Potentials and Thermodynamics of Cells (Ch. 2)

Basic Electrochemical Thermodynamics:
→ potential vs. chemical information

Reversibility
Free energy
Half-potential and cell potential
Nernst equation

Electrochemical potential

Liquid junction potential
Types of liquid junctions
Conductance, transference numbers, and mobility

Selective electrodes

Basic electrochemical thermodynamics

Reversibility: thermodynamically important

(a) Chemical reversibility

$Pt/H_2/H^+, Cl^-/AgCl/Ag$ 0.222 V

$H_2 + 2AgCl \rightarrow 2Ag + 2Cl^- + 2H^+$

Reversing the cell → reversed cell reaction "chemically reversible"

$Zn/ H^+, SO_4^{2-}/Pt$

Discharging the cell: $Zn + 2H^+ \rightarrow Zn^{2+} + H_2$ (hydrogen evolution)

Reversing the cell:

$2H^+ + 2e \rightarrow H_2$ (Zn electrode)

$2H_2O \rightarrow O_2 + 4H^+ + 4e$ (Pt electrode)

$2H_2O \rightarrow 2H_2 + O_2$ (Net)

→ "chemically irreversible"

(b) Thermodynamic reversibility: an infinitesimal reversal

Chemically reversible: thermodynamically reversible or not

(c) Practical reversibility

- Actual process at finite rate → depends on the time domain
- In electrochemistry, following Nernst equation (linkage E and concentrations)

$$O + ne = R$$

$$E = E^{0\prime} + (RT/nF)\ln(C_O/C_R)$$

→ electrochemically (or nernstian) reversible

Reversibility & Gibbs free energy

Reversible: net work from the cell = ΔG

Irreversible: net work from the cell < ΔG

Free energy & cell emf (electromotive force)

$$Zn/Zn^{2+}\ (a=1),\ Cl^{-}\ (a=1)/AgCl/Ag$$

Discharge the cell through $R = \infty$ (zero current) → reversible

→ ΔE (potential difference) is the equilibrium value (open-circuit)

$Zn + 2AgCl \rightarrow Zn^{2+} + 2Ag + 2Cl^{-}$ $E_{rxn} = 0.985$ V (spontaneous)

Reversed cell: -0.985 V

Positive E_{rxn} (spontaneous reaction

$$\Delta G = -nFE_{rxn}$$

$$\Delta G^0 = -nFE_{rxn}{}^0$$

$E_{rxn}{}^0$: standard emf of the cell reaction

$$\Delta S = -(\partial \Delta G/\partial T)_p = nF(\partial E_{rxn}/\partial T)_p$$

$$\Delta H = \Delta G + T\Delta S = nF[T(\partial E_{rxn}/\partial T)_p - E_{rxn}]$$

$$RT\ln K_{rxn} = -\Delta G^0 = nFE_{rxn}$$

Half-reactions & reduction potentials

Half-reaction emf to a standard reference electrode

- NHE (normal hydrogen electrode) or SHE (standard)

$Pt/H_2(a=)/H^+(a=1)$ E = 0 V at all temperatures

Reaction: $2H^+ + 2e = H_2$

Appendix C (p808-): standard electrode potentials for the reduction

$Pt/H_2(a=)/H^+(a=1)//Ag^+(a=1)/Ag$ 0.7999 V

→ $Ag^+ + e = Ag$ $E^0 = +0.7999$ V vs. NHE

cf. Ag_n, $n < 20$ → bulk Ag metal과 아주 다름

Ag_1: $Ag^+(aq) + e = Ag_1(aq)$ $E_1^0 = -1.8$ V

2.6 V more negative than bulk Ag: single Ag에서 전자 떼어내기가 훨씬 쉽다!!

Ag_2: $Ag^+ + Ag_1 + e = Ag_2$ $E_2^0 \sim 0$ V

Cluster size↑→ E_n^0 approaches bulk: greater surface energy of small cluster

emf & concentration

Consider $\nu H_2 + \nu_O O \rightarrow \nu_R R + \nu H^+$

$$\Delta G = \Delta G^0 + RT\ln(a_R^{\nu R} a_{H+}^{\nu H+}/a_O^{\nu O} a_{H2}^{\nu H2})$$

a: activity ($a_{H+} = a_{H2} = 1$), $\Delta G = -nFE$ & $\Delta G^0 = -nFE^0$

Nernst equation

$$E = E^0 - (RT/nF)\ln(a_R\nu^R a_{H+}^{\nu H+}/a_O^{\nu O} a_{H2}^{\nu H2}) = E^0 + (RT/nF)\ln(a_O^{\nu O}/a_R^{\nu R})$$

$$E_{rxn} = E_{right} - E_{left} > 0 \text{ (spontaneous reaction)}$$

Formal potential

Activity $a = \gamma[A]$, γ: activity coefficient → unconvenient to use activity due to unknown activity

$E = E^0 – RT/nF \, ln \, \gamma_R / \gamma_O – RT/nF \, ln \, [R]/[O]$

$E = E^{0'} – RT/nF \, ln \, [R]/[O]$

$E^{0'}$: formal potential (Table C.2 (p. 810))

- Ionic strength 가 activity coefficient에 영향을 미치기 때문에 formal potential 은 medium에 따라 다 다름 → standard potential은 다른 ionic strength에서 측정하여 zero ionic strength로 extrapolating함

Reference electrodes

NHE

Ag/AgCl/KCl (sat) 0.222 V vs. NHE

Saturated Calomel Electrode 0.2415 V vs. NHE

Non-Cl system: Hg/Hg2SO4/K2SO4

Nonaqueous system:

- quasireference electrode (QRE):

Ag or Pt wire in organic solvent (e.g., ferrocene/ferrocenium)

Interfacial potential differences

Potential at any point within a phase: $\Phi(x,y,z)$ work required to bring a unit positive charge from ∞ to point (x,y,z)

$$\Phi(x,y,z) = \int \quad -\varepsilon d\boldsymbol{l}$$

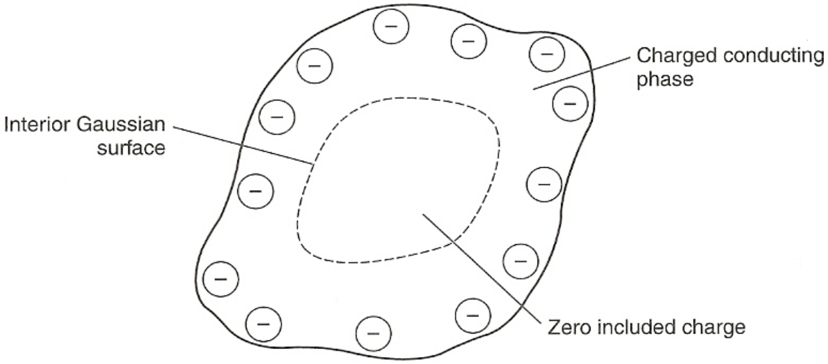
ε: electric field strength (force/unit charge)

Potential difference between (x´,y´,z´) and (x,y,z)

$$\Phi\,(x',y',z') - \Phi(x,y,z) = \int \quad -\varepsilon d\boldsymbol{l}$$

Charge q inside an imaginary surface (Gaussian surface)

$$q = \varepsilon_0 \oint \varepsilon d\mathbf{S}$$



given by an integral of the ε

ε_0 : permittivity, 8.85419 x 10^{-12} $C^2N^{-1}m^{-1}$

Excess charge resides on the surface of the conducting phase

→ space charge region (~Å - ~1000Å)

Interactions between conducting phases

When two conductors (e.g., metal & electrolyte) contact
→ electrical double layer

$$q^S = -q^M$$

→ <u>interfacial potential difference</u> ($\Phi^M - \Phi^S$)
depends on charge imbalance at the interface & physical size of the interface
that is, <u>charge density</u> (C/cm^2)

Measurement of potential differences

- No measurement of $\Delta\phi$ for single interface → Need two interfaces

Measurement of cell potential: a sum of several interfacial differences

$Cu/Zn/Zn^{2+}, Cl^{-}/AgCl/Ag/Cu'$

To focus a single
interfacial potential difference
→ maintain constant interfacial
Potential at all of the other junctions
In the cell

Electrochemical potentials

Electrochemical potential for species i with charge z_i in phase α

$$\bar{\mu}_i^{\alpha} = \mu_i^{\alpha} + z_i F \phi^{\alpha}$$

Chemical potential, $\mu_i^{\alpha} = (\partial G/\partial n_i)_{nj\neq i,\ P,\ T}$

Electrochemical potential, $\bar{\mu}_i^{\alpha} = (\partial \bar{G}/\partial n_i)_{T,P,nj\neq i}$

$\bar{G}$: electrochemical free energy

(a) Properties of electrochemical potential

1. For an uncharged species: $\bar{\mu}_i^{\alpha} = \mu_i^{\alpha}$
2. For any substance: $\mu_i^{\alpha} = \mu_i^{0\alpha} + RT\,ln\,a_i^{\alpha}$, where $\mu_i^{0\alpha}$ is the standard chemical potential, and a_i is the activity
3. For a pure phase at unit activity (e.g., solid Zn, AgCl, Ag, H_2): $\bar{\mu}_i^{\alpha} = \mu_i^{0\alpha}$
4. For electrons in a metal (z = -1): $\bar{\mu}_e^{\alpha} = \mu_e^{0\alpha} - F\phi^{\alpha}$
5. For a equilibrium of species i between phase α and β: $\bar{\mu}_i^{\alpha} = \bar{\mu}_i^{\beta}$

Cell potential

$$\mathrm{Cu/Zn/Zn^{2+}, Cl^{-}/AgCl/Ag/Cu'}$$

Cell reaction: $\mathrm{Zn + 2AgCl + 2e(Cu') = Zn^{2+} + 2Ag + 2Cl^{-} + 2e(Cu)}$

At equilibrium

→ Nernst equation for the cell

Fermi level & absolute potential

Electrochemical potential of electrons in a phase α, $\bar{\mu}_e^{\alpha}$: “Fermi level” or “Fermi energy”

→ electron energy E_F^{α}

Absolute potential (vs. potential of a free electron in vacuum) of NHE: 4.44 V

Energy to remove an electron from NHE to vacuum = 4.44 eV

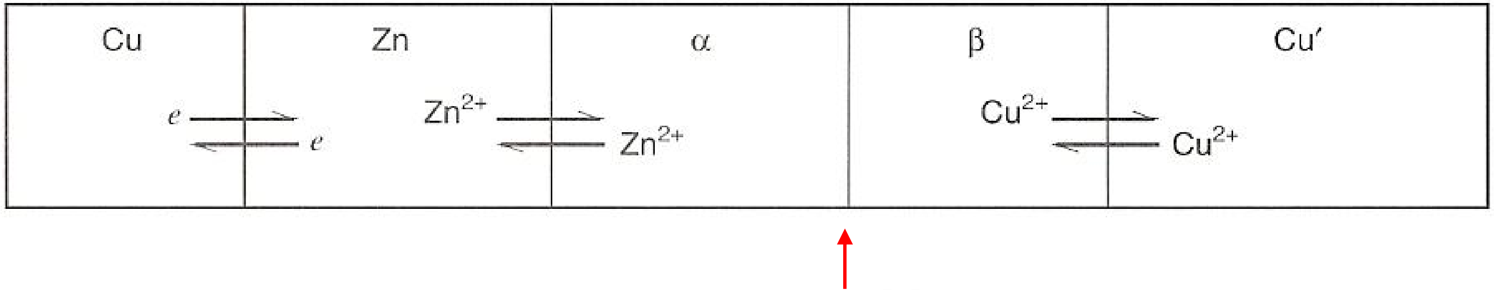
Liquid junction potentials

Interface (liquid junction) between two solutions: transport processes to mix the solutes

$$\underset{\alpha}{\mathrm{Cu/Zn/Zn^{2+}}}\mathrm{/}\underset{\beta}{\mathrm{Cu^{2+}}}\mathrm{/Cu'}$$

Overall cell potential at null current

$$E=\underbrace{[\phi^{Cu'} - \phi^{\beta}]}_{\text{Cu}} - \underbrace{[\phi^{Cu} - \phi^{\alpha}]}_{\text{Zn}} + \underbrace{[\phi^{\beta} - \phi^{\alpha}]}_{\text{liquid junction potential}}$$



Non-equilibrium

Types of liquid junctions

1. Two solutions of the same electrolyte at different concentrations
2. Two solutions at the same concentration with different electrolytes having an ion in common
3. Two solutions not satisfying conditions 1 or 2

Conductance, transference number, & mobility

$$\begin{array}{c} \qquad\qquad \alpha \qquad\qquad\quad \beta \\ (-)\ Pt/H_2(1\ atm)/H^+, Cl^-/H^+, Cl^-/H_2(1\ atm)/Pt'\ \ (+) \\ \qquad\qquad (a_1) \qquad\quad (a_2) \end{array}$$

$a_1 < a_2$

Galvanically operated:

Left electrode (oxidation): $H_2 \rightarrow 2H^+(\alpha) + 2e(Pt)$

Right electrode (reduction): $2H^+(\beta) + 2e(Pt') \rightarrow H_2$

→ positive charge↑ in α phase & negative charge↑ in β phase
H^+ movement to the right, Cl^- to the left

Transference number (or transport number)

The fraction of the current carried by H^+ and Cl^-: t_+ and t_-

$$t_+ + t_- = 1$$

$$\sum t_i = 1$$

e.g., Figure above: $t_+ = 0.8$, $t_- = 0.2$

Conductance ($S = \Omega^{-1}$), $L = \kappa A/l$

conductivity (κ, Scm^{-1}): contribution from all ionic species

$\propto$ ion conc, charge magnitude ($|z_i|$), index of migration velocity (u_i)

Mobility (u_i): limiting velocity of the ion in an electric field of unit strength

unit: $cm^2V^{-1}s^{-1}$ (cm/s per V/cm)

electric field, E → electric force → counterbalance with frictional drag → terminal velocity

Electric force = $|z_i|eE$ e: electronic charge

Frictional drag (Stokes law) = $6\pi\eta rv$

η :viscosity of medium, r: ion radius, v: velocity

When the terminal velocity is reached:

$$u_i = v/E = |z_i|e/\,6\pi\eta r$$

Conductivity

$$\kappa = F\sum|z_i|u_iC_i$$

Transference number for species i = conductivity by i /total conductivity

$$t_i = |z_i|u_iC_i/\sum|z_j|u_jC_j$$

For pure electrolytes (e.g., KCl, $CaCl_2$, HNO_3) → equivalent conductivity (Λ)
당량전도도

$$\Lambda = \kappa/C_{eq}$$

C_{eq}: concentration of + (or -) charges = $C|z|$

$$\Lambda = F(u_+ + u_-) = \lambda_+ + \lambda_-$$

equivalent ion conductivity, $\lambda_i = Fu_i$

$$t_i = \lambda_i/\Lambda = u_i/(u_+ + u_-)$$

- Table 2.3.1: t_+ → individual ionic conductivities, λ_i 측정 가능
- λ_i, t_i depend on concentration of pure electrolyte because interactions between ions tend to alter mobilities

→ Table 2.3.2: λ_{0i} (extrapolated to infinite dilution) → t_i 계산

For pure electrolyte: $t_i = \lambda_i/\Lambda$

For mixed electrolytes: $t_i = |z_i|C_i\lambda_i/\sum|z_j|C_j\lambda_j$

Solid electrolyte: ions move under electric field without solvent → 전도도 존재

→ batteries, fuel cells, and electrochemical devices

Calculation of liquid junction potentials

Metal-solution interfaces

$$1/2H_2 \rightarrow H^+(\alpha) + e(Pt)$$

$$H^+(\beta) + e(Pt') \rightarrow 1/2H_2$$

Charge transport at the liquid junction

$$t_+H^+(\alpha) + t_-Cl^-(\beta) = t_+H^+(\beta) + t_-Cl^-(\alpha)$$

$$\rightarrow \quad H^+(\beta) + e(Pt') = H^+(\alpha) + e(Pt)$$

Under null current conditions

$$\bar{\mu}_{H+}^{\beta} + \bar{\mu}_{e}^{Pt'} = \bar{\mu}_{H+}^{\alpha} + \bar{\mu}_{e}^{Pt}$$

$$FE = F(\Phi^{Pt'} - \Phi^{Pt}) = \bar{\mu}_{H+}^{\beta} - \bar{\mu}_{H+}^{\alpha}$$

$$E = (RT/F)\ln(a_2/a_1) + (\phi^{\beta} - \phi^{\alpha})$$

$$E_{cell} = E_{Nernst} + E_j$$

E_j: liquid junction potential

For type 1 junction involving 1:1 electrolytes

$$E_j = (\phi^\beta - \phi^\alpha) = (t_+ - t_-)(RT/F)\ln(a_2/a_1)$$

e.g.,

$(t_+ - t_-) \rightarrow 0$, $E_j \rightarrow 0$

For $a_1 = 0.01$ M, $a_2 = 0.1$ M HCl, $t_+ = 0.83$ & $t_- = 0.17$ (Table 2.3.1)

$E_j = (0.83 - 0.17)(59.1)\log(0.01/0.1) = -39.1$ mV

For a total cell, $E = (59.1)\log(a_2/a_1) + E_j = 59.1 - 39.1 = 20.0$ mV

→ liquid junction potential: 측정된 cell potential의 중요한 성분（큰 영향）

For type 2 junctions between 1:1 electrolytes

$$E_j = \pm(RT/F)\ln(\Lambda^\beta/\Lambda^\alpha)$$

Minimizing liquid junction potentials

대부분 E_j: additional troublesome → should be minimized! → salt bridge

(concentrated ions of nearly equal mobility)

$HCl(C_1)/NaCl(C_2) \rightarrow HCl(C_1)/KCl(C)/NaCl(C_2)$

C↑ → E_j↓ because ion transport at the two junctions is dominated more and more extensively by the massive amounts of KCl

Salt bridges: KCl ($t_+ = 0.49$, $t_- = 0.51$), KNO_3 ($t_+ = 0.51$, $t_- = 0.49$)
CsCl ($t_+ = 0.5025$), RbBr ($t_+ = 0.4958$), NH_4I ($t_+ = 0.4906$)

Junctions of two immiscible liquids

Biological membrane model

Selective electrodes

Two electrolytes phase but only a single ion could penetrate by selectively permeable membrane (t = 1 for the permeating ion i, t = 0 for other ions)

$$(RT/z_i)\ln(a_i^\beta/a_i^\alpha) + F(\phi^\beta - \phi^\alpha) = 0$$

$$E_m = -(RT/z_iF)\ln(a_i^\beta/a_i^\alpha)$$

E_m (membrane potential): potential difference between the two phases
→ ion-selective electrode의 핵심

Glass electrodes

pH 측정, alkali ion activity 특정

$Hg/Hg_2Cl_2/KCl(sat'd)/$test solution/Glass membrane/HCl(0.1 M)/AgCl/Ag

SCE (reference)   internal reference

Glass electrode (그림)

if the interface is selective toward a single species i

$$E = \text{constant} + (RT/z_iF)\,ln\,a_i^{soln}$$

constant: sum of potential differences at all of the other interfaces

Glass: affinity for certain cations

$$E_m = (\phi^{\beta} - \phi^{m''}) + (\phi^{m''} - \phi^{m}) + (\phi^{m} - \phi^{m'}) + (\phi^{m'} - \phi^{\alpha})$$

✓ 1st & last terms: interfacial potential difference from equilibrium balance of selective charge exchange across an interface → “Donnan equilibrium”

Suppose Na^+ & H^+ as active ions

✓ 2nd & 3rd terms: junction potentials within the glass membrane → “diffusion potentials”

Whole potential difference across the membrane

E_m =

(Donnan term) (Diffusion term)

Rearrangement

E_m =

$$\overline{\mu}_{Na+}^{\alpha} + \overline{\mu}_{H+}^{m'} = \overline{\mu}_{H+}^{\alpha} + \overline{\mu}_{Na+}^{m'}$$

$$Na^+(\alpha) + H^+(m') = H^+(\alpha) + Na^+(m')$$

Equilibrium constant $K_{H+,Na+} = a_{H+}^{\alpha} a_{Na+}^{m'} / a_{H+}^{m'} a_{Na+}^{\alpha}$

Same for β and m ″

$$E_m =$$

$K_{H+,Na+}$ and u_{Na+}/u_{H+} are constant → their product: "potentiometric selectivity coefficient" $k_{H+,Na+}^{pot}$

$$E_m =$$

β phase: internal filling solution (of constant composition) & α : test solution

Overall potential of the cell

$$E = \text{constant} + (RT/F)\ln(a_{H+}^{\alpha} + k_{H+,Na+}^{pot} a_{Na+}^{\alpha})$$

Cell potential is responsive to the activities of both Na^+ & H^+ in the test solution
Degree of selectivity between these species is defined $k_{H+,Na+}^{pot}$

If $k_{H+,Na+}^{pot}\, a_{Na+}^{\ \alpha} << a_{H+}^{\ \alpha}$, membrane responds exclusively to H^+

Glass membranes also respond to other ions, Li^+, K^+, Ag^+, NH_4^+
→ relative responses by potentiometric selectivity coefficients

Different types of electrodes (from different type of glass)
(a) pH electrodes with a selectivity order $H^+ >>> Na^+ > K^+.. > Ca^{2+}$
(b) sodium-sensitive electrodes with the order $Ag^+ > H^+ > Na^+ >> K^+..$
(c) cation-sensitive electrode

(d) Detection limits: $10^{-6} \sim 10^{-7}$ M

Gas-sensing electrodes

Typical potentiometric gas-sensing electrode: SO_2, NH_3, CO_2 penetrate the membrane → change in pH

ZrO_2 with Y_2O_3: O_2 at high T

Sensors for exhaust gas (CO & NO_x)

Enzyme-coupled devices

Polymer diaphragm filled with a matrix in which an enzyme is immobilized

e.g., urease in polymer gel → urea