Overhead Slides for

Chapter 18, Part 1

of

Fundamentals of Atmospheric Modeling

by

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Types of Equilibrium Equations

Reversible chemical reaction

$$\mathrm{d}n_{\mathrm{D}}\mathrm{D} + \mathrm{d}n_{\mathrm{E}}\mathrm{E} + \ldots \rightleftharpoons \mathrm{d}n_{\mathrm{A}}\mathrm{A} + \mathrm{d}n_{\mathrm{B}}\mathrm{B} + \ldots \qquad (18.1)$$

Divide each $\mathrm{d}n_i$ by smallest value of $\mathrm{d}n_i$

$$\nu_{\mathrm{D}}\mathrm{D} + \nu_{\mathrm{E}}\mathrm{E} + \ldots \rightleftharpoons \nu_{\mathrm{A}}\mathrm{A} + \nu_{\mathrm{B}}\mathrm{B} + \ldots \qquad (18.3)$$

Mass conservation

$$\sum_i k_i \left(\mathrm{d}n_i\right) m_i = 0 \qquad (18.2)$$

Solvent
Substance in which species dissolve in (*e.g.*, water)

Solute
The dissolving species

Solution
Combination of solute and solvent

Solids
Suspended material not in solution

Gas-Particle Equilibrium

Gas-particle reversible reaction

$$AB(g) \rightleftharpoons AB(aq) \quad (18.4)$$

Gas in equilibrium with solution at gas-solution interface

Examples

Hydrochloric acid

$$HCl(g) \rightleftharpoons HCl(aq) \quad (18.5)$$

Nitric acid

$$HNO_3(g) \rightleftharpoons HNO_3(aq)$$

Carbon dioxide

$$CO_2(g) \rightleftharpoons CO_2(aq)$$

Ammonia

$$NH_3(g) \rightleftharpoons NH_3(aq)$$

Sulfuric acid

$$H_2SO_4(g) \rightleftharpoons H_2SO_4(aq) \quad (18.5)$$

Electrolytes, Ions, and Acids

Electrolytes

Substances that undergo partial or complete dissociation into ions in solution

Ions

Charged atoms or molecules

Dissociation

Molecule breaks into simpler components, namely ions. Degree of dissociation depends on acidity.

Acidity

Measure of concentration of hydrogen ions (protons, H^+ ions) in solution

Electrolytes, Ions, and Acids

Acidity measured in terms of pH

$$pH = -\log_{10}\left[H^+\right] \qquad (18.6)$$

$[H^+]$ = molarity of H^+ (moles-H^+ L^{-1}-solution)

Protons in solution donated by acids

H_2CO_3 = carbonic acid

HCl = hydrochloric acid

HNO_3 = nitric acid

H_2SO_4 = sulfuric acid

Strong acids (dissociate readily at low pH)

HCl = hydrochloric acid

HNO_3 = nitric acid

H_2SO_4 = sulfuric acid

Weak acids (dissociate readily at higher pH)

H_2CO_3 = carbonic acid

Electrolytes, Ions, and Acids

Hydrochloric acid dissociation (pH above -6)

$$HCl(aq) \rightleftharpoons H^+ + Cl^- \quad (18.7)$$

Sulfuric acid dissociation (pH above -3)

$$H_2SO_4(aq) \rightleftharpoons H^+ + HSO_4^- \quad (18.8)$$

Bisulfate dissociation (pH above 2)

$$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-} \quad (18.8)$$

Nitric acid dissociation (pH above -1)

$$HNO_3(aq) \rightleftharpoons H^+ + NO_3^- \quad (18.9)$$

Carbon dioxide dissociation (pH above 6)

$$CO_2(aq) + H_2O(aq) \rightleftharpoons H_2CO_3(aq) \rightleftharpoons H^+ + HCO_3^- \quad (18.10)$$

Bicarbonate dissociation (pH above 10)

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-} \quad (18.10)$$

Bases

Base

Donates OH^- (hydroxide ion)

Hydroxide ions combine with hydrogen ions to form liquid water, increasing pH of solution

$$H_2O(aq) \rightleftharpoons H^+ + OH^- \quad (18.11)$$

Ammonia complexes with water and dissociates

$$NH_3(aq) + H_2O(aq) \rightleftharpoons NH_4^+ + OH^- \quad (18.12)$$

Solid Electrolytes

Suspended electrolytes not in solution

Precipitation / crystallization

Formation of solid electrolytes from ions

Dissociation

Separation of solid electrolytes into ions

Ammonium-containing solid reactions

$$NH_4Cl(s) \rightleftharpoons NH_4^+ + Cl^- \quad (18.15)$$

$$NH_4NO_3(s) \rightleftharpoons NH_4^+ + NO_3^- \quad (18.15)$$

$$(NH_4)_2SO_4(s) \rightleftharpoons 2NH_4^+ + SO_4^{2-} \quad (18.15)$$

Sodium-containing solid reactions

$$NaCl(s) \rightleftharpoons Na^+ + Cl^- \quad (18.16)$$

$$NaNO_3(s) \rightleftharpoons Na^+ + NO_3^- \quad (18.16)$$

$$Na_2SO_4(s) \rightleftharpoons 2Na^+ + SO_4^{2-} \quad (18.16)$$

Solid formation from the gas phase on surfaces

$$NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g) \quad (18.17)$$

$$NH_4NO_3(s) \rightleftharpoons NH_3(g) + HNO_3(g) \quad (18.17)$$

Equilibrium Relation and Constant

Equilibrium coefficient relation

$$\prod_i \{a_i\}^{k_i \nu_i} = \frac{\{A\}^{\nu_A}\{B\}^{\nu_B}\ldots}{\{D\}^{\nu_D}\{E\}^{\nu_E}\ldots} = K_{eq}(T) \qquad (18.18)$$

{}... = Activity

Effective concentration or intensity of substance

$$\{A(g)\} = p_{A,s} \qquad \text{(gas)} \qquad (18.19)$$

$$\{A^+\} = \mathbf{m}_{A^+}\gamma_{A^+} \qquad \text{(ion)} \qquad (18.20)$$

$$\{A(aq)\} = \mathbf{m}_A \gamma_A \qquad \text{(dissolved molecule)} \qquad (18.20)$$

$$\{H_2O(aq)\} = a_w = \frac{p_v}{p_{v,s}} = f_r \qquad \text{(liquid water)} \qquad (18.21)$$

$$\{A(s)\} = 1 \qquad \text{(solid)} \qquad (18.22)$$

Equilibrium Coefficient Relation

Gibbs free energy

$$G^* = H^* - TS^* = U^* + p_a V - TS^* \qquad (18.23)$$

Enthalpy

$$H^* = U^* + p_a V$$

Change in Gibbs free energy

Measure of maximum amount of useful work obtained from a change in enthalpy or entropy of the system

$$dG^* = d\left(H^* - TS^*\right) = dU^* + p_a dV + V dp_a - T dS^* - S^* dT \qquad (18.24)$$

Change in entropy

$$dS^* = dQ^* / T$$

Change in internal energy

$$dU^* = dQ^* - p_a dV = T dS^* - p_a dV \qquad (18.25)$$

Change in internal energy in presence of reversible reactions

$$dU^* = T dS^* - p_a dV + \sum_i k_i \left(dn_i\right) \mu_i \qquad (18.26)$$

Equilibrium Coefficient Relation

Substitute (18.26) into (18.24)

$$dG^* = V dp_a - S^* dT + \sum_i k_i (dn_i) \mu_i \qquad (18.27)$$

Hold temperature and pressure constant

$$dG^* = \sum_i k_i (dn_i) \mu_i \qquad (18.28)$$

Chemical potential (μ_i)

Measure of intensity of a substance or the measure of the change in free energy per change in moles of a substance = partial molar free energy

$$\mu_i = \left(\frac{\partial G_i^*}{\partial n_i} \right)_{T, p_a} = \mu_i^o(T) + R^* T \ln\{a_i\} \qquad (18.29)$$

Equilibrium occurs when dG* = 0 in (18.28)

$$\sum_i k_i \nu_i \mu_i = 0 \qquad (18.30)$$

Equilibrium Coefficient Relation

Substitute (18.29) into (18.30)

$$\sum_i k_i \nu_i \mu_i^o(T_0) + R^* T_0 \sum_i k_i \nu_i \ln\{a_i\} = \sum_i k_i \nu_i \Delta_f G_i^o + R^* T_0 \ln \prod_i \{a_i\}^{k_i \nu_i} = 0$$

(18.31)

where

$$\sum_i k_i \nu_i \ln\{a_i\} = \ln \prod_i \{a_i\}^{k_i \nu_i}$$

Standard molal Gibbs free energy of formation

$$\Delta_f G_i^o = \mu_i^o(T_0)$$

Rearrange (18.31)

$$\prod_i \{a_i\}^{k_i \nu_i} = \exp\left(-\frac{1}{R^* T_0} \sum_i k_i \nu_i \Delta_f G_i^o\right) \qquad (18.32)$$

The right side of (18.32) is the equilibrium coefficient

$$K_{eq}(T_0) = \exp\left(-\frac{1}{R^* T_0} \sum_i k_i \nu_i \Delta_f G_i^o\right) \qquad (18.33)$$

Temperature Dependence of Equilibrium Constant

Van't Hoff equation (similar to Arrhenius equation)

$$\frac{\mathrm{d}\ln K_{eq}(T)}{\mathrm{d}T} = \frac{1}{R^{*}T^{2}} \sum_i k_i \nu_i \Delta_f \mathrm{H}_i \qquad (18.34)$$

Molal enthalpy of formation (J mole^{-1}) of a substance

$$\Delta_f \mathrm{H}_i \approx \Delta_f \mathrm{H}_i^{\mathrm{o}} + c_{p,i}^{\mathrm{o}}\left(T - T_0\right) \qquad (18.35)$$

$c_{p,i}^{\mathrm{o}}$ = Standard molal heat capacity at constant pressure

$\Delta_f \mathrm{H}_i^{\mathrm{o}}$ = standard molal nthalpy of formation

Combine (18.34) and (18.35) and write integral

$$\int_{T_0}^{T} \mathrm{d}\ln K_{eq}(T) = \int_{T_0}^{T} \frac{1}{R^{*}T^{2}} \sum_i k_i \nu_i \left[\Delta_f \mathrm{H}_i^{\mathrm{o}} + c_{p,i}^{\mathrm{o}}\left(T - T_0\right)\right] \mathrm{d}T$$

(18.36)

Integrate

$$K_{eq}(T) = K_{eq}(T_0)\exp\left\{-\sum_i k_i \nu_i \left[\frac{\Delta_f \mathrm{H}_i^{\mathrm{o}}}{R^{*}T_0}\left(\frac{T_0}{T} - 1\right) + \frac{c_{p,i}^{\mathrm{o}}}{R^{*}}\left(1 - \frac{T_0}{T} + \ln\frac{T_0}{T}\right)\right]\right\}$$

(18.37)

Forms of Equilibrium Equations

Henry's law

In a dilute solution, the pressure exerted by a gas at the gas-liquid interface is proportional to the molality of the dissolved gas in solution

Henry's law relationship

$$HNO_3(g) \rightleftharpoons HNO_3(aq)$$

Equilibrium coefficient relationship

$$\frac{\{HNO_3(aq)\}}{\{HNO_3(g)\}} = \frac{\mathbf{m}_{HNO_3(aq)}\gamma_{HNO_3(aq)}}{p_{HNO_3(g),s}} = K_{eq}(T) \quad \frac{\text{moles}}{\text{kg atm}} \tag{18.38}$$

Activity Coefficients

Activity coefficients (γ)

- Account for deviation from ideal behavior of a solution.

- Infinitely dilute solution, no deviations, $\gamma = 1$

- Relatively dilute solutions, deviations from Coulombic (electric) forces of attraction and repulsion $\gamma < 1$

- Concentrated solutions, deviations caused by ionic interactions, $\gamma < 1$ or $\gamma > 1$

Geometric mean binary activity coefficient

$$\gamma_{\pm} = \left(\gamma_{+}^{\nu_{+}} \gamma_{-}^{\nu_{-}}\right)^{1/(\nu_{+}+\nu_{-})} \qquad (18.40)$$

Rewrite

$$\gamma_{\pm}^{\nu_{+}+\nu_{-}} = \gamma_{+}^{\nu_{+}} \gamma_{-}^{\nu_{-}} \qquad (18.41)$$

Electrolyte Dissociation

Univalent electrolyte

$HNO_3(aq) \rightleftharpoons H^+ + NO_3^-$ ---> $\nu_+ = 1$ and $\nu_- = 1$

---> $z_+ = +1$ and $z_- = -1$

Multivalent electrolyte

$Na_2SO_4(s) \rightleftharpoons 2Na^+ + SO_4^{2-}$ ---> $\nu_+ = 2$ and $\nu_- = 1$

---> $z_+ = +1$ and $z_- = -2$

Symmetric electrolyte

$$\nu_+ = \nu_-$$

Charge balance requirement

$$z_+\nu_+ + z_-\nu_- = 0$$

Equilibrium Rate Expression

Table. 18.3.

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1. $HNO_3(aq) \rightleftharpoons H^+ + NO_3^-$

$$\frac{\{H^+\}\{NO_3^-\}}{\{HNO_3(aq)\}} = \frac{\mathbf{m}_{H^+}\gamma_{H^+}\mathbf{m}_{NO_3^-}\gamma_{NO_3^-}}{\mathbf{m}_{HNO_3(aq)}\gamma_{HNO_3(aq)}} = \frac{\mathbf{m}_{H^+}\mathbf{m}_{NO_3^-}\gamma^2_{H^+,NO_3^-}}{\mathbf{m}_{HNO_3(aq)}\gamma_{HNO_3(aq)}} = K_{eq}(T) \quad \frac{\text{moles}}{\text{kg}}$$

(18.39)

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2. $Na_2SO_4(s) \rightleftharpoons 2Na^+ + SO_4^{2-}$

$$\frac{\{Na^+\}^2\{SO_4^{2-}\}}{\{Na_2SO_4(s)\}} = \frac{\mathbf{m}^2_{Na^+}\gamma^2_{Na^+}\mathbf{m}_{SO_4^{2-}}\gamma_{SO_4^{2-}}}{1.0} = \mathbf{m}^2_{Na^+}\mathbf{m}_{SO_4^{2-}}\gamma^3_{2Na^+,SO_4^{2-}} = K_{eq}(T) \quad \frac{\text{moles}}{\text{kg}^3}$$

(18.42)

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3. $HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$

$$\frac{\{H^+\}^2\{SO_4^{2-}\}}{\{H^+\}\{HSO_4^-\}} = \frac{\mathbf{m}^2_{H^+}\gamma^2_{H^+}\mathbf{m}_{SO_4^{2-}}\gamma_{SO_4^{2-}}}{\mathbf{m}_{H^+}\gamma_{H^+}\mathbf{m}_{HSO_4^-}\gamma_{HSO_4^-}} = \frac{\mathbf{m}_{H^+}\mathbf{m}_{SO_4^{2-}}\gamma^3_{2H^+,SO_4^{2-}}}{\mathbf{m}_{HSO_4^-}\gamma^2_{H^+,HSO_4^-}} = K_{eq}(T) \quad \frac{\text{moles}}{\text{kg}}$$

(moles kg^{-1}) (18.43)

Equilibrium Rate Expression

4. $NH_3(g) + HNO_3(g) \rightleftharpoons NH_4^+ + NO_3^-$

$$\frac{\{NH_4^+\}\{NO_3^-\}}{\{NH_3(g)\}\{HNO_3(g)\}} = \frac{\mathbf{m}_{NH_4^+}\gamma_{NH_4^+}\mathbf{m}_{NO_3^-}\gamma_{NO_3^-}}{p_{NH_3(g),s}\,p_{HNO_3(g),s}} = \frac{\mathbf{m}_{NH_4^+}\mathbf{m}_{NO_3^-}\gamma^2_{NH_4^+,NO_3^-}}{p_{NH_3(g),s}\,p_{HNO_3(g),s}} = K_{eq}(T)\quad \frac{\text{moles}^2}{\text{kg}^2\,\text{atm}^2}$$

(18.44)

5. $NH_3(aq) + H_2O(aq) \rightleftharpoons NH_4^+ + OH^-$

$$\frac{\{NH_4^+\}\{OH^-\}}{\{NH_3(aq)\}\{H_2O(aq)\}} = \frac{\mathbf{m}_{NH_4^+}\gamma_{NH_4^+}\mathbf{m}_{OH^-}\gamma_{OH^-}}{\mathbf{m}_{NH_3(aq)}\gamma_{NH_3(aq)} \times f_r} = \frac{\mathbf{m}_{NH_4^+}\mathbf{m}_{OH^-}\gamma^2_{NH_4^+,OH^-}}{\mathbf{m}_{NH_3(aq)}\gamma_{NH_3(aq)} \times f_r} = K_{eq}(T)\quad \frac{\text{moles}}{\text{kg}}$$

(18.45)

Mean Binary Activity Coefficients

Pitzer's method

$$\ln \gamma^{0}_{12b} = Z_1 Z_2 f^{\gamma} + \mathbf{m}_{12} \frac{2\nu_1\nu_2}{\nu_1+\nu_2} B^{\gamma}_{12} + \mathbf{m}^{2}_{12} \frac{2(\nu_1\nu_2)^{3/2}}{\nu_1+\nu_2} C^{\gamma}_{12} \qquad (18.46)$$

$$f^{\gamma} = -0.392\left[\frac{\mathbf{I}^{1/2}}{1+1.2\mathbf{I}^{1/2}} + \frac{2}{1.2}\ln\left(1+1.2\mathbf{I}^{1/2}\right)\right] \qquad (18.47)$$

$$B^{\gamma}_{12} = 2\beta^{(1)}_{12} + \frac{2\beta^{(2)}_{12}}{4\mathbf{I}}\left[1 - e^{-2\mathbf{I}^{1/2}}\left(1+2\mathbf{I}^{1/2}-2\mathbf{I}\right)\right] \qquad (18.48)$$

Ionic strength of solution (moles kg^{-1})

Measure of the interionic effects resulting from attraction and repulsion among ions

$$\mathbf{I} = \frac{1}{2}\left(\sum_{i=1}^{N_C}\mathbf{m}_{2i-1}Z^{2}_{2i-1} + \sum_{i=1}^{N_A}\mathbf{m}_{2i}Z^{2}_{2i}\right) \qquad (18.49)$$

Mean Binary Activity Coefficients

Table. 18.2. Pitzer parameters for three electrolytes.

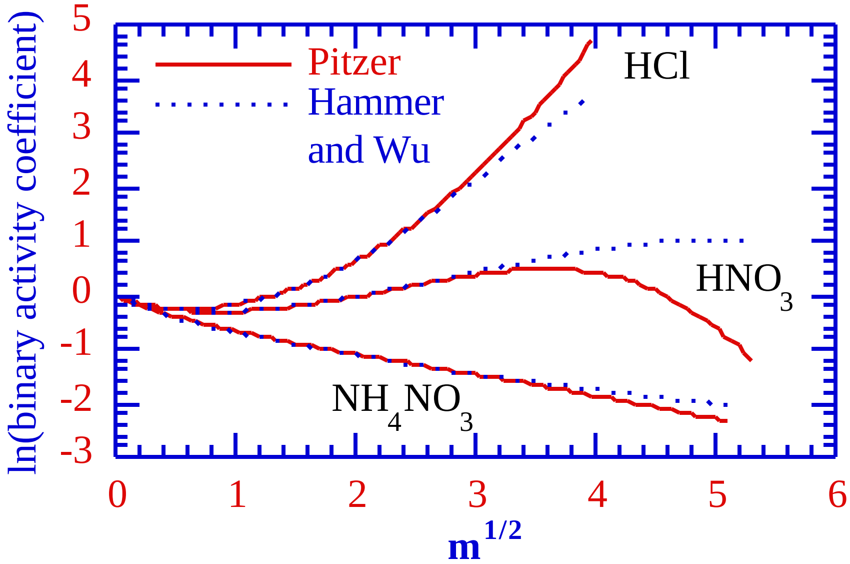
	$\beta_{12}^{(1)}$	$\beta_{12}^{(2)}$	C_{12}^{γ}
HCl	0.17750	0.2945	0.0012
HNO_3	0.1119	0.3206	0.0015
NH_4NO_3	-0.0154	0.112	-0.000045

Polynomial fit from data (valid to high molality)

$$\ln \gamma_{12b}^{0} = B_0 + B_1 \mathbf{m}_{12}^{1/2} + B_2 \mathbf{m}_{12} + B_3 \mathbf{m}_{12}^{3/2} + \ldots \qquad (18.51)$$

Mean Binary Activity Coefficients

Fig. 18.1. Comparison of measured (Hammer and Wu) and calculated (Pitzer) activity coefficient data



Equilibrium coefficient expression for hydrochloric acid

$$\frac{\mathbf{m}_{H^+}\mathbf{m}_{Cl^-}\gamma^2_{H^+,Cl^-}}{p_{HCl(g),s}} = 1.97 \times 10^6 \qquad (18.50)$$

Equilibrium coefficient expression for nitric acid

$$\frac{\mathbf{m}_{H^+}\mathbf{m}_{NO_3^-}\gamma^2_{H^+,NO_3^-}}{p_{HNO_3(g),s}} = 2.51 \times 10^6$$

Temperature Dependence of Mean Binary Activity Coefficients

Temperature dependent equation

$$\ln \gamma_{12b}(T) = \ln \gamma_{12b}^{0} \qquad (18.52)$$

$$+ \frac{T_L}{(\nu_1+\nu_2)R^* T_0}\left(\varphi_L + \mathbf{m}\frac{\partial \varphi_L}{\partial \mathbf{m}}\right) + \frac{T_C}{(\nu_1+\nu_2)R^*}\left(\varphi_{c_p} + \mathbf{m}\frac{\partial \varphi_{c_p}}{\partial \mathbf{m}} - \varphi_{c_p}^{o}\right)$$

Temperature-dependent parameters

$$T_L = \frac{T_0}{T} - 1 \qquad (18.53)$$

$$T_C = 1 + \ln\left(\frac{T_0}{T}\right) - \frac{T_0}{T}$$

Polynomial for relative apparent molal enthalpy

$$\varphi_L = U_1 \mathbf{m}^{1/2} + U_2 \mathbf{m} + U_3 \mathbf{m}^{3/2} + \ldots \qquad (18.54)$$

Polynomial for apparent molal heat capacity

$$\varphi_{c_p} = \varphi_{c_p}^{o} + V_1 \mathbf{m}^{1/2} + V_2 \mathbf{m} + V_3 \mathbf{m}^{3/2} + \ldots$$

$\gamma_{12b}(T)$	= binary activity coef. at temperature T
φ_L	= relative apparent molal enthalpy (J mole^{-1})
φ_{c_p}	= apparent molal heat capacity (J mole^{-1} K^{-1})
$\varphi_{c_p}^{o}$	= apparent molal heat capacity at infinite dilution

Temperature Dependence of Mean Binary Activity Coefficients

Combine (18.51) - (18.54) -->

$$\ln \gamma_{12b}(T) = F_0 + F_1 \mathbf{m}^{1/2} + F_2 \mathbf{m} + F_3 \mathbf{m}^{3/2} + \ldots \qquad (18.55)$$

Coefficients

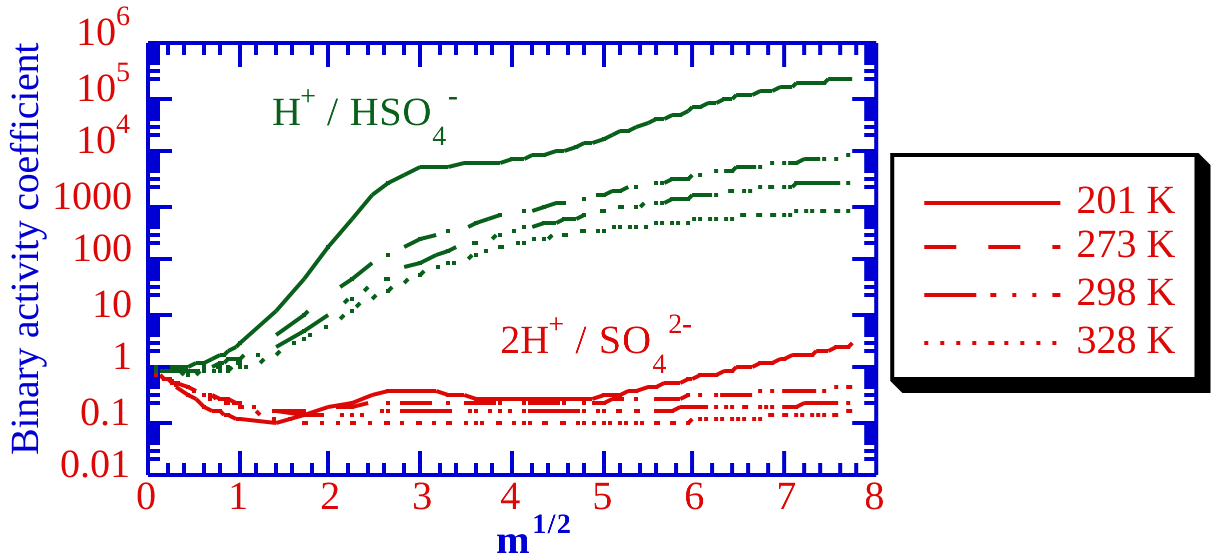
$$F_0 = B_0, \quad F_j = B_j + G_j T_L + H_j T_C \quad j = 1\ldots \qquad (18.56)$$

$$G_j = \frac{0.5(j+2)U_j}{(\nu_1 + \nu_2)R^* T_0} \qquad (18.57)$$

$$H_j = \frac{0.5(j+2)V_j}{(\nu_1 + \nu_2)R^*}$$

Sulfate and Bisulfate

Fig. 18.2. Binary activity coefficients of sulfate and bisulfate, each alone in solution. Results valid for 0 - 40 m.



Mean Mixed Activity Coefficients

Bromley's method

Binary activity coefficient of an electrolyte in a mixture

$$\log_{10}\gamma_{12m}(T) = -A_\gamma \frac{Z_1 Z_2 \mathbf{I}_m^{1/2}}{1+\mathbf{I}_m^{1/2}} + \frac{Z_1 Z_2}{Z_1+Z_2}\left(\frac{W_1}{Z_1}+\frac{W_2}{Z_2}\right) \qquad (18.58)$$

$$W_1 = Y_{21}\left(\log_{10}\gamma_{12b}(T) + A_\gamma \frac{Z_1 Z_2 \mathbf{I}_m^{1/2}}{1+\mathbf{I}_m^{1/2}}\right) + Y_{41}\left(\log_{10}\gamma_{14b}(T) + A_\gamma \frac{Z_1 Z_4 \mathbf{I}_m^{1/2}}{1+\mathbf{I}_m^{1/2}}\right) + \qquad (18.59)$$

$$W_2 = X_{12}\left(\log_{10}\gamma_{12b}(T) + A_\gamma \frac{Z_1 Z_2 \mathbf{I}_m^{1/2}}{1+\mathbf{I}_m^{1/2}}\right) + X_{32}\left(\log_{10}\gamma_{32b}(T) + A_\gamma \frac{Z_3 Z_2 \mathbf{I}_m^{1/2}}{1+\mathbf{I}_m^{1/2}}\right) + \cdots \qquad (18.60)$$

$$Y_{21} = \left(\frac{Z_1+Z_2}{2}\right)^2 \frac{\mathbf{m}_{2,m}}{\mathbf{I}_m} \qquad X_{12} = \left(\frac{Z_1+Z_2}{2}\right)^2 \frac{\mathbf{m}_{1,m}}{\mathbf{I}_m} \qquad (18.61)$$

Molalities of binary electrolyte found from

$$\mathbf{I}_m = \frac{1}{2}\left(\mathbf{m}_{1,b} Z_1^2 + \mathbf{m}_{2,b} Z_2^2\right) = \frac{1}{2}\left(\nu_+ \mathbf{m}_{12,b} Z_1^2 + \nu_- \mathbf{m}_{12,b} Z_2^2\right) \qquad (18.62)$$

Molalities of cation, anion alone in solution

$$\mathbf{m}_{1,b} = \nu_+ \mathbf{m}_{12,b} \qquad \mathbf{m}_{2,b} = \nu_- \mathbf{m}_{12,b}$$

Molality of binary electrolyte giving ionic strength of mixture

$$\mathbf{m}_{12,b} = \frac{2\,\mathbf{I}_m}{\nu_+ Z_1^2 + \nu_- Z_2^2} \qquad (18.63)$$