Electrolyte Solutions

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  - introduction, definition
- Phase equilibruim
  - predictive model
- Thermodynamics
  - properties, data source, activity models

Aqueous chemistry (1)

- Aqueous electrolyte system
  - Aqueous-based environmental applications
    - gas treatment, waste water treatment (chromatographic separations, membrane separations, pH controlled neutralization) chemical waste disposal
  - Typical applications
    - bio separations, corrosion, oilfield research, geothermal wells, paper production

- Difficulties of phase equilibrium models
  - describing the nonideal behavior
    - mean activity coefficient
  - different standard state
  - complex chemistry

Aqueous chemstry (2)

- Aqueous systems terminology
  - Phase
    - physical state of chemical species. (g, l, aq, s)
  - Electrolyte
    - some solubility in water and reacts in water.
  - Nonelectrolyte
    - some solubility in water and remains nearly totally in the molecular form.
  - Ionic species
    - dissolved in water and possessing charge, cation or anion
  - Molecular species
    - dissolved in water and no charge

Aqueous Chemistry (3)

- Complex, ion pair
  - composed of both cationic and anionic portions, charged or uncharged
- Strong electrolyte
  - completely dissociates to base ions
- Weak electrolyte
  - partially dissociates
- Aqueous electrolyte equilibrium
  - thermodynamic equilibrium involving all species in the aqueous phase
- Aqueous phase equilibrium
  - thermodynamic description of physical equilibrium between aqueous phase and other phase.

Aqueous Chemistry (4)

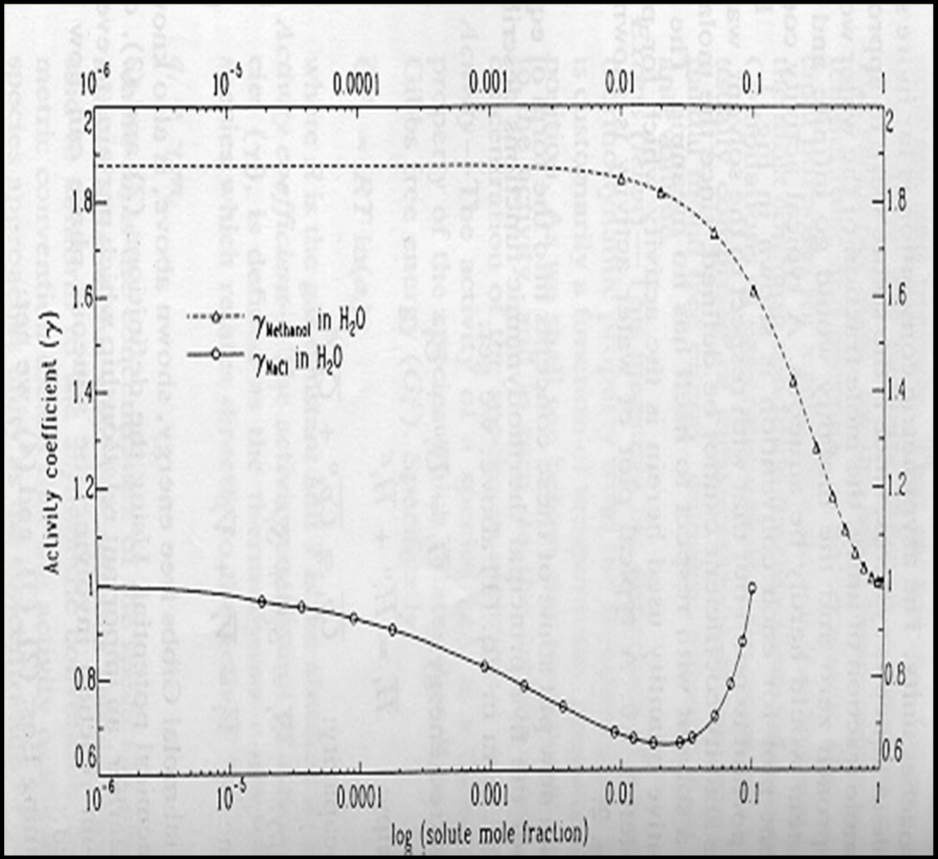
- Aqueous Thermodynamic Definitions
  - Solvent
  - Solute - dissolved in water
  - Molality
    - moles of an aqueous phase species per kg of water
  - Thermodynamic properties - G, H, S, Cp, V

$$\overline{P_i} = \overline{P_i}^0 + \overline{P_i}^E$$

  - Standard state term - at defined state (c, T, P)
  - Reference state - at specific standard state

Aqueous Chemistry (5)

- Excess term - nonideal contributions, activity
  - Activity, Activity coefficient (symmetric, asymmetric)



Aqueous Chemistry (6)

- Equilibrium Constants
  - equilibrium reaction

$$aA + bB = cC + dD$$

$$K = \frac{(\gamma_C m_C)^c (\gamma_D m_D)^d}{(\gamma_A m_A)^a (\gamma_B m_B)^b}$$

$$= \exp[-\Delta \overline{G}_{rxn}(T) / RT]$$

Phase equilibrium (1)

- Predictive model (water - chlorine system)

$$H_2 0(vap) = H_2O(aq)$$

$$Cl_2(vap) = Cl_2(aq)$$

$$Cl_2(aq) + H_2O = H^+(ion) + Cl^-(ion) + HClO(aq)$$

$$HClO(aq) = H^+(ion) + ClO^-(ion)$$

$$H_2O(aq) = H^+(ion) + OH^-(ion)$$

- Given : T, P , M^0 of H_2O, m^0 of Cl_2
- Calculate : v, P_1, P_2, m_{HClO}, m_{Cl2}, m_{H} + , m_{OH}-, m_{Cl}, m_{ClO}, m_{H2O}(aq) - 10 unknowns.

Phase equilibrium (2)

- Equilibrium constant (5)
- Electroneutrality equation : cation = anion (1)

$$m_{H+} = m_{Cl-} + m_{OH-} + m_{ClO-}$$

- material balance (4)

$$3M_{H2O}{}^{0} + 2m_{Cl2}{}^{0} = 3M_{H2O} + M_{H2O}/55.51(3m_{HClO} + m_{Cl}{}^{-}$$
$$+ 2m_{OH^-} + m_{H^+} + 2m_{Cl2(aq)}) + v$$

$$2m_{Cl2}{}^{0} = M_{H2O}/55.51(m_{HClO} + m_{Cl^-} + m_{ClO^-}) + vP_2/P$$

$$2M_{H2O}{}^{0} = 2M_{H2O} + M_{H2O}/55.51(m_{HClO} + m_{H^+} + m_{OH^-}) + vP_1/P$$

$$P = P_1 + P_2$$

Thermodynamics(1)

- Representation of the thermodynamic properties

$$P_T = \sum_i^n \overline{P_i} N_i$$

  - thermodynamic consistency
  - Gibbs free energy
    - activity coefficient

$$\overline{S_i} = -\left(\frac{\partial \overline{G_i}}{\partial T}\right)_{P,m}$$

$$\overline{H_i} = \overline{G_i} + T\overline{S_i}$$

$$\overline{C_{pi}} = \left(\frac{\partial \overline{H_i}}{\partial T}\right)_{P,m}$$

$$\overline{V_i} = \left(\frac{\partial \overline{G_i}}{\partial P}\right)_{T,m}$$

Thermodynamics(2)

- Sources of Data
  - Compilations of G, H, S, Cp
    - Chase et al.(1985) : ref. state (s, l, g)
    - Cox et al.(1989) : ref. state (s, l, g, aq)
    - Daubert and Danner (1989) : ref. T dependent
    - Glushko et al. (1965-1981) : ref. (aq), NBS
    - Kelly (1960) : ref. state H, Cp, S (s)
  - Compilations of Equilibrium Constants
    - Baes and Mesmer (1976) : hydrolysis equilbria for metal cations
    - Smith and Martell (1975-1989) : complexation equilibria for anions, organic anions

Thermodynamics(3)

- Compilations of Activity Coefficient Data
  - Goldberg (1981) : univalent and bivalent electrolytes
  - Goldberg and Nutall (1978) : alkalin metals
  - Hammer and Wo (1972) : univalent electrolytes
  - Lobo (1989) : activity coefficient data , viscosity, transport, density, osmotic coeffient data

- Compilations of Solubility data
  - Horvath(1982) : halogenated hydrocarbons
  - Linke and Seidell (1958, 1965) : inorganic compounds
  - Stephen and Stephen (1963) : organic compounds

Thermodynamics(4)

- Standard State Properties $\overline{G_i}^0, \overline{H_i}^0, \overline{S_i}^0, \overline{C_{pi}}^0, \overline{V_i}^0$

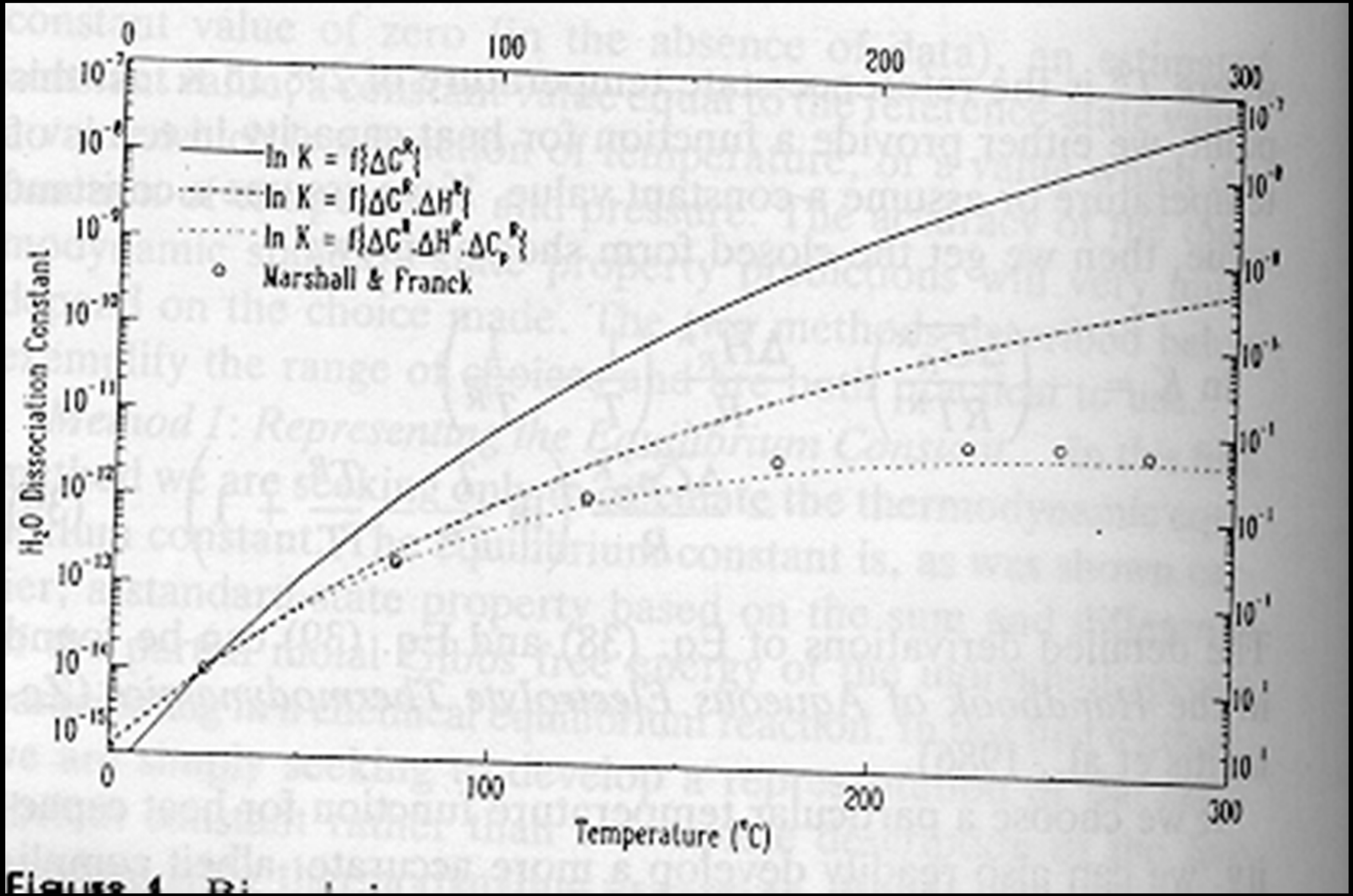
  - Representing the Equilbrium Constant

$$\ln K = -\left(\frac{\Delta\overline{G_{Rxn}}^R}{RT^R}\right) - \frac{\Delta\overline{H_{Rxn}}^R}{R}\left(\frac{1}{T} - \frac{1}{T^R}\right) - \frac{\Delta\overline{C_p}^R}{R}\left(\ln\frac{T}{T^R} - \frac{T^R}{T} + 1\right)$$

  - Helgeson Equation of State :

ϖ, c1, c2, a1, a2, a3, a4 - 7 coefficients

Thermodynamics(5)



Thermodynamics(6)

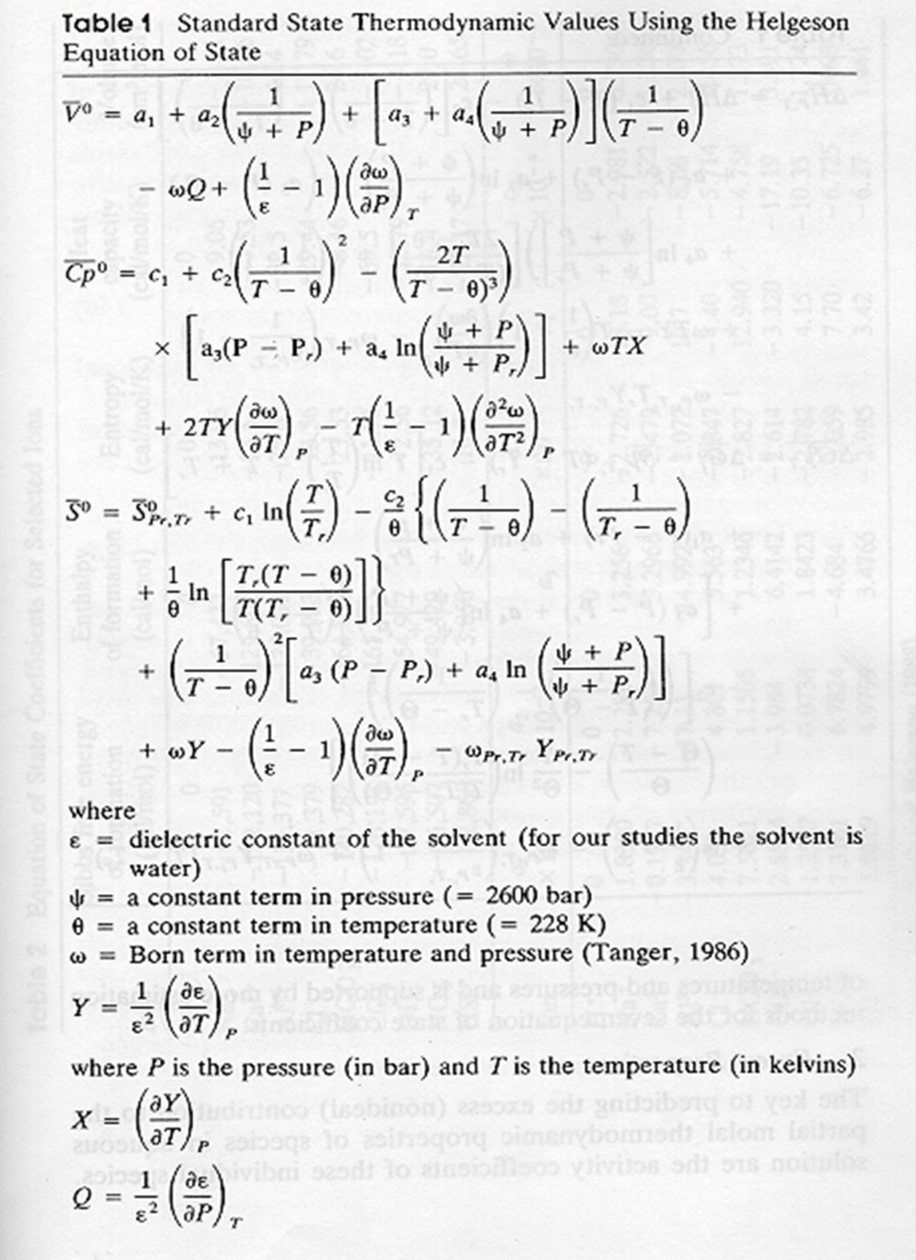


Table 1 Standard State Thermodynamic Values Using the Helgeson Equation of State

$$\overline{V}^0 = a_1 + a_2\left(\frac{1}{\psi + P}\right) + \left[a_3 + a_4\left(\frac{1}{\psi + P}\right)\right]\left(\frac{1}{T - \theta}\right)$$

$$- \omega Q + \left(\frac{1}{\varepsilon} - 1\right)\left(\frac{\partial \omega}{\partial P}\right)_T$$

$$\overline{Cp}^0 = c_1 + c_2\left(\frac{1}{T - \theta}\right)^2 - \left(\frac{2T}{(T - \theta)^3}\right)$$

$$\times \left[a_3(P - P_r) + a_4 \ln\left(\frac{\psi + P}{\psi + P_r}\right)\right] + \omega T X$$

$$+ 2TY\left(\frac{\partial \omega}{\partial T}\right)_P - T\left(\frac{1}{\varepsilon} - 1\right)\left(\frac{\partial^2 \omega}{\partial T^2}\right)_P$$

$$\overline{S}^0 = \overline{S}^0_{Pr,Tr} + c_1 \ln\left(\frac{T}{T_r}\right) - \frac{c_2}{\theta}\left\{\left(\frac{1}{T - \theta}\right) - \left(\frac{1}{T_r - \theta}\right)\right.$$

$$\left. + \frac{1}{\theta} \ln\left[\frac{T_r(T - \theta)}{T(T_r - \theta)}\right]\right\}$$

$$+ \left(\frac{1}{T - \theta}\right)^2\left[a_3(P - P_r) + a_4 \ln\left(\frac{\psi + P}{\psi + P_r}\right)\right]$$

$$+ \omega Y - \left(\frac{1}{\varepsilon} - 1\right)\left(\frac{\partial \omega}{\partial T}\right)_P - \omega_{Pr,Tr} Y_{Pr,Tr}$$

where

ε = dielectric constant of the solvent (for our studies the solvent is water)

ψ = a constant term in pressure (= 2600 bar)

θ = a constant term in temperature (= 228 K)

ω = Born term in temperature and pressure (Tanger, 1986)

$$Y = \frac{1}{\varepsilon^2}\left(\frac{\partial \varepsilon}{\partial T}\right)_P$$

where P is the pressure (in bar) and T is the temperature (in kelvins)

$$X = \left(\frac{\partial Y}{\partial T}\right)_P$$

$$Q = \frac{1}{\varepsilon^2}\left(\frac{\partial \varepsilon}{\partial P}\right)_T$$

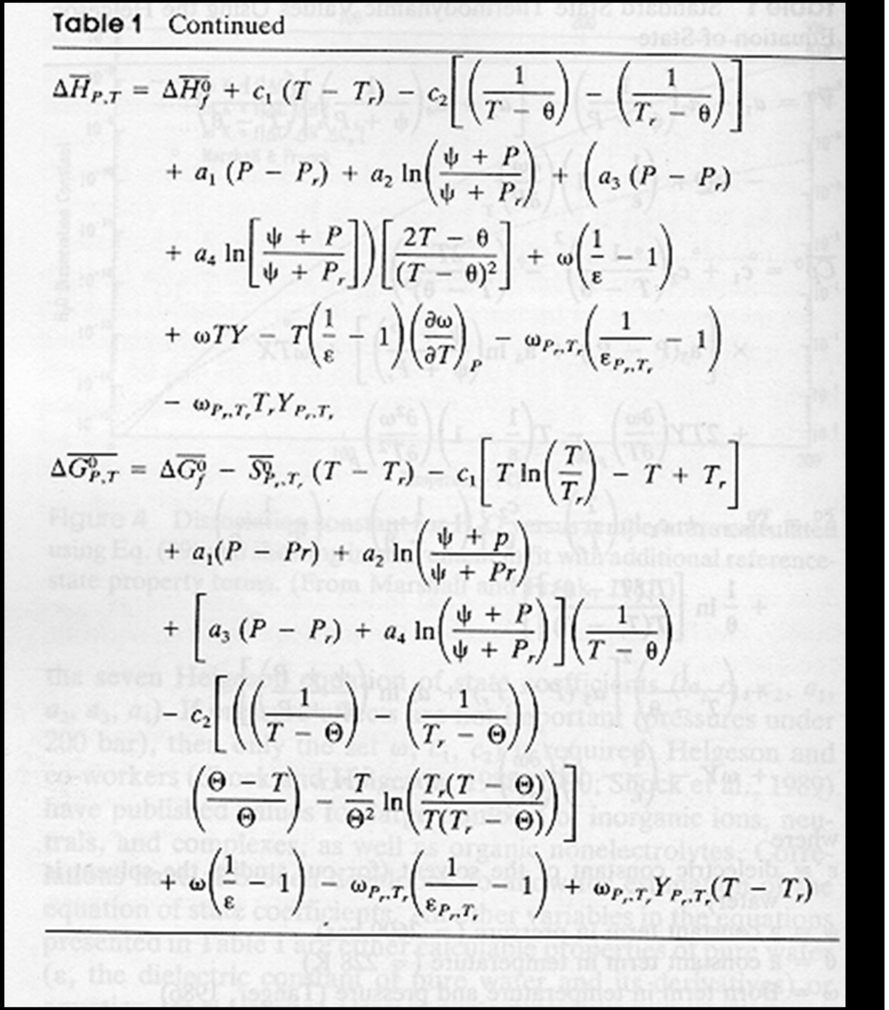


Table 1 Continued

$$\Delta \overline{H}_{P,T} = \Delta \overline{H^0_f} + c_1(T - T_r) - c_2\left[\left(\frac{1}{T - \theta}\right) - \left(\frac{1}{T_r - \theta}\right)\right]$$

$$+ a_1(P - P_r) + a_2 \ln\left(\frac{\psi + P}{\psi + P_r}\right) + \left(a_3(P - P_r)\right.$$

$$\left. + a_4 \ln\left[\frac{\psi + P}{\psi + P_r}\right]\right)\left[\frac{2T - \theta}{(T - \theta)^2}\right] + \omega\left(\frac{1}{\varepsilon} - 1\right)$$

$$+ \omega TY - T\left(\frac{1}{\varepsilon} - 1\right)\left(\frac{\partial \omega}{\partial T}\right)_P - \omega_{P_r,T_r}\left(\frac{1}{\varepsilon_{P_r,T_r}} - 1\right)$$

$$- \omega_{P_r,T_r} T_r Y_{P_r,T_r}$$

$$\Delta \overline{G^0_{P,T}} = \Delta \overline{G^0_f} - \overline{S^0}_{P_r,T_r}(T - T_r) - c_1\left[T \ln\left(\frac{T}{T_r}\right) - T + T_r\right]$$

$$+ a_1(P - Pr) + a_2 \ln\left(\frac{\psi + p}{\psi + Pr}\right)$$

$$+ \left[a_3(P - P_r) + a_4 \ln\left(\frac{\psi + P}{\psi + P_r}\right)\right]\left(\frac{1}{T - \theta}\right)$$

$$- c_2\left[\left(\left(\frac{1}{T - \Theta}\right) - \left(\frac{1}{T_r - \Theta}\right)\right)\right.$$

$$\left.\left(\frac{\Theta - T}{\Theta}\right) - \frac{T}{\Theta^2} \ln\left(\frac{T_r(T - \Theta)}{T(T_r - \Theta)}\right)\right]$$

$$+ \omega\left(\frac{1}{\varepsilon} - 1\right) - \omega_{P_r,T_r}\left(\frac{1}{\varepsilon_{P_r,T_r}} - 1\right) + \omega_{P_r,T_r} Y_{P_r,T_r}(T - T_r)$$

Thermodynamics & Properties LAB
KOREA University

Thermodynamics(7)

- Excess Properties
  - Ionic strength
    $$I = \frac{1}{2}\sum_{i=1}^{nI} z_i^2 m_i$$
  - activity coefficient
    - long range term : dilute solutions

      Debye and Hückel term or modified D-H
    - short range term : concentranted solution

      ion-ion, ion-molecule interaction
  - mean activity coefficient
    $$\gamma_{\pm} = (\gamma_{+}^{x}\gamma_{-}^{y})^{1/(x+y)}$$

Thermodynamics(8)

- History of activity coefficient models
  - Debye-Hückel model
  - Guggenheim’s equation : one parameter
    - Davies’ equation
    - Bromley’s equation
  - Meissner’s equation : reduced activity coefficients
  - Pitzer’s equation : 3~4 parameters model
  - Helgeson : EoS approach
  - Chen’s equation : short and long range interactons using two parameters

Thermodynamics(9)

- Debye-Hückel (1920') : from electric potential

$$\log \gamma_{\pm} = \frac{-A|z_+ z_-|\sqrt{I}}{(1+a_0 B\sqrt{I})} + CI$$

- Guggenheim's (1935)

$$\log \gamma_{c,a} = -\frac{\alpha|z_+ z_-|\sqrt{I}}{1+\sqrt{I}} + \frac{2v_+}{v_+ + v_-}\sum_{a'} \beta_{c,a`} m_{a`} + \frac{2v_-}{v_+ + v_-}\sum_{c'} \beta_{c`,a} m_{a`}$$

- Davies's (1938)

$$\log \gamma_{\pm} = \frac{A|z_+ z_-|\sqrt{I}}{1+\sqrt{I}} + Bm$$

Thermodynamics(10)

- Bromley's (1972)

$$\log \gamma_{\pm} = -\frac{A|z_{+}z_{-}|\sqrt{I}}{1+\rho\sqrt{I}} + \frac{(B_0 - B)I}{(1+aI^2)} + BI + CI^2$$

- Meissner's (1978) : reduced activity coefficients

$$\Gamma^{o} = \{1 + B(1+0.1I)^{q} - B\}\Gamma^{*} \qquad \Gamma^{o} = \gamma_{\pm}^{1/z_{+}z_{-}}$$

- Pitzer (1973~1978)

$$\ln \gamma_{\pm} = |z_{+}z_{-}| f` + m\left(\frac{2v_{+}v_{-}}{v}\right)B_{\pm}^{\gamma} + m^2\left[\frac{2(v_{+}v_{-})^{1.5}}{v}\right]C_{\pm}^{\gamma}$$

Thermodynamics(11)

- Helgeson (1981)
- Chen (1982)
  - NRTL method, long range and short range contribution

$$\ln f_{\pm} = \ln f_{\pm}^{P} + \ln f_{\pm}^{lc}$$

- Temperature effect

Thermodynamics(13)