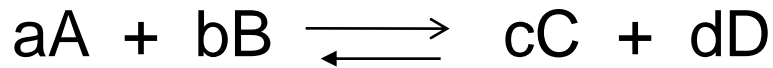


# CHEMICAL EQUILIBRIUM

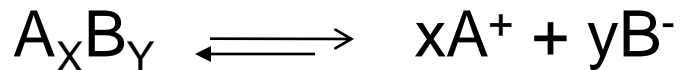
**NANIK DWI NURHAYATI, S.SI,M.SI**

- <http://nanikdn.staff.uns.ac.id>
- E-mail : nanikdn@uns.ac.id

# IONIC EQUILIBRIUM



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



elektrolite activity

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

$$a = \gamma m$$

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

$\gamma$  = 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 <sub>2</sub> (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 <sub>3</sub> (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 <sub>2</sub> SO <sub>4</sub> (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 <sub>4</sub> (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 <sub>3</sub> Fe(CN) <sub>6</sub> (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 
$$\mu = \mu^\circ + RT \ln \frac{m}{m^\circ} + RT \ln \gamma$$

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

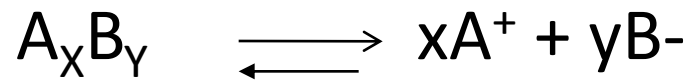
## Mean ionic activity coefficient

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

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

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

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



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

$$s = x + y$$

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

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

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

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

## DEBYE HUCKEL LAW

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

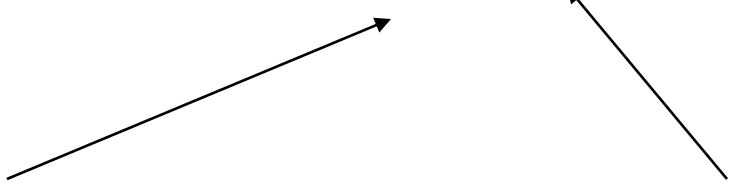
$$A = 0,509 \text{ mol/kg}$$

# 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.

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

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



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

Ionic Strength

# IONIC STRENGTH, I

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

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

$z_i$  = charge for all



# Ionic Strength Example

Find the ionic strength of

1.  $\text{CaCl}_2$  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.  $\text{NaCl}$  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 relationship between activity, concentration, and activity coefficient. It features a central cyan box containing the equation  $A_c = [C] \gamma_c$ . To the left of this box is an orange arrow pointing right, labeled "Activity of C". To the right of the box is another orange arrow pointing left, 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**