

## CHAPTER IV

### APPLICATION OF GRAPH TO STRONG ELECTROLYTES SYSTEM

#### Dilute Solutions of Strong Electrolytes $A^+B^-$ Dissolve in Solvent C

The partition function of the mixture A, B, and C with interaction potential between molecules of type A and B only can be defined as

$$Q_C = Q_T \frac{Q_N}{N_A! N_B!} \quad \text{---(4.1)}$$

where

$$Q_T = \left( \frac{2\pi m_A kT}{h^2} \right)^{3/2 N_A} \left( \frac{2\pi m_B kT}{h^2} \right)^{3/2 N_B} \left( \frac{2\pi m_C kT}{h^2} \right)^{3/2 N_C}$$

$$Q_N = Q_{\text{latt.}} Q_{\text{Vib}}$$

$Q_{\text{Vib}}$  can neglect because it is unaffected at normal temperature, therefore, we have

$$Q_N = \int \dots \int e^{-\beta U} d\vec{r}_1 \dots d\vec{r}_{N_A} d\vec{r}'_1 \dots d\vec{r}'_{N_B} \quad \text{---(4.2)}$$

where  $\beta = 1/kT$

Equation (4.1) becomes

$$Q_C = \left( \frac{2\pi m_A kT}{h^2} \right)^{3/2 N_A} \left( \frac{2\pi m_B kT}{h^2} \right)^{3/2 N_B} \left( \frac{2\pi m_C kT}{h^2} \right)^{3/2 N_C} \frac{Q_N}{N_A! N_B!} \quad \text{---(4.3)}$$

For one type of molecule, we have Eq.(3.10)

$$Q_N = V^N \exp \left[ N \sum_{k=1}^{\infty} \rho^k \frac{\beta_{k+1}}{k+1} \right] \quad \text{---(4.4)}$$

For A,B interacting molecules, we have

$$N = N_A + N_B, \quad \rho = \frac{N_A + N_B}{V}$$

Thus,

$$Q_N = V^{N_A + N_B} \exp \left[ (N_A + N_B) \sum_{k=1}^{\infty} \rho^k \frac{\beta_{k+1}}{k+1} \right] \quad \text{---(4.5)}$$

By the definition of the irreducible cluster integral, we have

$$\beta_k = \frac{1}{k!V} \int \dots \int \sum_{k+1 \geq i > j \geq 1} \mathbb{H} f_{ij} d\vec{r}_1 \dots d\vec{r}_{k+1} \quad \text{---(4.6)}$$

For 2-particles,

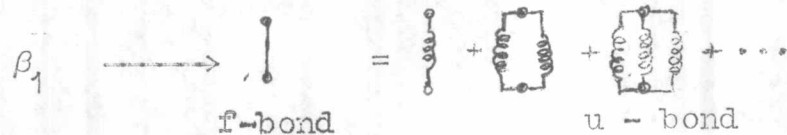
$$\begin{aligned} \beta_1 &= \frac{1}{V} \iint f_{12} d\vec{r}_1 d\vec{r}_2 \\ &= \iint (e^{-\beta u_{12}} - 1) dr_{12} \end{aligned} \quad \text{---(4.7)}$$

where  $\beta = 1/kT$ ,  $u_{12} = u(r_{12}) = \frac{z_1 z_2 e^2}{\epsilon r_{12}}$

Consider the term  $f_{12}$ ,

$$f_{12} = (e^{-\beta u_{12}} - 1) = -\beta u_{12} + \frac{1}{2}(\beta u_{12})^2 - \frac{1}{3!}(\beta u_{12})^3 + \dots \quad \text{---(4.8)}$$

Eq.(4.8) we can write in diagram



But we have found that the higher order terms of u-bond have negligible values in comparison with the leading term. So we define  $\beta_{ko}$  for u-bond with neglecting higher terms. Therefore, we have

$$\beta_k \equiv \beta_{ko} \quad (\text{neglecting higher order terms}) \quad \text{---(4.9)}$$

Next, we define

$$\beta_{ko} = \sum_{\alpha_1, \dots, \alpha_{k+1}} x_{\alpha_1} x_{\alpha_2} \dots x_{\alpha_{k+1}} \beta_{ko}^{\alpha_1 \alpha_2 \dots \alpha_{k+1}} \quad \text{---(4.10)}$$

$$\beta_{10} = \sum_{\alpha_1, \alpha_2} x_{\alpha_1} x_{\alpha_2} \beta_{10}^{\alpha_1 \alpha_2}$$

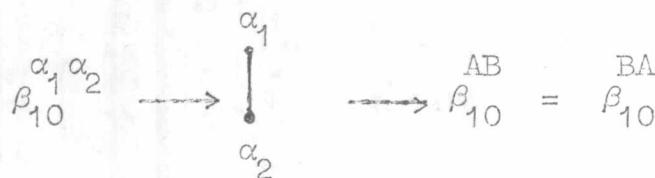
For A, B interacting molecules, we have

$$x_A = \frac{N_A}{N_A + N_B}, \quad x_B = \frac{N_B}{N_A + N_B}$$

Thus, we obtain

$$\beta_{10} = x_A^2 \beta_{10}^{AA} + x_A x_B (\beta_{10}^{AB} + \beta_{10}^{BA}) + x_B^2 \beta_{10}^{BB}$$

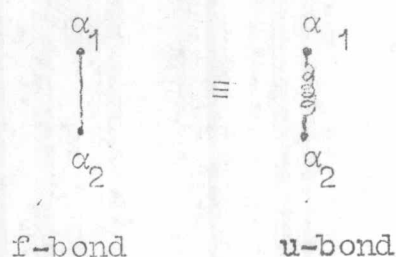
by graph



so

$$\beta_{10} = x_A^2 \beta_{10}^{AA} + 2x_A x_B \beta_{10}^{AB} + x_B^2 \beta_{10}^{BB} \quad \text{---(4.11)}$$

From Eq.(4.9), we have



Therefore, we can write

$$\beta_{10}^{AA} = -\frac{\beta}{V} \int \int u_{AA} d\vec{r}_1 d\vec{r}_2 = -\beta \int \frac{e^2 z_A^2}{\epsilon r_{12}} dr_{12}$$

$$\beta_{10}^{AB} = -\frac{\beta}{V} \int \int u_{AB} d\vec{r}_1 d\vec{r}_2 = -\beta \int \frac{e^2 z_A z_B}{\epsilon r_{12}} dr_{12}$$

$$\beta_{10}^{BB} = -\frac{\beta}{V} \int \int u_{BB} d\vec{r}_1 d\vec{r}_2 = -\beta \int \frac{e^2 z_B^2}{\epsilon r_{12}} dr_{12}$$

Equation (4.11) becomes

$$\beta_{10} = -\frac{\beta e^2}{\epsilon} (x_A^2 z_A^2 + 2x_A x_B z_A z_B + x_B^2 z_B^2) \int \frac{1}{r_{12}} dr_{12}$$

$$= -\frac{\beta e^2}{\epsilon} (x_A z_A + x_B z_B)^2 \int \frac{1}{r_{12}} dr_{12} \quad \text{---(4.12)}$$

By electroneutrality, we have

$$x_A z_A + x_B z_B = 0$$

Therefore, we obtain

$$\beta_{10} = 0 \quad \text{---(4.13)}$$

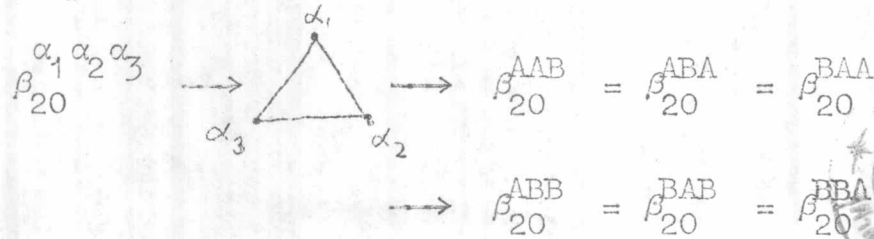
Next, we consider  $\beta_{20}$ ,

$$\beta_{20} = \sum_{\alpha_1 \alpha_2 \alpha_3} x_{\alpha_1} x_{\alpha_2} x_{\alpha_3} \beta_{20}^{\alpha_1 \alpha_2 \alpha_3}$$

For A, B interacting molecules, we have

$$\beta_{20} = x_A^3 \beta_{20}^{AAA} + x_A^2 x_B (\beta_{20}^{AAB} + \beta_{20}^{ABA} + \beta_{20}^{BAA}) \\ + x_A x_B^2 (\beta_{20}^{ABB} + \beta_{20}^{BAB} + \beta_{20}^{BBA}) + x_B^3 \beta_{20}^{BBB}$$

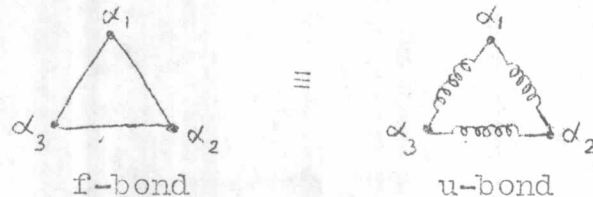
but by graph



so

$$\beta_{20} = x_A^3 \beta_{20}^{AAA} + 3x_A^2 x_B \beta_{20}^{AAB} + 3x_A x_B^2 \beta_{20}^{ABB} + x_B^3 \beta_{20}^{BBB} \quad (4.14)$$

From Eq. (4.9), we have



Therefore, we can write

$$\begin{aligned} \beta_{20}^{AAA} &= \frac{(-\beta)^3}{2V} \iiint u_{AA}(r_{12}) u_{AA}(r_{23}) u_{AA}(r_{31}) d\bar{r}_1 d\bar{r}_2 d\bar{r}_3 \\ &= \frac{(-\beta)^3}{2V} z_A^6 \iiint \left( \frac{e^2}{\epsilon r_{12}} \right) \left( \frac{e^2}{\epsilon r_{23}} \right) \left( \frac{e^2}{\epsilon r_{31}} \right) d\bar{r}_1 d\bar{r}_2 d\bar{r}_3 \\ \beta_{20}^{AAB} &= \frac{(-\beta)^3}{2V} z_A^4 z_B^2 \iiint \left( \frac{e^2}{\epsilon r_{12}} \right) \left( \frac{e^2}{\epsilon r_{23}} \right) \left( \frac{e^2}{\epsilon r_{31}} \right) d\bar{r}_1 d\bar{r}_2 d\bar{r}_3 \\ \beta_{20}^{ABB} &= \frac{(-\beta)^3}{2V} z_A^2 z_B^4 \iiint \left( \frac{e^2}{\epsilon r_{12}} \right) \left( \frac{e^2}{\epsilon r_{23}} \right) \left( \frac{e^2}{\epsilon r_{31}} \right) d\bar{r}_1 d\bar{r}_2 d\bar{r}_3 \\ \beta_{20}^{BBB} &= \frac{(-\beta)^3}{2V} z_B^6 \iiint \left( \frac{e^2}{\epsilon r_{12}} \right) \left( \frac{e^2}{\epsilon r_{23}} \right) \left( \frac{e^2}{\epsilon r_{31}} \right) d\bar{r}_1 d\bar{r}_2 d\bar{r}_3 \end{aligned}$$

Equation (4.14) becomes

$$\beta_{20} = \frac{(-\beta)^3}{2V} (x_A z_A^2 + x_B z_B^2)^3 \iiint \left( \frac{e^2}{\epsilon r_{12}} \right) \left( \frac{e^2}{\epsilon r_{23}} \right) \left( \frac{e^2}{\epsilon r_{31}} \right) d\bar{r}_1 d\bar{r}_2 d\bar{r}_3 \quad (4.15)$$

By induction, we obtain

$$\beta_{k0} = \frac{(-\beta)^{k+1}}{2V} (x_A z_A^2 + x_B z_B^2)^{k+1} \int \dots \int \left( \frac{e^2}{\epsilon r_{12}} \right) \dots \left( \frac{e^2}{\epsilon r_{k+1,1}} \right) d\bar{r}_1 \dots d\bar{r}_{k+1} \quad (4.16)$$

or

$$\beta_{k0} = \frac{(-\beta)^{k+1}}{2V} \left( \sum x_{\alpha_1} x_{\alpha_2} \dots x_{\alpha_{k+1}} z_{\alpha_1}^2 z_{\alpha_2}^2 \dots z_{\alpha_{k+1}}^2 \right) \times \int \dots \int \left( \frac{e^2}{\epsilon r_{12}} \right) \dots \left( \frac{e^2}{\epsilon r_{k+1,1}} \right) d\bar{r}_1 \dots d\bar{r}_{k+1} \quad (4.17)$$

By Fourier transform,

$$\begin{aligned} & \int \dots \int \left( \frac{e^2}{\epsilon r_{12}} \right) \dots \left( \frac{e^2}{\epsilon r_{k+1,1}} \right) d\bar{r}_1 \dots d\bar{r}_{k+1} \\ &= \frac{V}{(2\pi)^3} \int \left[ (2\pi)^{3/2} \left( \frac{2}{\pi} \right)^{1/2} \left( \frac{e^2}{\epsilon p^2} \right) \right]^{k+1} d\bar{p} \quad (4.18) \end{aligned}$$

Thus,

$$\beta_{k0} = \frac{(-\beta)^{k+1}}{2} (x_A z_A^2 + x_B z_B^2)^{k+1} \cdot \left( \frac{1}{2\pi} \right)^3 \int \left[ \frac{4\pi e^2}{\epsilon p^2} \right]^{k+1} d\bar{p} \quad (4.19)$$

We now consider only ring without additional line for  $Q_N$ ,

therefore, we can replace  $\beta_k$  with  $\beta_{k0}$ , Eq.(4.5) becomes

$$Q_N = V^{N_A + N_B} \exp \left[ (N_A + N_B) \sum_{k=1}^{\infty} \rho^k \frac{\beta_{k0}}{k+1} \right] \quad (4.20)$$

$$\text{Let } S(\rho') = \sum_{k=1}^{\infty} \beta_{k0} \rho'^k \quad (4.21)$$

$$\int_0^{\rho} S(\rho') d\rho' = \sum_{k=1}^{\infty} \beta_{k0} \frac{\rho^{k+1}}{k+1}$$

$$\sum_{k=1}^{\infty} \beta_{k0} \frac{\rho^k}{k+1} = \frac{1}{\rho} \int_0^{\rho} S(\rho') d\rho' \quad \text{---(4.22)}$$

Substitute Eq.(4.22) in Eq.(4.20), we obtain

$$Q_N = V^{N_A+N_B} \exp\left[\frac{(N_A+N_B)}{\rho} \int_0^{\rho} S(\rho') d\rho'\right] \quad \text{---(4.23)}$$

By substituting  $\beta_{k0}$  from Eq.(4.19) in Eq.(4.21), we have

$$S(\rho') = \sum_{k=1}^{\infty} \rho'^k \frac{(-\beta)^{k+1}}{2} (x_A z_A^2 + x_B z_B^2)^{k+1} \left(\frac{1}{2\pi}\right)^3 \int \left[ \frac{4\pi e^2}{\epsilon p^2} \right]^{k+1} d\bar{p}$$

$$= \frac{\rho'}{2(2\pi)^3} \left[ (-\beta)(x_A z_A^2 + x_B z_B^2) \left(\frac{4\pi e^2}{\epsilon p^2}\right) \right]^2 \times$$

$$\int \sum_{k=1}^{\infty} \left[ (-\beta)(x_A z_A^2 + x_B z_B^2) \left(\frac{4\pi e^2}{\epsilon p^2}\right) \right]^{k-1} \rho'^{k-1} d\bar{p}$$

$$\text{Let } a = \left[ (-\beta)(x_A z_A^2 + x_B z_B^2) \left(\frac{4\pi e^2}{\epsilon p^2}\right) \right]$$

$$S(\rho') = \frac{\rho' a^2}{2(2\pi)^3} \int \sum_{k=1}^{\infty} a^{k-1} \rho'^{k-1} d\bar{p}$$

$$= \frac{\rho' a^2}{2(2\pi)^3} \int \sum_{k=0}^{\infty} a^k \rho'^k d\bar{p}$$

$$= \frac{\rho' a^2}{2(2\pi)^3} \int \frac{1}{1-\rho' a} d\bar{p} \quad \text{---(4.24)}$$

Use symmetrical spherical coordinate

$$d\bar{p} = 4\pi p^2 dp,$$

equation (4.24) becomes

$$\begin{aligned}
 S(\rho') &= \frac{\rho' a^2}{2(2\pi)^3} \int_0^\infty \frac{1}{1-\rho' a} \cdot 4\pi p^2 dp \\
 &= \frac{4\rho' \beta^2 e^4 (x_A z_A^2 + x_B z_B^2)^2}{\epsilon^2} \int_0^\infty \frac{1}{p^2 + \rho' \beta (x_A z_A^2 + x_B z_B^2) \left(\frac{4\pi e^2}{\epsilon}\right)} \cdot dp \\
 S(\rho') &= \left[ \frac{\beta e^2}{\epsilon} (x_A z_A^2 + x_B z_B^2) \right]^{3/2} \frac{1}{\pi^2} \rho'^{1/2} \quad \text{-----(4.25)}
 \end{aligned}$$

Substitute  $S(\rho')$  in Eq.(4.23), we obtain

$$\begin{aligned}
 Q_N &= V^{N_A+N_B} \exp \left[ \frac{(N_A+N_B)}{\rho} \left\{ \frac{\beta e^2}{\epsilon} (x_A z_A^2 + x_B z_B^2) \right\}^{3/2} \frac{1}{\pi^2} \int_0^\rho \rho'^{1/2} d\rho' \right] \\
 &= V^{N_A+N_B} \exp \left[ \frac{2}{3} (N_A+N_B) \left\{ \frac{\beta e^2}{\epsilon} (x_A z_A^2 + x_B z_B^2) \right\}^{3/2} \frac{1}{\pi^2} \rho^{1/2} \right] \quad \text{-----(4.26)}
 \end{aligned}$$

or

$$Q_N = V^{N_A+N_B} \exp \left[ \frac{2}{3} (N_A+N_B) \left\{ \frac{\beta e^2}{\epsilon} (N_A z_A^2 + N_B z_B^2) \right\}^{3/2} \frac{\pi^2}{V^{1/2}} \right] \quad \text{-----(4.27)}$$

where

$$\rho = \frac{N}{V}, \quad x_A = \frac{N_A}{N}, \quad x_B = \frac{N_B}{N}, \quad N = N_A + N_B.$$

Consider the partition function of the mixture A,B,C from

Eq.(4.3) and substitute  $Q_N$  from Eq.(4.27), therefore

$$\begin{aligned}
 Q_C &= \left( \frac{2\pi m_A kT}{h^2} \right)^{3/2 N_A} \left( \frac{2\pi m_B kT}{h^2} \right)^{3/2 N_B} \left( \frac{2\pi m_C kT}{h^2} \right)^{3/2 N_C} \cdot \frac{V^{N_A+N_B}}{N_A! N_B!} \times \\
 &\quad \exp \left[ \frac{2}{3} \left\{ \frac{\beta e^2}{\epsilon} (N_A z_A^2 + N_B z_B^2) \right\}^{3/2} \times \frac{\pi^2}{V^{1/2}} \right] \quad \text{-----(4.28)}
 \end{aligned}$$

From thermodynamics, the Helmholtz free energy is defined by

$$A = -k T \ln Q_C$$

Thus,



$$\begin{aligned}
 A = & -kT \left[ \ln \left\{ \left( \frac{2\pi m_A kT}{h^2} \right)^{3/2 N_A} \left( \frac{2\pi m_B kT}{h^2} \right)^{3/2 N_B} \left( \frac{2\pi m_C kT}{h^2} \right)^{3/2 N_C} \right\} \right] \\
 & - \frac{2}{3} kT \frac{\pi^{1/2}}{V^{1/2}} \left[ \frac{\beta e^2}{\epsilon} (N_A z_A^2 + N_B z_B^2) \right]^{3/2} - kT \left[ (N_A + N_B) \ln V - \ln N_A! N_B! \right]
 \end{aligned}
 \tag{4.29}$$

The first term is the kinetic energy term, the second term is interacting term, the third term is non interacting term.

$$\text{Let } A = A' + A''$$

$A' \rightarrow$  kinetic energy term + non interacting term

$A'' \rightarrow$  interacting term

Consider the interacting term, from thermodynamics, the chemical potential is defined by

$$\mu_i = \left( \frac{\partial A}{\partial N_i} \right)_{V,T} = kT \ln \gamma_i \tag{4.30}$$

where  $\gamma_i$  is called the activity coefficient.

Therefore, we have

$$\begin{aligned}
 \mu_A'' & = \left( \frac{\partial A''}{\partial N_A} \right)_{V,T} = kT \ln \gamma_A \\
 \ln \gamma_A & = -\pi^{1/2} \left( \frac{\beta e^2}{\epsilon} \right)^{3/2} \left( \frac{N_A z_A^2 + N_B z_B^2}{V} \right)^{1/2} z_A^2
 \end{aligned}
 \tag{4.31}$$

$$\begin{aligned}
 \mu_B'' & = \left( \frac{\partial A''}{\partial N_B} \right)_{V,T} = kT \ln \gamma_B \\
 \ln \gamma_B & = -\pi^{1/2} \left( \frac{\beta e^2}{\epsilon} \right)^{3/2} \left( \frac{N_A z_A^2 + N_B z_B^2}{V} \right)^{1/2} z_B^2
 \end{aligned}
 \tag{4.32}$$

For one molecule of the mixture, we have

$$A_2B = 2A^+ + B^-$$

so

$$\mu''_{A_2B} = 2\mu''_A + \mu''_B = kT \ln \gamma_{A_2B} = 3kT \ln \gamma_{\pm} \quad \text{---(4.33)}$$

$$\mu''_{A_2B} = -kT \pi^{\frac{1}{2}} \left(\frac{\beta e^2}{\epsilon}\right)^{3/2} \left(\frac{N_A z_A^2 + N_B z_B^2}{V}\right)^{\frac{1}{2}} (2z_A^2 + z_B^2) \quad \text{---(4.34)}$$

$$\ln \gamma_{\pm} = -\frac{1}{3} (2z_A^2 + z_B^2) \pi^{\frac{1}{2}} \left(\frac{\beta e^2}{\epsilon}\right)^{3/2} \left(\frac{N_A z_A^2 + N_B z_B^2}{V}\right)^{\frac{1}{2}} \quad \text{---(4.35)}$$

For  $z_A = +1$ ,  $z_B = -2$ ,

$$\ln \gamma_{\pm} = -2 \pi^{\frac{1}{2}} \left(\frac{N_A + 4N_B}{V}\right)^{\frac{1}{2}} \left(\frac{\beta e^2}{\epsilon}\right)^{3/2} \quad \text{---(4.36)}$$

Consider the kinetic energy term and non interacting term, we obtain

$$\mu'_{A_2B} = \overset{\circ}{\mu}(T) + 3kT \ln \rho_{\pm} \quad \text{---(4.37)}$$

Therefore, the chemical potential of a mole of the mixture A, B and C is

$$\mu_{A_2B} = \mu'_{A_2B} + \mu''_{A_2B}$$

$$\mu_{A_2B} = \overset{\circ}{\mu}(T) + 3kT \ln \rho_{\pm} + 3kT \ln \gamma_{\pm} \quad \text{---(4.38)}$$

$$\mu_{A_2B} = \overset{\circ}{\mu}(T) + 3kT \ln \rho_{\pm} \gamma_{\pm} \quad \text{---(4.39)}$$

Consider the term  $\ln \gamma_{\pm}$ , from Eq. (4.33), we have

$$3kT \ln \gamma_{\pm} = 2kT \ln \gamma_A + kT \ln \gamma_B \quad \text{----- (4.40)}$$

$$\ln \gamma_{\pm} = \ln (\gamma_A^2 \gamma_B)^{1/3}$$

$$\gamma_{\pm} = (\gamma_A^2 \gamma_B)^{1/3} \quad \text{----- (4.41)}$$



$\gamma_{\pm}$  is called the mean activity coefficient of electrolytes

Next consider the term  $\ln \rho_{\pm}$ , from Eq. (4.37), we have

$$3kT \ln \rho_{\pm} = 2kT \ln \rho_A + kT \ln \rho_B \quad \text{----- (4.42)}$$

where  $\rho_i = \frac{N_i}{V}$  is the mean number density of the  $i$ th species for the total volume of solution.

If we treat  $\rho_i$  as the number of ion per cc. We may replace  $\rho_i$  by  $Nc_i/1000$ , where  $c_i$  is the number of gram ions per liter of solution and  $N$  is Avogadro's number. Since the solutions under consideration are very dilute, the number of moles per liter,  $c_i$ , closely approximates the product  $m_i \rho$ , where  $m_i$  is the molality and  $\rho$  in this case is the solvent density (rather than a charge density). So, we have

$$\rho_i \longrightarrow Nc_i/1000, \quad c_i \longrightarrow m_i \rho \quad \text{----- (4.43)}$$

Thus, Eq. (4.42) becomes

$$3kT \ln m_{\pm} = 2kT \ln m_A + kT \ln m_B$$

$$\ln m_{\pm} = \ln (m_A^2 m_B)^{1/3}$$

$$m_{\pm} = (m_A^2 m_B)^{1/3} \quad \text{----- (4.44)}$$

$m_{\pm}$  is called mean molality of electrolyte.

Comparison with Debye-Hückel Limiting Law

We now consider our result, Eq.(4.35), we have

$$\ln \gamma_{\pm} = -\frac{1}{3}(2z_A^2 + z_B^2) \pi^{\frac{1}{2}} \left(\frac{\beta e^2}{\epsilon}\right)^{3/2} \left(\frac{N_A z_A^2 + N_B z_B^2}{V}\right)^{\frac{1}{2}} \quad (4.45)$$

or

$$\ln \gamma_{\pm} = -\frac{1}{3}(2z_A^2 + z_B^2) \pi^{\frac{1}{2}} \left(\frac{e^2}{\epsilon kT}\right)^{3/2} (\rho_A z_A^2 + \rho_B z_B^2)^{\frac{1}{2}}$$

By Eq.(4.43), we can write

$$\begin{aligned} \ln \gamma_{\pm} &= -\frac{1}{3}(2z_A^2 + z_B^2) \pi^{\frac{1}{2}} \left(\frac{e^2}{\epsilon kT}\right)^{3/2} \left(\frac{N\rho}{1000}\right)^{\frac{1}{2}} (m_A z_A^2 + m_B z_B^2)^{\frac{1}{2}} \\ &= -\frac{1}{3}(2z_A^2 + z_B^2) \left(\frac{e^2}{\epsilon kT}\right) \left(\frac{\pi N e^2 \rho}{1000 \epsilon kT}\right)^{\frac{1}{2}} \left(\sum_i m_i z_i^2\right)^{\frac{1}{2}} \\ &= -\frac{1}{3}(2z_A^2 + z_B^2) \left(\frac{e^2}{2\epsilon kT}\right) \left(\frac{8\pi N e^2 \rho}{1000 \epsilon kT}\right)^{\frac{1}{2}} \left(\sum_i \frac{1}{2} m_i z_i^2\right)^{\frac{1}{2}} \\ &= -\frac{1}{3}(2z_A^2 + z_B^2) \left(\frac{e^2}{2\epsilon kT}\right) \left(\frac{8\pi N e^2 \rho}{1000 \epsilon kT}\right)^{\frac{1}{2}} I^{\frac{1}{2}} \quad (4.46) \end{aligned}$$

where

$$I = \sum_i m_i z_i^2 \quad (4.47)$$

is called the ionic strength of a solution.

Equation (4.46), we can write in the other form as

$$\ln \gamma_{\pm} = -\frac{1}{3}(2z_A^2 + z_B^2) \left(\frac{e^2}{\epsilon kT}\right) K \quad (4.48)$$

where

$$K = \left(\frac{8\pi N e^2 \rho}{1000 \epsilon kT}\right)^{\frac{1}{2}} I^{\frac{1}{2}} \quad (4.49)$$

is a parameter in Debye - Hückel Limiting Law (see ref. No.1 p.412).

The simplified form of Eq.(4.48), may write as

$$\log_{10} \gamma_{\pm} = -\frac{1}{3} (2Z_A^2 + Z_B^2) A \sqrt{I} \quad \text{-----(4.50)}$$

where

$$A = 1.8025 \times 10^6 \frac{\rho^{\frac{1}{2}}}{(\epsilon T)^{\frac{3}{2}}} \text{ mol}^{-\frac{1}{2}} \text{ liter}^{\frac{1}{2}} \text{ deg}^{\frac{1}{2}}.$$

For  $Z_A = +1$ ,  $Z_B = -2$ , Eq.(4.50) becomes

$$\log_{10} \gamma_{\pm} = -2A\sqrt{I} \quad \text{-----(4.51)}$$

The result show that our calculations using graph agree with the calculations of Debye - Hückel limiting law (See. ref. No.1 pp.412-414 and ref. No.3 pp.289-293).