

Thermodynamics of materials

31. Energy Conversions and Electrochemistry

Kunok Chang
kunok.chang@khu.ac.kr

Kyung Hee University

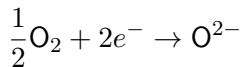
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 - Electrode Reactions and Electrode Potentials
 - Standard Electrode Potential
 - Cell Reactions and Cell Voltage
 - Voltage Derive from Chemical Composition Difference

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Electrode Reactions and Electrode Potentials

- Assume the typical cathodic reaction



if the reaction is under the equilibrium,

$$\frac{1}{2}\mu_{\text{O}_2}^c + 2\tilde{\mu}_e^c = \tilde{\mu}_{\text{O}^{2-}}^c$$

where c superscript represents that the reaction takes place at cathode.

- In other form,

$$\frac{1}{2}\mu_{\text{O}_2}^c + 2\mu_e^c - 2\mathcal{F}\phi_{\text{electrode}}^c = \mu_{\text{O}^{2-}}^c - 2\mathcal{F}\phi_{\text{electrolyte}}^c$$

where $\phi_{\text{electrolyte}}^c$ is the electric potential at the electrode side of cathode/electrolyte interface and $\phi_{\text{electrode}}^c$ is the potential on the electrode side.



Electrode Reactions and Electrode Potentials

- We introduce the quantity cathode electrode potential E^c by

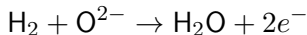
$$E^c = \phi_{\text{electrode}}^c - \phi_{\text{electrolyte}}^c = -\frac{\mu_{\text{O}^{2-}}^c - \frac{1}{2}\mu_{\text{O}_2}^c - 2\mu_e^c}{2\mathcal{F}} = -\frac{\Delta G^c}{2\mathcal{F}}$$

where ΔG^c is the Gibbs free energy change for the cathode reaction.



Electrode Reactions and Electrode Potentials

- The reaction at the anode of the fuel cell is



At equilibrium for the anode reaction,

$$\mu_{\text{H}_2}^a + 2\mu_{\text{O}^{2-}}^a - 2\mathcal{F}\phi_{\text{electrolyte}}^a = \mu_{\text{H}_2\text{O}}^a + 2\mu_e^a - 2\mathcal{F}\phi_{\text{electrode}}^a$$

- We introduce the quantity cathode electrode potential E^c by

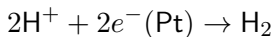
$$E^a = \phi_{\text{electrolyte}}^a - \phi_{\text{electrode}}^a = -\frac{\mu_{\text{H}_2\text{O}}^a + 2\mu_e^a - \mu_{\text{H}_2}^a - \mu_{\text{O}^{2-}}^a}{2\mathcal{F}} = -\frac{\Delta G^a}{2\mathcal{F}}$$

where ΔG^c is the Gibbs free energy change for the anode reaction.



Standard Electrode Potential

- For the hydrogen electrode reaction



at equilibrium,

$$2\tilde{\mu}_{\text{H}^+} + 2\tilde{\mu}_{e^-}^{\text{Pt}} = \mu_{\text{H}_2}$$

where $\tilde{\mu}_{\text{H}^+}$ and $\tilde{\mu}_{e^-}$ are the electrochemical potentials of H^+ and electrons.

- The electric potential drop across the electrode/electrolyte interface at the electrode is given by

$$E_{\text{H}_2/\text{H}^+} = -\frac{\mu_{\text{H}_2}^\circ - \mu_{\text{H}^+}^\circ - 2\mu_{e^-}^{\text{Pt}}}{2\mathcal{F}} - \frac{RT}{2\mathcal{F}} \ln \frac{p_{\text{H}_2}}{a_{\text{H}^+}}$$

- The electric potential of standard hydrogen electrode (SHE) is

$$E_{\text{SHE}}^\circ = -\frac{\mu_{\text{H}_2}^\circ - \mu_{\text{H}^+}^\circ - 2\mu_{e^-}^{\text{Pt}}}{2\mathcal{F}}$$



Standard Electrode Potential

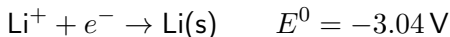
- Then we have

$$E_{\text{H}_2/\text{H}^+} = E_{\text{SHE}}^\circ - \frac{RT}{2\mathcal{F}} \ln \frac{p_{\text{H}_2}}{a_{\text{H}^+}}$$

- Now we set the standard potential $E_{\text{SHE}}^\circ = 0$, the electrode potential of the hydrogen electrode at nonstandard conditions is given by

$$E_{\text{H}_2/\text{H}^+} = -\frac{RT}{2\mathcal{F}} \ln \frac{a_{\text{H}^+}}{p_{\text{H}_2}}$$

- The standard electrode potential of Li relative to the standard hydrogen electrode is given by

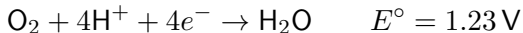


A negative value for the standard potential for Li indicates that it is more difficult to reduce Li^+ to Li metal than H^+ to H_2 , or it is easier to oxidize Li than H_2 .



Standard Electrode Potential

- The standard electrode potential of oxygen relative to standard hydrogen electrode potential is



Cell Reactions and Cell Voltage

- An electrochemical cell consists of a cathode, an anode, an electrolyte, a separator separating the cathode and anode, and metallic contacts to an external device. A short-hand notation is

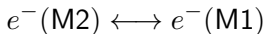


- M1 is a metallic electrode, $M1^{z+}$ is the corresponding ion of valence z , and M2(I) and M2(II) are the metallic connects of the same metal M2 to an external device.



Cell Reactions and Cell Voltage

- At the junction M1|M2(II), at equilibrium,



$$\mu_e^{\text{M2(II)}} - \mathcal{F}\phi^{\text{M2(II)}} = \mu_e^{\text{M1}} - \mathcal{F}\phi^{\text{M1}}$$

where $\mu_e^{\text{M2(II)}}$ and μ_e^{M1} are chemical potentials of electrons in metal M2 and electrode M1, respectively, $\phi^{\text{M2(II)}}$ and ϕ^{M1} are electric potentials in M2 and M1.

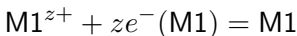
- Hence the potential drop at the junction M1|M2(II) at equilibrium is

$$\phi^{\text{M2(II)}} - \phi^{\text{M1}} = \frac{\mu_e^{\text{M2(II)}} - \mu_e^{\text{M1}}}{\mathcal{F}} = \frac{\mu_e^{\text{M2(II)}}}{\mathcal{F}} - \frac{\mu_e^{\text{M1}}}{\mathcal{F}}$$



Cell Reactions and Cell Voltage

- For the electrode reaction at $M1^{z+}|M1$ electrolyte/electrode interface at equilibrium,



$$\mu_{M1^{z+}} + z\mathcal{F}\phi^{\text{electrolyte}} + z\mu_e^{M1} - z\mathcal{F}\phi^{M1} = \mu_{M1}$$

where $\mu_{M1^{z+}}$ and μ_{M1} are chemical potentials of $M1^{z+}$ and $M1$ and $\phi^{\text{electrolyte}}$ is the electric potential in the electrolyte.

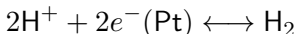
- The electrode potential for $M1^{z+}|M1$ is then

$$\phi^{M1} - \phi^{\text{electrolyte}} = \frac{\mu_{M1^{z+}} + z\mu_e^{M1} - \mu_{M1}}{z\mathcal{F}} = \frac{\mu_{M1^{z+}} - \mu_{M1}}{z\mathcal{F}} + \frac{\mu_e^{M1}}{\mathcal{F}}$$



Cell Reactions and Cell Voltage

- For the Pt electrode at equilibrium,



$$2\mu_{\text{H}^+} + 2\mathcal{F}\phi^{\text{electrolyte}} + 2\mu_{e^-}^{\text{Pt}} - 2\mathcal{F}\phi^{\text{Pt}} = \mu_{\text{H}_2}$$

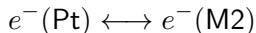
where μ_{H^+} and μ_{H_2} are chemical potentials of H^+ and H_2 , and $\mu_{e^-}^{\text{Pt}}$ is the chemical potential of electrons in Pt.

- The Pt electrode potential is

$$\phi^{\text{electrolyte}} - \phi^{\text{Pt}} = \frac{\mu_{\text{H}_2} - 2\mu_{\text{H}^+}}{2\mathcal{F}} - \frac{\mu_{e^-}^{\text{Pt}}}{\mathcal{F}}$$

Cell Reactions and Cell Voltage

- At the $M2(I)|Pt$ junction at equilibrium,



$$\mu_{e^{-}}^{Pt} - \mathcal{F}\phi^{Pt} = \mu_{e^{-}}^{M2(I)} - \mathcal{F}\phi^{M2(I)}$$

where ϕ^{Pt} and $\phi^{M2(I)}$ are electric potentials in Pt and the left metallic contact M2.

- The potential drop at the junction is

$$\phi^{Pt} - \phi^{M2(I)} = \frac{\mu_{e^{-}}^{Pt}}{\mathcal{F}} - \frac{\mu_{e^{-}}^{M2(I)}}{\mathcal{F}}$$

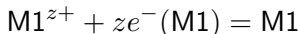
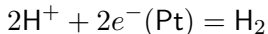
- Summing up,

$$\phi^{M2(II)} - \phi^{M2(I)} = \frac{2\mu_{M1^{z+}} + \mu_{H_2} - 2\mu_{M1} - 2z\mu_{H^+}}{2z\mathcal{F}}$$

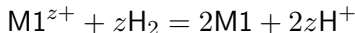


Cell Reactions and Cell Voltage

- The open-circuit voltage or potential drop for the entire cell is independent of the chemical potentials of electrons in electrodes or in the metallic contacts as long as the two metallic contacts are the same metal M2.
- Consider two reactions,



the overall reaction is



- The thermodynamic driving force for the above overall reaction is

$$D = -\Delta G = 2\mu_{\text{M1}^{z+}} + z\mu_{\text{H}_2} - 2\mu_{\text{M1}} - 2z\mu_{\text{H}^+}$$



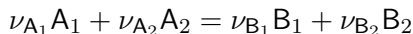
Cell Reactions and Cell Voltage

- The open-circuit electric voltage of an electrochemical cell,

$$E = \phi^{M2(II)} - \phi^{M2(I)} = \frac{D}{2z\mathcal{F}} = -\frac{\Delta G}{2z\mathcal{F}}$$

where $2z$ represents the number of moles of electrons involved in the reaction.

- For a reaction



- Then, the Gibbs energy of the reaction is

$$\Delta G = \Delta G^\circ + RT \ln \frac{a_{B_1}^{\nu_{B_1}} a_{B_2}^{\nu_{B_2}}}{a_{A_1}^{\nu_{A_1}} a_{A_2}^{\nu_{A_2}}} = \Delta G^\circ + RT \ln K$$



Cell Reactions and Cell Voltage

- Therefore, the voltage variation with activity is given by

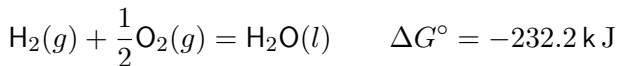
$$E = E^\circ - \frac{RT}{z\mathcal{F}} \ln K$$

which is often referred to the Nernst equation. E° is the standard cell voltage when all the species involved in the reaction are in their standard states,

$$E^\circ = -\frac{\Delta G^\circ}{z\mathcal{F}}$$

where ΔG° is the standard Gibbs free energy of reaction involving z moles of electrons.

- For example at room temperature,

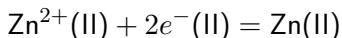
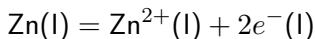


$$E^\circ = -\frac{\Delta G^\circ}{z\mathcal{F}} = -\frac{-232200}{2 \times 96480} = 1.23 \text{ V}$$

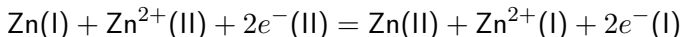


Voltage Derive from Chemical Composition Difference

- For this cell, the half-cell reactions are



- The overall reaction is



at equilibrium,

$$\mu_{\text{Zn}}^{\text{I}} + \mu_{\text{Zn}^{2+}}^{\text{II}} + 2\mathcal{F}\phi_{\text{electrolyte}}^{\text{II}} + 2\mu_{e^{-}}^{\text{II}} - 2\mathcal{F}\phi_{\text{electrode}}^{\text{II}} = \mu_{\text{Zn}}^{\text{II}} + \mu_{\text{Zn}^{2+}}^{\text{I}} + 2\mathcal{F}\phi_{\text{electrolyte}}^{\text{I}}$$



Voltage Derive from Chemical Composition Difference

- The contribution of chemical potentials of electrons disappears if external metallic connections of the same metal are considered. The cell voltage is

$$E = \phi_{\text{electrode}}^{\text{II}} - \phi_{\text{electrode}}^{\text{I}} = \frac{(\mu_{\text{Zn}}^{\text{I}} - \mu_{\text{Zn}}^{\text{II}}) + (\mu_{\text{Zn}^{2+}}^{\text{II}} - \mu_{\text{Zn}^{2+}}^{\text{I}})}{2\mathcal{F}}$$

- For pure Zn electrode,

$$E = \frac{RT}{2\mathcal{F}} \ln \frac{a_{\text{Zn}^{2+}}^{\text{II}}}{a_{\text{Zn}^{2+}}^{\text{I}}}$$

- When concentration of Zn^{2+} is uniform in electrolyte, we have

$$E = \frac{RT}{2\mathcal{F}} \ln \frac{a_{\text{Zn}}^{\text{I}}}{a_{\text{Zn}}^{\text{II}}}$$

