

CH365 Chemical Engineering Thermodynamics

Lesson 37

The Ideal Solution Model and Excess Properties

Block 6 – Solution Thermodynamics

Gibbs Energy “Generating Function”^{Slide 2}

Pure substances: Lesson 27 slides 21-22 and Lesson 28 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*.

For example, enthalpy:

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

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

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

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

(10.3, L34 slide 7)

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

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

(Eq. 10.5, L34 slide 7)

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

Ideal Solution Model

For Gases:

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

ig = ideal gas
id = ideal solution

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

For Liquids:

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

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:

$$\bar{V}_i^{id} = \left(\frac{\partial \bar{G}_i^{id}}{\partial P} \right)_{T,x} = \left(\frac{\partial G_i}{\partial P} \right)_{T,x} \Rightarrow V_i = \left(\frac{\partial G_i}{\partial P} \right)_{T,x} \Rightarrow \boxed{\bar{V}_i^{id} = V_i} \\ \text{(Eq. 10.18)} \qquad \qquad \qquad \text{(Eq. 10.4)} \qquad \qquad \qquad \text{(Eq. 10.76 page 393)}$$

$$\bar{S}_i^{id} = - \left(\frac{\partial \bar{G}_i^{id}}{\partial T} \right)_{P,x} = - \left(\frac{\partial G_i}{\partial T} \right)_{P,x} - R \ln x_i \Rightarrow S_i = - \left(\frac{\partial G_i}{\partial T} \right)_{P,x} \Rightarrow \boxed{\bar{S}_i^{id} = S_i - R \ln x_i} \\ \text{(Eq. 10.19)} \qquad \qquad \qquad \text{(Eq. 10.5)} \qquad \qquad \qquad \text{(Eq. 10.77)}$$

$$\bar{H}_i^{id} = \bar{G}_i^{id} + T \bar{S}_i^{id} \Rightarrow \bar{H}_i^{id} = G_i^{id} + RT \ln x_i + T(S_i - R \ln x_i) \Rightarrow \boxed{\bar{H}_i^{id} = H_i} \\ = G_i^{id} + T S_i \qquad \qquad \qquad \text{(Eq. 10.78)}$$

Summability

Re-constructing the total solution properties

$$M = \sum_i x_i \bar{M}_i \quad (\text{Eq. 10.11, Lesson 34, Slide 12})$$

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

eq. 10.75, previous slide

$$G^{\text{id}} = \sum_i x_i G_i + RT \sum_i x_i \ln x_i \quad (\text{Eq. 10.79 p. 393})$$

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

eq. 10.77, previous slide

$$S^{\text{id}} = \sum_i x_i S_i - R \sum_i x_i \ln x_i \quad (\text{Eq. 10.80 p. 393})$$

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

eq. 10.78, previous slide

$$H^{\text{id}} = \sum_i x_i H_i \quad (\text{Eq. 10.82 p. 393})$$

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

eq. 10.76, previous slide

$$V^{\text{id}} = \sum_i x_i V_i \quad (\text{Eq. 10.81 p. 393})$$

$$\hat{f}_i^{\text{id}} = x_i f_i \quad (\text{Eq. 10.83 p. 394})$$

(Lewis-Randall Rule)

$$\hat{\phi}_i^{\text{id}} = x_i \phi_i \quad (\text{Eq. 10.84})$$

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
- $M = V, U, H, S, \text{ or } G$

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

$$M \equiv M^{\text{ig}} + M^R$$

- Excess Properties
- $M^E = V^E, U^E, H^E, S^E, \text{ or } G^E$

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

$$M \equiv M^{\text{id}} + M^E$$

$$G^E \equiv G - G^{\text{id}}$$

$$H^E \equiv H - H^{\text{id}}$$

$$S^E \equiv S - S^{\text{id}}$$

$$M^E = M^R - \sum_i x_i M^R \quad (\text{Eq. 10.87 page 395})$$

Derived on pp. 394-395 by
subtracting M^{ig} from M^{id} .

$$\bar{M}^E \equiv \bar{M}_i - \bar{M}^{\text{id}} \quad (\text{Eq. 10.88 page 395})$$

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

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

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:

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

Questions?