
Chapter 5

Oxidation and Reduction

한 화학종에서 다른 화학종으로 전자전이가 일어나는 과정
전연자원에 (MO, MS)서 원소(M)를 추출하는 과정

Redox 속도론/열역학

Reducing agent (Reductant); Oxidizing agent (Oxidant)

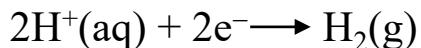
Anode (산화), Cathode (환원)

Reduction Potentials:

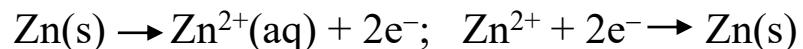
환원반응의 driving force: 이온을 금속으로 환원시키는데 요구되는 전위차

5.1 Redox Half-Reaction

a reduction half-reaction, gains e

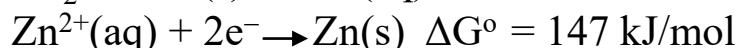
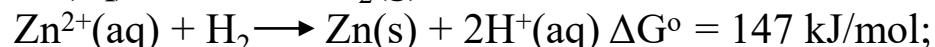
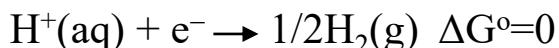


an oxidation reaction, loses e

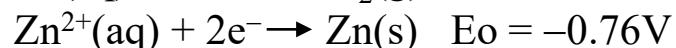
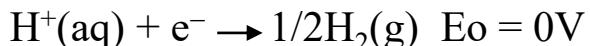


5.2 Standard Potentials

$\Delta G^\circ = -RT\ln K$ = negative (= $K > 1$: favorable, spontaneous)



$\Delta G^\circ = -nFE^\circ$ E° =standard potential, F = Faraday const =96.48 kcal/mol



전체반응 $E^\circ = 0.76\text{V}$

emf= 두 반반응 standard potential 차이: cell potential, V = 1 cal당 1J의 일

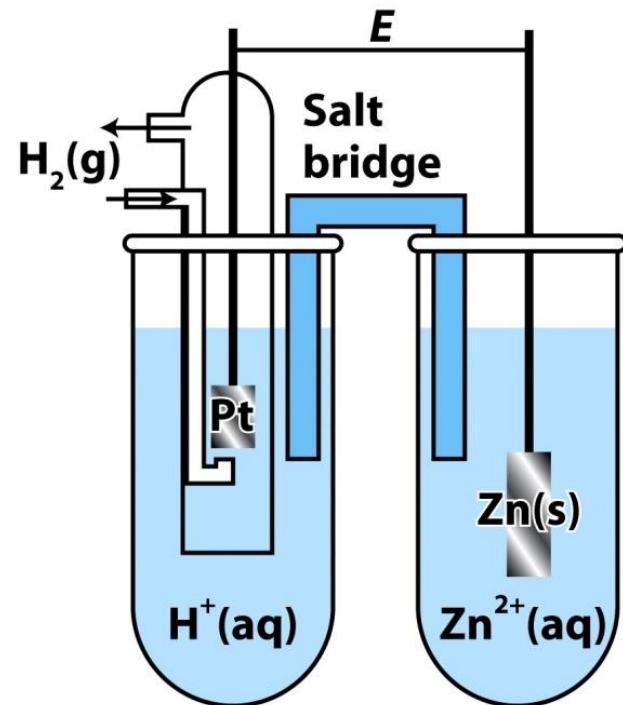


Figure 5-1
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5.3 Trends in Standard Potentials:

금속의 원자화, 이온화, 이온의 수화엔탈피 등 모두가 Standard potential에 기여

$-T\Delta S$ 는 큰 영향 없음

Table 5.1 Thermodynamic contributions to E^\ominus for a selection of metals at 298 K*

	Li	Na	Cs	Ag
$\Delta_{\text{sub}}H^\ominus / (\text{kJ mol}^{-1})$	+161	+109	+79	+284
$I / (\text{kJ mol}^{-1})$	520	495	376	735
$\Delta_{\text{hyd}}H^\ominus / (\text{kJ mol}^{-1})$	-520	-406	-264	-468
$\Delta_f H^\ominus(\text{M}^+, \text{aq}) / (\text{kJ mol}^{-1})$	+167	+206	+197	+551
E^\ominus / V	-3.04	-2.71	-3.03	+0.80

* $\Delta_f H^\ominus(H^+, \text{aq}) = +455, \text{ kJ mol}^{-1}$.

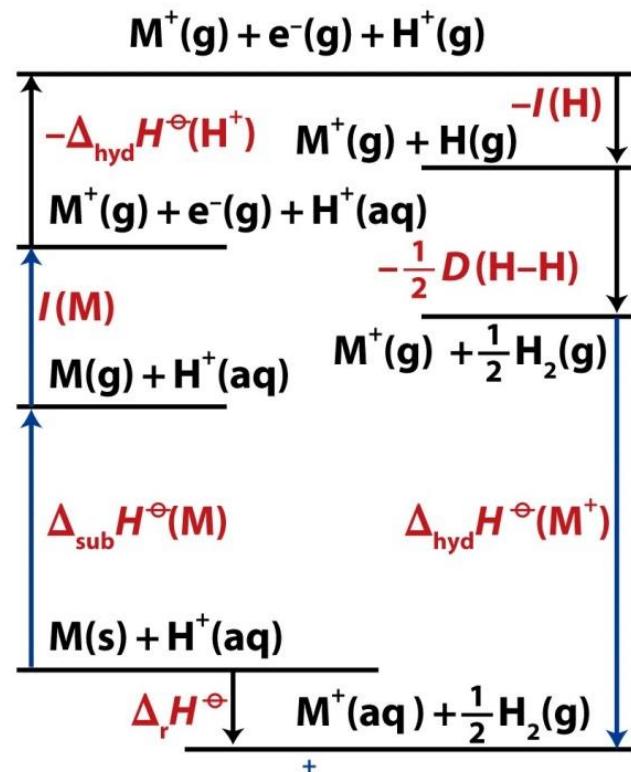


Figure 5-2

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5.4 Electrochemical Series:

E° 가 positive and large 이면 strong oxidizing agent
 E° 가 negative and large 이면 strong reducing agent

Series의 중요한 특징: couple의 산화수를 환원
 시키는 열역학적 경향

Table 5.2 Selected standard potentials at 298 K*

Couple	E^\ominus / V
$\text{F}_2(\text{g}) + 2 \text{e}^- \rightarrow 2 \text{F}^-(\text{aq})$	+2.87
$\text{Ce}^{4+}(\text{aq}) + \text{e}^- \rightarrow \text{Ce}^{3+}(\text{aq})$	+1.76
$\text{MnO}_4^-(\text{aq}) + 8 \text{H}^+(\text{aq}) + 5 \text{e}^- \rightarrow \text{Mn}^{2+}(\text{aq}) + 4 \text{H}_2\text{O}(\text{l})$	+1.51
$\text{Cl}_2(\text{g}) + 2 \text{e}^- \rightarrow 2 \text{Cl}^-(\text{aq})$	+1.36
$\text{O}_2(\text{g}) + 4 \text{H}^+(\text{aq}) + 4 \text{e}^- \rightarrow 2 \text{H}_2\text{O}(\text{l})$	+1.23
$[\text{IrCl}_6]^{2-}(\text{aq}) + \text{e}^- \rightarrow [\text{IrCl}_6]^{3-}(\text{aq})$	+0.87
$\text{Fe}^{3+}(\text{aq}) + \text{e}^- \rightarrow \text{Fe}^{2+}(\text{aq})$	+0.77
$[\text{PtCl}_4]^{2-}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Pt}(\text{s}) + 4 \text{Cl}^-(\text{aq})$	+0.76
$\text{I}_3^-(\text{aq}) + 2 \text{e}^- \rightarrow 3\text{I}^-(\text{aq})$	+0.54
$[\text{Fe}(\text{CN})_6]^{3-}(\text{aq}) + \text{e}^- \rightarrow [\text{Fe}(\text{CN})_6]^{4-}(\text{aq})$	+0.36
$\text{AgCl}(\text{s}) + \text{e}^- \rightarrow \text{Ag}(\text{s}) + \text{Cl}^-(\text{aq})$	+0.22
$2 \text{H}^+(\text{aq}) + 2 \text{e}^- \rightarrow \text{H}_2(\text{g})$	0
$\text{AgI}(\text{s}) + \text{e}^- \rightarrow \text{Ag}(\text{s}) + \text{I}^-(\text{aq})$	-0.15
$\text{Zn}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Zn}(\text{s})$	-0.76
$\text{Al}^{3+}(\text{aq}) + 3 \text{e}^- \rightarrow \text{Al}(\text{s})$	-1.68
$\text{Ca}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Ca}(\text{s})$	-2.87
$\text{Li}^+(\text{aq}) + \text{e}^- \rightarrow \text{Li}(\text{s})$	-3.04

* Further values are included in *Resource section 3*.

5.5 The Nernst Equation: cell의 emf 관계식

$$\Delta G = \Delta G^\circ + RT \ln(Q) \text{에서 } Q\text{는 반응지수}$$

$$-nFE = -nF\mathcal{E}^\circ + RT \ln(Q)$$

$$\mathcal{E} = \mathcal{E}^\circ - \frac{RT}{nF} \ln(Q) : \text{Nernst 식}$$

25°C에서

$$\mathcal{E} = \mathcal{E}^\circ - \frac{0.0591}{n} \log(Q)$$

$$\ln K = nFE^\circ/RT$$

Table 5.3 The relation between K and E^\ominus

E^\ominus /V	K
+2	10^{34}
+1	10^{17}
0	1
-1	10^{-17}
-2	10^{-34}

Table 5-3

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5.7. The Influence of pH

산화환원 반응: 전자와 H+ 이동 동반 \rightarrow pH에 significant 영향 받음

Redox Stability: 용매, 다른 용질, 용질 자신, 용존 산소

5.7 Reactions with Waters

물, oxidizing agent H_2 로 환원

물, reducing agent O_2 로 산화

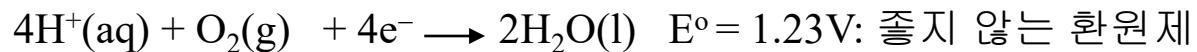
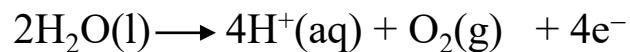
Oxidation by water: 큰 음의 표준전위를 갖는 금속이 aqueous acid와 반응하면

수소를 발생 (부동화(Passivation) 산화막이 형성되지 않으면..)



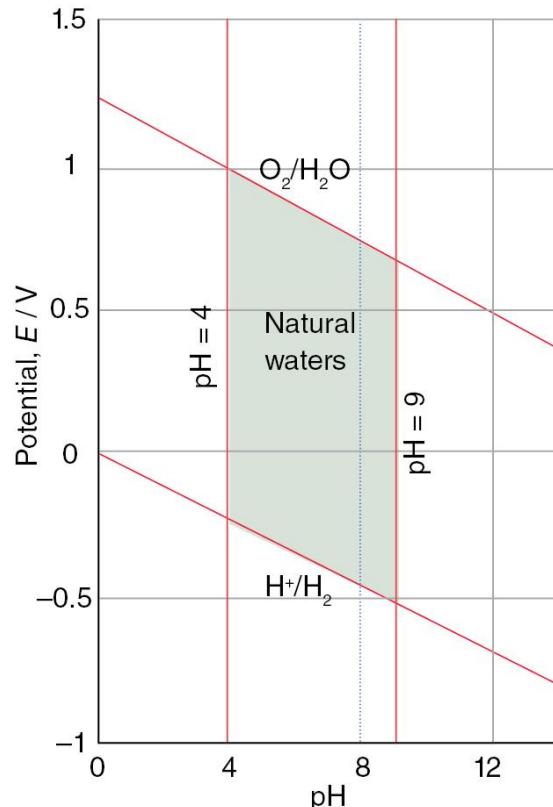
cf. Mg, Al 쉽게 산화되지만 바깥 산화막에 의해 보호되어
몇 년 동안 안정하게 유지

Reduction by Water:



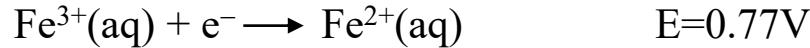
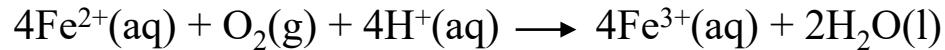
$$E^\circ (Co^{3+}, Co^{2+}): 1.82V \text{이므로 } E^\circ = 0.59V$$

The stability field of water:



5.8 Oxidation by Atmospheric Oxygen:

용액이 공기와 접촉을 하고 있다면 용질과 산소의 반응 고려



$$\text{Cell } E = 0.46 - (0.059 \times \text{pH}) \text{ V}$$

5.9 Disproportionation and Comproportionation:

표준전위가 불균화/균일화 반응항으로 다른 산화상태의 안정성 및 불안정성을 정의

ex) $E(\text{Cu}^+, \text{Cu}) = 0.52\text{V}$; $E(\text{Cu}^{2+}, \text{Cu}^+) = 0.16\text{V}$

물의 안정한 영역속에 있으므로 Cu^+ 이온이 물을 산화환원시키지도 못함



(위 두 반반응의 차이)

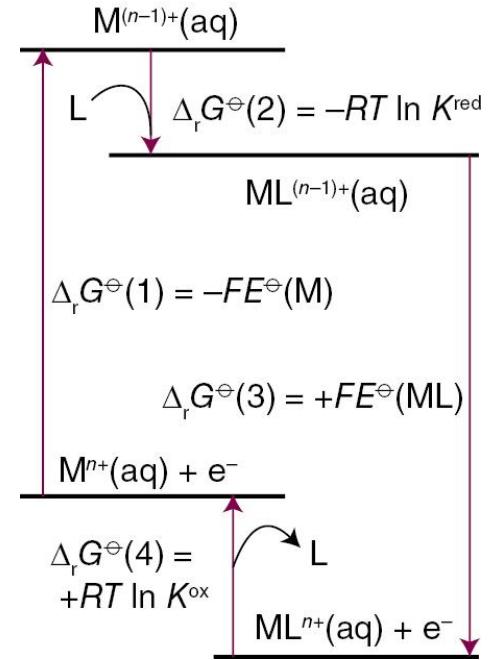
HClO도 불균화반응이 쉽게 일어남

Comproportionation



5.10 The Influence of Complexation:

금속착물의 형성은 Standard potential에 영향: 각 착물의 전자 수용/기여 정도가 다르기 때문



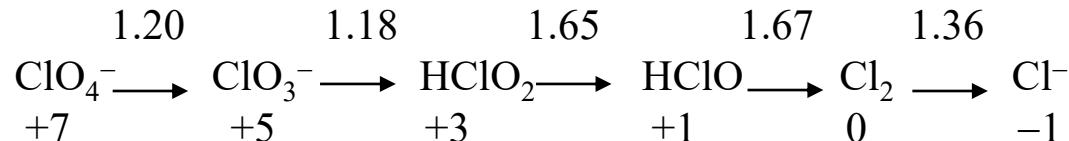
5.11 The Relation between Solubility and Standard Potentials; Determination of sparingly soluble compound K_{sp}

The Diagrammatic Presentation of Potential Data:

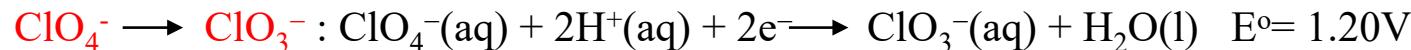
여러 가지 화학종이 존재할 수 있는 산화상태에 따른 열역학적 안정성

5.12 Latimer Diagrams: 원소 각각에 대한 수치적 표현에 적절: 부록 3

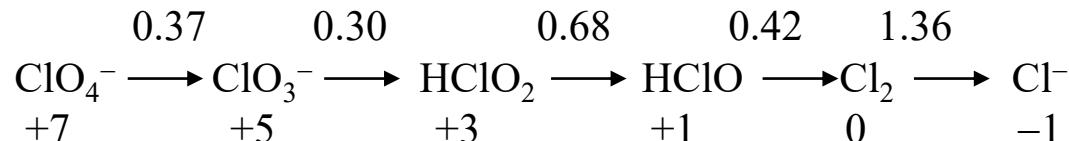
Acidic soln.



특징: 산화수는 왼쪽에서 오른쪽으로 갈수록 감소하고 E^o값이 화살표 위에...



Basic soln.



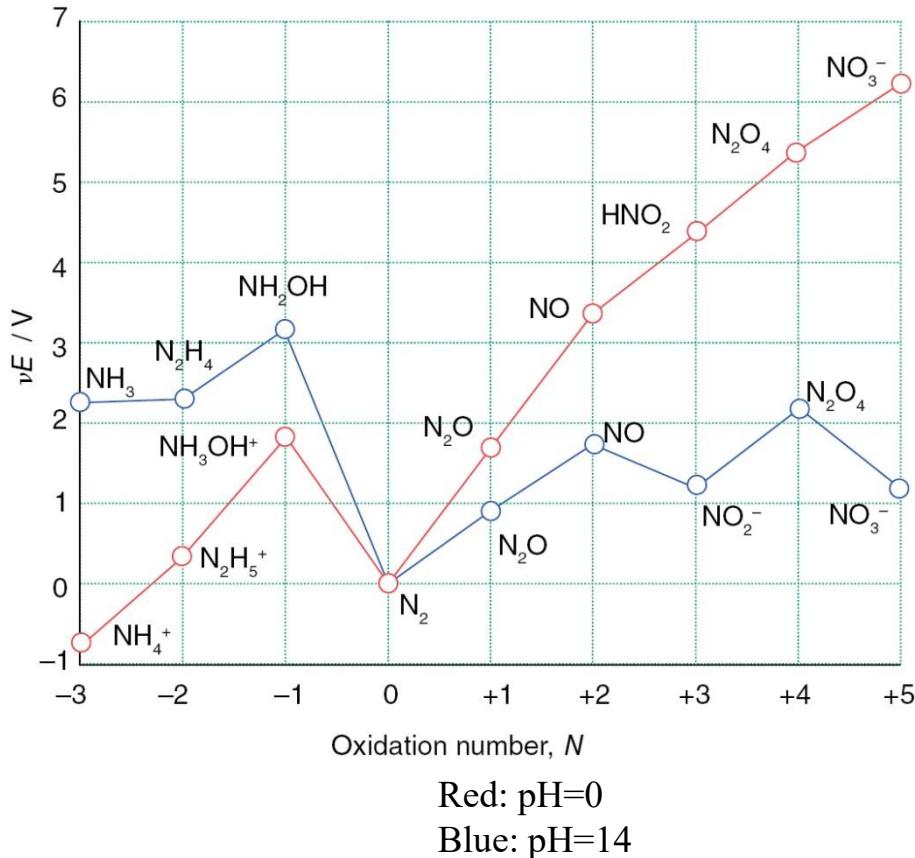
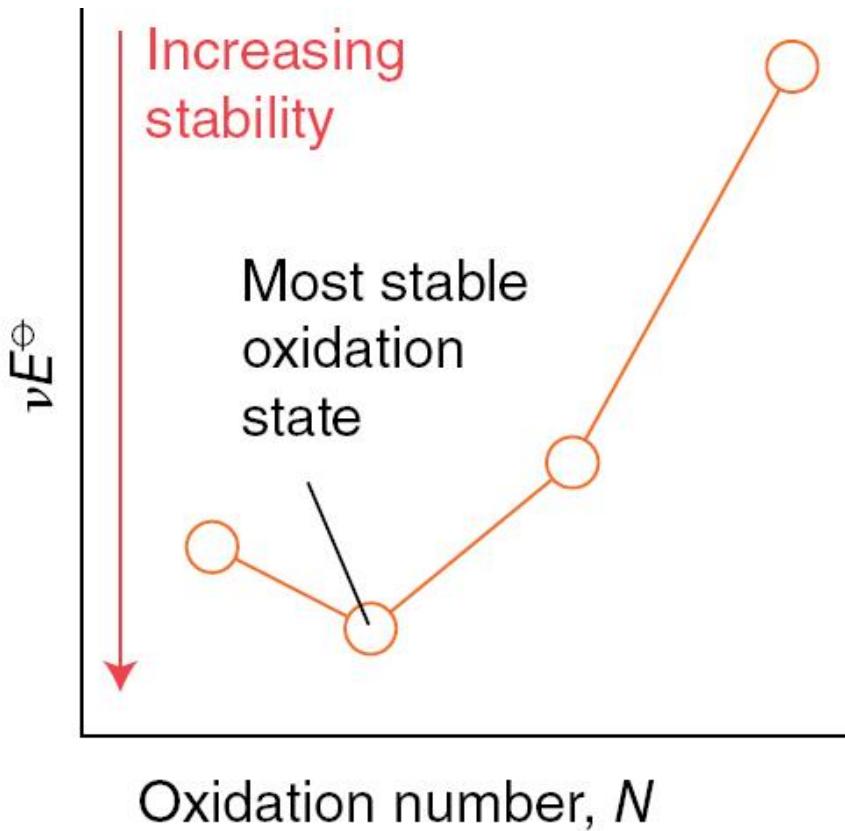
인접하지 않는 환원전위도 가능

$$\Delta G^{\circ} = \Delta G^{\circ'} + \Delta G^{\circ'':} - nFE^{\circ} = n'FE^{\circ'} - n''FE^{\circ'':} \quad E^{\circ} = (n'FE^{\circ'} + n''FE^{\circ'':})/(n' + n'')$$

문화반은 설명에도 있어

5.13 Frost Diagrams:

여러 산화상태들에 대한 상대적인 안정성의 표현을 정성적으로..
 다른 산화상태에서의 상대적 안정성: 화학종이 산화제인지 환원제인지...



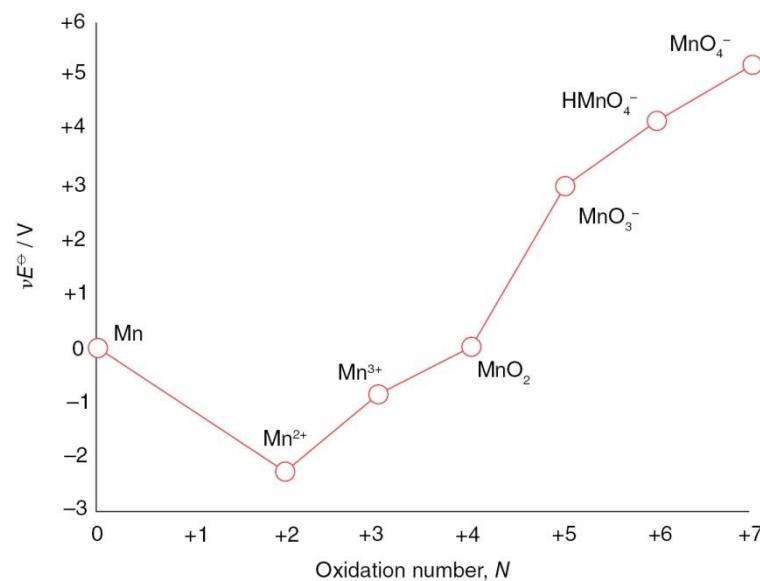
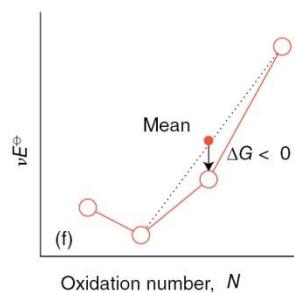
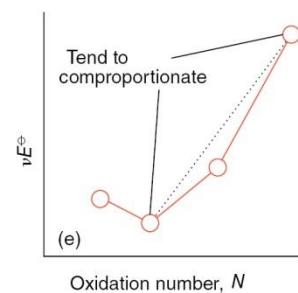
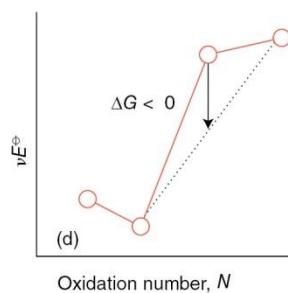
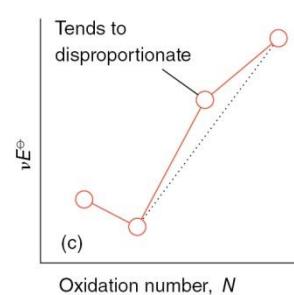
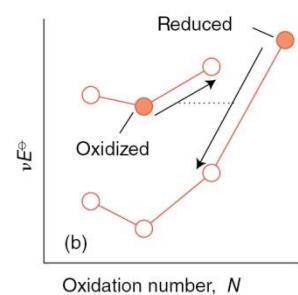
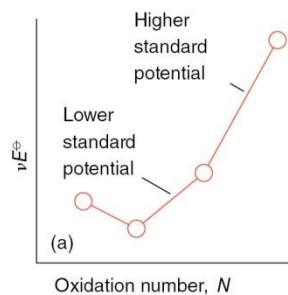
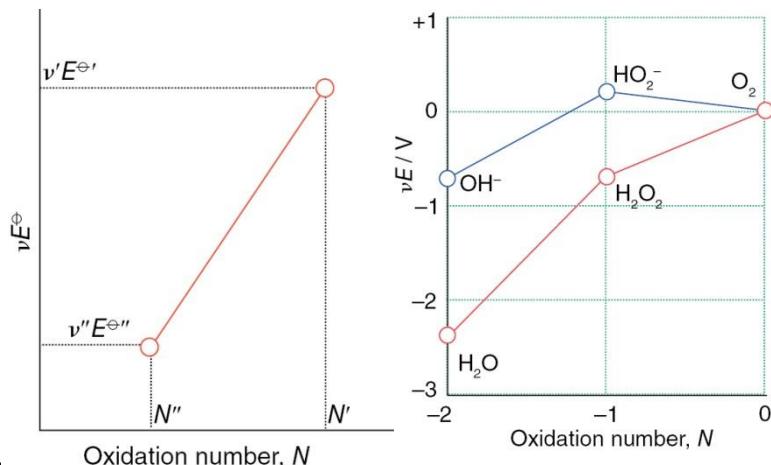
- 두 점을 잇는 기울기는 두 점에 의해 형성된 표준전위

- 한 쌍에서 산화제가 보다 양의 기울기를 가지면
(Positive E) 쉽게 환원

- 한 쌍에서 환원제가 양의 기울기가 작아지면
(작은 Positive E) 산화의 반응 속도 빠름

- 양 옆에 있는 종을 연결 한 것보다 위에 있으면 불균화 반응

- 양 옆에 있는 종을 연결 한 것보다 아래에 있으면 균등화 반응



5.12 The Dependence of Stability on pH:

어느 pH에서 전위 데이터: pH=7에서는 생화학연구에 유용

5.14 Pourbaix Diagram: Redox activity vs Bronstead Acidity

화학종의 열역학적으로 안정한 pH와 전위 영역

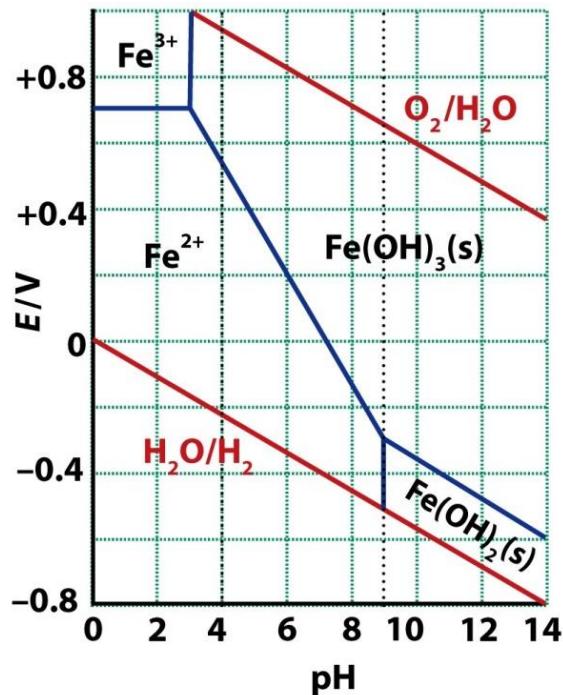


Figure 5-11
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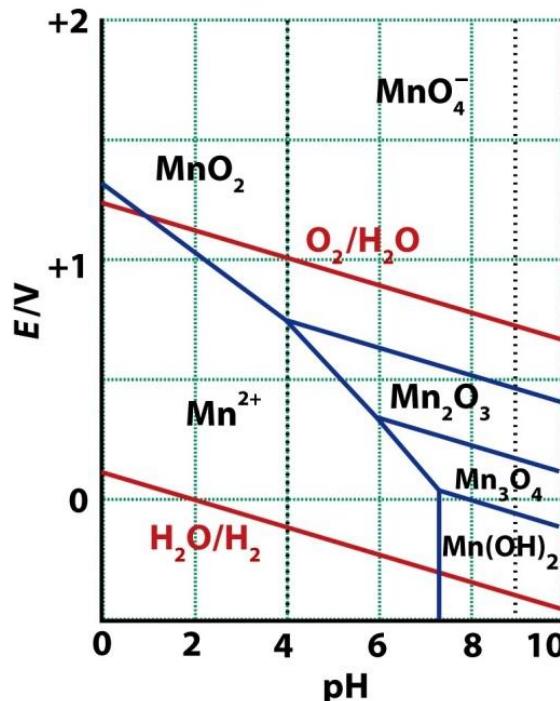


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5.15 Applications in Environmental Chemistry: Natural Waters

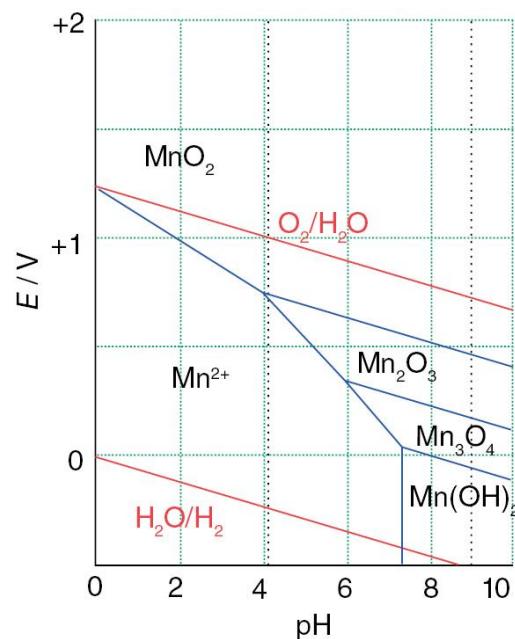
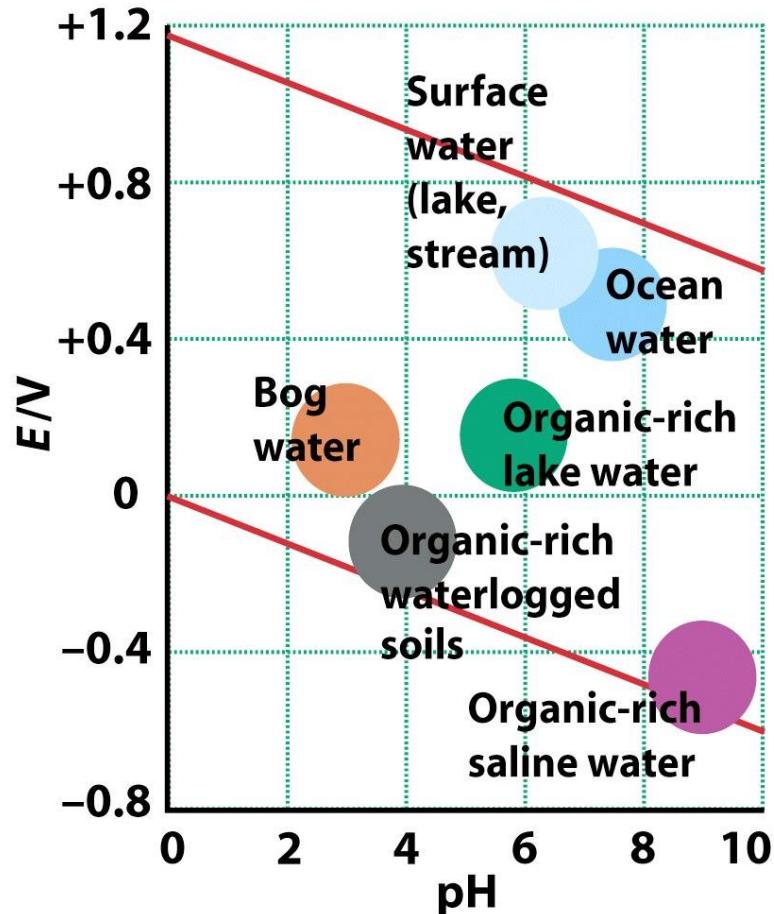
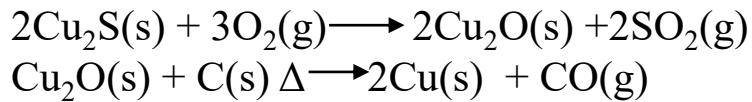


Figure 5-12

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5.16 Chemical Reduction: 원소 추출



Thermodynamic Aspect

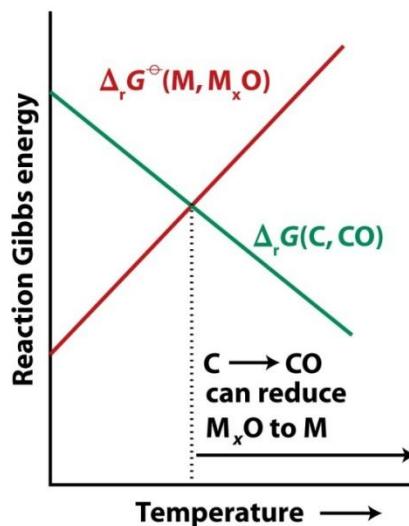


Figure 5-14
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Two line의 intersection 보다 높은 온도에서 반응

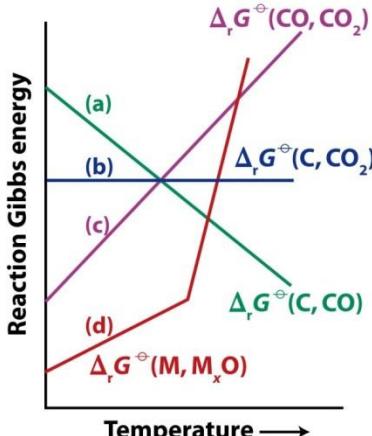


Figure 5-15
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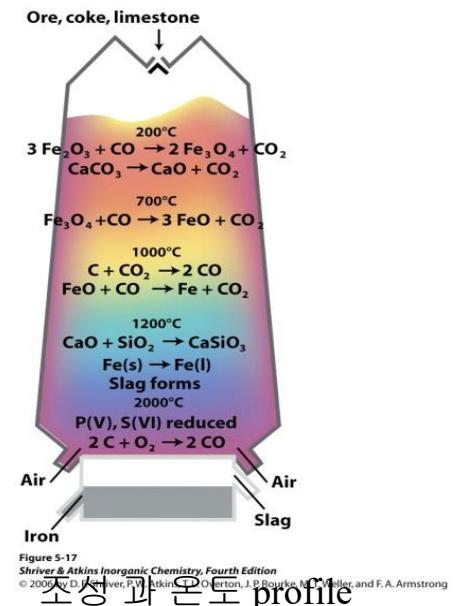
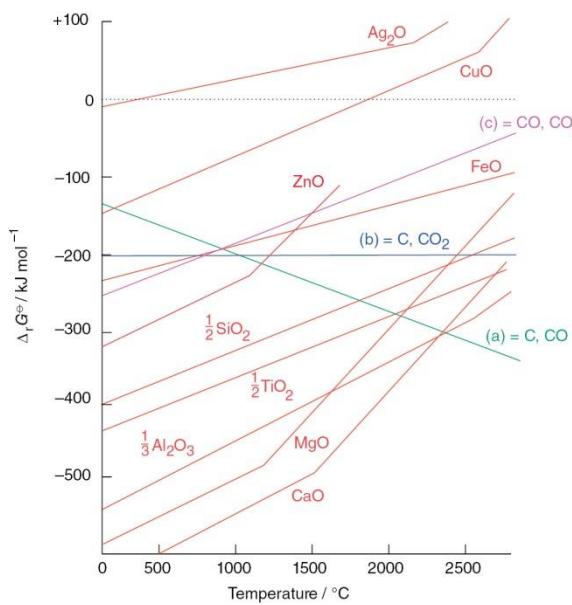
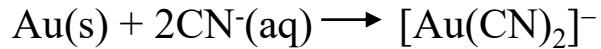
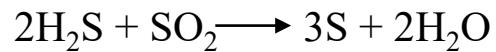
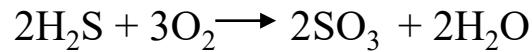


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조성과 온도 profile

5.17 Chemical Oxidation: 무거운 할로겐, S, 희귀 금속



5.17 Elelctrochemical Extraction

전기화학 환원: Al: $2\text{Al}_2\text{O}_3 + 3\text{C} \rightarrow 4\text{Al} + 3\text{CO}_2$ Bayer process : aluminum hydroxide:
Al: Hall-Heroult process

전기화학 산화: Cl₂: $2\text{Cl}^-(\text{aq}) + 2\text{H}_2\text{O(l)} \rightarrow 2\text{OH}^-(\text{aq}) + \text{H}_2(\text{g}) + \text{Cl}_2(\text{g})$