Chapter 7 Chemical Equilibrium

7.1 $\Delta G^{o}$and the Equilibrium Constant

1. 化學方程式 $a\mathrm{A} + b\mathrm{B} = c\mathrm{C} + d\mathrm{D}$, 用通式$\sum v_{\mathrm{i}} \mathrm{X}_{\mathrm{i}} = 0$表之 ($v_{\mathrm{i}}$ of product爲正, retactant爲負)

constant T. P. 下 $dG = \sum_{i} \mu_i dn_i$

定義 extent of reaction ξ (或叫 progress variable):

$n_i = n_{i,\mathrm{o}} + v_i \xi$ ($n_{i,\mathrm{o}}$爲 initial condition)

(A) 等於對係數v_{i}作 normalization

(B) 對 forward rx., ξ爲正

則 $dn_i = v_i d\xi$

$$\Rightarrow dG = \sum \mu_i v_i d\xi$$

$$\left(\frac{\partial G}{\partial \xi}\right)_{\mathrm{T,P}} = \sum_{i} \mu_i v_i \begin{cases} > 0 & \text{spontaneous backward rx. (才能使 } dG \text{ 變小)} \\ = 0 & \text{平衡} \\ < 0 & \text{spontaneous forward rx.} \end{cases}$$

2. 又 $\mu_{\mathrm{i}} = \mu_{\mathrm{i}}^{\mathrm{o}} + \mathrm{R}T \ln a_{\mathrm{i}}$

$$\text{故} \left(\frac{\partial G}{\partial \xi}\right)_{\mathrm{T,P}} = \sum_{i} v_i \mu_i^{o} + \mathrm{R}T \sum_{i} v_i \ln a_i$$

$$= \underset{\uparrow}{\Delta G^{\circ}} + \mathrm{R}T \sum_{i} v_i \ln a_i$$

Gibbs energy change for std. state

$$= \Delta G^{\circ} + \mathrm{R}T \ln Q \quad , \quad Q = \prod a_i^{v_i}$$

activity quotient ← 不一定是 K, 平衡時之 Q 才是 K

平衡時 $\left(\frac{\partial G}{\partial \xi}\right)_{\mathrm{T,P}} = 0$, 即 $\Delta G^{\circ} = -\mathrm{R}T \ln Q_{\mathrm{eq}} = -\mathrm{R}T \ln K$

3. 以 $a\mathrm{A}_{(g)} + b\mathrm{B}_{(g)} \rightarrow c\mathrm{C}_{(g)}$ 爲例:

平衡時 P_{A} P_{B} P_{C} $\Delta G = 0$

std. state P° P° P° $\Delta G = \Delta G^{\circ}$ -----------------⓪

考慮 $a\mathrm{A}_{(g)} (P = P_{\mathrm{A}}) \rightarrow a\mathrm{A}_{(g)} (P = P^{\circ})$, $\Delta G = a\mathrm{R}T \ln(P^{\circ}/P_{\mathrm{A}})$ ------①

$b\mathrm{B}_{(g)} (P = P_{\mathrm{B}}) \rightarrow b\mathrm{B}_{(g)} (P = P^{\circ})$, $\Delta G = b\mathrm{R}T \ln(P^{\circ}/P_{\mathrm{B}})$ ------②

$c\mathrm{C}_{(g)} (P = P^{\circ}) \rightarrow c\mathrm{C}_{(g)} (P = P_{\mathrm{C}})$, $\Delta G = c\mathrm{R}T \ln(P_{\mathrm{C}}/P^{\circ})$ ------③

⓪+①+②+③ $a\mathrm{A}_{(g)} (P = P_{\mathrm{A}}) + b\mathrm{B}_{(g)} (P = P_{\mathrm{B}}) \rightarrow c\mathrm{C}_{(g)} (P = P_{\mathrm{C}})$ 平衡

即 $\Delta G^{\circ} + a\mathrm{R}T \ln(P^{\circ}/\mathrm{P_A}) + b\mathrm{R}T \ln(P^{\circ}/\mathrm{P_B}) + c\mathrm{R}T \ln(P_{\mathrm{C}}/P^{\circ}) = 0$

$$\Delta G^{\circ} + \mathrm{R}T \ln\left(P_{\mathrm{C}}{}^{\mathrm{c}} / P_{\mathrm{A}}{}^{\mathrm{a}} P_{\mathrm{B}}{}^{\mathrm{b}}\right) = 0$$

$$\Delta G^{\circ} + \mathrm{R}T \ln K = 0, \Delta G^{\circ} = -\mathrm{R}T \ln K$$

7.2 Reactions Involving Gases and Pure Solids or Liquids

1. 平衡常數表示法

① 全是理想之氣態: $a_{\mathrm{i}} = P_{\mathrm{i}}/P°$ 故即: $K = \prod_i = \left(\frac{P_i}{P^o}\right)^{\upsilon_i}$ 以 bar 爲單位之 P 代入 activity

② 含有 pure condensed phase: $a_{\mathrm{i}} \cong 1$ for condensed phase 所以其“濃度”可以省略

③ solution:

通常對 solute: $a_i = \gamma_i m_i / m^\circ$ molality 之單位 (下一節再詳細討論)

☆ 但此時 standard state 爲 $m = 1$ 之 solution

對 solvent: $a_1 = \gamma_1 x_1 \approx 1$ for dilute solutions

☆此時 standard state 爲 x=1 之 pure solvent

☆稀薄水溶液中，水之 m 爲 55.5 m$^{\mathrm{o}}$, 但不會用 $a = \gamma m/m^\circ$, 而是用 $a = \gamma x \cong 1$

2. $\Delta G_{\mathrm{(soln)}}$ 如何導出？

(1) 如能由表查出 (如：$\Delta G_{\mathrm{f(soln)}}$) 則直接加減

(2) $\Delta G°_{\mathrm{(soln)}}$ from $\Delta G°_{\mathrm{(gas)}}$

假設滿足 Henry's law, 則 $P_{\mathrm{i}} = k_{\mathrm{i}}^{(\mathrm{H})} x_{\mathrm{i}}$ 或 $k_{\mathrm{m,i}}^{(\mathrm{H})} m_{\mathrm{i}}$

$$\mu_{\mathrm{g}} = \mu_{\mathrm{soln}} \quad \text{即} \ \mu_{\mathrm{g,i}}^{\mathrm{o}} + \mathrm{R}T \ln\left(\frac{P_{\mathrm{i}}}{P^{\mathrm{o}}}\right) = \mu_{\mathrm{soln,i}}^{\mathrm{o}} + \mathrm{R}T \ln \frac{P_{\mathrm{i}}}{k_{\mathrm{m,i}}^{(\mathrm{H})} m^{\mathrm{o}}}$$

$$\boxed{\mu_{\mathrm{soln,i}}^{\mathrm{o}} = \mu_{\mathrm{g,i}}^{\mathrm{o}} + \mathrm{R}T \ln\left(\frac{k_{\mathrm{m,i}}^{(\mathrm{H})} m^{\mathrm{o}}}{P^{\mathrm{o}}}\right)}$$

convention Ⅱ, 即 Henry's law 之 ref. state 之 μ

例：CO_2 溶於水中, solubility $m \cong 3.4\times10^{-2}\ m^{\mathrm{o}}$ for $P = 1\,\mathrm{bar}$, 即 $1 = k_{\mathrm{m}}^{(\mathrm{H})} \cdot 3.4\times10^{-2}$

$k_{\mathrm{m}}^{(\mathrm{H})} = 29.4$, 故 $\mu_{\mathrm{soln}}^{\mathrm{o}} = \mu_{\mathrm{g}}^{\mathrm{o}} + \mathrm{R}T \ln 29.4$

$m = 1$ $= -394.4 + 8.4\ \mathrm{kJ\,mol^{-1}}$

(3) $\Delta G^\circ_{\mathrm{(soln)}}$ from $\Delta G^\circ_{\mathrm{(s)}}$:省略 "i" subscript

saturated solution 之 activity

$$\mu_{\mathrm{(s)}} = \mu_{\mathrm{(saturated\ soln)}} \quad \text{即} \ \mu_{\mathrm{(s)}}^{\mathrm{o}} = \mu_{\mathrm{soln}}^{\mathrm{o}} + \mathrm{R}T \ln a$$

故要知道 saturated soln 之 activity 或 activity coefficient 及濃度

$\mu_{\mathrm{soln}}^{\mathrm{o}} = \mu_{\mathrm{(s)}}^{\mathrm{o}} - \mathrm{R}T \ln a$ 如 $a > 1$, 則 $\mu_{\mathrm{soln}}^{\mathrm{o}}$ 較 $\mu_{\mathrm{(s)}}^{\mathrm{o}}$ more negative

$a < 1$, 則 $\mu_{\mathrm{soln}}^{\mathrm{o}}$ 較 $\mu_{\mathrm{(s)}}^{\mathrm{o}}$ more positive

〈觀念〉: $\mathrm{A_{(s)}} \rightarrow \mathrm{A_{(sat.\,soln,\ \ell m^\circ)}}$, $\Delta G = 0$, 即 $\mu_{\mathrm{(s)}}^{\mathrm{o}} = \mu_{\mathrm{soln}}^{\mathrm{o}} + \mathrm{R}T \ln \ell$

$\mathrm{A_{(s)}} \rightarrow \mathrm{A_{(soln,\ m\,m^\circ)}}$, $\Delta G = \mathrm{R}T \ln \frac{\mathrm{m}}{\ell}$

即

$\mathrm{A_{(s)}} \rightarrow \mathrm{A_{(soln,\ 1m^\circ)}}$, $\Delta G = \mathrm{R}T \ln \frac{1}{\ell} = -\mathrm{R}T \ln \ell$

即 std. soln

7.3 Chemical Equilibrium in Solutions

1. 如爲強電解質， 1 個分子 $\rightarrow$ ν_+ cation $+$ ν_- anion $\text{total} = \nu = \nu_+ + \nu_-$

(1) ideal solution 修正“個數”即可

如： 解離度爲α，原濃度爲m } 則解離後有 $(1-\alpha)m + \nu\alpha m$

$$= \left[1 + (\nu - 1)\alpha\right]m$$

↖ $\boxed{\text{gross molality}}$

$\Pi = icRT$ 此時 i 即$1 + (\nu - 1)\alpha$ ，故 $\boxed{\alpha = \dfrac{i-1}{\nu - 1}}$

(2) non-ideal solution：考慮 activity & activity coefficient

(A) $\mu_{\text{salt}} = \nu_+\mu_+ + \nu_-\mu_-$，分解爲$\nu_+$個電荷爲 z_+及ν_-個電荷爲 z_-的離子,電中性即：$\sum \upsilon_i z_i = 0$

如：Na_2SO_4中$\nu_+ = 2,\ z_+ = 1,\ \nu_- = 1,\ z_- = -2$

又 $\mu_i = \mu_i^o + RT\ln a_i$ ， 知 $\ln a_{\text{salt}} = \nu_+\ln a_+ + \nu_-\ln a_-$

$a_{\text{salt}} = a_+^{\nu_+}a_-^{\nu_-} = a_\pm^{\nu},\quad (\nu = \nu_+ + \nu_-)$

定義 mean ionic activity $\boxed{a_\pm = \left(a_+^{\nu_+}a_-^{\nu_-}\right)^{1/\nu}}$ ， 即 $a_{salt} = a_\pm^{\nu}$

↗ 注意：a_{salt}指的是ν個離子之a, $a_\pm$指的是 1 個離子之平均a

(B) 但 $a_+ = \gamma_+ m_+$ ， $a_- = \gamma_- m_-$

故 $a_+^{\nu_+}a_-^{\nu_-} = \gamma_+^{\nu_+}m_+^{\nu_+}\gamma_-^{\nu_-}m_-^{\nu_-} = \left(\gamma_+^{\nu_+}\gamma_-^{\nu_-}\right)\left(m_+^{\nu_+}m_-^{\nu_-}\right)$

定義 mean ionic activity coefficient $\boxed{\gamma_\pm = \left(\gamma_+^{\nu_+}\gamma_-^{\nu_-}\right)^{1/\nu}}$

mean ionic molality $\boxed{m_\pm = \left(m_+^{\nu_+}m_-^{\nu_-}\right)^{1/\nu}}$

則 $a_\pm = \gamma_\pm m_\pm$ 或 $a_{\text{salt}} = \left(\gamma_\pm m_\pm\right)^{\nu}$

⟨Note⟩：$m_\pm$ 和 m 之關係：

$m_+ = \nu_+ m$ ， $m_- = \nu_- m$ ， 故 $\boxed{m_\pm = \left(\nu_+^{\nu_+}\nu_-^{\nu_-}\right)^{1/\nu} m = \nu_\pm m}$

個數比 1：1 電解質 $m_\pm = m$

2：1 電解質 $m_\pm = 4^{1/3} m$

3：1 電解質 $m_\pm = 27^{1/4} m$

2：2 電解質 $m_\pm = 2m$

2. Ionic strength: $I = \dfrac{1}{2}\sum_i m_i z_i^2$

charge 比 1：－1 electrolyte $I = m$ ， $m_\pm = m$

1：－2 electrolyte $I = 3m$ ， $m_\pm = 4^{1/3} m$

2：－2 electrolyte $I = 4m$ ， $m_\pm = m$ (if 個數比 1:1)

〈例〉: 0.01 m° $Na_2SO_4 + 0.02$m° NaCl

(1 kg H_2O加上0.01 mole之Na_2SO_4 及0.02 mole之NaCl, 不是指兩個solu混合)

則 $Na^+ = 0.01 \times 2 + 0.02 = 0.04\ m°$

$Cl^- = 0.02\ m°$

$SO_4^{-2} = 0.01\ m°$

$$I = \frac{1}{2}(0.04 + 0.02 + 0.01 \times 4) = 0.05\, m°$$

Na_2SO_4 之 I 爲 $0.03\, m°$， NaCl爲 $0.02\, m°$， 故 $\boxed{I \text{ 可加成}}$

7.4 Debye-Hϋckel Theory

Peter J. W. Debye (1884-1966) 荷蘭裔美國人 1936 年 Nobel Prize (dipole moment)

Erich Hϋckel (1896-1980 德國人)

兩個帶電荷粒子之作用力 $F_{12} = \vec{e}_r \dfrac{Q_1 Q_2}{4\pi\varepsilon {r_{12}}^2}$,

$\varepsilon = \varepsilon_0 \varepsilon_{\text{rel}}$,

利用統計的方法，看離子隨距離之分布情形， $\boxed{a : \text{excluded radius}}$

$$n_{\text{j}}(\text{r}) = \frac{-\text{z}_{\text{j}} \text{e}^2 \exp[-\kappa(\text{r}-a)]}{4\pi\varepsilon\, r(1+\kappa\, a)} \qquad \boxed{1/\kappa = \text{Debye length}}$$

↑

average net change per unit volume at distance *r*

$$\kappa = \text{e}\sqrt{\frac{2\text{N}_{\text{A}}\rho_1 I}{\varepsilon\, \text{k}_{\text{B}} T}} = \boxed{\beta\sqrt{I}}$$

ρ_1 : density of solvent

I : ionic strength

§ κ for water at 298 K

因 $\varepsilon_0 = 8.8545\times10^{-12}\,\text{Fm}^{-1}$, $\varepsilon_{\text{rel}} = 78.54$
↑ for water

$\rho_1 = 997.14\ \text{kg}\,\text{m}^{-3}$

$\text{e} = 1.60218\times10^{-19}\,\text{C}$

$\text{k}_{\text{B}} = 1.3807\times10^{-23}\ \text{J}\,\text{K}^{-1}$

$\beta = 3.282\times10^9\ \text{kg}^{1/2}\text{mol}^{-1/2}\text{m}^{-1}$

$\kappa = \beta\sqrt{I}$

total net charge $dQ = 4\pi\, r^2 n_j(r) dr$ at distance *r* (算整個球殼)

$$\frac{d}{dr} r\exp[-\kappa(r-a)] = \exp[-\kappa(r-a)] + r(-\kappa)\exp[-\kappa(r-a)]$$

故 $r = \dfrac{1}{\kappa}$ 有 max

~43 Å for 1:1 electrolyte at 0.005 m

最後結果：

$$\boxed{\ln\gamma_{\pm} = -\frac{\alpha|\text{z}_+\text{z}_-|\sqrt{I}}{1+\beta a\sqrt{I}}}$$

(I 以 m^{o} 爲單位) 如果根號內用 I/m^{o} 表示較周全，但麻煩

其中 $\alpha = \sqrt{2\pi\,\text{N}_{\text{A}}\rho_1}\left(\dfrac{\text{e}^2}{4\pi\varepsilon\,\text{k}_{\text{B}}T}\right)^{3/2}$ 對 H_2O at 298 K , $\boxed{\alpha = 1.171\,\text{kg}^{1/2}\ \text{mol}^{-1/2}}$

〈簡化〉: 因 $a \cong 3\overset{o}{A}$， 故 $\beta a \cong 1$

$$\boxed{\ln\gamma_\pm = -1.171|z_+z_-|\frac{\sqrt{I}}{1+\sqrt{I}}} \quad \text{infinite dilution 則} \quad \frac{\sqrt{I}}{1+\sqrt{I}} \to \sqrt{I}$$

或 $$\boxed{\log_{10}\gamma_\pm = -0.510|z_+z_-|\frac{\sqrt{I}}{1+\sqrt{I}}}$$

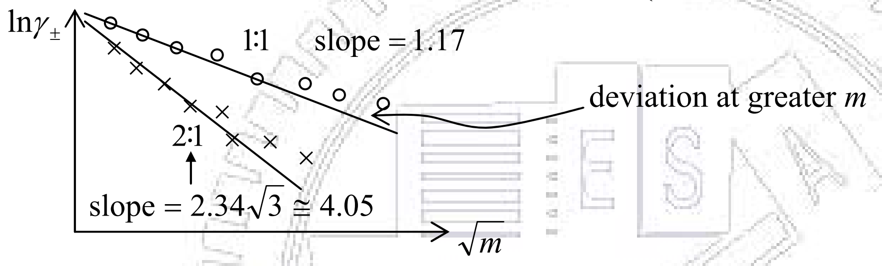
通常只適用於0.01 m^o以下之soln.,

對於1:1之電解質, $I = m$, $\log_{10}\gamma_\pm = -0.510\dfrac{\sqrt{m}}{1+\sqrt{m}} \approx -am^{1/2} + bm$

〈修正〉加一項修正項: Davies equation

$$\frac{\sqrt{I}}{1+\sqrt{I}} \to \left(\frac{\sqrt{I}}{1+\sqrt{I}} - 0.30\,I\right)$$

或 Guggenheim eq. $\ln\gamma_\pm = -\alpha|z_+z_-|\dfrac{\sqrt{I}}{1+\sqrt{I}} + 2\left(\dfrac{\nu_+\nu_-}{\nu_+ + \nu_-}\right)\beta m$



1. K_{sp} 之計算

以前用 m ，現在要用 $\underset{\uparrow}{m_\pm^\nu}\,\gamma_\pm^\nu$

因 $\gamma_\pm$ 受 I 而改變 (通常 I 變大, $\gamma_\pm$ 變小)
此即salting out之原理

原來 $K_{sp} = m_+^{\nu_+}m_-^{\nu_-}$ 現 $K_a = a_+^{\nu_+}a_-^{\nu_-}$

$$= \left(m_+^{\nu_+}m_-^{\nu_-}\right)\left(\gamma_+^{\nu_+}\gamma_-^{\nu_-}\right)$$

例：AgCl solubility = 1.27×10^{-5} m^o

ideal solution	real solution
$K_{sp} = 1.61\times10^{-10}$ m	$\ln\gamma_\pm = \dfrac{-1.171\sqrt{1.27\times10^{-5}}}{1+\sqrt{1.27\times10^{-5}}} = -0.00418$ $\gamma_\pm = 0.996$ $K_a = (m_\pm)^2\cdot(0.996)^2 = 1.60\times10^{-10}$ $\cong (m_\pm)^2$ 可忽略 $\gamma_\pm$ 之修正

如加入 0.1 m NaCl

則 solubility 減爲 $1.61\times10^{-9}\ m^o$

但是加了 0.1 m NaCl 後

$$\ln\gamma_{\pm}=\frac{-1.171\sqrt{0.1}}{1+\sqrt{0.1}}\qquad \gamma_{\pm}=0.754$$

$$m_{+}m_{-}=\frac{1.6\times10^{-10}}{(0.754)^2}=2.81\times10^{-10}\qquad K_{\mathrm{a}}\ \text{才是不變的}$$

故 solubility = $\boxed{2.81\times10^{-9}\ m^o}$

較 'real'多出約 75%

事實上 (1)濃度太高, DHG equation 幾乎已不適用

(2) Cl^- 很多，$AgCl_2^-$ 可能形成

2. 平衡只牽涉到 solutes

$$K=\prod_{i=2}^{c}\left(\frac{\gamma_i m_i}{m^{\mathrm{o}}}\right)^{\nu_i}$$

如牽涉到 solute 及 solvent, 則

$$K=(\gamma_1 x_1)^{\nu_1}\prod_{i=2}^{c}\left(\frac{\gamma_i m_i}{m^{\mathrm{o}}}\right)^{\nu_i}\approx\prod_{i=2}^{c}\left(\frac{\gamma_i m_i}{m^{\mathrm{o}}}\right)^{\nu_i}\quad \text{for diluted soln}$$

3. Reactions with Electrolyte Solutes

例：

其實是

net：

但其實無法測定單一離子之 ΔH_f, ΔG_f , ΔS

故定 $H^+_{(aq)}$ $1m^{\mathrm{o}}$ 之 ΔH_f, ΔG_f , S 均爲零

亦即：把 $HCl_{(aq)}$ 的 state function 均歸諸於 $_{(aq)}$, $HNO_{3(aq)}$均歸諸於

strong acid (完全解離)：

HCl, HClO4, HI, HBr, HNO_3, H2SO4

strong base：

金屬氧化物, 如：NaOH, KOH

weak acid or base：不完全解離

例： (課本例 7.9)

查表, $\Delta G^{\circ}=127.087$ kJ，可導出 at 298K

$$K_b = \frac{\gamma_{NH_4^+} m_{NH_4^+} \gamma_{OH^-} m_{OH^-}}{\gamma_{NH_3} m_{NH_3} \gamma_{H_2O} x_{H_2O}} = \frac{\gamma_{\pm}{}^2 m_{\pm}{}^2}{m_{NH_3}} \qquad m_{\pm} = m \quad \text{in this case}$$

如 initial [NH_3]爲 0.100 m^o, 則 $K_b = \dfrac{\gamma_{\pm}{}^2 m^2}{0.100 - m}$, $m = 0.00133$ if $\gamma_{\pm} = 1$

代入 Debye-Hückel law, $\log_{10}\gamma_{\pm} = -0.510\left(\dfrac{\sqrt{m}}{1+\sqrt{m}} - 0.30m\right) = -0.01774$

$\gamma_{\pm}$=0.960, 再代入上式, $m = 0.00140$

4. 強電解質之平衡 以 HCl 爲例

$$\mu(\text{HCl, aq}) = \mu(\text{H}^+) + \mu(\text{Cl}^-)$$

因 HCl 不可能不解離, 故用 m' 取代 1 m^o 作爲 reference state, m' 遠較 1 m^o 小

即$\mu°(\text{HCl, aq}) + RT \ln a(\text{HCl, aq})$

$= \mu°(\text{HCl, aq}) + RT \ln \gamma_{HCl} m_{eq}(\text{HCl})/m'$

$= \mu°(\text{H}^+) + RT \ln \gamma_{H^+} m_{eq}(\text{H}^+)/m°$

$\quad + \mu°(\text{Cl}^-) + RT \ln \gamma_{Cl^-} m_{eq}(\text{Cl}^-)/m°$

standard states

H^+ , Cl^- → 1 $m°$, $\gamma = 1$

$HCl_{(aq)}$ → m' , $\gamma = 1$

因解離很大 , m_{eq}(HCl) 很小 , 量不出

又 $\mu°(\text{HCl, aq}) = \mu°(\text{H}^+) + \mu°(\text{Cl}^-)$ ← 由此決定 m'

故 $a(\text{HCl, aq}) = \gamma_{HCl} \cdot m(\text{HCl})/m'$ (由HCl side 來看)

$= \gamma_{H^+}\gamma_{Cl^-} m_{eq}(\text{H}^+) m_{eq}(\text{Cl}^-)/m°m°$ (由H^+及Cl^- side 來看)

$= \dfrac{\gamma_+\gamma_- m_+ m_-}{(m°)^2}$

即 $\Delta G° = 0$ for $HCl_{(aq)} = H^+_{(aq)} + Cl^-_{(aq)}$

故 $K = 1 = \dfrac{\gamma_+ m_+ \gamma_- m_- /(m°)^2}{\gamma_{HCl}(m_{HCl}/m')}$, 但不表示 $m_{HCl} \approx m_+ m_-$, 因 $m' \neq m°$

通常只考慮正負離子(即a_+, a_-)而不考慮electrolyte(HCl)以避開麻煩

又$\mu(\text{HCl, aq}) = \mu(\text{HCl, g}) = \mu°(\text{HCl, g}) + RT \ln P_{HCl}/P°$

即 $\mu°(\text{HCl, g}) + RT \ln P_{HCl}/P° = \mu^o_+ + \mu^o_- + RT \ln \dfrac{\gamma_+\gamma_- m_+ m_-}{(m^o)^2}$

$$\text{故} \quad P_{HCl} = \gamma_+\gamma_- m_{\pm}{}^2 \underbrace{\boxed{\left(\frac{P°}{(m°)^2}\right) e^{\frac{\mu°(H^+)+\mu°(Cl^-)-\mu°(HCl,\ g)}{RT}}}}_{k_{\pm}^{(m)}}$$

Note: $P_{HCl} = k_{\pm}^{(m)} \gamma_{\pm}{}^2 m_{\pm}{}^2$ 而非如非電解質的 Henry's law $\propto m$

例:The partial vapor pressure of a 5.00 mol kg^{-1} aqueous solution of HCl at 298.15 K is equal to 6.97 × 10^{-5} atm. The mean ionic activity coefficient is equal to 2.38. Find the value of $k_{\pm}^{(m)}$ and of .

Solution

$$k_{\pm}^{(m)}=\frac{P(\mathrm{HCl})}{\gamma_{\pm}^{2}m^{2}}=\frac{6.97\times10^{-5}\ \mathrm{atm}}{(2.38)^{2}\left(5.00\ \mathrm{mol\,kg^{-1}}\right)^{2}}=4.92\times10^{-7}\ \mathrm{atm\,kg^{2}\ mol^{-2}}$$

$= (8.3145$

J

$\mathrm{K}^{(-1)}\ \mathrm{mol}^{(-1)})\ (298.15\ \mathrm{K})\times\ln[((4.92\times10^{(-7)}\ \mathrm{atm})\ (1\ \mathrm{mol\ kg}^{(-1)})^{2})/(1\ \mathrm{bar})\ ((1.01325\ \mathrm{bar})/(1\ \mathrm{atm}))]$

$= -3.60\times10^{4}$ J $= -36.0$ kJ

7.5 Buffer Solutions

(1) 過去 $pH = -\log_{10}[\text{H}^+]$

現在 $pH = -\log_{10} a_{\text{H}^+} = -\log_{10} \dfrac{\gamma_{\text{H}^+} m_{\text{H}^+}}{\text{m}^\circ}$

<例 1> ① $\text{CH}_3\text{COOH} = \text{CH}_3\text{COO}^- + \text{H}^+ \qquad K_{\text{eq}} = ?$

$\Delta G_f(\text{H}^+)$是 zero (爲了方便, 否則要由H之IP及H$^+$之solvation)

查 table A.8 (ao 表1m°之狀態, 未解離)

$$\Delta G^\circ = -369.31 + 0 - (-396.46) = 27.15 \text{ kJ mol}^{-1}$$

$$K = \exp\left[\frac{-\Delta G^\circ}{\text{R}T}\right] = 1.75\times10^{-5}$$

② 0.1 m 之 CH_3COOH 之 pH 值?

先設 $\gamma = 1$，則 $\dfrac{x^2}{0.1-x} = 1.75\times10^{-5}$ ， $x = 1.31\times10^{-3}\ m^\circ$

由 Davies Eq., $\log_{10}\gamma_\pm = -0.510|z_+z_-|\cdot\left[\dfrac{\sqrt{I}}{1+\sqrt{I}} - 0.30I\right]$

$I = \dfrac{1}{2}\sum m_i z_i^2 = 1.31\times10^{-3}$ ， 代入 $\gamma_\pm \approx 0.9655$

則 $\dfrac{\gamma^2 x^2}{0.1-x} = 1.75\times10^{-5}$ ， $x \approx 1.36\times10^{-3}$

$pH = -\log_{10} 1.36\times10^{-3}\times0.9655 = 2.88$

$\nwarrow$假設 $\gamma_+ = \gamma_\pm$

(2) Buffer Solution：強鹼滴定弱酸 或 弱酸+弱酸鹽

$$\text{HA} = \text{H}^+ + \text{A}^-$$

$$K_\text{a} = \frac{a_{\text{H}^+} a_{\text{A}^-}}{a_{HA}} = \frac{a_{\text{H}^+}\gamma_{\text{A}^-} m_{\text{A}^-}}{m_{\text{HA}}} \qquad (\gamma_{\text{HA}} \cong 1)$$

$$m_{\text{HA}} = \frac{n_a}{1\text{ kg solvent}} \quad , \quad m_{\text{A}^-} = \frac{n_s}{1\text{ kg solvent}}$$

故 $pH = pK_a + \log_{10}\left(\dfrac{n_s\gamma_A}{n_a}\right)$ ← 較準確

$\approx pK_a + \log_{10}\left(\dfrac{n_s}{n_a}\right)$ if $\gamma_{A^-} \cong 1$, 即和高中所學一樣

〈即Henderson - Hasselbalch Eq.〉不考慮 γ

生物體中之 buffering：血中之碳酸根

$CO_{2\,(g)} \rightleftharpoons CO_{2\,(aq)}$ $\qquad k^{(H)} = 1.24\times10^{6}$ Torr $\quad$ at 298 K

$CO_{2\,(aq)} + H_2O = H_2CO_{3\,(aq)}$ $\qquad K = 2.58\times10^{-3}$

由此單位即可知是以 x 爲濃度，而壓力以 Torr

如忽略 ionization，則此平衡常數決定 $CO_{2\,(aq)}$ 與 $H_2CO_{3(aq)}$ 之比例

但 $H_2CO_{3\,(aq)} = H^{+}_{(aq)} + HCO^{-}_{3\,(aq)}$ $\qquad K_1 = 1.70\times10^{-4}$

$HCO^{-}_{3\,(aq)} = H^{+}_{(aq)} + CO^{-2}_{3\,(aq)}$ $\qquad K_2 = 4.69\times10^{-11}$

① 760 Torr 下 CO_2 溶於水中, $pH = ?$

$$x_{CO_2} = \frac{P_{CO_2}}{k^{(H)}} = \frac{P_{CO_2}}{1.24\times10^{6}} = \frac{760}{1.24\times10^{6}} = 6.13\times10^{-4} \text{ ，又 } x = \frac{m}{m+\dfrac{1}{M_1}} \approx mM_1$$

MW of solvent in kg

$$m_{CO_2} = \frac{6.13\times10^{-4}}{0.018} = 0.034\ m^{o}$$

② 通常分辨不出 $CO_{2\,(aq)}$ 及 $H_2CO_{3\,(aq)}$，即只能量出 $[CO_2]+[H_2CO_3]$

故 $\dfrac{(H^{+})(HCO_3^{-})}{(H_2CO_3)} = K_1$ 改爲 $\dfrac{(H^{+})(HCO_3^{-})}{\{(H_2CO_3)+(CO_2)\}} = K_1{}'$

由 $2.58\times10^{-3} = \dfrac{a_{H_2CO_3}}{a_{CO_2}}$ 知 $a_{CO_2} = 388\, a_{H_2CO_3}$

故 $K_1{}' = K_1 \dfrac{(H_2CO_3)}{\{\cancel{(H_2CO_3)}+(CO_2)\}} = \dfrac{1}{389}\times1.7\times10^{-4} = 4.37\times10^{-7}$

幾乎可忽略了

忽略第二解離常數，$4.37\times10^{-7} = \dfrac{x^2}{0.034-x}$ ，$x = 1.22\times10^{-4}\ m^{o}$

$(\, x = a_{H^+} \approx m_{H^+})$

> <Note> 數學上如此做並不正確, 其實應該是 $\dfrac{x^2}{\dfrac{0.034}{389}-x} = 1.7\times10^{-4}$
>
> 其中 0.034/389 爲 $a_{H_2CO_3}$ 故 $\dfrac{x^2}{0.034-389x} = \dfrac{1.7\times10^{-4}}{389} = 4.37\times10^{-7}$

$pH = -\log_{10}(0.000122) = 3.91$

③ 如果用 $\gamma_{\pm}$，則 $\gamma_{\pm} = 0.987$，代入 $pH = 3.91$

(3) 人的血液之 pH 值可因$[CO_2]$減少而昇高

換氣過度 (hyperventilation)

快速呼吸→血中 pH 變高 ，因 CO_2 移走

pH 高會頭昏→將袋子罩住口鼻呼吸即可增 CO_2→降 pH 值

7.6 Temp. Dependence 前面已教過 $\frac{\partial \Delta G/T}{\partial 1/T} = \Delta H$ 或 $\frac{\partial \Delta G/T}{\partial T} = -\frac{\Delta H}{T^2}$

ΔH 如果不是 constant, 用 $\Delta H^\circ(T) = \Delta H^\circ(T_1) + \Delta C_p\,(T - T_1)$ 代入

則 $$\ln\frac{K(T_2)}{K(T_1)} = -\frac{\Delta H^\circ(T_1)}{\mathrm{R}}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) + \frac{\Delta C_p}{\mathrm{R}}\left[\ln\left(\frac{T_2}{T_1}\right) + \frac{T_1}{T_2} - 1\right]$$

Principle of Le Châtelier 系統 respond to “stress” by 可以減小“stress” 效應之反應

例：① 對放熱反應, 加熱會使平衡向左(使加的熱變少)

② 氣體反應, 如 mole 數變小, 則加壓使平衡向右(使壓力變大)

$$K_\mathrm{x} = \left(P_\mathrm{T}/P^\circ\right)^{-\Delta\nu} K_\mathrm{p}$$

如果 $\Delta\nu$ 是負值(mole 數變小),加壓, K_x 變大, 產物變多

7.7 Biological Systems

① $\mathrm{ATP} + \mathrm{H_2O} \rightarrow \mathrm{ADP} + \mathrm{P}$ 促使許多原本不會進行之反應進行，如：$\mathrm{glucose} \rightarrow \mathrm{glucose\,6\text{-}phosphate}$

ATP 和 ADP 常與 $\mathrm{Ca^{+2}}$、$\mathrm{Mg^{+2}}$ 形成 complex，此時 $[\mathrm{H^+}]$ 及 $[\mathrm{M^+}]$ 之 activity 不一定要定爲1

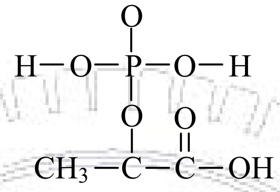
通常用“modified standard state” (因真正的 standard state 太不“real”了)，例：$\Delta G^{\circ\prime} = -29.3\ \mathrm{kJ\ mol^{-1}}$

for 298.15K, $pH = 7.00$, $p\mathrm{Mg} = 4.00$ ATP/ADP 之離子與之 complex

$$p\mathrm{Mg} = -\log_{10} a_{\mathrm{Mg^{+2}}} = -\log_{10}\left[\gamma_{\mathrm{Mg^{+2}}} c_{\mathrm{Mg^{+2}}} / c^\circ\right]$$

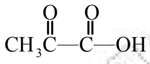
而 ADP 再靠別反應變回 ATP：

$$
\begin{array}{lll}
\text{例:} & \mathrm{PEP + H_2O = P_y + P} & \Delta G = -53.6 \\
+) & \mathrm{ADP\ +\ P\ = H_2O + ATP} & 29.3 \\
\hline
\text{故} & \mathrm{ADP + PEP = ATP + P_y} & -24.3
\end{array}
$$



PEP：phosphoenolypyruvic acid

$\mathrm{P_y}$：pyruvic acid



$\mathrm{CH_3\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-OH}$

P：$\mathrm{HPO_3^{-2}}$

實際上要靠 enzyme (pyruvate kinase)

$$\begin{cases} \mathrm{E + PEP = EP + P_y} \\ \mathrm{EP + ADP = E + ATP} \end{cases}$$

② 低濃度→高濃度 “active transport” $\mathrm{ADP+PEP = ATP+P_y}$

參考課本Figure 7.4

右邊比左邊濃度低 (因 $\mathrm{CA \rightarrow C' + A}$)

所以②是 spontaneous

spontaneous

enzyme

carrier C 有 2 種形式：$\begin{cases} \text{C — 易與 A 結合} \\ \text{C}' \text{ — 不易與 A 結合} \end{cases}$

在人體中，利用 ATP → ADP 以及 enzyme 可以使許多 nonspontaneous 的 process 發生

有機化學家如只會用加熱來促進化學反應，未免太遜了

另例： $\mathrm{HS + CO \rightarrow H + OCS}$ $\Delta H^o = 52\ \mathrm{kJ\ mol^{-1}}$

但 $\mathrm{HS + CO \leftrightarrow HSCO}$ $\Delta H^o \approx 0$

$\mathrm{HSCO + O_2 \rightarrow HO_2 + OCS}$ $\Delta \mathrm{H}^\circ = -164\ \mathrm{kJ\ mol^{-1}}$

即：利用 $\mathrm{H + O_2 \rightarrow HO_2}$ 之 $\Delta H^\circ = 216\ \mathrm{kJ\,mol^{-1}}$ 極度放熱來促成反應