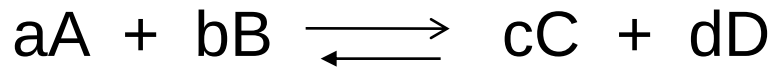


CHEMICAL EQUILIBRIUM

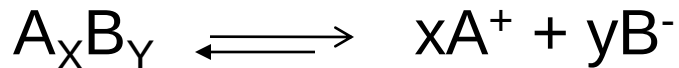
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IONIC EQUILIBRIUM



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



elektrolite activity

$$\gamma = \frac{a}{m}$$

$$a = \gamma m$$

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

γ = ionic activity coefficient

a = ionic activity

m = molality (m)

cation activity $a_{x^+} = \gamma^+ m^+$

anion $a_{y^-} = \gamma^- m^-$

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

Anion $\gamma^- = \frac{a^-}{m^-}$

Ionic Activity, Molality, & Activity Coefficients

We can define single-ion activity coefficients...

$$a_{+} = m_{+} \gamma_{+}$$

$$a_{-} = m_{-} \gamma_{-}$$

Mean ionic activity becomes...

$$m_{\pm}^{\nu}$$

Mean ionic molality

$$\gamma_{\pm}^{\nu}$$

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)	$a_2 = a_+ a_-^3 = a_{\pm}^4 = m_{\pm}^4 \gamma_{\pm}^4 = (m_+)(m_-)^3 \gamma_{\pm}^4 = (m)(3m)^3 \gamma_{\pm}^4 = 27m^4 \gamma_{\pm}^4$
2-1	
Na ₂ SO 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 ₃ Fe(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

$$\mu = \mu^{\circ} + RT \ln a \quad ,$$

$$a = \frac{\gamma m}{m^{\circ}}$$

HENRY LAW,

$\gamma \longrightarrow 1$, and $a \longrightarrow m/m^{\circ}$ than $m \longrightarrow 0$

So
$$\mu = \mu^{\circ} + RT \ln \frac{m}{m^{\circ}} + RT \ln \gamma$$

$$\mu = \mu^{\circ} + RT \ln \gamma$$

Mean ionic activity coefficient

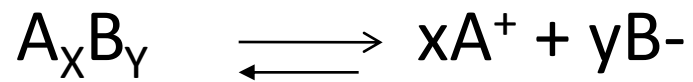
$$G = \mu_{+} + \mu_{-}$$

$$\mu_{+} = \mu^{\circ}_{+} + RT \ln \gamma_{+}$$

$$G = G^{\circ} + RT \ln \gamma$$

$$G = \mu^{\circ}_{+} + \mu^{\circ}_{-} + RT \ln \gamma_{+} + RT \ln \gamma_{-}$$

$$G = G^{\circ} + RT \ln \gamma_{+} \gamma_{-}$$



$$\gamma_{\pm} = (\gamma_+^x \cdot \gamma_-^y)^{1/s}$$

$$s = x + y$$

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

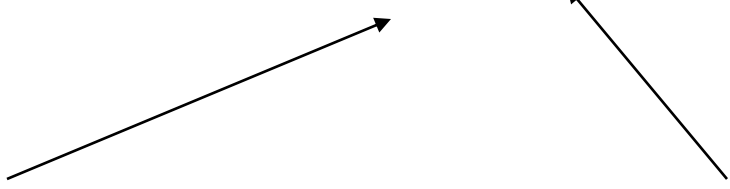
$$G = G^\circ + X RT \ln \gamma_+ + Y RT \ln \gamma_-$$

$$\mu = \mu^\circ + RT \ln \gamma_{\pm}$$

$$G^\circ = \mu_+^\circ + \mu_-^\circ$$

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.

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


The diagram shows two arrows originating from below. One arrow points from the definition of A to the 'A' term in the equation. The other arrow points from the formula for I_c to the 'I_c' term in the equation.

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

$$A = (2\pi N_A)^{1/2} \left(\frac{e}{4\pi\epsilon_0\epsilon_r k_B T} \right)^{3/2}$$

Ionic Strength

IONIC STRENGTH, I

$$I = \frac{1}{2} \sum m_i z_i^2$$

Where c_i = concentration of the i^{th} species
ions in solution

z_i = charge for all

DEBYE HUCKEL LAW

$$\text{Log } \gamma_{\pm} = -A |z_+ z_-| \sqrt{I}$$

$$A = 0,509 \text{ mol/kg}$$

Ionic Strength Example

Find the ionic strength of

1. CaCl_2 1 mol/kg

$$I = \frac{1}{2} (m_{\text{Ca}^{2+}} \times 2^2) + (2 \times m_{\text{Cl}^-} \times 1^2)$$

$$I = \frac{1}{2} (1 \times 4) + (2 \times 1) = 3$$

2. NaCl 0,5 mol/kg

$$I = \frac{1}{2} (m_{\text{Na}^+} \times 1^2) + (m_{\text{Cl}^-} \times 1^2)$$

$$I = \frac{1}{2} (1/2 \times 1) + (1/2 \times 1) = 1/2$$

Determine mean ionic activity coefficient :

1. HCl 0,01 mol/kg

$$I = \frac{1}{2} \sum m_i Z_i^2$$

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

$$I = 0,01$$

$$\begin{aligned} \log \gamma_{\pm} &= -0,509 Z_A \cdot Z_B \sqrt{I} \\ &= 0,5 (1) (1) \sqrt{0,01} \\ &= 0,05 \end{aligned}$$

$$\gamma_{\pm} = 0,889 \quad \text{table 0,9}$$

2. KCl 0,001 mol/kg at 25° C

$$I = \frac{1}{2} \sum m_i Z_i^2$$

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

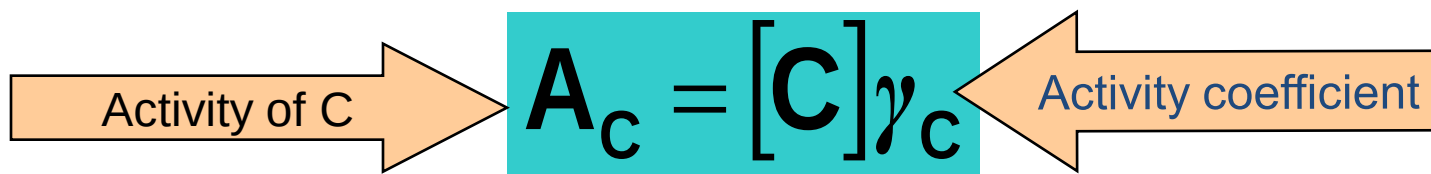
$$I = 0,001$$

$$\begin{aligned} \log \gamma_{\pm} &= -0,509 Z_A \cdot Z_B \sqrt{I} \\ &= 0,509 (1) (1) \sqrt{0,001} \\ &= 0,0161 \end{aligned}$$

$$\gamma_{\pm} = 0,964 \quad \text{table 0,966}$$

ACTIVITY COEFFICIENTS

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



The diagram illustrates the equation $A_c = [C]\gamma_c$ within a light blue rectangular box. An orange arrow points from the left towards the box, labeled "Activity of C". Another orange arrow points from the right towards the box, labeled "Activity coefficient".

$$A_c = [C]\gamma_c$$

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