CH365 Chemical Engineering Thermodynamics

Lesson 37
The Ideal Solution Model and Excess Properties

Block 6 – Solution Thermodynamics

Gibbs Energy "Generating Function"

Pure substances: Lesson 27 slides 21-22 and Lesson28 slide 3
Generalized for Solutions: Lesson 34 Slides 9-13

When the Gibbs energy is expressed as a function of its canonical variables, it plays the role of a generating function, providing the means for calculation of all other thermodynamic properties by simple mathematical operations (differentiation and elementary algebra), and implicitly represents complete property information.

(10.3, L34 slide 7)

$$dG = VdP - SdT + \sum_i \mu_i dx_i$$

$$dG = \left(\frac{\partial G}{\partial P}\right)_{T,x_i} dP + \left(\frac{\partial G}{\partial T}\right)_{P,x_i} dT + \sum_i \left(\frac{\partial G}{\partial x_i}\right)_{T,P} dx_i$$

For example, enthalpy:

$$G = H - T \cdot S$$

$$H = G + T \cdot S \qquad -\left(\frac{\partial G}{\partial T}\right)_{P,x} = S$$

(Eq. 10.5, L34 slide 7)

$$H = G - T \cdot \left(\frac{\partial G}{\partial T}\right)_{P,x}$$

All other thermodynamic properties can be calculated from Gibbs Energy expressed as a function of its canonical variables.

Ideal Solution Model

For Gases: $\mu_i^{ig} \equiv \bar{G}_i^{ig} = G_i^{ig} + RT\ln y_i$ (ideal gas mixture model)
(Eq. 10.24 page 374, Lesson 35 slide 5 circled)

ig = ideal gas
id = ideal solution

entropy of mixing, lesson 35, is the same in solids, liquids and gases

For Liquids: $\mu_i^{id} \equiv \bar{G}_i^{id} \equiv G_i + RT\ln x_i$ (defined by extension of 10.24)
(Eq. 10.75 page 392, definition)

pure component i in real physical state (gas, liquid, or solid)

Equation 10.24 is a special case of an ideal solution in the gas state with x_i replaced by y_i.

By extension, all other properties follow from previous derivations:

$$\bar{V}_i^{id} = \left(\frac{\partial \bar{G}_i^{id}}{\partial P}\right)_{T,x} = \left(\frac{\partial G_i}{\partial P}\right)_{T,x} \Rightarrow V_i = \left(\frac{\partial G_i}{\partial P}\right)_{T,x} \Rightarrow \boxed{\bar{V}_i^{id} = V_i}$$

(Eq. 10.18) (Eq. 10.4) (Eq. 10.76 page 393)

$$\bar{S}_i^{id} = -\left(\frac{\partial \bar{G}_i^{id}}{\partial T}\right)_{P,x} = -\left(\frac{\partial G_i}{\partial T}\right)_{P,x} - R\ln x_i \Rightarrow S_i = -\left(\frac{\partial G_i}{\partial T}\right)_{P,x} \Rightarrow \boxed{\bar{S}_i^{id} = S_i - R\ln x_i}$$

(Eq. 10.19) (Eq. 10.5) (Eq. 10.77)

$$\bar{H}_i^{id} = \bar{G}_i^{id} + T\bar{S}_i^{id} \Rightarrow \bar{H}_i^{id} = G_i^{id} + RT\ln x_i + T(S_i - R\ln x_i) = G_i^{id} + TS_i \Rightarrow \boxed{\bar{H}_i^{id} = H_i}$$

(Eq. 10.78)

Summability

Re-constructing the total solution properties

$$M = \sum_i x_i \bar{M}_i$$

(Eq. 10.11, Lesson 34, Slide 12)

$\bar{G}_i^{id} = G_i + RT \ln x_i$

eq. 10.75, previous slide

$$G^{id} = \sum_i x_i G_i + RT \sum_i x_i \ln x_i$$

(Eq. 10.79 p. 393)

$\bar{S}_i^{id} = S_i - R \ln x_i$

eq. 10.77, previous slide

$$S^{id} = \sum_i x_i S_i - R \sum_i x_i \ln x_i$$

(Eq. 10.80 p. 393)

$\bar{H}_i^{id} = H_i$

eq. 10.78, previous slide

$$H^{id} = \sum_i x_i H_i$$

(Eq. 10.82 p. 393)

$\bar{V}_i^{id} = V_i$

eq. 10.76, previous slide

$$V^{id} = \sum_i x_i V_i$$

(Eq. 10.81 p. 393)

$$\hat{f}_i^{id} = x_i f_i$$

(Eq. 10.83 p. 394)
(Lewis-Randall Rule)

$$\hat{\phi}_i^{id} = x_i \phi_i$$

(Eq. 10.84)

Derived by subtraction of gamma-form equations on page 394. See Lesson 35 Slide 11 and Lesson 36 Slides 2 and 3 for examples.

Note that equations 10.79, 10.80, and 10.82 are very similar to the ideal gas equations from Lesson 35 Slide 7 (Equations 10.25, 10.26, and 10.27)

Excess Properties

- Residual Properties
- M = V, U, H, S, or G

$$M^R \equiv M - M^{ig} \qquad \text{(Eq. 6.41)} \qquad M \equiv M^{ig} + M^R$$

- Excess Properties
- $M^E = V^E, U^E, H^E, S^E$, or G^E

$$M^E \equiv M - M^{id} \qquad \text{(Eq. 6.41)} \qquad M \equiv M^{id} + M^E$$

$$G^E \equiv G - G^{id} \qquad H^E \equiv H - H^{id} \qquad S^E \equiv S - S^{id}$$

$$M^E = M^R - \sum_i x_i M^R$$

(Eq. 10.87 page 395)

Derived on pp. 385-386 by subtracting M^{ig} from M^{id}.

$$\bar{M}^E \equiv \bar{M}_i - \bar{M}^{id}$$

(Eq. 10.88 page 395)

Note that excess properties have no meaning for pure species, whereas residual properties exist for species and solutions

Table 10.1: Summary of Equations for the Gibbs Energy and Related Properties

M in Relation to G	*M^R in Relation to G^R*	*M^E in Relation to G^E*
$V = \left(\partial G / \partial P\right)_{T,x}$ (10.4)	$V^R = \left(\partial G^R / \partial P\right)_{T,x}$	$V^E = \left(\partial G^E / \partial P\right)_{T,x}$
$S = -\left(\partial G / \partial T\right)_{P,x}$ (10.5)	$S^R = -\left(\partial G^R / \partial T\right)_{P,x}$	$S^E = -\left(\partial G^E / \partial T\right)_{P,x}$
$H = G + TS$ $= G - T\left(\partial G / \partial T\right)_{P,x}$ $= -RT^2 \left[\frac{\partial (G/RT)}{\partial T}\right]_{P,x}$	$H^R = G^R + TS^R$ $= G^R - T\left(\partial G^R / \partial T\right)_{P,x}$ $= -RT^2 \left[\frac{\partial (G^R/RT)}{\partial T}\right]_{P,x}$	$H^E = G^E + TS^E$ $= G^E - T\left(\partial G^E / \partial T\right)_{P,x}$ $= -RT^2 \left[\frac{\partial (G^E/RT)}{\partial T}\right]_{P,x}$
$C_P = \left(\partial H / \partial T\right)_{P,x}$ $= -T\left(\partial^2 G / \partial T^2\right)_{P,x}$	$C_P^R = \left(\partial H^R / \partial T\right)_{P,x}$ $= -T\left(\partial^2 G^R / \partial T^2\right)_{P,x}$	$C_P^E = \left(\partial H^E / \partial T\right)_{P,x}$ $= -T\left(\partial^2 G^E / \partial T^2\right)_{P,x}$

Example 10.11

(a) If C_P^E is a constant, independent of temperature, find expressions for G^E, S^E, and H^E as functions of T.

(b) From the equations developed in part (a), find values for G^E, S^E, and H^E for an equimolar solution of benzene(1)/n-hexane(2) at 323.15 K, given the following excess-property values for an equimolar solution at 298.15 K:

$$C_P^E = -2.86 \,\frac{\text{J}}{\text{mol}\cdot\text{K}} \qquad H^E = 897.9 \,\frac{\text{J}}{\text{mol}} \qquad G^E = 384.5 \,\frac{\text{J}}{\text{mol}}$$

Questions