal mixture.

Solution

For an ideal mixture Eqs. 9.3-1a and b must be satisfied at all conditions. To see if this is s we start with the relation between the Gibbs energy and volume and use the equation above obtain

$$\underline{V}_{mix} = \left(\frac{\partial \underline{G}_{mix}}{\partial P}\right)_{T,N} = \sum_{i=1}^{2} x_i \left(\frac{\partial \underline{G}_i}{\partial P}\right)_{T,N} = \sum x_i \underline{V}_i(T, P)$$

Therefore,

$$\bar{V}_1(T, P) = \left.\frac{\partial (N\underline{V}_{mix})}{\partial N_1}\right|_{T,N_2} = \frac{\partial}{\partial N_1}\left(N_1 \underline{V}_1(T, P) + N_2 \underline{V}_2(T, P)\right)_{T,N_2} = \underline{V}_1(T, P)$$

Similarly, $\bar{V}_2(T, P) = \underline{V}_2(T, P)$, so Eq. 9.3-1b is satisfied. We now move on to Eq. 9.3-1a b starting with

$$\left.\frac{\partial}{\partial T}\right|_P \left(\frac{\underline{G}}{T}\right) = \frac{1}{T}\left(\frac{\partial \underline{G}}{\partial T}\right)_P - \frac{\underline{G}}{T^2} = \frac{1}{T}(-\underline{S}) - \frac{(\underline{H} - T\underline{S})}{T^2} = -\frac{\underline{H}}{T^2}$$

or

$$\underline{H} = -T^2 \left.\frac{\partial}{\partial T}\right|_P \left(\frac{\underline{G}}{T}\right)$$

Therefore,

$$\underline{H}_{mix} = -T^2 \left.\frac{\partial}{\partial T}\right|_P \left[\sum x_i \frac{\underline{G}_i}{T} + R\sum x_i \ln x_i + \frac{a}{T} x_1 x_2\right]$$

$$= -T^2\left[\sum x_i \left(-\frac{\underline{H}_i}{T^2}\right) - \frac{a}{T^2} x_1 x_2\right] = \sum x_i \underline{H}_i + a x_1 x_2$$

Then

$$\bar{H}_1(T,P,\underline{x}) = \frac{\partial}{\partial N_1}\bigg|_{T,P,N_2} N\underline{H}_{\text{mix}} = \frac{\partial}{\partial N_1}\bigg|_{T,P,N_2}\left(N_1\underline{H}_1 + N_2\underline{H}_2 + \frac{aN_1N_2}{N_1+N_2}\right)$$

$$= \underline{H}_1(T,P) + a\left[\frac{N_2}{N_1+N_2} - \frac{N_1N_2}{(N_1+N_2)^2}\right]$$

$$= \underline{H}_1(T,P) + a(x_2 - x_1x_2) = \underline{H}_1(T,P) + ax_2(1-x_1)$$

$$= \underline{H}_1(T,P) + ax_2^2$$

Similarly, $\bar{H}_2(T,P,\underline{x}) = \underline{H}_2(T,P) + ax_1^2$.

Therefore, Eq. 9.3-1a is not satisfied, and the mixture described by Eq. * is not an ideal mixture.

COMMENT

Clearly, for this mixture $\underline{G}^{ex} = ax_1x_2$ and $\underline{A}^{ex} = ax_1x_2$. Since the excess Gibbs energies of mixing are not zero, this also shows that the mixture cannot be ideal. ■

ILLUSTRATION 9.3-3

Developing Expressions for Activity Coefficients and Species Fugacities from the Gibbs Energy

Develop an expression for the activity coefficients and species fugacities using the Gibbs energy function of the previous illustration.

SOLUTION

We start from

$$\underline{G}^{ex} = \underline{G}_{\text{mix}} - \underline{G}_{\text{mix}}^{\text{IM}}$$

$$= \left(\sum_{i=1}^{2} x_i\underline{G}_i + RT\sum_{i=1}^{2} x_i \ln x_i + ax_1x_2\right) - \left(\sum_{i=1}^{2} x_i\underline{G}_i + RT\sum_{i=1}^{2} x_i \ln x_i\right) = ax_1x_2$$

Then, by definition,

$$\bar{G}_1^{ex} = \left(\frac{\partial N\underline{G}^{ex}}{\partial N_1}\right)_{T,P,N_2} = \frac{\partial}{\partial N_1}\bigg|_{T,P,N_2} Nax_1x_2 = \frac{\partial}{\partial N_1}\bigg|_{T,P,N_2} \frac{aN_1N_2}{(N_1+N_2)}$$

$$= a\left[\frac{N_2}{N_1+N_2} - \frac{N_1N_2}{(N_1+N_2)^2}\right] = a(x_2 - x_1x_2)$$

$$= ax_2(1-x_1) = ax_2^2 = RT\ln\gamma_1(x_1)$$

or

$$\gamma_1(x_1) = \exp\left[\frac{ax_2^2}{RT}\right] = \exp\left[\frac{a(1-x_1)^2}{RT}\right]$$

Similarly,

$$\bar{G}_2^{ex} = ax_1^2 = a(1-x_2)^2 \quad \text{and} \quad \gamma_2(x_2) = \exp\left[\frac{ax_1^2}{RT}\right] = \exp\left[\frac{a(1-x_2)^2}{RT}\right]$$

From Eq. 9.3-3, the activity coefficient is equal to unity for species in ideal mixtures, and for nonideal mixtures

$$\gamma_i(T,P,\underline{x}) = \exp\left(\frac{\bar{G}_i^{ex}}{RT}\right) = \exp\left(\frac{1}{RT}\int_0^P \left[\bar{V}_i(T,P,\underline{x}) - \underline{V}_i(T,P)\right] dP\right)$$

$$0 = \underline{S}\, dT - \underline{V}\, dP + \sum_{i=1}^{C} x_i\, d\bar{G}_i$$

$$0 = \underline{S}^{IM}\, dT - \underline{V}^{IM}\, dP + \sum_{i=1}^{C} x_i\, d\bar{G}_i^{IM}$$

Subtracting, we get the Gibbs-Duhem relation for excess properties

$$0 = \underline{S}^{ex}\, dT - \underline{V}^{ex}\, dP + \sum_{i=1}^{C} x_i\, d\bar{G}_i^{ex}$$

But $\bar{G}_i^{ex} = RT\ln\gamma_i,$ ***and*** $\underline{G}^{ex} = \sum x_i\bar{G}_i^{ex} = \underline{H}^{ex} - T\underline{S}^{ex}$ ***Thus***

$$0 = \frac{\underline{H}^{ex}}{T}\, dT - \underline{V}^{ex}\, dP + RT\sum_{i=1}^{C} x_i\, d\ln\gamma_i$$

Therefore, for constant T and P, we have the Gibbs-Duhem relation for activity

$$0 = \sum_{i=1}^{C} x_i\, d\ln\gamma_i\Big|_{T,P}$$

For binary mixtures:

$$x_1\left(\frac{\partial\ln\gamma_1}{\partial x_1}\right)_{T,P} + x_2\left(\frac{\partial\ln\gamma_2}{\partial x_1}\right)_{T,P} = 0$$

ILLUSTRATION 9.3-4

Testing Whether an Activity Coefficient Model Satisfies the Gibbs-Duhem Equation

Determine whether the activity coefficient expressions derived in the previous illustration satisfy the Gibbs-Duhem equation, Eq. 9.3-17.

SOLUTION

From the previous illustration, we have

$$\ln \gamma_1(x_1) = \frac{a}{RT} x_2^2 = \frac{a}{RT}(1 - x_1)^2$$

and

$$\ln \gamma_2(x_2) = \frac{a}{RT} x_1^2 = \frac{a}{RT}(1 - x_2)^2$$

Consequently,

$$\left(\frac{\partial \ln \gamma_1}{\partial x_1}\right)_{T,P} = \frac{-2a}{RT}(1 - x_1) = \frac{-2ax_2}{RT} \quad \text{and} \quad \left(\frac{\partial \ln \gamma_2}{\partial x_1}\right)_{T,P} = \frac{2ax_1}{RT}$$

so that

$$x_1 \left(\frac{\partial \ln \gamma_1}{\partial x_1}\right)_{T,P} + x_2 \left(\frac{\partial \ln \gamma_2}{\partial x_1}\right)_{T,P} = -\frac{2ax_1x_2}{RT} + \frac{2ax_1x_2}{RT} = 0$$

as required by Eq. 9.3-17.

Dependence on P

$$\ln \gamma_i(T, P, \underline{x}) = \frac{\bar{G}_i^{ex}(T, P, \underline{x})}{RT} = \frac{1}{RT} \int_0^P \left[\bar{V}_i(T, P, \underline{x}) - \underline{V}_i(T, P)\right] dP$$

Then

$$\left(\frac{\partial \ln \gamma_i(T, P, \underline{x})}{\partial P}\right)_{T,\underline{x}} = \frac{\partial}{\partial P}\left(\frac{1}{RT} \int_0^P \left[\bar{V}_i(T, P, \underline{x}) - \underline{V}_i(T, P)\right] dP\right)_{T,\underline{x}}$$

$$= \frac{\bar{V}_i(T, P, \underline{x}) - \underline{V}_i(T, P)}{RT} = \frac{\bar{V}_i^{ex}(T, P, \underline{x})}{RT}$$

So that

$$\gamma_i(T, P_2, \underline{x}) = \gamma_i(T, P_1, \underline{x}) \exp\left[\int_{P_1}^{P_2} \frac{\bar{V}_i^{ex}(T, P, \underline{x})}{RT}\, dP\right]$$

$$\simeq \gamma_i(T, P_1, \underline{x}) \exp\left[\frac{\bar{V}_i^{ex}(T, \underline{x})(P_2 - P_1)}{RT}\right]$$

Not too easy to use. We do not have an excess volume "equation of state"

Dependence on T

$$\left(\frac{\partial \ln \gamma_i(T, P, \underline{x})}{\partial T}\right)_{P, \underline{x}} = \frac{\partial}{\partial T}\left(\frac{\bar{G}_i^{ex}}{RT}\right)_{P, \underline{x}} = -\frac{\bar{H}_i^{ex}(T, P, \underline{x})}{RT^2}$$

$$\boxed{\gamma_i(T_2, P, \underline{x}) = \gamma_i(T_1, P, \underline{x}) \exp\left[-\int_{T_1}^{T_2} \frac{\bar{H}_i^{ex}(T, P, \underline{x})}{RT^2}\, dT\right]}$$

For small T changes the excess enthalpy can be assumed constant. Then

$$\gamma_i(T_2, P, \underline{x}) = \gamma_i(T_1, P, \underline{x}) \exp\left[\frac{\bar{H}_i^{ex}(\underline{x})}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right]$$

FUGACITY IN GASEOUS MIXTURES

Amagat's Law (experimental)

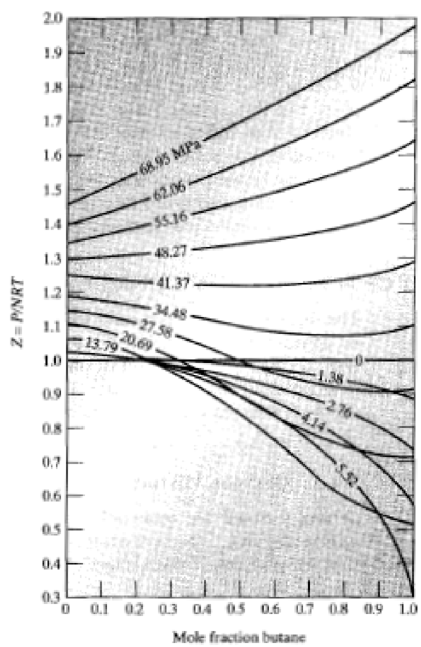
$$V_{mix}(T, P, N_1, N_2, \ldots) = \sum_{i=1}^{C} N_i \underline{V}_i(T, P)$$

Multiply by P/NRT

$$Z_{mix}(T, P, \underset{\sim}{y}) = \sum_{i=1}^{C} y_i Z_i(T, P)$$

Here $Z = PV/NRT$ is the compressibility of the mixture, Z_i is the compressibility of the pure component i, and $y_i = N_i/N$ is the mole fraction of species i. (*Hereafter y_i will be used to indicate a gas-phase mole fraction and x_i to denote a mole fraction in the liquid phase or in equations that are applicable to both gases and liquids.*)

This formula (linearity) is true, but only sometimes



Thus, from $\bar{V}_i(T, P, \underline{y}) = \underline{V}_i(T, P)$ *and from*

$$RT \ln \left\{ \frac{\bar{f}_i(T, P, \underline{x})}{x_i f_i(T, P)} \right\} = \int_0^P (\bar{V}_i - \underline{V}_i)\, dP$$

We get the ***LEWIS AND RANDALL RULE***

$$\boxed{\bar{f}_i^{\mathrm{V}}(T, P, \underline{y}) = y_i f_i^{\mathrm{V}}(T, P)}$$

More accurate is to start with

$$\ln \frac{\bar{f}_i^{\mathrm{V}}(T, P, \underline{y})}{y_i P} = \ln \bar{\phi}_i^{\mathrm{V}}(T, P, \underline{y}) = \frac{1}{RT} \int_{\underline{V}=\infty}^{\underline{V}=Z^{\mathrm{V}} RT/P} \left[\frac{RT}{\underline{V}} - N \left(\frac{\partial P}{\partial N_i} \right)_{T, V, N_{j \neq i}} \right] d\underline{V} - \ln Z^{\mathrm{V}}$$

and use an equation of state… (see illustrations)

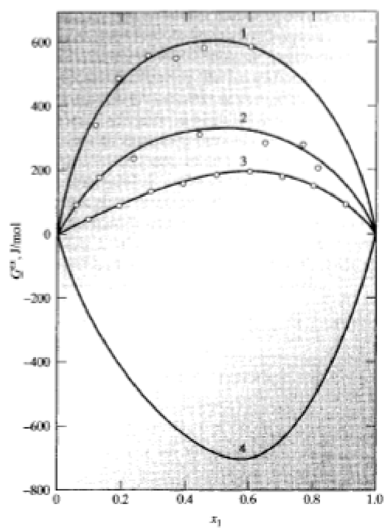
MIXTURE ACTIVITY MODELS

We have

$$\Delta_{\text{mix}}\underline{G} = \Delta_{\text{mix}}\underline{G}^{\text{IM}} + \underline{G}^{\text{ex}} = RT\sum_{i=1}^{C} x_i \ln x_i + \underline{G}^{\text{ex}}(\underline{x})$$

One constant Margules model

Some experimental data



which suggests

$$\boxed{\underline{G}^{\text{ex}} = Ax_1x_2}$$

Then

$$\bar{G}_1^{\text{ex}} = \left.\frac{\partial(N\underline{G}^{\text{ex}})}{\partial N_1}\right|_{T,P,N_2} = \frac{\partial}{\partial N_1}\left(\frac{AN_1N_2}{N_1+N_2}\right)$$

$$= A\left\{\frac{N_2}{N_1+N_2} - \frac{N_1N_2}{(N_1+N_2)^2}\right\} = Ax_2^2$$

$$\gamma_1(\underline{x}) = \exp\left\{\frac{\bar{G}_1^{\text{ex}}}{RT}\right\} = \exp\left\{\frac{Ax_2^2}{RT}\right\} = \exp\left\{\frac{A(1-x_1)_2^2}{RT}\right\}$$

Similarly

$$\gamma_2(x) = \exp\left\{\frac{Ax_1^2}{RT}\right\} = \exp\left\{\frac{A(1-x_2)_2^2}{RT}\right\}$$

or

$$RT\ln\gamma_1 = Ax_2^2$$
$$RT\ln\gamma_2 = Ax_1^2$$

Other

Two constant Margules

$$RT\ln\gamma_1 = \alpha_1 x_2^2 + \beta_1 x_2^3$$
$$RT\ln\gamma_2 = \alpha_2 x_1^2 + \beta_2 x_1^3$$

Van Laar

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

Wilson

$$\ln\gamma_1 = -\ln(x_1 + x_2\Lambda_{12}) + x_2\left[\frac{\Lambda_{12}}{x_1+x_2\Lambda_{12}} - \frac{\Lambda_{21}}{x_1\Lambda_{21}+x_2}\right]$$
$$\ln\gamma_2 = -\ln(x_2 + x_1\Lambda_{21}) - x_1\left[\frac{\Lambda_{12}}{x_1+x_2\Lambda_{12}} - \frac{\Lambda_{21}}{x_1\Lambda_{21}+x_2}\right]$$

NRTL

$$\ln\gamma_1 = x_2^2\left[\tau_{21}\left(\frac{G_{21}}{x_1+x_2G_{21}}\right)^2 + \frac{\tau_{12}G_{12}}{(x_2+x_1G_{12})^2}\right]$$
$$\ln\gamma_2 = x_1^2\left[\tau_{12}\left(\frac{G_{12}}{x_2+x_1G_{12}}\right)^2 + \frac{\tau_{21}G_{21}}{(x_1+x_2G_{21})^2}\right]$$

See section 9.11 for recommendations

REVIEW OF REFERENCE STATES

1 bar and some T and ideal gas behaviour
Pure liquid at 1 bar and some T

The need for STANDARD STATES arrives from the use of activity coefficients

In these cases the reference T is the T of the system (P is usually 1 bar).

In general different states are used depending on the state of aggregation
Gases: Pure component as an ideal gas at a fix temp. Then

$$\bar{G}_i(T, P, \underline{x}) = \underline{G}_i^\circ(T) + RT \ln \frac{\bar{f}_i(T, P, \underline{x})}{1 \text{ bar}}$$

$$\underline{H}_i^\circ(T) = -T^2 \frac{d\left(\frac{\underline{G}_i^\circ(T)}{T}\right)}{dT} = -T^2 \frac{d\left(\frac{\mu_i^\circ(T)}{T}\right)}{dT}$$

$$\mu_i(T, P, \underline{x}) = \mu_i^\circ(T) + RT \ln \frac{\bar{f}_i(T, P, \underline{x})}{1 \text{ bar}}$$

$$\underline{S}_i^\circ(T) = -\frac{d\underline{G}_i^\circ(T)}{dT} = -\frac{d\mu_i^\circ(T)}{dT}$$

Liquids: Pure component at same T at 1 bar.

Non-Simple Mixtures

We know that the Lewis and Randall rule helps finding the fugacity of a specie in the vapor phase

$$\bar{f}_i^V(T, P, \underline{y}) = y_i f_i^V(T, P)$$

For this we need the fugacity of the pure specie. This might not exist!
For liquids it is similar:

$$\bar{f}_i^L(T, P, \underline{x}) = x_i \gamma_i(T, P, \underline{x}) f_i^L(T, P)$$

And some species might not exist as pure liquids at that T and P.

What to do:

a) ***Equations of state for the mixture!! Avoids using the above formula and one can compute the fugacity directly using the methods of section 9-4.***
b) ***Use the above formulas anyway with some estimates of the fugacities of the pure species.***

Liquid fugacity of a component that is vapor at the chosen P and T

At low P, the fugacity of a liquid is equal to the vapor pressure (even if it is larger than P)

Vapor fugacity of a component that is liquid at the chosen P and T

Use corresponding states and 7-4-10…

(ignore subcooled liquids)

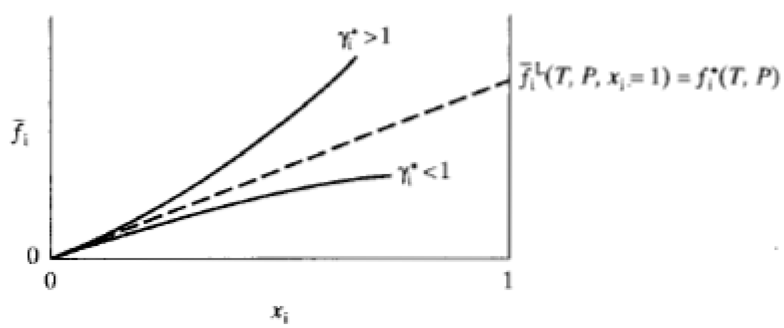
Gases dissolved in liquids

Experimental Observation (Henry Law)

$$\bar{f}_i^L(T, P, \underline{x}) = x_i H_i(T, P) \quad \text{as } x_i \to 0$$

At higher concentration we introduce another activity coefficient (pitiful!!)

$$\boxed{\bar{f}_i^L(T, P, \underline{x}) = x_i \gamma_i^*(T, P, \underline{x}) H_i(T, P)}$$



A different activity coefficient!! (Ignore discussion after eq 9-7-10)