Lectures 9

Reaction Equilibria

O'Connell & Haile
Chapter 10.3 - 10.5

Topics:

- States of systems with reactions
- Reaction equilibrium relations
  - Stoichiometric
  - Nonstoichiometric
- Properties of formation
- Reaction equilibrium expressions
- Suggested strategies for solving phase & reaction equilibrium problems

THERMODYNAMIC STATE OF REACTING SYSTEMS AT EQUILIBRIUM

To change a state $\mathcal{V} = \mathcal{C} + 2 - \mathcal{S}_{ext}$

Still get Duhem's Theorem for closed ($\mathcal{S}_{ext} = \mathcal{C}$)

To identify final state $\mathcal{F}_a = \mathcal{C} + 2 - \mathcal{S}$

$\mathcal{S}$ has $\mathcal{R}$ reaction equilibrium constraints

$\mathcal{A}_j = 0 \quad j = 1, 2, \ldots \mathcal{R}$

$\mathcal{F}' = \mathcal{C}+1-\mathcal{S}$; for phase+reaction equilibria

$\mathcal{F} = \mathcal{C}+2-\mathcal{P}-\mathcal{R}-\mathcal{S}$: $\mathcal{S}$=other internal constraints

To get desired initial state, want $\mathcal{F}'$ value

REACTION EQUILIBRIUM RELATIONS

Reaction equilibrium species constraint:

$\sum_{i=1}^{C} \overline{G}_i dN_i = 0$ & element constraint $\sum_{i=1}^{C} a_{ki} dN_i = 0$

where a_{ki} = # atoms of k on species i

(*e.g.*, for C_2H_6(1), $a_{C1} = 2$, $a_{H1} = 6$)

2 forms: stoichiometric & nonstoichiometric

Stoichiometric has $\mathcal{A}_j$, ν_{ij} & ξ_j of Ch. 7

Solves $\mathcal{R}$ nonlinear equations for ξ_j to get $\{N\}, T, P$

Nonstoichiometric has $\frac{\Delta g_f^o}{RT}, a_i, a_{ki}$

Solves constrained optimization $\mathcal{C}+m_e$ equations to get $\{x\}, \lambda_k$

STOICHIOMETRIC DEVELOPMENT (10.3.2)

Basic equations (10.3.8) - (10.3.9)

$$\mathcal{A}_j = 0 = \mathcal{A}_j^o(T, P^o, \{x^o\}) - RT \ln \prod_i^C \left(\frac{f_i(T,P,\{x\})}{f_i^o(T,P^o,\{x^o\})} \right)^{\nu_{ij}} \quad j = 1, 2, \ldots, \mathcal{R}$$

$$K_j(T) \equiv \prod_i^C \left(\frac{f_i(T,P,\{x\})}{f_i^o(T;P_i^o)} \right)^{\nu_{ij}}$$

$$\Rightarrow \quad = \exp\left[\frac{-\sum_{i=1}^{C} \nu_{ij} \overline{G}_i^o(T)}{RT} \right] \equiv \exp\left[\frac{-\Delta g_j^o(T)}{RT} \right] \qquad (10.3.13)$$

NOTE: K_j only $f(T)$ - constrains $\{x\}$, P

Standard State Affinity $\mathcal{A}_j^o = -\sum_{i=1}^{C} \nu_{ij} \overline{G}_i^o(T)$

can have any value:

$\mathcal{A}_j^o > 0$, goes to products, if < 0, get reactants

$K_j > 0$: if > 1, to products, if < 1, to reactants

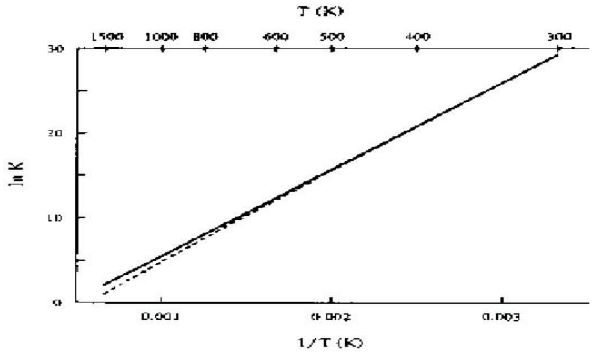
NH_3 - Ex. 10.3.3 gets *K*, decisions on FFF, SS

***K_j* varies with *T* via $\Delta h_j^o(T)$**

(Gibbs-Helmholtz Eq.) $\ln \frac{K_j(T_2)}{K_j(T_1)} \approx \frac{-\Delta h_j^o}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$

(more accurate with Δc_{pj}^o)

Example (10.3.5)



NONSTOICHIOMETRIC DEVELOPMENT

Optimization problem is Eq. (10.3.34)

$$\text{Min}\left[\sum_{i=1}^{C} N_i \overline{G}_i + \sum_{k=1}^{m_e}\left(\sum_{i=1}^{C} a_{ki} N_i - b_k\right)\lambda_k\right]$$

where b_k = total # atoms *k* (conserved), a_{ki} = atoms of *k* in species *i*

Solve for {*x*} & $\{\lambda\}$ via equations (10.3.37-8)

$$\overline{G}_i^o + RT\ln\frac{f_i}{f_i^o} + \sum_{k=1}^{m_e} a_{ki}\lambda_k = 0; \quad i = 1,\ldots,C \quad \textbf{(10.3.38)}$$

$$\sum_{i=1}^{C} a_{ki} N_i - b_k = 0 \qquad k = 1,\ldots,m_e \quad \textbf{(10.3.37)}$$

Standard states depend on phase & FFF

Gases: ig@ f_i^o=1 pressure unit (*e.g.*, 1 atm., 1 bar)

FFF #1 $a_i(T,P,\{x\}) \equiv \frac{f_i}{f_i^o} = x_i\varphi_i(T,P,\{x\})P$

Liquids - use with FFF #2-5 with, *e.g.*, pure saturated liquid *i* at *T*

$f_i^o = f_{pure\ i}(T;P_i^s) = \varphi_i^s(T)P_i^s(T)$

or Henry's Law standard state $f_i^o = H_i(T)$

Solids - pure solid *i* @ *T* & *P* =1 (bar,atm.,.)

Don't "see" SS but it is in <u>both</u> *K* & γ_i)

PROPERTIES OF FORMATION (10.4.2)

Measure {x_{eq}} to get K_j (*T*), $\Delta g_j^o(T)$ **&** $\Delta h_j^o(T)$

("play game backwards") get $\Delta g_{if}^o(T^o), \Delta h_{if}^o(T^o)$

Compute Δg_j^o, Δh_j^o **& K_j(*T*) from tabulations of** $\Delta g_{if}^o, \Delta h_{if}^o$ **at *T*^{o} ("play game forwards")**

since $\Delta g_i^o(T^o,P^o) = \sum_{i=1}^{C} v_{ij}\Delta g_{if}^o(T^o)$ **(10.4.18)**

Then correct to *T* from *T*^{o} via Eq. (10.4.19)

Note phase changes (esp. solids, p. 461)!

$\Delta g_{if}^o, \Delta h_{if}^o$ **tabulations in several places (Refs.)**

Note: Δg_j^o **±1 kJ at *T* = 500 K ⇒ ± 27% in K_j!**

Stoichiometric Expressions (10.4.3)

General

$$K_j \equiv \prod_i^C a_i^{\nu_{ij}}$$

Gases FFF #1 (10.4.26)

$$K_j = \prod_i^C (x_i \varphi_i)^{\nu_{ij}} P^{\nu_{ij}} = P^{\sigma_j} \prod_i^C (x_i \varphi_i)^{\nu_{ij}}$$

Liquid/Solid FFF #3 (10.4.27)

$$K_j = \prod_i^C (x_i \gamma_i)^{\nu_{ij}} \exp\left[\frac{\nu_{ij}}{RT} \int_{P_i^s}^{P} v_{\text{pure i}}(T, \pi) d\pi\right]$$

FFF #5 (10.4.28)

$$K_j = \prod_i^C (x_i \gamma_i)^{\nu_{ij}} \exp\left[\frac{\nu_{ij}}{RT} \int_{P_i^s}^{P} \bar{V}_i(T, \pi, \{x\}) d\pi\right]$$

Nonstoichiometric Forms (10.4.5)

NH_3 Examples: 10.4.4 & 10.4.6

Selecting relation forms for application

Decisions, decisions!

1. Assess the risk

a. What is inherent uncertainty of case?
b. What should happen if you are wrong?

2. Make reasonable assumptions at appropriate places of analysis

a. Phase, behaviors, types of substances, etc.
b. Sensitivity to errors?

3. Available resources

a. Values from data, models, computation

Rules of Thumb

FFF #1 for gases & perhaps liquids

FFF #2-5 for solids & perhaps liquids
Pure component Standard State to 1.2 T_c
Henry's Law SS only when necessary

Use phi-phi (EoS) if possible for VLE
Complex substances have complex combining & mixing rules

Use gamma-phi (EoS/G^E) for understanding of VLE/LLE phase & simplicity when useful

Always obtain number of independent reactions among species first
Do not confuse "mechanism" with reaction

Use stoichiometric method for few & known reactions among simple species

Use nonstochiometric method for larger systems or unknown reactions