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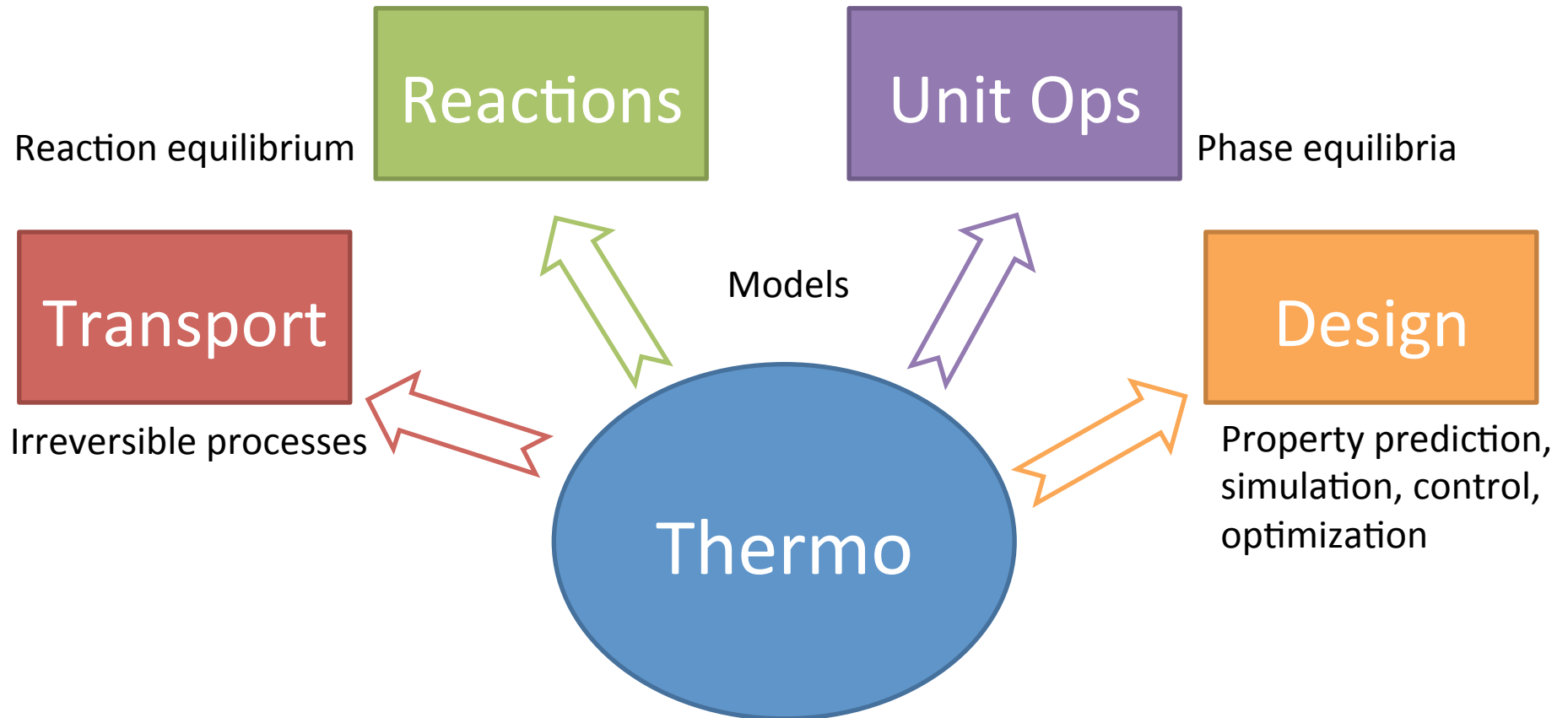
ChemE Thermodynamics

Review Session

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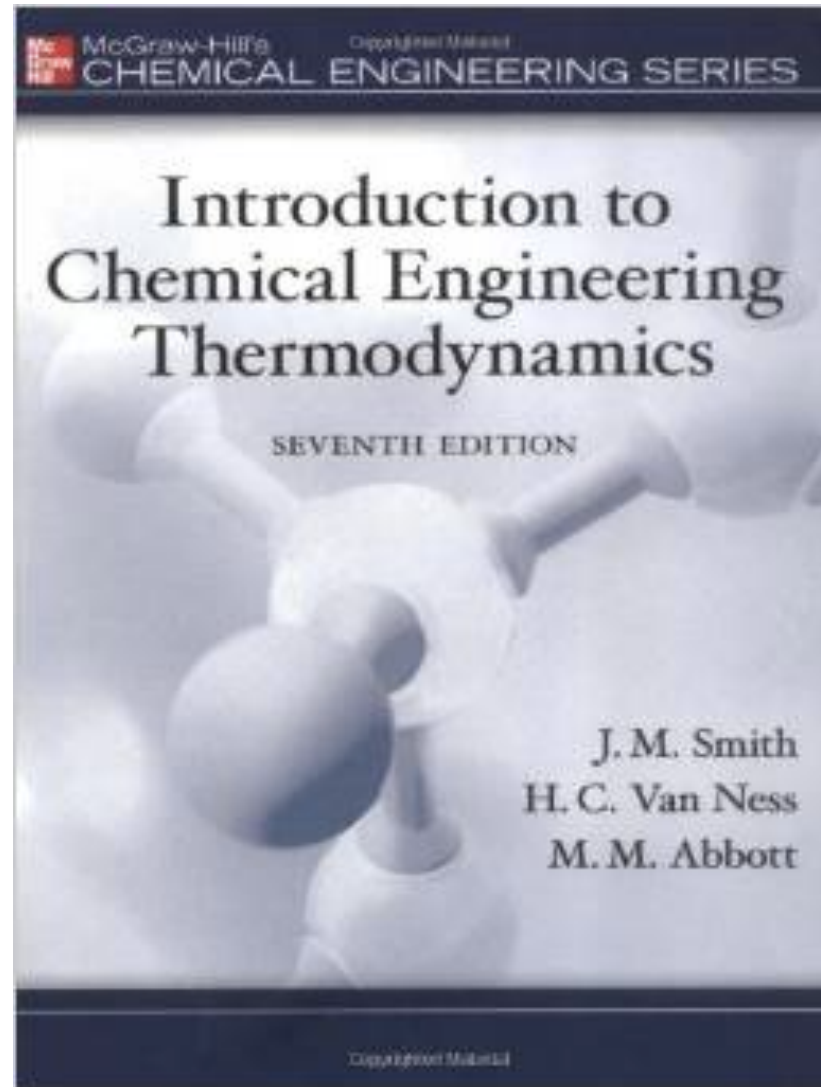
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Why Thermodynamics?



Material and Energy Balance

Textbook



Chemical Potential

- Single-phase, *open* system (material can pass through boundaries)

$$nG = g(P, T, n_1, n_2, \dots, n_i, \dots)$$

- Total differential of nG

$$d(nG) = \left[\frac{\partial(nG)}{\partial P} \right]_{T,n} dP + \left[\frac{\partial(nG)}{\partial T} \right]_{P,n} dT + \sum_i \underbrace{\left[\frac{\partial(nG)}{\partial n_i} \right]_{P,T,n_{j \neq i}}}_{\mu_i} dn_i$$

(chemical potential by **definition**)

- Interpretation
 - Partial molar free energy.
 - Form of potential energy that can be absorbed or released during a chemical reaction.
 - The total sum of chemical potentials is **zero** at chemical equilibrium or in phase equilibrium. See Chapter 11 (Sections 11.1 and 11.2).

Introducing Fugacity

- The Gibbs energy, and hence μ_i , is defined in relation to internal energy (whose absolute value is unknown) and entropy.
- Less desirable characteristics of $\mu_i \rightarrow$ *fugacity*.
- **Fugacity**: effective pressure of a real gas, which replaces the true mechanical pressure in accurate chemical equilibrium calculations. Potential quantity that characterizes equilibrium partitioning of mass.

$$dG = VdP - SdT \quad (6.10)$$

$$dG_i^{ig} = V_i^{ig}dP = \frac{RT}{P}dP = RTd \ln P \quad (\text{constant } T)$$

Integration yields

$$G_i^{ig} = \Gamma_i(T) + RT \ln P \quad (11.28)$$

For a real gas, the following **definition** is given

$$G_i \equiv \Gamma_i(T) + RT \ln f_i \quad (11.31)$$

Fugacity Coefficient

- Subtracting (11.28) from (11.31) gives

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

where G_i^R is the *residual* Gibbs energy.

- By **definition**, the fugacity coefficient is the ratio f_i/P

$$\phi_i \equiv \frac{f_i}{P} \quad (11.34)$$

- Therefore, using equation (6.49),

$$\frac{G_i^R}{RT} = \ln \phi_i = \int_0^P (Z - 1) \frac{dP}{P} \quad (\text{constant } T) \quad (11.35)$$

- Can be integrated numerically (e.g., Trapezoid Method) if experimental data are available, or evaluated analytically if model for Z is assumed.

Calculation of Fugacity: Pure Species (I/II)

- **Ideal Gas**

$$f_i^{ig} = P \quad \phi_i^{ig} = 1$$

- **Pure Gas**

- Virial equation of state up to second coefficient

$$\ln \phi_i = \frac{B_{ii}P}{RT} \quad (11.36)$$

- Cubic equation of state

$$\ln \phi_i = Z_i - 1 - \ln(Z_i - \beta_i) - q_i I_i \quad (11.37)$$

where

$$\beta_i = \Omega \frac{P_{r,i}}{T_{r,i}} \quad (3.53)$$

(see Table 3.1)

Remember:

$$f_i = \phi_i P \quad q_i = \frac{\Psi \alpha(T_{r,i})}{\Omega T_{r,i}} \quad (3.54)$$

Calculation of Fugacity: Pure Species (II/II)

- **Pure Liquid**

- Approximation to equation (11.43):

$$f_i = \phi_i^{\text{sat}} P_i^{\text{sat}} \exp \left[\frac{V_i^l (P - P_i^{\text{sat}})}{RT} \right] \quad (11.44)$$

$$\ln \phi_i^{\text{sat}} = \int_0^{P_i^{\text{sat}}} (Z_i^v - 1) \frac{dP}{P} \quad (11.42)$$

where the exponential in (11.44) is known as Poynting correction factor.

- Need:

- Values of Z_i^v (experiments, equation of state, generalized correlation),
- Liquid-phase molar volume V_i^l (usually value for saturated liquid),
- Value for P_i^{sat} .

Fugacity of Species in Solution

- Analogous to the case of pure species. Interaction between different species is accounted for with *mixing rules*.

Real Gas Mixture

$$\hat{\phi}_i^v = \frac{\hat{f}_i^v}{y_i P}$$

Real Liquid Solution

$$\hat{\phi}_i^l = \frac{\hat{f}_i^l}{x_i P}$$

- **Ideal Gas**

$$\hat{f}_i^{ig} = y_i P \quad \hat{\phi}_i^{ig} = 1$$

- **Virial Equation of State up to Second Coefficient**

$$\hat{\phi}_k = \frac{P}{RT} \left[B_{kk} + \frac{1}{2} \sum_i \sum_j y_i y_j (2\delta_{ik} - \delta_{ij}) \right] \quad (11.64)$$

where $\delta_{ik} \equiv 2B_{ik} - B_{ii} - B_{kk}$

- Expressions for cubic equations of state are more complicated (reference: *Poling, B. E., Prausnitz, J. M., & O'Connell, J. P. (2001). The Properties of Gases and Liquids. 5th Edition. The McGraw-Hill Companies, Inc. New York, NY. USA.*).

Ideal Solution and Excess Properties

- By **definition**

$$\mu_i^{id} = G_i(T, P) + RT \ln x_i \quad (11.75)$$

- Lewis/Randall rule

$$\hat{f}_i^{id} = x_i f_i \quad (11.83)$$

Consequence:

$$\hat{\phi}_i^{id} = \phi_i \quad (11.84)$$

- Real liquid solutions are often more easily dealt with through properties that measure their *departures* from ideal-solution behavior rather than ideal-gas behavior.
- Analogously to a residual property M^R , **define** M^E as an excess property

$$M^E \equiv M - M^{id} \quad (11.85)$$

- The reason for not using the same formulation as gas is that there is no good, easy model for fugacity coefficient for liquid mixtures.

Excess Gibbs Energy and Activity Coefficient

- Manipulating equations,

$$\bar{G}_i^E = \bar{G}_i - \bar{G}_i^{id} = RT \ln \frac{\hat{f}_i}{x_i f_i}$$

where we **define** the activity coefficient as follows

$$\gamma_i \equiv \frac{\hat{f}_i}{x_i f_i} \quad (11.90)$$

- Important result: $\ln \gamma_i$ is a partial property with respect to G^E/RT :

$$\frac{G^E}{RT} = \sum_i x_i \ln \gamma_i \quad (11.99)$$

- Several models for G^E/RT , hence activity coefficients:
 - Margules
 - van Laar
 - Wilson
 - NRTL
 - UNIQUAC
 - UNIFAC

Application: Vapor-Liquid Equilibria (VLE)

- Equilibrium (isofugacity) condition:

$$\hat{f}_i^v = \hat{f}_i^l \quad (11.48)$$

- Putting together the expressions for vapor and liquid fugacity in mixtures:

$$\hat{\phi}_i y_i P = \gamma_i x_i \phi_i^{\text{sat}} P_i^{\text{sat}} \exp \left[\frac{V_i^l (P - P_i^{\text{sat}})}{RT} \right]$$

↗ non-ideality in gas mixture ↖ non-ideality in liquid solution

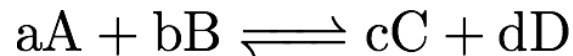
This is sometimes called the γ - ϕ approach to VLE.

- Rearranging, K -values (i.e., partition coefficients used in flash and distillation calculations).

$$K_i = \frac{y_i}{x_i} = \frac{\gamma_i \phi_i^{\text{sat}} P_i^{\text{sat}} \exp \left[\frac{V_i^l (P - P_i^{\text{sat}})}{RT} \right]}{\hat{\phi}_i P}$$

Application: Chemical Reaction Equilibria

- Given general equilibrium reaction



its equilibrium is determined by the equilibrium constant K .

- By **definition**, we relate K and the standard Gibbs energy as follows:

$$\Delta G^\circ = -RT \ln K \quad (13.11)$$

- The equilibrium is defined in terms of the *fugacity* of the components:

$$K = \frac{\hat{f}_C^c \hat{f}_D^d}{\hat{f}_A^a \hat{f}_B^b} \left(\frac{1}{P^\circ} \right)^{c+d-a-b} \quad (\text{see equation (13.25)})$$

- Using fugacity coefficients (typically in gas-phase reactions):

$$\hat{f}_i = y_i \hat{\phi}_i P$$

$$K = \frac{(y_C \hat{\phi}_C)^c (y_D \hat{\phi}_D)^d}{(y_A \hat{\phi}_A)^a (y_B \hat{\phi}_B)^b} \left(\frac{P}{P^\circ} \right)^{c+d-a-b} \quad (\text{see equation (13.26)})$$

- Expressions for ideal gas mixture (13.28), liquid-phase (13.31) etc.

Extent of Reaction

- Also known as coordinate of reaction: ϵ
 - Extent to which the reaction has taken place.

$$dn_i = \nu_i d\epsilon \quad (13.3)$$

where ν is the stoichiometric coefficient of species i (positive if product, negative if reactant).

- Relationship between mole fraction and ϵ (see Section 13.1).
 - Single reaction

$$y_i = \frac{n_i}{n} = \frac{n_{i0} + \nu_i \epsilon}{n_0 + \nu \epsilon} \quad (13.5)$$

- Multiple reactions

$$y_i = \frac{n_i}{n} = \frac{n_{i0} + \sum_j \nu_{i,j} \epsilon_j}{n_0 + \sum_j \nu_j \epsilon_j} \quad (13.7)$$

where i indexes species and j indexes reactions.

- Procedure for ideal gas mixture: substitute y_i into expression for K and solve for ϵ . See Examples 13.1, 13.2, and 13.3.