CH365 Chemical Engineering Thermodynamics

Lesson 35
Ideal Gas Mixtures and Fugacity

Block 6 – Solution Thermodynamics

<u>Today</u>:
Properties of ideal gas mixtures
Excess properties (of ideal gas mixtures)
Fugacity

Recap of Lesson 34

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

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

Chemical Potential:

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

Equilibrium Condition:

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

Partial Molar Properties:

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

Gibbs-Duhem

$$\sum_i x_i\,d\overline{M}_i = 0$$

(Eq. 10.14)

Summability

$$M = \sum_i x_i\,\overline{M}_i$$

(Eq. 10.11)

Ideal Gas Mixture Model - Volume

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

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- Partial molar volume (species molar volume as it exists in solution) is the same as total molar volume. All species occupy the same volume.

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

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

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

$$n = n_i + n_j + \ldots$$

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

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

(species volume = total volume)

- Partial pressure is not a molar quantity (partial pressure of species *i* in an ideal gas mixture is defined as the pressure *i* would exert if it alone occupied the total volume of the mixture.

Ideal Gas Mixture Model - Enthalpy

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.

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

$$V_i^{ig} = \frac{RT}{P} \qquad \overline{V}_i^{ig} \neq \frac{RT}{p_i} \qquad \left(\text{because } \overline{V}_i^{ig} = \frac{RT}{P}\right)$$

But for other properties like enthalpy H in an IG:

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

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

<u>Application of Gibbs' Theorem</u>

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

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

Entropy S: $\quad dS_i^{ig} = C_P^{ig}\dfrac{dT}{T} - R\, d\ln P \quad$ (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: $\quad S_i^{ig}(T,P) - S_i^{ig}(T,p_i) = -R\ln\dfrac{P}{p_i} \quad = -R\ln\dfrac{P}{y_i P} \quad = +R\ln y_i$

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

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

(Eq. 10.23, p 373)

Ideal Gas Mixture Model – G, μ

Gibb's Theorem

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

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

Partial Gibbs Energy:
$$\overline{G}_i^{ig} = \overline{H}_i^{ig} - T\,\overline{S}_i^{ig}$$

$$\overline{H}_i^{ig} = H_i^{ig} \qquad\qquad \overline{S}_i^{ig} = S_i^{ig} - R\,\ln y_i$$

(Eq. 10.22) $\qquad\qquad$ (Eq. 10.23)

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

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

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

$$\boxed{\mu_i = \overline{G}_i^{ig} = G_i^{ig} + RT\,\ln y_i \quad \text{(Eq. 10.24 page 374)}} \quad \text{(used in slide 9)}$$

Summability Revisited

Reconstruct Total Properties from Partial Molar Properties

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

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

(Eq. 10.11)

Enthalpy H:

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

$$\boxed{H^{ig} = \sum_i y_i H_i^{ig}} \quad \text{(Eq. 10.25 p. 374)}$$

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

Entropy S:

$$S^{ig} = S = \sum_i y_i \bar{S}_i^{ig} = \sum_i y_i \left(S_i^{ig} - R \ln y_i \right) = \sum_i y_i S_i^{ig} - R \sum_i y_i \ln y_i$$

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

$$\bar{G}_i^{ig} = G_i^{ig} + R T \ln y_i \quad \text{(Eq. 10.24)}$$

Gibbs Energy G:

$$G^{ig} = G = \sum_i y_i \bar{G}_i^{ig} = \sum_i y_i \bar{G}_i^{ig} = \sum_i y_i G_i^{ig} + R T \sum_i y_i \ln y_i$$

$$\boxed{G^{ig} = \sum_i y_i G_i^{ig} + R T \sum_i y_i \ln y_i} \quad \text{(Eq. 10.27 p. 374)}$$

Excess Properties – Ideal Mixtures

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

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

Difference: total enthalpy – weighted average of species enthalpies

"Enthalpy change of mixing" $\implies$ zero for ideal gases

makes sense – no IMF's

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

$$S^{ig} - \sum_i y_i S_i^{ig} = \boxed{R \sum_i y_i \ln \frac{1}{y_i}} \qquad \text{mixing term}$$

"Entropy change of mixing"

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

Alternative Form of μ

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

(Eq. 6.11)

$$dG_i^{ig} = V_i^{ig} dP - S_i^{ig} dT \qquad \xrightarrow{\text{(Const T)}} \qquad dG_i^{ig} = V_i^{ig} dP = \frac{RT}{P} dP = RT \, d \ln P$$

$$dG_i^{ig} = RT \, d \ln P \quad \longrightarrow \quad \int dG_i^{ig} = \int RT \, d \ln P \quad \longrightarrow \quad G_i^{ig} = RT \ln P + C \quad \overset{\text{Integration constant}}{\underset{C=C(T)=\Gamma_i(T)}{\longleftarrow}}$$

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

Γ is a species-dependent function of T

(Eq. 10.28, page 374)

(Eq. 10.24)

$$\mu_i^{ig} \equiv \overline{G}_i^{ig} = G_i^{ig} + RT \ln y_i = \left(RT \ln P + \Gamma_i(T) \right) + RT \ln y_i = RT \ln \left(y_i P \right) + \Gamma_i(T)$$

(combined nat log terms)

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

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

(Eq. 10.11)

$$G^{ig} = \sum_i y_i \left(RT \ln \left(y_i P \right) + \Gamma_i(T) \right) = \sum_i y_i \Gamma_i(T) + RT \sum_i y_i \ln \left(y_i P \right)$$

(Eq. 10.30 p. 375)

Gilbert Newton Lewis
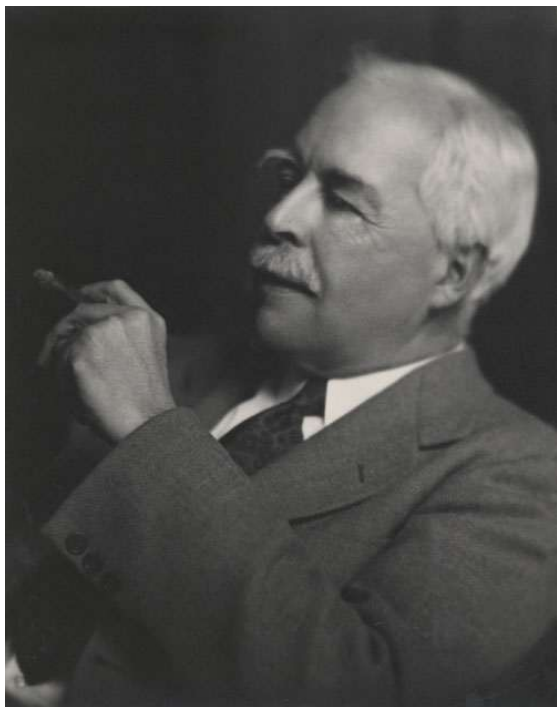
- Born October 23, 1875, died March 23, 1946
- Developed the electron-pair theory of acid-base reactions in 1923
- Lewis electron dot structures
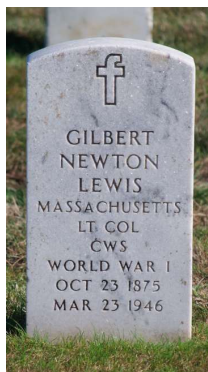
Golden Gate National Cemetery, San Bruno, San Mateo County, California, USA
Plot: K BLK, 3166-A

- Nominated 41 times for Nobel Prize

- known for partial properties, concept of ideal solutions, and modern formulation of chemical potential

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

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

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

- 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

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

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

for ideal gases:

$$f_i^{ig} = P$$

(Eq. 10.32)

$$G_i - G_i^{ig} = RT \ln \frac{f_i}{P}$$

for real gases, *residual Gibbs energy*:

$$G_i^R = G_i - G_i^{ig}$$

(Definition Eq. 6.41)

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

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

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

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

Evaluation of Fugacity

Lesson 28 slide 7:

$$\frac{G_i^R}{RT} = \int_0^P (Z_i - 1)\,dP \qquad \text{(Eq. 6.49, page 227)}$$

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

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

Evaluate integral for cubic equations of state:

Lesson 28 slide 8:

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

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

$$\beta_i = \Omega \frac{P_{r_i}}{T_{r_i}} \qquad q_i = \frac{\Psi \alpha}{\Omega T_{r_i}} \qquad I_i = \frac{1}{\sigma - \varepsilon} \ln\left(\frac{Z_i + \sigma\beta}{Z_i + \varepsilon\beta} \right) \qquad I_i = \frac{\beta_i}{Z_i}$$

$$\text{(Eq. 3.50)} \qquad\qquad \text{(Eq. 3.51)} \qquad\qquad \text{(Eq. 13.72)} \qquad\qquad \text{(vdW)}$$

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?