CHEMICAL EQUILIBRIUM

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IONIC EQUILIBRIUM

$$aA + bB \rightleftharpoons cC + dD$$

$$K = \frac{(C)c \quad (D)d}{(A)_a \quad (B)_b}$$

$$A_X B_Y \rightleftharpoons xA^+ + yB^-$$

elektrolite activity $a = (a^{x+})(a^{y-})$

$\gamma = \frac{a}{m}$ γ = ionic activity coefficient

a = ionic activity

$a = \gamma\, m$ m = molality (m)

cation activity $ax^+ = \gamma^+ \; m^+$ anion $ay- = \gamma- \; m-$

activity coefficient cation $\gamma+ = \frac{a^+}{m+}$ Anion $\gamma- = \frac{a-}{m-}$

Ionic Activity, Molality, & Activity Coefficients

We can define single-ion activity coefficients…

$$a_+ = m_+ \gamma_+ \qquad a_- = m_- \gamma_-$$

Mean ionic activity becomes…

$$m_\pm^\nu \qquad \gamma_\pm^\nu$$

Mean ionic molality

Mean ionic activity coefficient

Table Activity and electrolytes

The relations between the activity of a strong electrolyte, its molality, and its mean ionic activity coefficient for various types of strong electrolytes.

Type	
1–1	
KCl(aq)	$a_2 = a_+ a_- = a_\pm^2 = m_\pm^2 \gamma_\pm^2 = (m_+)(m_-)\gamma_\pm^2 = m^2 \gamma_\pm^2$
1–2	
$CaCl_2$(aq)	$a_2 = a_+ a_-^2 = a_\pm^3 = m_\pm^3 \gamma_\pm^3 = (m_+)(m_-)^2\gamma_\pm^3 = (m)(2m)^2\gamma_\pm^3 = 4m^3 \gamma_\pm^3$
1–3	
$LaCl_3$(aq)	$a_2 = a_+ a_-^3 = a_\pm^4 = m_\pm^4 \gamma_\pm^4 = (m_+)(m_-)^4\gamma_\pm^4 = (m)(3m)^3\gamma_\pm^4 = 27m^4 \gamma_\pm^4$
2–1	
Na_2SO_4(aq)	$a_2 = a_+^2 a_- = a_\pm^3 = (m_+)^2(m_-)\gamma_\pm^3 = (2m)^2(m)\gamma_\pm^3 = 4m^3 \gamma_\pm^3$
2–2	
$ZnSO_4$(aq)	$a_2 = a_+ a_- = a_\pm^2 = m_\pm^2 \gamma_\pm^2 = (m_+)(m_-)\gamma_\pm^2 = m^2 \gamma_\pm^2$
3–1	
$Na_3Fe(CN)_6$(aq)	$a_2 = a_+^3 a_- = a_\pm^4 = m_\pm^4 \gamma_\pm^4 = (m_+)^3(m_-)\gamma_\pm^4 = (3m)^3(m)\gamma_\pm^4 = 27m^4 \gamma_\pm^4$

CHEMICAL POTENTIAL

$\mu = \mu^o + RT \ln a$, $a = \dfrac{\gamma\ m}{m^0}$

HENRY LAW,

$\gamma \longrightarrow 1$, and $a \longrightarrow m/mo$ than $m \longrightarrow 0$

So $\mu = \mu^o + RT \ln \dfrac{m}{m^0} + RT \ln \gamma$

$\mu = \mu^o + RT \ln \gamma$

Mean ionic activity coefficient

$G = \mu_+ + \mu_-$ $\mu_+ = \mu^o_+ + RT \ln \gamma_+$

$G = G^o + RT \ln \gamma$

$G = \mu^o_+ + \mu^o_- + RT \ln \gamma_+ + RT \ln \gamma_-$

$G = G^o + RT \ln \gamma_+ \gamma_-$

$$A_X B_Y \rightleftharpoons xA^+ + yB-$$

$$\gamma_{\pm} = (\gamma^X_+ \cdot \gamma^Y_-)^{1/s}$$

$$s = x + y$$

$$G = X\,\mu_+ + Y\,\mu_-$$

$$G = G^o + X\,RT\ln\gamma_+ + Y\,RT\ln\gamma_-$$

$$\mu = \mu o + RT\ln\gamma_{\pm}$$

$$G^o = \mu^o_+ + \mu^o_-$$

Debye-Hückel Theory

Debye-Hückel Theory: Assumes ions are point ions (no radii) with purely Coulombic interactions and activity coefficients depend only on the ion charges and the solvent properties.

$$\ln \gamma_{\pm} = -\left| z_{+} z_{-} \right| A I_c^{1/2}$$

$$I_c = \frac{1}{2} \sum_{j=1}^{s} z_j^2 c_j$$

$$A = \left(2\pi N_A\right)^{1/2} \left(\frac{e}{4\pi\varepsilon_0 \varepsilon_r k_B T} \right)^{3/2}$$

Ionic Strength

IONIC STRENGTH, I

$$I = \tfrac{1}{2} \Sigma\, m_i \;\; Z_i^2$$

Where c_i = concentration of the i^{th} species z_i = charge for all ions in solution

DEBYE HUCKEL LAW

$\text{Log}\, \gamma\underline{+} = -A\, |\, Z_{+.}\;\; Z_{-}\, |\, \sqrt{I}$ A = 0,509 mol/kg

Ionic Strength Example

Find the ionic strength of

1. $CaCl_2$ 1 mol/kg

   $I = ½ (mCa^{2} + x\ 2^{2}) + (2x\ mCl- x\ 1^{2})$

   $I = ½ (1x\ 4) + (2 x 1) = 3$

2. NaCl 0,5 mol/kg

   $I = ½ (mNa+ x\ 1^{2}) + (mCl- x\ 1^{2})$

   $I = ½ (1/2 x 1) + (½ x 1) = ½$

Determine mean ionic activity coefficient :

1. HCl 0,01 mol/kg

$I = \frac{1}{2} \Sigma\, m_i\ Zi^2$

$I = \frac{1}{2}((\ 0,01\ (1)^2\ + 0,01\ (1)^2\ )$

$I = 0,01$

$\log \gamma\underline{+} = -0,509\ Z_A.\ Z_B\ \sqrt{I}$

$= 0,5\ (1)\ (1)\ \sqrt{0,01}$

$= 0,05$

$\gamma\underline{+} = 0,889$ table 0,9

2. KCl 0,001 mol/kg at 25^o C

$I = \frac{1}{2} \Sigma\, m_i\ Zi^2$

$I = \frac{1}{2}((\ 0,001\ (1)^2\ + 0,001\ (1)^2\ )$

$I = 0,001$

$\log \gamma\underline{+} = -0,509\ Z_A.\ Z_B\ \sqrt{I}$

$= 0,509\ (1)\ (1)\ \sqrt{0,001}$

$= 0,0161$

$\gamma\underline{+}$ = 0,964 **table 0,966**

ACTIVITY COEFFICIENTS

To account for the effect of ionic strength, concentrations are replaced by activities.

Activity of C → $$A_C = [C]\gamma_C$$ ← Activity coefficient

And general form of equilibrium constant is:

$$K = \frac{A_C^{\,c} A_D^{\,d}}{A_A^{\,a} A_B^{\,b}} = \frac{[C]^c \gamma_C^{\,c} [D]^d \gamma_D^{\,d}}{[A]^a \gamma_A^{\,a} [B]^b \gamma_B^{\,b}}$$

THANK YOU