

## APPENDIX A

### Thermodynamic Calculations

#### ACTIVITY COEFFICIENTS

Extended Debye-Hückel Equation:

$$\log \gamma = - \frac{AZ^2\sqrt{I}}{1 + Ba\sqrt{I}} \quad (\text{A-1})$$

where:  $\gamma$  = activity coefficient

$I$  = ionic strength ( $1 \times 10^{-2} \text{M}$ )

$Z$  = charge of ion

$A = 1.82 \times 10^6 (\epsilon T)^{-1.5}$  where  $\epsilon$  = dielectric constant of water (Table A-1)

$B = 50.3 (\epsilon T)^{-0.5}$  (Table A-1)

$a$  = parameter for ion size (Table A-2)

Table A-1: Coefficients “A” and “B” for Extended Debye-Hückel Equation.

Temp (°C)	Temp (K)	$\epsilon$	A	B
5	278.15	86.30	0.489	0.325
25	298.15	78.85	0.505	0.328

Table A-2: Parameter “a” for Extended Debye-Hückel Equation.

Ion	a
H <sup>+</sup>	9
OH <sup>-</sup>	3
Fe <sup>+2</sup>	6
Ca <sup>+2</sup>	6
CO <sub>3</sub> <sup>-2</sup>	5
Fe <sup>+3</sup>	9
PO <sub>4</sub> <sup>-3</sup>	4

#### SOLUBILITY CORRECTIONS

van't Hoff Equation:

$$\ln \frac{K_2}{K_1} = \frac{\Delta H_r^\circ}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \quad (\text{A-2})$$

where:  $K_2$  and  $K_1$  are the solubility products at temperatures  $T_2$  and  $T_1$ , respectively

$\Delta H_r^\circ$  = enthalpy of reaction

$R$  = gas constant = 8.314 J/K/mole

The enthalpy of reaction is calculated by summing the heats of formation ( $\Delta H_f^\circ$ ) of the individual components.  $\Delta H_f^\circ$  values do vary with temperature, but can be considered constant over the range 5–35°C<sup>1</sup>.

1. Stumm, W. & Morgan, J.J. *Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters*. John Wiley & Sons, Inc, New York, NY (Third Edition, 1996).