Chapter 8 The Thermodynamics of Electrochemical Systems

8.1 The Chemical Potential and the Electric Potential

① electric field $\varepsilon = \dfrac{\vec{F}}{Q}$, 單位：$\dfrac{\text{N}}{\text{Coul.}} = \dfrac{\text{Volt}}{\text{m}}$ (即Force/charge)

② electric potential φ , $\varepsilon = -\nabla\varphi$ 單位：volt, ∇：gradient

(即： potential energy/charge)

③ electrostatic potential energy $V = Q\varphi$ 單位： Joule (或 eV)

$$\mu_i = \mu_{i(\text{chem})} + \boxed{N_{\text{A}} e z_i}\,\varphi \qquad e = 1.60\times10^{-19}\ \text{C}$$

$$= \mu_{i(\text{chem})} + z_i F\varphi \qquad F\text{: Faraday's constant} = 96485\ \text{C mol}^{-1}$$

$$1\ \text{eV} = 96.485\ \text{kJ mol}^{-1} = 23.06\ \text{kcal mol}^{-1}$$

對 2 個可導電之金屬, 其平衡時 μ 相同, 但 $\mu_{i(\text{chem})}$ 可不同, 由 $z_i F\varphi$ compensate

對電解質溶液而言

$$\mu_i = \nu_+\mu_+ + \nu_-\mu_-$$

$$= \nu_+\mu_{+(\text{chem})} + \nu_-\mu_{-(\text{chem})} + (\nu_+ z_+ + \nu_- z_-)F\varphi$$

$$= \nu_+\mu_{+(\text{chem})} + \nu_-\mu_{-(\text{chem})} = \mu_{i(\text{chem})}$$

即： electrostatic part 抵銷了, 只管 chemistry 即可

8.2 Electrochemical Cells

1. 名詞：

$$\begin{cases}\text{electrolytic cell—要外加電流才會產生反應}\\ \text{galvanic cell—產生電流}\\ \text{equilibrium electrochemical cell—即：reversible cell (外加電壓來平衡)}\end{cases}$$

參考課本Figure 8.2

cell without liquid junction

half - reaction

cathode

anode

hydrogen electrode

Ag - AgCl electrode

左：oxidation: anode (陽極) $H_{2(g)} \rightarrow 2H^+_{(aq)} + 2e^-$

右：reduction: cathode $AgCl_{(s)} + e^- \rightarrow Ag_{(s)} + Cl^-_{(aq)}$

$$2AgCl_{(s)} + H_{2(g)} = 2H^+_{(aq)} + 2Cl^-_{(aq)} + 2Ag_{(s)}$$

2. 電池之表示法：
   - (1) 左邊係 oxidation, 右邊 reduction
   - (2) 用“ | ”表 phase separation, “ || ”表 salt bridge 或 drop 極小之 liquid junction, “ ⋮ ”表 liquid junction
   - (3) 通常不必用解離之形式, 如：$CuSO_{4(aq)}$ 即可, 不必用 Cu^{+2} , SO_4^{-2}
   - (4) 註明 phase 及 conc.
   - (5) 不參與反應之電極也要寫出

係 physical description, 而非反應

例：$\text{Pt}\ |H_2(0.99\ \text{atm})|\text{HCl}(0.5\ m^\circ)|AgCl_{(s)}|\text{Ag}\ |\overbrace{\text{Pt}}^{\text{可有可無}}$

例：$Zn_{(s)}\ |ZnSO_{4(aq)} \vdots CuSO_{4(aq)}\ |Cu_{(s)}$ Daniel 電池

量 emf 要用 potentiometer，量 reversible potential difference

用還原電位

$$E = \Delta\varphi = \varphi(R) - \varphi(L)$$

(V) 右邊減左邊 > 0 爲 spontaneous

3. Nernst Eq. $\mu = \mu^\circ + \mathrm{R}T\ln a$, $\Delta G = \Delta G^\circ + \mathrm{R}T\ln Q$, 因 $\Delta G = -nF\varepsilon$, non-PV work

$$\varepsilon = \varepsilon^\circ - \frac{\mathrm{R}T}{nF}\ln Q \qquad \text{(注意是負號)}$$

上述電池 $\varepsilon = \varepsilon^\circ - \dfrac{\mathrm{R}T}{nF}\ln\dfrac{a_{\mathrm{HCl}}^2}{P_{\mathrm{H_2}}}$

$$= \varepsilon^\circ - \frac{RT}{2nF}\ln\left(\frac{\gamma_\pm^4 m^4}{P_{\mathrm{H_2}}}\right) \qquad (\gamma_+\gamma_- m_+ m_-)^2$$

$$\frac{\mathrm{R}T}{F} = \frac{8.314\times298.15}{96485} = 0.0257\ \mathrm{V}$$

〈例〉：$\mathrm{Zn_{(s)}|ZnCl_{2(aq,\,\mathit{m}=1)}|AgCl_{(s)}|Ag_{(s)}}$

左： $\mathrm{Zn} \rightarrow \mathrm{Zn^{+2}} + 2\,\mathrm{e^-}$ $\qquad \varepsilon = 0.7628\ \mathrm{V}$

右： $\mathrm{2AgCl_{(s)} + 2\,e^- \rightarrow 2Ag + 2Cl^-}$ $\qquad \varepsilon = 0.2225\ \mathrm{V}$

$\mathrm{Zn_{(s)} + 2AgCl_{(s)} = 2Ag_{(s)} + ZnCl_{2(aq)}}$ $\qquad \varepsilon = 0.9853\ \mathrm{V}$

故 $\varepsilon = 0.9853 - \dfrac{\mathrm{R}T}{nF}\ln Q$

$$= 0.9853 - \frac{8.314\times298.15}{2\times96500}\ln a_{\mathrm{ZnCl_2}}$$

$$= 0.9853 - \frac{0.0257}{2}\ln(4m^3\gamma_\pm^3)$$

因 $\mathrm{ZnCl_2 \rightarrow Zn^{+2} + 2Cl^-}$

$$a = a_+ a_-^2 = m\gamma_+(4m^2)\gamma_-^2 = 4m^3\gamma_\pm^3$$

$m = 1$, $\log\gamma_\pm = -0.510\times2\dfrac{\sqrt{3}}{1+\sqrt{3}} = -0.645$, $\gamma_\pm = 0.226$, $I = 3m$ (濃度太大不適用)

用Davies Eq. 則 $\log\gamma_\pm = -0.510\times2\left(\dfrac{\sqrt{3}}{1+\sqrt{3}} - 0.3\cdot3\right)\cdot\gamma_\pm > 1$, 不好 (濃度太大不適用)

實際上 $\gamma_\pm = 0.325$

故 $\varepsilon = 0.9853 - 0.0128\ln\left(4\times1\times0.325^3\right) = 0.9853 - (-0.0255) = 1.011\ \mathrm{V}$

4. 實驗上測量 ε°

因爲 ε° 之 standard state 未必存在, 未必能直接測

通常用稀釋法來 approach ε°

以 $H_{2(g)} + 2AgCl_{(s)} = 2HCl_{(aq)} + 2Ag_{(s)}$ 爲例

$$\varepsilon = \varepsilon^\circ \underbrace{- \frac{2RT}{F}\ln m\gamma_\pm}_{\uparrow} = \varepsilon^\circ - \frac{2RT}{F}\ln m - \frac{2RT}{F}\ln \gamma_\pm$$

設 $P_{H_2} = P^\circ = 1$, 則 $\dfrac{-RT}{2F}\ln\left(\dfrac{\gamma_\pm^4 m^4}{P_{H_2}}\right) = \dfrac{-2RT}{F}\ln m\gamma_\pm$

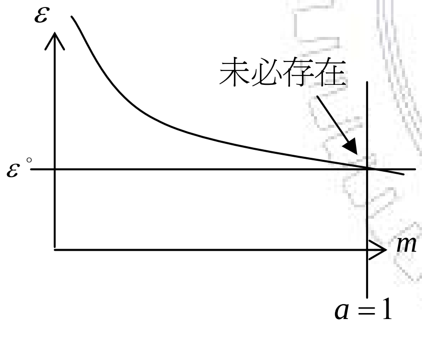
$$= \varepsilon^\circ - \frac{2RT}{F}\ln m - \frac{2RT}{F}\times\left(-1.171\frac{\sqrt{m}}{1+\sqrt{m}} + bm\right)$$

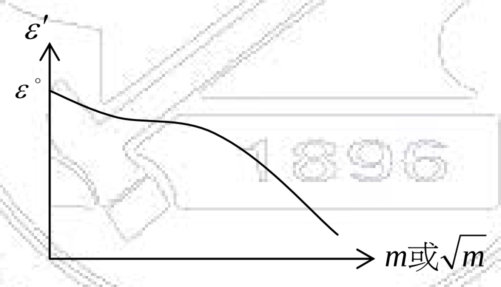
① 定義 $\varepsilon' = \varepsilon + \dfrac{2RT}{F}\ln m$, 則 $\varepsilon' = \varepsilon^\circ - \dfrac{2RT}{F}\ln\gamma_\pm$, 極稀時 $\gamma_\pm \to 1$, 故 $\varepsilon' \to \varepsilon^\circ$

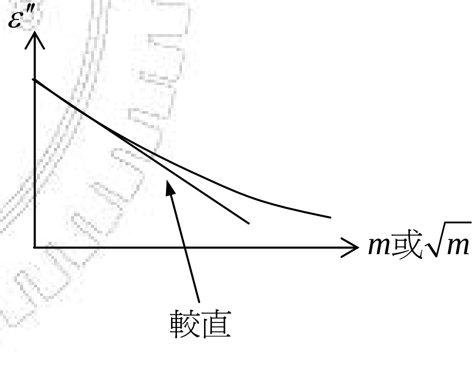
② $\varepsilon' = \varepsilon^\circ - \dfrac{2RT}{F}\left(-1.171\dfrac{\sqrt{m}}{1+\sqrt{m}} + bm\right) \square\ \varepsilon^\circ + \dfrac{2RT}{F}1.171\sqrt{m}$, 故可對 $\sqrt{m}$ 作圖外插

③ 定義 $\varepsilon'' = \varepsilon + \dfrac{2RT}{F}\left(\ln m - \dfrac{1.171\sqrt{m}}{1+\sqrt{m}}\right)$, 則 $\varepsilon'' = \varepsilon^\circ - \dfrac{2RT}{F}bm$, $m \to 0$, $\varepsilon'' \to \varepsilon^\circ$

(課本 Eq. 8.2-21符號有錯)







8.3 Half-cell Potentials and Cell Potentials

1. 定義：

hydrogen electrode 在左邊時所測得之 ε°

即爲右邊半電池之 standard reduction potential

或稱 standard half-cell potential

指的仍是還原電位

$\varepsilon = \varepsilon(\text{右}) - \varepsilon(\text{左})$

不能用 ε° 相加減, 例： $2e^- + 2H^+ + ClO_4^- \rightarrow ClO_3^- + H_2O$, $\varepsilon^\circ = 1.19\ V$, $\Delta G^\circ = -2 \cdot F \cdot 1.19$

$6e^- + 6H^+ + ClO_3^- \rightarrow Cl^- + 3H_2O$, $\varepsilon^\circ = 1.38\ V$, $\Delta G^\circ = -6 \cdot F \cdot 1.38$

$8e^- + 8H^+ + ClO_4^- \rightarrow Cl^- + 4H_2O$, $\varepsilon^\circ \neq 2.57\ V$, $\varepsilon^\circ = -\dfrac{1.19 \times 2 + 1.38 \times 6}{8} = 1.33\ V$

2. Cell with liquid junction

有時無法只有一種 solution, 因可能形成沉澱, 或 electrode 可能與另一半電池反應

例： $Zn \rightarrow Zn^{+2} + 2e^-$

$Cu^{+2} + 2e^- \rightarrow Cu$ 則 Cu^{+2} 即會直接與 Zn 作用, 無法由外面淺路導電

參考課本Figure 8.6

即 Daniel Cell 古時電話,鐵路號誌用

☆ 也可以用濃 $CuSO_4$ (較重)在下面, 稀 $ZnSO_4$ 在上面 (但不能斷路)

〈性質〉: (1) 無法有 persistent metastable state,

因 ions 會 diffuse, even 在 open circuit

(2) 效率受影響, 因有 transference 之問題

(3) 不 reversible, 因有 liquid junction potential

此時 $\varepsilon = \varepsilon^\circ + \varepsilon_{LJ} - \dfrac{RT}{nF}\ln Q$

§ ① 用 salt bridge 減少 LJ potential (~ mV)

KCl suspended in agar gel

〈原因〉: (1) K^+ 及 Cl^- 之 transference number 類似 (後詳)

(2) 可以極 concentrated, dominate LJ potential

替代品：NH_4NO_3 (Cl^- 如遇有 Ag^+, Pb^{+2} 時, 會沉澱)

② 用 concentration cell 去避免 LJ potential

3. Concentration cell

$$\varepsilon = \varepsilon^\circ - \frac{RT}{nF}\ln Q$$

$$= \varepsilon^\circ - \frac{RT}{nF}\ln\frac{a_1}{a_2} = -\frac{RT}{nF}\ln\frac{a_1}{a_2}$$

利用濃度不同之相同電極亦可產生 emf

〈每一 factor of 2 : $\frac{RT}{nF}\ln 2 = \frac{8.314\times 298.15}{n\cdot 96485}\ln 2 = \frac{0.018\text{V}}{n}$ 〉

① Electrode concentration cell

例： $\text{Pt}|\text{H}_2(\text{g}, P_1)|\text{H}^+(\text{aq, m})|\text{H}_2(\text{g}, P_2)|\text{Pt}$

或 $\text{Pt}|\text{H}_2(\text{g}, P_1)|\text{HCl(m)}|\text{AgCl(s)}|\text{Ag}|\text{AgCl(s)}|\text{HCl(m)}|\text{H}_2(\text{g}, P_2)|\text{Pt}$

Rx. $\text{H}_2(P_1)\rightarrow \text{H}_2(P_2)$

P_1 要較大才可以

$$\varepsilon = \frac{-RT}{2F}\ln\frac{P_2}{P_1} = 0.0128\ \text{volt}\times\ln\frac{P_1}{P_2},\ \Delta G = -n\varepsilon F = RT\ln\frac{P_2}{P_1}$$

比較： reversible expansion at constant T , $w = RT\ln\frac{P_2}{P_1}$, 和上式相同

可視爲作不同形式的功 (電功 vs. 膨脹功)

double cell :

參考課本Figure 8.8 或 參考課本Figure 8.9

可排除 liquid junction 之影響

② Electrolyte concentration cell

例： $\text{Pt}|\text{H}_2(P_1)|\text{HCl}(m_1)||\text{HCl}(m_2)|\text{H}_2(P_1)|\text{Pt}$

Rx. $\Rightarrow \text{HCl}(m_2)\rightarrow \text{HCl}(m_1)$ ← Note: 不是 $m_1 \rightarrow m_2$, 因陽極 $\text{H}_{2(g)} \rightarrow 2\text{H}^+(m_1)$

陰極 $2\text{H}^+(m_2) \rightarrow \text{H}_{2(g)}$

$$\varepsilon = -\frac{RT}{F}\ln\frac{a_1(\text{HCl})}{a_2(\text{HCl})}$$

$$= -\frac{RT}{F}\ln\frac{(\gamma_{\pm 1}m_1)^2}{(\gamma_{\pm 2}m_2)^2} = -\frac{2RT}{F}\ln\frac{\gamma_{\pm 1}m_1}{\gamma_{\pm 2}m_2}$$ ← Note: 不要忘了 $\gamma_\pm$

可視爲把稀釋作用拿來作電功

8.4. Determination of $a_\pm$ and $\gamma_\pm$ of Electrolytes

1. 對 volatile compds , 由 vapor pressure 可得知

〈例〉: 10 m 之 HCl solution 有 $P_{\mathrm{HCl}} = 4.2$ torr

$k_\pm^{(m)} = 4.92 \times 10^{-7}$ atm kg^{2}mol^{-2}

$$\text{因}\ P_{\mathrm{HCl}} = k_\pm^{(m)} \gamma_\pm^2 m^2\ ,\ \gamma_\pm^2 = \frac{P_{\mathrm{HCl}}}{k_\pm^{(m)} m^2} = \frac{4.2/760}{4.92 \times 10^{-7} \cdot 10^2} = 112$$

$$\gamma_\pm = 10.6$$

注意: 即使此時不遵守 Henry's law, 還是用 $k_\pm^{(m)}$, 因爲其爲 reference

(即上式γ=1)

2. 由 Emf 測知

〈例〉: Pt|H_2(g)|HCl(aq)|AgCl(s)|Ag(s)|Pt

$$\varepsilon = \varepsilon^\circ - \frac{\mathrm{R}T}{2F} \ln \frac{a_{\mathrm{HCl}}^2}{P(\mathrm{H_2})/P^\circ}$$

$$P = 1\ \text{bar 時},\ \ln a_{\mathrm{HCl}} = 2\ln(\gamma_\pm m) = \frac{F(\varepsilon^\circ - \varepsilon)}{\mathrm{R}T}$$

$$\varepsilon = 0.3524\ \mathrm{V},\ \varepsilon^\circ = 0.2223\ \mathrm{V},\ \text{則}\ \ln a_{\mathrm{HCl}} = 5.064 = 2\ln(\gamma_\pm m)$$

$$\left(\begin{array}{l} \text{for } m_{\mathrm{HCl}} = 0.1 \\ \text{及 } P_{\mathrm{H_2}} = 1\ \text{bar} \end{array}\right) \qquad \gamma_\pm = \frac{e^{-2.532}}{0.1} = 0.795$$

3. 由 Osmotic pressure 測量

由 KCl soln. 之 osmotic pressure 測 ϕ (水的)

再因 2 個 soln. 的水的 ϕ 相同, 用 ϕ 測 sucrose 之 γ

以“1”表 H_2O (solvent)

phase I reference soln

phase II 待測 soln.

平衡時

$$a_1(\mathrm{I}) = a_1(\mathrm{II}) \qquad [\text{指 } \mathrm{H_2O}]$$
$$\|$$
$$\gamma_1(\mathrm{I}) x_1(\mathrm{I})$$

定義 molar osmotic coefficient $\phi = \dfrac{-\ln a_1}{m_2 \nu\ M_1} = \dfrac{-\left(\mu_1^\circ - \mu_1\right)}{\mathrm{R}T\ M_1 \nu\ m_2}$,即一個分子變ν個離子後, non-ideal之修正

$$\text{出處}:\ \Pi = ic\mathrm{R}T\ \ ,\ \ \Pi V_1 = \nu\phi n_2 \mathrm{R}T\ ,\ \Pi \bar{V}_1 = \nu\phi \frac{n_2}{n_1} \mathrm{R}T$$
$$\|$$
$$-\mathrm{R}T \ln a_1$$

$$\text{故}\ \phi = -\frac{n_1}{n_2 \nu} \ln a_1 \cong -\frac{1}{\nu m_2 M_1} \ln a_1\ \ (\text{因}\ n_2 = m_2 n_1 M_1) \quad \text{Note: } x_2 = \frac{n_2}{n_1 + n_2} \approx \frac{n_2}{n_1}\ ,\ \text{又}\ x_2 = \frac{m_2}{m_2 + \frac{1}{M_1}} \approx m_2 M_1$$

$\ln a_1 \cong -\nu m_2 M_1 \phi$ ← <另種看法> $\ln a_1 = -\Pi\bar{V}/RT = -icRT\bar{V}/RT$

$\mu_1 = \mu_1^{\circ} - RTM_1\nu\, m_2\phi$　　　　$= -\nu\phi\dfrac{n_2}{n_1} = -\nu\phi M_1 m_2$

$\mu_2 = \mu_2^{\circ} + \nu RT\ln(\gamma_2 m_2)$

(省略 $\gamma_{2\pm}$ 及 $m_{2\pm}$ 的±號)

再用 $n_1 d\mu_1 + n_2 d\mu_2 = 0$

則 $-n_1RTM_1\nu(m_2 d\phi + \phi dm_2) + (m_2 n_1 M_1)\nu RT\left[d\ln\gamma_2 + \overset{\frac{dm_2}{m_2}}{\boxed{d\ln m_2}}\right] = 0$

$$\Rightarrow\quad -m_2 d\phi - \phi dm_2 + m_2 d\ln\gamma_2 + dm_2 = 0$$

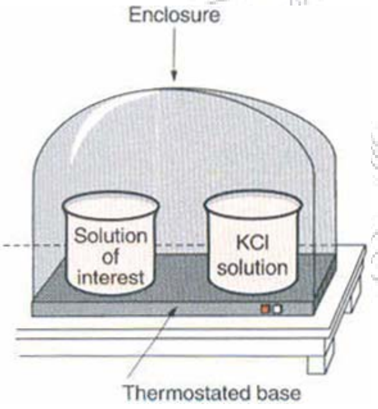
$$d\ln\gamma_2 = d\phi + \frac{\phi-1}{m_2}dm_2$$

$$\int_{m_2=0}^{m_2} d\ln\gamma_2 = \int_{m_2=0}^{m_2} d\phi + \int_{m_2=0}^{m_2}\frac{\phi-1}{m_2}dm_2$$

$$\ln\gamma_1(m_2) = \phi(m_2) - 1 + \int_0^{m_2}\frac{\phi-1}{m_2}dm_2$$

實驗上測 ϕ

4. 非常不 volatile 之 compd. 例如： sucrose in $H_2O_{(l)}$



恆溫

isopiestic method

使之平衡，再測兩 solution 中 solvent 之 mole fraction
以下之討論其實和上一節相同，
但把 1 和 2 改爲 A 和 B，且用不同 approach，
讓同學可以真正瞭解

利用 Gibbs-Duhem eq. 由 $H_2O_{(l)}$ 之 a 推得 sucrose 之 a

$n_A d\mu_A + n_B d\mu_B = 0$，即 $n_A d\ln a_A + n_B d\ln a_B = 0$

如用 molality 表示，則 $n_B = m = mM_A n_A$

〈 A 爲 solvent，B 爲 solute 〉 $n_A = 1/M_A$　(用 SI unit)

故 $d\ln a_B = -\dfrac{n_A}{n_B}d\ln a_A$

$$= -\frac{1}{mM_A}d\ln a_A$$

如 B 爲 electrolyte, $\rightarrow \nu_+ + \nu_- = \nu$ 個離子

則 $d\ln a_B = -\dfrac{1}{m\nu M_A} d\ln a_A$

定義 ϕ ： molal osmotic coefficient (是濃度之 function)

$$\phi = \frac{-\ln a_A}{m\nu M_A}$$

<Note>

ϕ 即 $\Pi = icRT$ 之 "i" ，但考慮了 ν

$$\Pi V = \phi \nu n_B RT$$

$$\Pi \overline{V_A^{\bullet}} = \frac{\phi n_B \nu}{n_A} RT = -RT\ln a_A$$

故 $\phi = -\ln a_A \dfrac{n_A}{\nu n_B}$

$$= -\ln a_A \frac{1}{\nu m M_A}$$

$$d\phi = \frac{-d\ln a_A}{\nu m M_A} + \frac{\ln a_A}{m^2 \nu M_A} dm$$

因 $\dfrac{-d\ln a_A}{\nu m M_A} = d\ln a_B$

$$d\ln a_B = d\phi + \frac{\phi}{m} dm$$

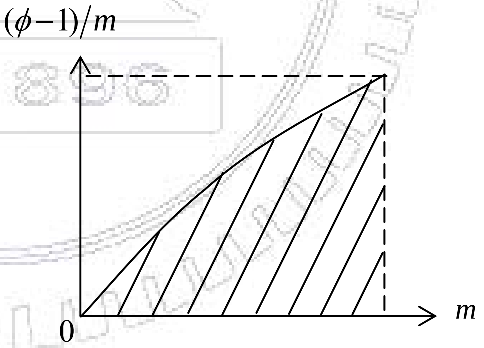
$$d\ln \gamma_\pm + \frac{dm}{m} = d\phi + \frac{\phi}{m} dm$$

$$\boxed{d\ln \gamma_\pm = d\phi + \frac{\phi - 1}{m} dm}$$

$$\int_0^m d\ln \gamma_\pm = \int_{\phi_{m=0}}^{\phi_{m=m}} d\phi + \int_0^m \frac{\phi - 1}{m} dm$$

$$\ln \gamma_\pm = \phi(m) - 1 + \int_0^m \frac{\phi - 1}{m} dm$$

$m \rightarrow 0$ 時, $\phi \rightarrow 1$



因 $\ln a_A \approx \ln x_A = \ln(1 - x_B) \approx -x_B = -\nu m \Big/ \dfrac{1}{M_A} = -\nu_m M_A$, 由定義 $\phi \rightarrow 1$

或由 $m \rightarrow 0$ 時, solvent 爲 ideal, 故 ϕ=1

8.5 Determination of pH

$\mathrm{pH} = -\log_{10} a_{\mathrm{H}^+}$ 但 a_{H^+} 不能精確地單獨被量出

如假設 $a_{\mathrm{H}^+} \cong a_\pm$, 可被量出 , 則可測 pH

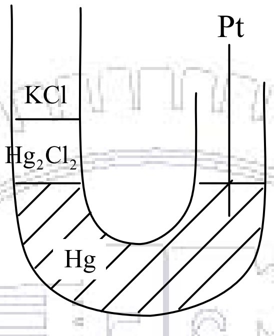
Calomel electrode

$$\mathrm{H}_{2\,(g)} \rightarrow 2\mathrm{H}^+_{(aq)} + 2e^-$$

$$2e^- + \mathrm{Hg_2Cl}_{2\,(s)} \rightarrow 2\mathrm{Hg}_{(l)} + 2\mathrm{Cl}^-_{(aq)}$$

$$\mathrm{H}_{2\,(g)} + \mathrm{Hg_2Cl}_{2\,(s)} \rightarrow 2\mathrm{HCl}_{(aq)} + 2\mathrm{Hg}_{(l)}$$

"saturated"及"normal"
calomel electrode



$$\mathrm{KCl}(aq, m)|\mathrm{Hg_2Cl}_{2(s)}|\mathrm{Hg}_{(l)}|\mathrm{Pt}$$

$$\mathrm{Hg_2Cl}_{2(s)} + 2e^- \rightarrow 2\mathrm{Hg}^+ + 2\mathrm{Cl}^-$$

$m = 0.1\ m \qquad \varepsilon = 0.3338\ \mathrm{V}$

$= 1\ m \qquad \varepsilon = 0.2802\ \mathrm{V}$ normal

$= \text{saturated} \qquad \varepsilon = 0.2415\ \mathrm{V}$

測量時

參考課本Figure 8.10

$$則\ \ \varepsilon = 0.2415\ \mathrm{V} + \mathrm{E_{LJ}} - \frac{RT}{F}\ln\frac{a_{\mathrm{H}^+}a_{\mathrm{Cl}^-}}{\left(P_{\mathrm{H}_2}/P^\circ\right)^{1/2}}$$

〈困難 1〉： a_{Cl^-} 不易精確量

解決： 測量 reference pH soln. 比較, 通常可假設 ① E_{LJ} 相近 ② a_{Cl^-} 相近

$$\varepsilon^{\mathrm{II}} - \varepsilon^{\mathrm{I}} = -\frac{RT}{F}\ln\frac{a_{\mathrm{H}^+}(\mathrm{II})}{a_{\mathrm{H}^+}(\mathrm{I})}$$

$$亦即\ \ \mathrm{pH}^{(\mathrm{II})} - \mathrm{pH}^{(\mathrm{I})} = \frac{F}{RT\ln 10}\left(\varepsilon^{(\mathrm{II})} - \varepsilon^{(\mathrm{I})}\right)$$

〈困難 2〉： H_2 有危險性, 且 f_{H_2} 不易量精確

解決： glass electrode 取代 H_2 electrode

雖然 voltage 與 glass 及 a_{H^+} 有關

但如與 reference soln. 相較, 可抵消

參考課本Figure 8.11

◎ 溫度要量精確

因 ε dep. on T

8.6 Thermodynamic for Electrochemistry

$$-nF\varepsilon^\circ = \Delta G^\circ = -\mathrm{R}T\ln K,\ \varepsilon^\circ = \frac{\mathrm{R}T}{nF}\ln K$$ (注意：沒有負號)

$$K = \exp\left[nF\varepsilon^\circ / \mathrm{R}T\right]$$

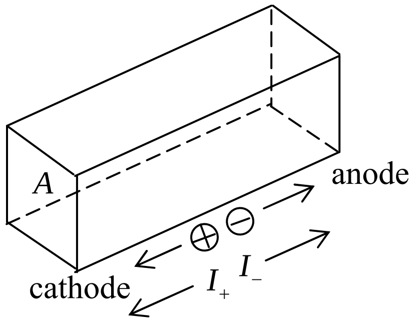
$$\Delta S^\circ = -\left(\frac{\partial \Delta G^\circ}{\partial T}\right)_\mathrm{P} = nF\left(\frac{\partial \varepsilon^\circ}{\partial T}\right)_\mathrm{P}$$

$$\Delta H^\circ = -nF\varepsilon^\circ + nFT\left(\frac{\partial \varepsilon^\circ}{\partial T}\right) = -nF\left[\varepsilon^\circ - T\left(\frac{\partial \varepsilon^\circ}{\partial T}\right)\right]$$

$$\varepsilon^\circ = \frac{\Delta H^\circ}{-nF} + T\left(\frac{\partial \varepsilon^\circ}{\partial T}\right)$$

8.7 Ion Mobility and Transference Number (補充)

1. Ion Mobility



$$I = I_+ + I_-$$

但 $I_i = \frac{\mathrm{d}Q}{\mathrm{d}t} = |z_i|e\frac{\mathrm{d}N_i}{\mathrm{d}t}$

$$= |z_i|e\underbrace{\frac{N_i}{V}(Av_i)}$$

單位時間通過 A 截面積之數目,

$\frac{N_i}{V}$ 是密度, Aν_i是單位時間掃過之體積

但離子之速度受 $\left.\begin{cases}\text{庫侖力}\\ \text{friction drag}\end{cases}\right\}$ 平衡後達到 steady state velocity

即 $z_i eE = fv_i$ （$f = 6\pi\eta r$）

η: viscosity , r: radius of sphere

故 $v_i = \frac{z_i eE}{f}$ 重要的是 $v_i \propto E$，故定義 $\boxed{u_i = \frac{v_i}{E} \quad \text{mobility}}$

單位：$\frac{\text{energy}}{\text{L}} = \text{kg}\cdot\frac{\text{m}}{\text{s}^2} = \underbrace{\boxed{\frac{\text{kg}}{\text{s}}}}_{f}\underbrace{\boxed{\frac{\text{m}}{\text{s}}}}_{v}$

〈 嚴格說 v_i 仍與濃度有關, 因爲必須考慮

"electrophoretic effect"-離子帶動附近之 solvent

"relaxation effect"-離子從原來之 ionic atmosphere 離開, 會有一股"拉回來"之力量 〉

因此 $I_i = |z_i|e\frac{N_i}{V}Au_iE$ electric field

$= |z_i|e\frac{N_i}{V}Au_i\frac{\varepsilon}{l}$ emf

$= \alpha u_i F\nu_i|z_i|\frac{n_i}{V}\frac{A\varepsilon}{l}$

$N_i = \alpha\nu_i N_\mathrm{A} n_i$ (其中 α 爲解離率)

而 $eN_\mathrm{A} = F$

① 電中性 $\nu_+|z_+| = \nu_-|z_-|$

故 $\frac{I_+}{I_-} = \frac{u_+}{u_-}$ 即： mobility 大者, 對帶電之"責任"較大

② 同樣之 positive ion 中,

則 $\frac{I_A}{I_\mathrm{B}} = \frac{u_\mathrm{A}\nu_\mathrm{A}\left(n_\mathrm{A}/V\right)|z_\mathrm{A}|}{u_\mathrm{B}\nu_\mathrm{B}\left(n_\mathrm{B}/V\right)|z_\mathrm{B}|}$ 和 $\left.\begin{cases}\text{mobility}\\ \text{濃度}\\ \text{帶電荷數}\end{cases}\right\}$ 有關

2. Transference Number

(或稱 transport number)

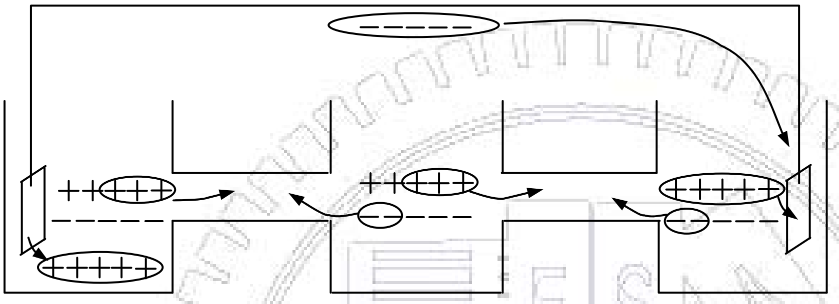
(1) 定義：

$$t_+ = \frac{I_+}{I_+ + I_-} = \frac{u_+}{u_+ + u_-} \quad ; \quad t_- = \frac{I_-}{I_+ + I_-} = \frac{u_-}{u_+ + u_-}$$

即：“導電能力”之比例

transference number t_+ 、 t_- 不同, 即可導致電解質在兩電極間濃度之不同

例：



如果 $\frac{u_+}{u_-} = \frac{3}{2}$

結果： $-------$ $-----$ $---$

濃度之改變即可造成ε之改變, 此即$\varepsilon_{\mathrm{LJ}}$

(2) Cell with transference (即：concentration cell with liquid junction)

例： $\mathrm{Na(Hg)|NaCl(aq,}\ m_1\mathrm{)|NaCl(aq,}\ m_2\mathrm{)Na(Hg)}$

Left: $\mathrm{Na(Hg)} \rightarrow \mathrm{Na}^+(m_1) + \mathrm{e}^-$

LJ: $t_+\mathrm{Na}^+(m_1) \rightarrow t_+\mathrm{Na}^+(m_2)$

$t_-\mathrm{Cl}^-(m_2) \rightarrow t_-\mathrm{Cl}^-(m_1)$ 因⊖逆向而行

Right: $\mathrm{Na}^+(m_2) + \mathrm{e}^- \rightarrow \mathrm{Na(Hg)}$

相加, $\mathrm{Na}^+(m_2) + t_+\mathrm{Na}^+(m_1) + t_-\mathrm{Cl}^-(m_2) \rightarrow \mathrm{Na}^+(m_1) + t_+\mathrm{Na}^+(m_2) + t_-\mathrm{Cl}^-(m_1)$

即： $(1-t_+)\mathrm{Na}^+(m_2) + t_-\mathrm{Cl}^-(m_2) \rightarrow (1-t_+)\mathrm{Na}^+(m_1) + t_-\mathrm{Cl}^-(m_1)$

即： $t_-\mathrm{NaCl}(m_2) \rightarrow t_-\mathrm{NaCl}(m_1)$

$$\varepsilon = -\frac{\mathrm{R}T}{F}\ln\left(\frac{a_1}{a_2}\right)^{t_-} = \underset{\uparrow \atop \text{打折扣}}{t_-}\left[\frac{-\mathrm{R}T}{F}\ln\frac{a_1}{a_2}\right]$$

(此不是$\varepsilon_{\mathrm{LJ}}$
而是ε when LJ present) ↗ ε

① 如是 concentration cell with liquid junction, 則ε要打折扣

② 如是考慮有 liquid junction, 則會有$\varepsilon_{\mathrm{LJ}}$

其大小由t_+(或t_-)及濃度差異來決定

§ 可以設計 cell 使$\varepsilon_{\mathrm{LJ}}$變很小

〈例 1〉: $\mathrm{Pt|H_2}(P_1)\mathrm{|HCl}(m_1)\mathrm{||HCl}(m_2)\mathrm{|H_2}(P_1)\mathrm{|Pt}$

$\Rightarrow$ $\mathrm{Pt|H_2}(P_1)\mathrm{|HCl}(m_1)\mathrm{|AgCl(s)|Ag|AgCl(s)|HCl}(m_2)\mathrm{|H_2}(P_1)\mathrm{|Pt}$

Ag 導電性好, 聯接 2 cell 可免去 LJ

〈例 2〉: 利用鹽橋且 $t_+ = t_-$ (如：KCl, $\mathrm{NH_4Cl}$, $\mathrm{NH_4NO_3}$)

由前之討論 $\varepsilon = t_-\left(\dfrac{-\mathrm{R}T}{nF}\ln\dfrac{a_1}{a_2}\right) = 2t_-\left(\dfrac{-\mathrm{R}T}{nF}\ln\dfrac{m_1\gamma_{1\pm}}{m_2\gamma_{2\pm}}\right)$

但 $\varepsilon_{\mathrm{Nernst}} = -\dfrac{\mathrm{R}T}{F}\ln\dfrac{m_1\gamma_{1\pm}}{m_2\gamma_{2\pm}}$

$t_-\mathrm{NaCl}(m_2) = t_-\mathrm{NaCl}(m_1)$

$\mathrm{Na}^+(m_2) = \mathrm{Na}^+(m_1)$

$\varepsilon = \varepsilon_{\mathrm{Nernst}} + \varepsilon_{\mathrm{LJ}}$, $\varepsilon_{\mathrm{LJ}} = \varepsilon - \varepsilon_{\mathrm{Nernst}}$

$$\varepsilon_{\mathrm{LJ}} = (1-2t_-)\frac{\mathrm{R}T}{F}\ln\frac{m_1\gamma_{1\pm}}{m_2\gamma_{2\pm}}$$

$$= (t_+ - t_-)\frac{\mathrm{R}T}{F}\ln\frac{m_1\gamma_{1\pm}}{m_2\gamma_{2\pm}}$$

故 $t_+ = t_-$ 時，$\varepsilon_{\mathrm{LJ}} \to 0$