

CH365 Chemical Engineering Thermodynamics

Lesson 35 Ideal Gas Mixtures and Fugacity

Block 6 – Solution Thermodynamics

Today:

Properties of ideal gas mixtures
Excess properties (of ideal gas mixtures)
Fugacity

Recap of Lesson 34

$$d(nG) = (nV)dP - (nS)dT \quad (\text{Eq. 6.7, page 216})$$

$$d(nG) = (nV)dP - (nS)dT + \sum_i \mu_i dn_i \quad (\text{Eq. 10.2, page 359})$$

Chemical Potential:

$$\mu_i \equiv \left[\frac{\partial(nG)}{\partial n_i} \right]_{P,T,n_{j\neq i}} = \left(\frac{\partial G}{\partial x_i} \right)_{T,P,x_{j\neq i}} \quad (\text{Eq. 10.1, page 359})$$

Equilibrium Condition:

$$\mu_i^\alpha = \mu_i^\beta = \dots = \mu_i^\pi \quad (\text{Eq. 10.6, page 361})$$

Partial Molar Properties:

$$\bar{M}_i \equiv \left[\frac{\partial(nM)}{\partial n_i} \right]_{P,T,n_j} \quad (\text{Eq. 10.7, page 361})$$

Gibbs-Duhem

$$\sum_i x_i d\bar{M}_i = 0 \quad (\text{Eq. 10.14})$$

Summability

$$M = \sum_i x_i \bar{M}_i \quad (\text{Eq. 10.11})$$

Ideal Gas Mixture Model

- limited ability to describe actual mixtures but approximates reality in the limit of low P, is analytically simple, and provides a good conceptual basis

“Solution” of ideal gases

$$V^{\text{ig}} = \frac{RT}{P} \quad (\text{Eqs. 3.7 and 10.20})$$

$$V \neq \sum_i x_i \bar{V}_i^{\text{ig}}$$

$$\bar{M}_i = \left[\frac{\partial(nM)}{\partial n_i} \right]_{P,T,n_j} \quad (\text{Eq. 10.7, p 352})$$

Response function: adding 1ml of an ig to 1000 mL of an ig results in 1001 mL

$$\bar{V}_i^{\text{ig}} = \left[\frac{\partial(nV^{\text{ig}})}{\partial n_i} \right]_{T, P, n_j} = \left[\frac{\partial(nRT / P)}{\partial n_i} \right]_{T, P, n_j} = \frac{RT}{P} \left(\frac{\partial n}{\partial n_i} \right)_{n_j} = \frac{RT}{P}$$

$$n = n_i + n_j + \dots$$

$$\frac{\partial n}{\partial n_i} = \frac{\partial n_i}{\partial n_i} + \frac{\partial n_j}{\partial n_i} + \dots = 1$$

(Volume does not have a partial molar interpretation)

$$\therefore \bar{V}_i^{\text{ig}} = \frac{RT}{P} = V^{\text{ig}} = V_i^{\text{ig}} \quad (\text{Eq. 10.20, p 363})$$

(species volume = total volume)

No “Dalton’s Law” for partial volumes; all species occupy the same volume.

- partial pressure of species i in an ideal gas mixture is defined as the pressure i would exert if it alone occupied the molar volume of the mixture

$$\bar{p}_i = \frac{\partial P}{\partial n_i} = \frac{\partial}{\partial n_i} \frac{RT}{nV^{\text{ig}}} \neq p_i$$

$$p_i \equiv y_i P = y_i \frac{RT}{V^{\text{ig}}}$$

(Partial pressure is *not* a partial molar property)

$$P \neq \sum_i y_i \bar{p}_i \quad \left(= - \frac{RT}{n^2 V^{\text{ig}}} \right)$$

$$\sum_i p_i = \sum_i y_i P = P \sum_i y_i = P$$

(Pressure is *not* a molar property of any kind)

The only molar property in the ideal gas equation is V^{ig}

Ideal Gas Mixture Model

Because IG molecules have zero volume and do not interact, the thermodynamic properties (*other than molar volume*) of the constituent species are independent of one another (and each species has its own individual set of properties).

Gibbs' Theorem

A partial molar property (other than volume) of a constituent species in an ideal gas mixture is equal to the corresponding property of the species as a pure ideal gas at the mixture temperature but at a pressure equal to its partial pressure in the mixture.

$$\bar{M}_i^{ig}(T, P) = M_i^{ig}(T, p_i) \quad \text{for } \bar{M}_i^{ig} \neq \bar{V}_i^{ig} \quad (\text{Eq. 10.21, p 373})$$

$$V_i^{ig} = \frac{RT}{P} \quad \bar{V}_i^{ig} \neq \frac{RT}{p_i} \quad \text{because } \bar{V}_i^{ig} = \frac{RT}{P}$$

But for other properties like enthalpy H in an IG:

$$\bar{H}_i^{ig}(T, P) = H_i^{ig}(T, p_i) = H_i^{ig}(T, P) \quad \bar{H}_i^{ig} = H_i^{ig}$$

Ideal gas H is independent of pressure by equation 6.23

(Eq. 10.22, p 373)

$$H_i^{ig} = \int_{T_{REF}}^T C_{p,i}^{ig} dT$$

Ideal Gas Mixture Model – Entropy

Gibbs' Theorem

$$\bar{M}_i^{ig}(T, P) = M_i^{ig}(T, p_i) \quad \text{for } \bar{M}_i^{ig} \neq \bar{V}_i^{ig} \quad (\text{Eq. 10.21, p 373})$$

Enthalpy H: $\bar{H}_i^{ig}(T, P) = H_i^{ig}(T, p_i) = H_i^{ig}(T, P) \rightarrow \bar{H}_i^{ig} = H_i^{ig} \quad (\text{Eq. 10.22, p 373})$

Entropy S: $dS_i^{ig} = C_P^{ig} \frac{dT}{T} - R d \ln P \quad (\text{Eq. 6.24, p 220})$

$$dS_i^{ig} = -R d \ln P \quad (\text{Eq. 6.24 at constant T})$$

Integrating from p_i to P : $S_i^{ig}(T, P) - S_i^{ig}(T, p_i) = -R \ln \frac{P}{p_i} = -R \ln \frac{P}{y_i P} = +R \ln y_i$

$$S_i^{ig}(T, p_i) = S_i^{ig}(T, P) - R \ln y_i$$

$$\therefore \bar{S}_i^{ig}(T, P) = S_i^{ig}(T, P) - R \ln y_i \rightarrow \bar{S}_i^{ig} = S_i^{ig} - R \ln y_i$$

(By Gibbs' Theorem)

(Eq. 10.23, p 373)

Ideal Gas Mixture Model – G, μ

Gibb's Theorem

$$\bar{M}_i^{ig}(T, P) = M_i^{ig}(T, p_i) \quad \text{for } \bar{M}_i^{ig} \neq \bar{V}_i^{ig} \quad (\text{Eq. 10.21, p 373})$$

Gibbs energy G:

$$G^{ig} = H^{ig} - T S^{ig} \quad (\text{Eq. 6.4, p 211})$$

Partial Gibbs Energy:

$$\bar{G}_i^{ig} = \bar{H}_i^{ig} - T \bar{S}_i^{ig}$$

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

(Eq. 10.22)

$$\bar{S}_i^{ig} = S_i^{ig} - R \ln y_i$$

(Eq. 10.23)

$$\bar{G}_i^{ig} = H_i^{ig} - T(S_i^{ig} - R \ln y_i) = H_i^{ig} - TS_i^{ig} + RT \ln y_i = G_i^{ig} + RT \ln y_i$$

$$\underbrace{H_i^{ig} - TS_i^{ig}}_{G_i^{ig}}$$

$$\mu_i \equiv \bar{G}_i^{ig}$$

$$\mu_i = \bar{G}_i^{ig} = G_i^{ig} + RT \ln y_i \quad (\text{Eq. 10.24 page 374})$$

Summability Revisited

Reconstruct Total Properties from Partial Molar Properties

$$M = \sum_i y_i \bar{M}_i^{ig}$$

(Eq. 10.11)

$$\text{Enthalpy } H: \quad H^{ig} = H = \sum_i y_i \bar{H}_i^{ig} = \sum_i y_i H_i^{ig}$$

$\bar{H}_i^{ig} = H_i^{ig}$ (Eq. 10.22)

$$H^{ig} = \sum_i y_i H_i^{ig}$$

(Eq. 10.25 p. 374)

$$\text{Entropy } S: \quad S^{ig} = S = \sum_i y_i \bar{S}_i^{ig} = \sum_i y_i (S_i^{ig} - R \ln y_i) = \sum_i y_i S_i^{ig} - R \sum_i y_i \ln y_i$$

$\bar{S}_i^{ig} = S_i^{ig} - R \ln y_i$ (Eq. 10.23)

$$S^{ig} = \sum_i y_i S_i^{ig} - R \sum_i y_i \ln y_i$$

(Eq. 10.26 p. 374)

$$\text{Gibbs Energy } G: \quad G^{ig} = G = \sum_i y_i \bar{G}_i^{ig} = \sum_i y_i (\bar{G}_i^{ig} + RT \ln y_i) = \sum_i y_i G_i^{ig} + RT \sum_i y_i \ln y_i$$

$\bar{G}_i^{ig} = G_i^{ig} + RT \ln y_i$ (Eq. 10.24)

$$G^{ig} = \sum_i y_i G_i^{ig} + RT \sum_i y_i \ln y_i$$

(Eq. 10.27 p. 374)

Excess Properties – Ideal Mixtures

Enthalpy H: $H^{ig} = \sum_i y_i H_i^{ig}$ (Eq. 10.25 p. 374)

$$H^{ig} - \sum_i y_i H_i^{ig} = 0 \quad \text{no heat transfer}$$

Difference: total enthalpy – weighted average of species enthalpies

“Enthalpy change of mixing” \rightarrow zero for ideal gases

makes sense – no IMF's

Entropy S: $S^{ig} = \sum_i y_i S_i^{ig} - R \sum_i y_i \ln y_i$ (Eq. 10.26 p. 374)

$$S^{ig} - \sum_i y_i S_i^{ig} = R \sum_i y_i \ln \frac{1}{y_i}$$

mixing term

“Entropy change of mixing”

$$\frac{1}{y_i} > 1 \quad \therefore S^{ig} - \sum_i y_i S_i^{ig} > 0 \quad (2^{\text{nd}} \text{ Law})$$

Alternative Form of μ

$$\mu_i^{ig} \equiv \bar{G}_i^{ig} = G_i^{ig} + RT \ln y_i \quad (\text{Eq. 10.24}) \quad (\text{From Slide 6})$$

$$(\text{Eq. 6.11}) \quad dG_i^{ig} = V_i^{ig}dP - S_i^{ig}dT \xrightarrow{(\text{Const } T)} dG_i^{ig} = V_i^{ig}dP = \frac{RT}{P}dP = RTd \ln P$$

$$dG_i^{ig} = RTd \ln P \rightarrow \int dG_i^{ig} = \int RTd \ln P \rightarrow G_i^{ig} = RT \ln P + C \quad \begin{array}{l} \text{Integration constant} \\ C=C(T)=\Gamma_i(T) \end{array}$$

$$G_i^{ig} = RT \ln P + \Gamma_i(T)$$

Γ is a species-dependent function of T
(Eq. 10.28, page 374)

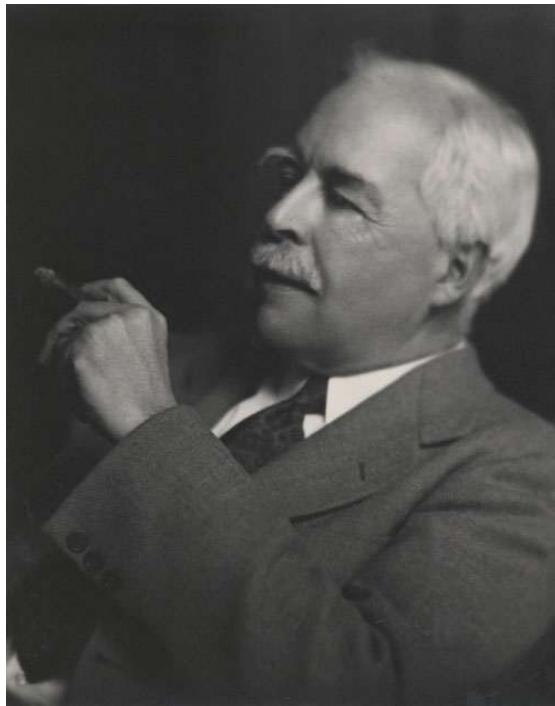
$$(\text{Eq. 10.24}) \quad \mu_i^{ig} \equiv \bar{G}_i^{ig} = G_i^{ig} + RT \ln y_i = (RT \ln P + \Gamma_i(T)) + RT \ln y_i = RT \ln (y_i P) + \Gamma_i(T) \quad (\text{combined ln terms})$$

$$M = \sum_i y_i \bar{M}_i^{ig} \quad (\text{Eq. 10.11})$$

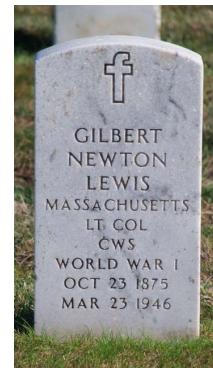
$$\mu_i^{ig} = RT \ln (y_i P) + \Gamma_i(T) \quad (\text{Eq. 10.29, page 375})$$

$$G^{ig} = \sum_i y_i \left(\underbrace{RT \ln (y_i P) + \Gamma_i(T)} \right) = \sum_i y_i \Gamma_i(T) + RT \sum_i y_i \ln (y_i P) \quad (\text{Eq. 10.30 p. 375})$$

Gilbert Newton Lewis



- Born October 23, 1875, died March 23, 1946
- Developed the electron-pair theory of acid-base reactions in 1923
- Lewis electron dot structures



Golden Gate National Cemetery, San Bruno, San Mateo County, California, USA
Plot: K BLK, 3166-A

- Nominated 41 times for Nobel Prize
- known for partial properties, concept of ideal solutions, and modern formulation of chemical potential

$$\mu_i^{ig} \equiv \bar{G}_i^{ig} = G_i^{ig} + RT \ln y_i \quad (\text{Eq. 10.24, page 374})$$

$$\mu_i^{ig} = RT \ln (y_i P) + \Gamma_i(T) \quad (\text{Eq. 10.29, page 375})$$

$$\therefore \mu_i^\alpha = \mu_i^\beta = \dots = \mu_i^\pi \quad (\text{Eq. 10.6, page 361})$$

- problem: μ approaches negative infinity as either y_i or P approach zero
- invented fugacity and formulated it as a new thermodynamic property

Fugacity

f_i has units of pressure
“escaping tendency”

tendency of a substance to pass from one phase to another

for ideal gases:

$$f_i^{\text{ig}} = P \quad (\text{Eq. 10.32})$$

$$G_i^{\text{ig}} = \Gamma_i(T) + RT \ln P \quad (\text{Eq. 10.28, page 374})$$

$$G_i = \Gamma_i(T) + RT \ln f_i \quad (\text{Eq. 10.31, page 376})$$

$$G_i - G_i^{\text{ig}} = RT \ln \frac{f_i}{P} \quad \text{for real gases, } \textit{residual Gibbs energy:}$$

$$G_i^R = G_i - G_i^{\text{ig}} \quad (\text{Definition Eq. 6.41})$$

$$G_i^R = RT \ln \phi_i \quad (\text{Eq. 10.33})$$

$$\phi_i \equiv \frac{f_i}{P} \quad (\text{Eq. 10.34})$$

The fugacity (or fugacity coefficient) is functionally related to the residual Gibbs energy of component i in a mixture

$$\lim_{P \rightarrow 0} (\ln \phi_i) = \lim_{P \rightarrow 0} \ln \left(\frac{f_i}{P} \right) = 0 \quad (\text{Since } f \text{ approaches } P \text{ as } P \text{ approaches 0})$$

Evaluation of Fugacity

$$\frac{G^R}{RT} = \int_0^P (Z - 1) dP \quad (\text{Eq. 6.49, page 227})$$

$$Z = 1 + \beta - q\beta \frac{Z - \beta}{(Z + \varepsilon\beta)(Z + \sigma\beta)} \quad (\text{Eq. 3.48})$$

$$G_i^R = RT \ln \phi_i \quad (\text{Eq. 10.33 p. 376})$$

$$\ln \phi_i = \int_0^P (Z_i - 1) dP \quad (\text{Eq. 10.35 p. 377})$$

Integrated form for cubic equations of state:

Similar to calculation
of residual properties,
Lesson 28 or WPR3

$$\ln \phi_i = Z_i - 1 - \ln(Z_i - \beta_i) - q_i I_i \quad (\text{Eq. 13.85 p. 501})$$

$$\beta_i = \Omega \frac{P_{r_i}}{T_r} \quad (\text{Eq. 3.50})$$

$$q_i = \frac{\Psi \alpha}{\Omega T_{r_i}} \quad (\text{Eq. 3.51})$$

$$I_i = \frac{1}{\sigma - \varepsilon} \ln \left(\frac{Z_i + \sigma\beta}{Z_i + \varepsilon\beta} \right) \quad I_i = \frac{\beta_i}{Z_i} \quad (\text{vdW}) \quad (\text{Eq. 13.72})$$

Computer Procedure for Cubic Equations of State

1. Collect the critical pressure, critical temperature, and acentric factor from table B.1 on pp. 663-665 or from the DIPPr website, CC, or A+. Note your source.
2. Collect σ , ε , Ω , and Ψ from Table 3.1 on p. 100 for the desired equation of state.
3. Use given T and P to calculate the reduced temperature and pressure.
4. Determine the correct expression for α from Table 3.1.
5. Calculate β from Eq. 3.50 and q from Eq. 3.51 on page 99.
6. Write the equation for compressibility (Z) for the cubic equation of state, Eq. 3.48 on p. 99, solve it for Z, and select the correct value for Z.
7. Determine the correct form for the integral (I) in Eqns. 13.71 and 13.72 on p. 496 and calculate the value of I .
8. Use Eqn. 13.85 on page 501 (or slide 12) to evaluate ϕ_i .

Questions?