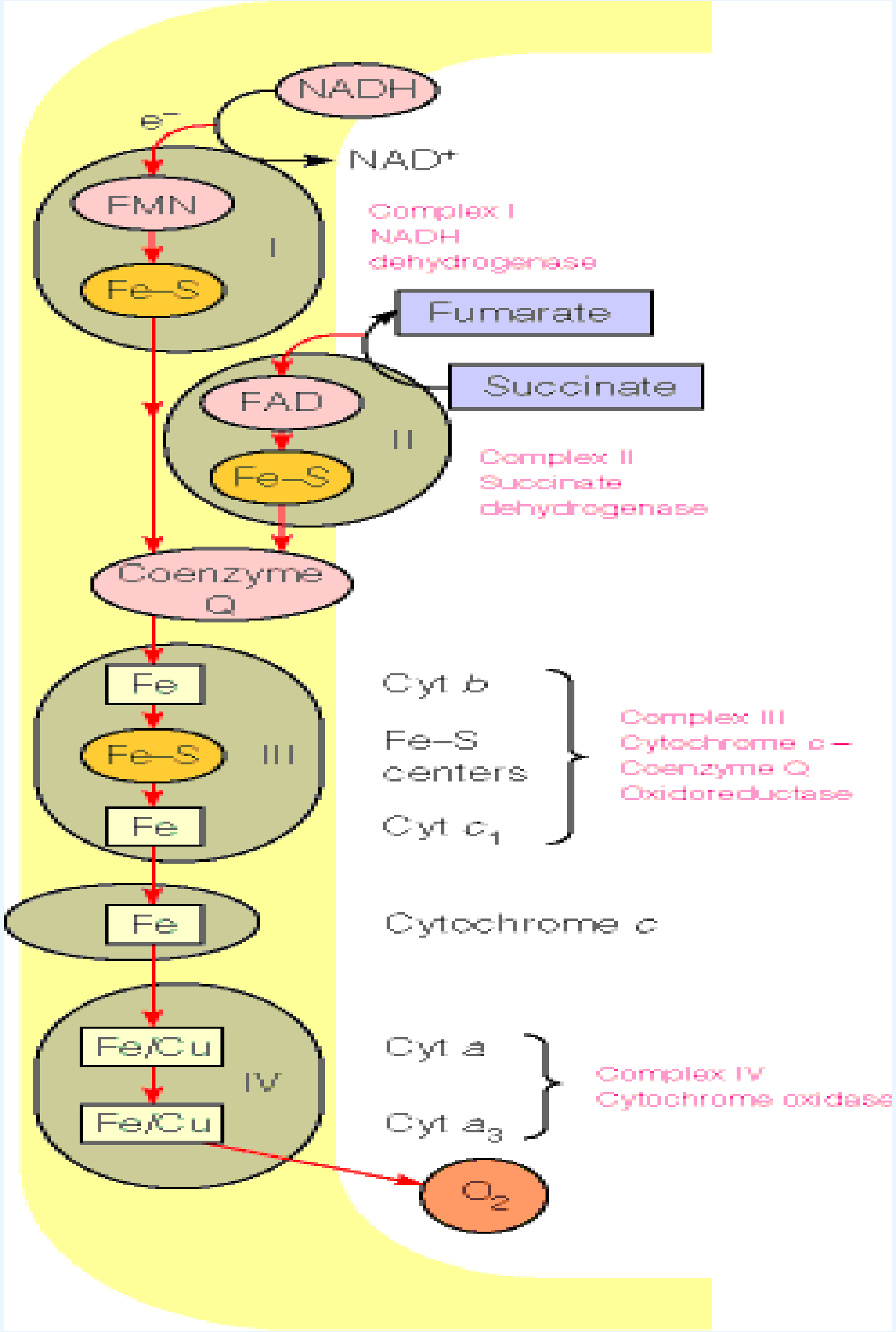
Oxidation-Reduction

Biology

Industry

Environment

Biology



NADH
e⁻
NAD+
FMN
Fe–S
I
Complex I
NADH
dehydrogenase
Fumarate
Succinate
FAD
Fe–S
II
Complex II
Succinate
dehydrogenase
Coenzyme Q
Fe
Fe–S
Fe
III
Cyt b
Fe–S centers
Cyt c1
Complex III
Cytochrome c –
Coenzyme Q
Oxidoreductase
Fe
Cytochrome c
Fe/Cu
Fe/Cu
IV
Cyt a
Cyt a3
Complex IV
Cytochrome oxidase
O2

Biology

Selected Biologically Important Redox Couples

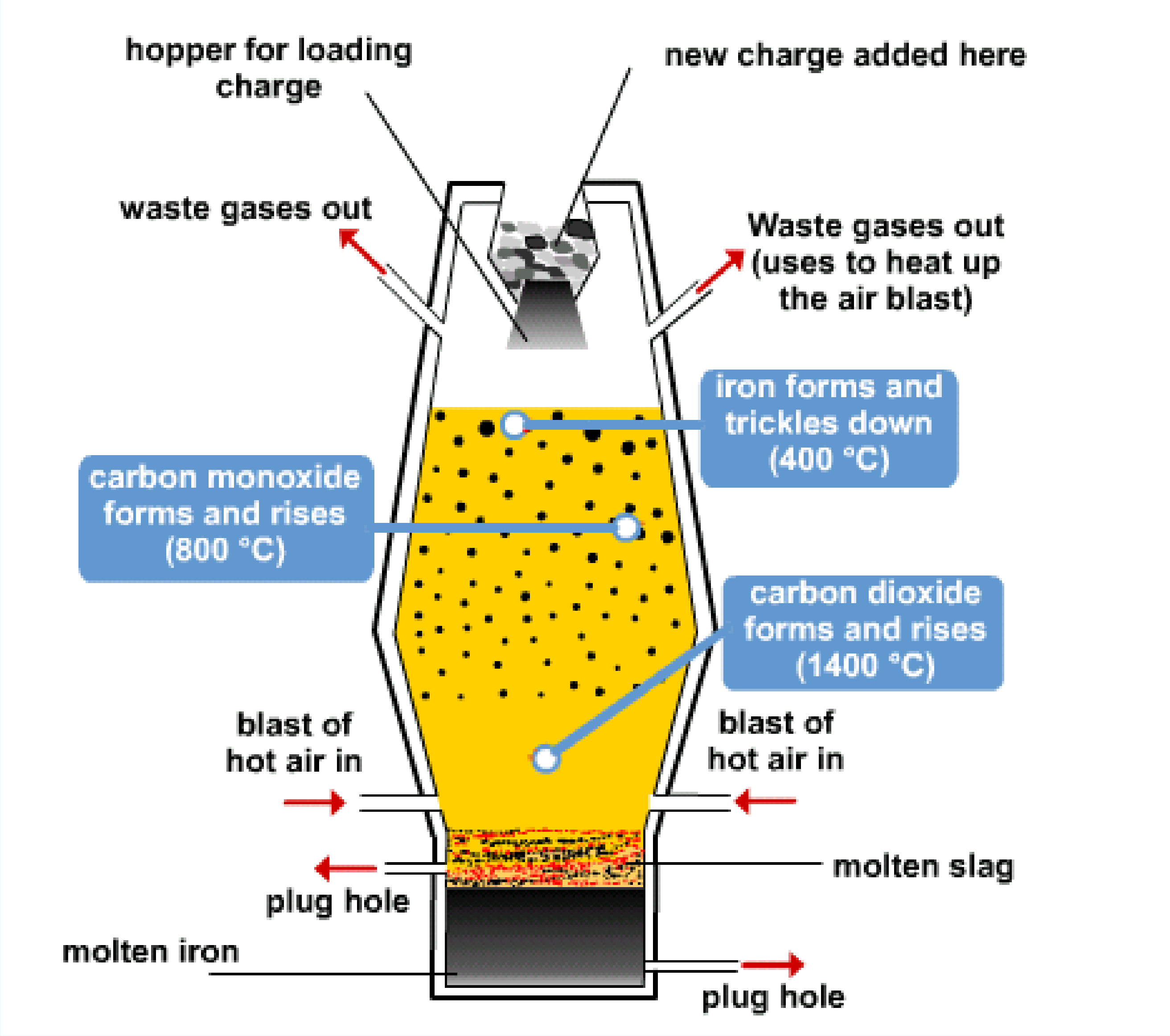
Redox Couple	E'_0 (Volts) [a]
$2H^+ + 2e^- \longrightarrow H_2$	−0.42
Ferredoxin(Fe^{3+}) + $e^- \longrightarrow$ ferredoxin (Fe^{2+})	−0.42
$NAD(P)^+ + H^+ + 2e^- \longrightarrow NAD(P)H$	−0.32
$S + 2H^+ + 2e^- \longrightarrow H_2S$	−0.274
Acetaldehyde + $2H^+ + 2e^- \longrightarrow$ ethanol	−0.197
$\text{Pyruvate}^- + 2H^+ + 2e^- \longrightarrow \text{lactate}^{2-}$	−0.185
$FAD + 2H^+ + 2e^- \longrightarrow FADH_2$	−0.18[b]
$\text{Oxaloacetate}^{2-} + 2H^+ + 2e^- \longrightarrow \text{malate}^{2-}$	−0.166
$\text{Fumarate}^{2-} + 2H^+ + 2e^- \longrightarrow \text{succinate}^{2-}$	0.031
Cytochrome *b* (Fe^{3+}) + $e^- \longrightarrow$ cytochrome *b* (Fe^{2+})	0.075
Ubiquinone + $2H^+ + 2e^- \longrightarrow$ ubiquinone H_2	0.10
Cytochrome *c* (Fe^{3+}) + $e^- \longrightarrow$ cytochrome *c* (Fe^{2+})	0.254
Cytochrome *a* (Fe^{3+}) + $e^- \longrightarrow$ cytochrome *a* (Fe^{2+})	0.29
Cytochrome a_3 (Fe^{3+}) + $e^- \longrightarrow$ cytochrome a_3 (Fe^{2+})	0.35
$NO_3^- + 2H^+ + 2e^- \longrightarrow NO_2^- + H_2O$	0.421
$NO_2^- + 8H^+ + 6e^- \longrightarrow NH_4^+ + 2H_2O$	0.44
$Fe^{3+} + e^- \longrightarrow Fe^{2+}$	0.771[c]
$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$	0.815

[a] E'_0 is the standard reduction potential at pH 7.0.

[b] The value for $FAD/FADH_2$ applies to the free cofactor because it can vary considerably when bound to an apoenzyme.

[c] The value for free Fe, not Fe complexed with proteins (e.g., cytochromes).

Industry **Extraction of elements** **Synthesis of different compounds**



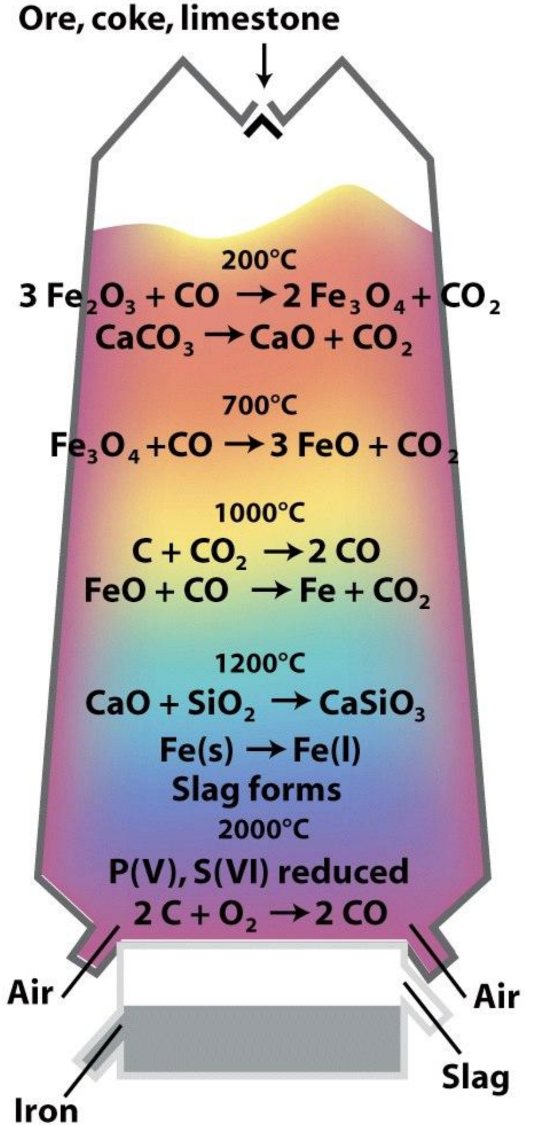
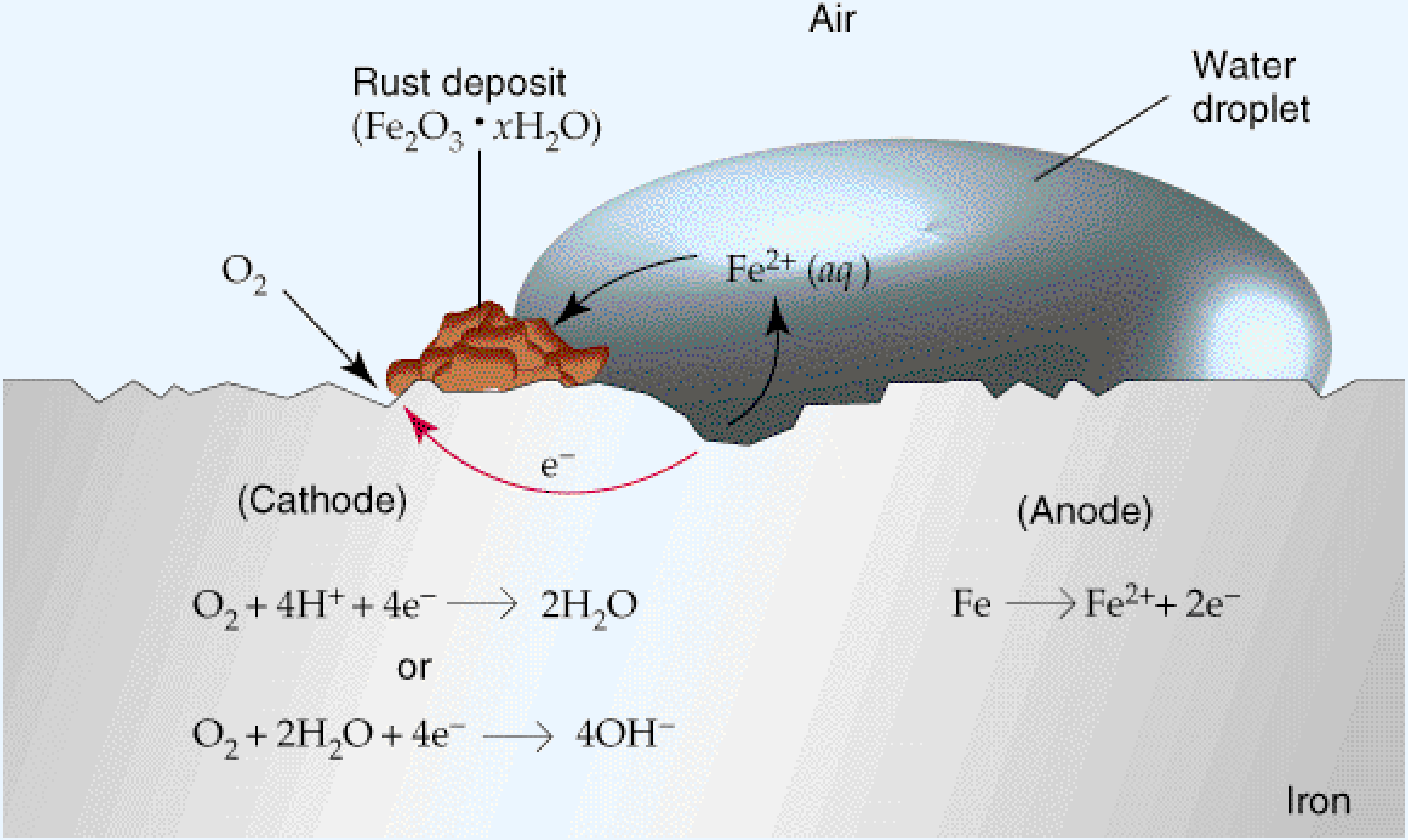


Figure 5-17
Shriver & Atkins Inorganic Chemistry, Fourth Edition

Environment



Redox reactions - transfer of electrons between species.

reduction by gain of electrons

$$Cu^{2+} + Mg \longrightarrow Cu + Mg^{2+}$$

oxidation by loss of electrons

All the redox reactions have two parts:

Oxidation

Reduction

- **The Loss of Electrons is Oxidation.**
- **An element that loses electrons is said to be oxidized.**
- **The species in which that element is present in a reaction is called the reducing agent.**

- **The Gain of Electrons is Reduction.**
- **An element that gains electrons is said to be reduced.**
- **The species in which that element is present in a reaction is called the oxidizing agent.**

$$Mg \longrightarrow Mg^{2+}$$

$$Cu^{2+} \longrightarrow Cu$$

Balancing Redox Equations

$$Fe^{2+} + MnO_4^- + H^+ \longrightarrow Mn^{2+} + Fe^{3+} + H_2O$$

1. Assign oxidation numbers to each atom.
2. Determine the elements that get oxidized and reduced.
3. Split the equation into half-reactions.
4. Balance all atoms in each half-reaction, except H and O.
5. Balance O atoms using H_2O.
6. Balance H atoms using H^+.
7. Balance charge using electrons.
8. Sum together the two half-reactions, so that: e^- lost = e^- gained
9. If the solution is basic, add a number of OH^- ions to each side of the equation equal to the number of H^+ ions shown in the overall equation. Note that $H^+ + OH^- \rightarrow H_2O$

Example

$$Fe^{2+} + MnO_4^- + H^+ \longrightarrow Mn^{2+} + Fe^{3+} + H_2O$$

$MnO_4^- \longrightarrow Mn^{2+}$ **Reduction half reaction**

(+7) (+2)

$Fe^{2+} \longrightarrow Fe^{3+}$ **Oxidation half reaction**

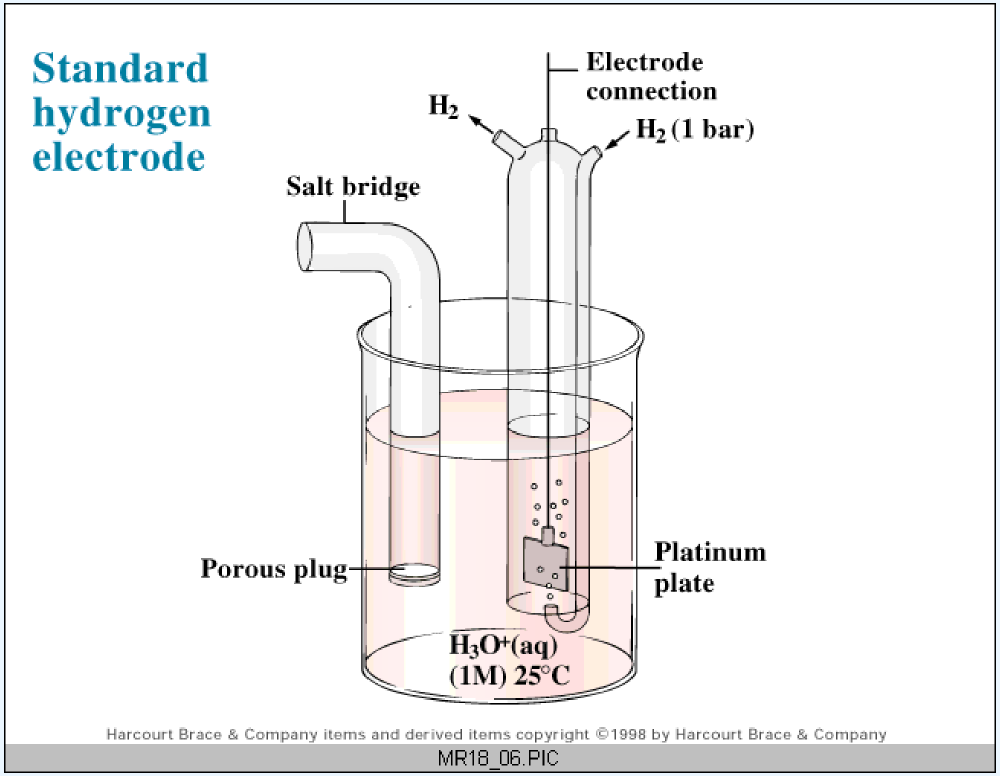
$$MnO_4^- + 8H^+ + 5e \longrightarrow Mn^{2+} + 4H_2O$$

$$5Fe^{2+} \longrightarrow 5Fe^{3+} + 5e$$

$$5Fe^{2+} + 8MnO_4^- + 8H^+ \longrightarrow 8Mn^{2+} + 5Fe^{3+} + 4H_2O$$

Hydrogen Electrode

- consists of a platinum electrode covered with a fine powder of platinum around which $H_{2(g)}$ is bubbled. Its potential is defined as zero volts.

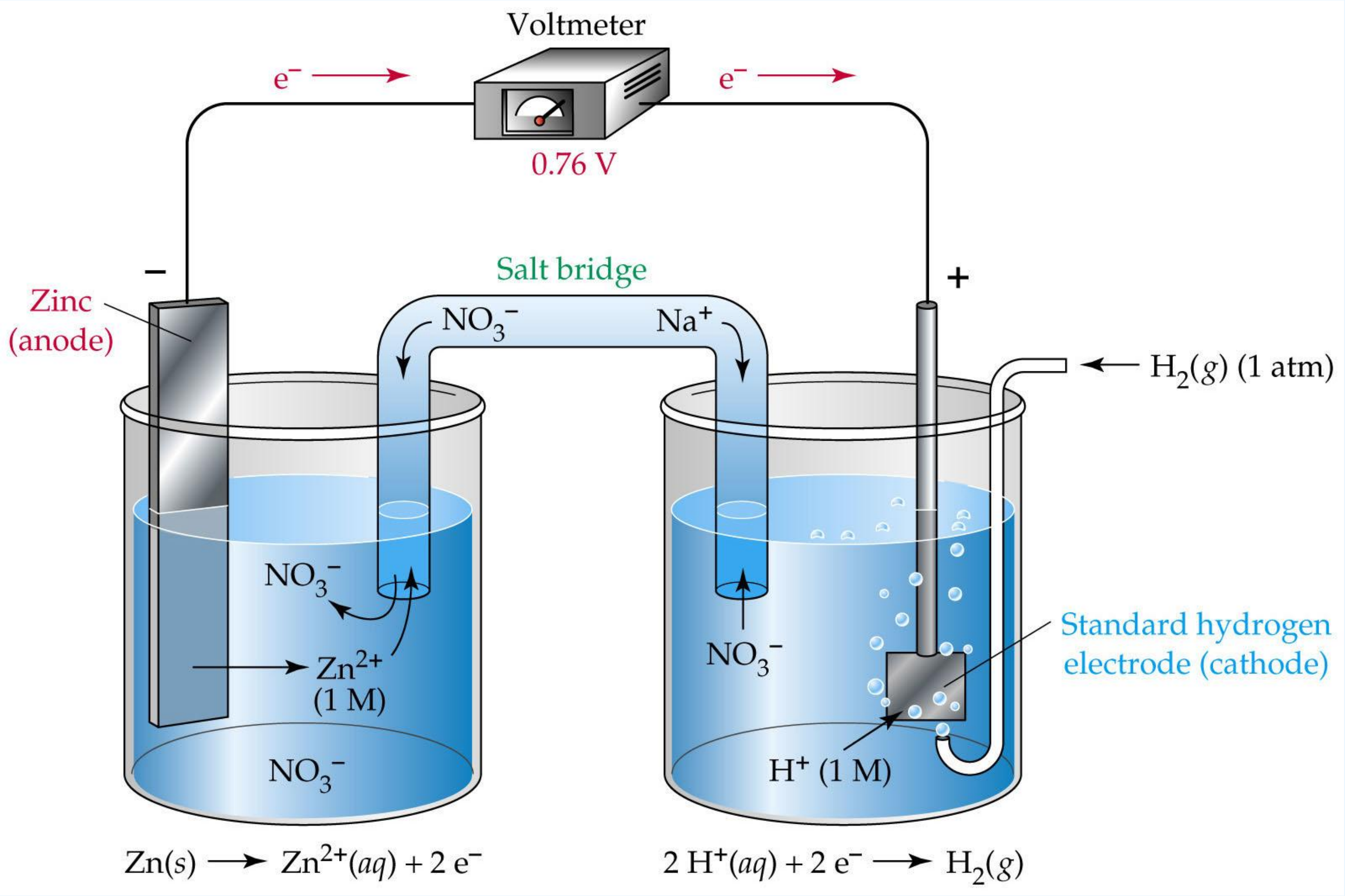


Hydrogen Half-Cell

$$H_{2(g)} \;=\; 2\,H^{+}_{(aq)} \;+\; 2\,e^{-}$$

reversible reaction

Galvanic Cell



Nernst Equation

$$aOx_1 + bRed_2 \longrightarrow a'Red_1 + b'Ox_2$$

$$Q = \frac{[Red_1]^{a'}\,[Ox_2]^{b'}}{[Ox_1]^{a}\,[Red_2]^{b}} \qquad E = E^0 - \frac{RT}{nF}\ln Q$$

E^0 = Standard Potential

R = Gas constant 8.314 J/K.mol

F- Faraday constant = 94485 J/V.mol

n- number of electrons

$$\Delta G^0 = -\, n\, F\, \Delta E^0$$

Note: if $\Delta G^0 < 0$, then ΔE^0 must be >0

A reaction is favorable if $\Delta E^0 > 0$

(a) $2H^+ (aq) + 2e \longrightarrow H_2(g)$ $\qquad E^0 (H^+, H_2) = 0$

(b) $Zn^{2+} (aq) + 2e \longrightarrow Zn(s)$ $\qquad E^0 (Zn^{2+}, Zn) = -0.76\ V$

(a-b) $2H^+ (aq) + Zn(s) \longrightarrow Zn^{2+}(aq) + H_2(g)$ $\qquad E^0 = +0.76\ V$

Reaction is favorable

TABLE 18.1 Standard Reduction Potentials at 25°C

Stronger oxidizing agent | Weaker reducing agent

Reduction Half-Reaction		E° (V)
$F_2(g) + 2e^-$	$\longrightarrow 2F^-(aq)$	2.87
$H_2O_2(aq) + 2H^+(aq) + 2e^-$	$\longrightarrow 2H_2O(l)$	1.78
$MnO_4^-(aq) + 8H^+(aq) + 5e^-$	$\longrightarrow Mn^{2+}(aq) + 4H_2O(l)$	1.51
$Cl_2(g) + 2e^-$	$\longrightarrow 2Cl^-(aq)$	1.36
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^-$	$\longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$	1.33
$O_2(g) + 4H^+(aq) + 4e^-$	$\longrightarrow 2H_2O(l)$	1.23
$Br_2(l) + 2e^-$	$\longrightarrow 2Br^-(aq)$	1.09
$Ag^+(aq) + e^-$	$\longrightarrow Ag(s)$	0.80
$Fe^{3+}(aq) + e^-$	$\longrightarrow Fe^{2+}(aq)$	0.77
$O_2(g) + 2H^+(aq) + 2e^-$	$\longrightarrow H_2O_2(aq)$	0.70
$I_2(s) + 2e^-$	$\longrightarrow 2I^-(aq)$	0.54
$O_2(g) + 2H_2O(l) + 4e^-$	$\longrightarrow 4OH^-(aq)$	0.40
$Cu^{2+}(aq) + 2e^-$	$\longrightarrow Cu(s)$	0.34
$Sn^{4+}(aq) + 2e^-$	$\longrightarrow Sn^{2+}(aq)$	0.15
$2H^+(aq) + 2e^-$	$\longrightarrow H_2(g)$	0
$Pb^{2+}(aq) + 2e^-$	$\longrightarrow Pb(s)$	−0.13
$Ni^{2+}(aq) + 2e^-$	$\longrightarrow Ni(s)$	−0.26
$Cd^{2+}(aq) + 2e^-$	$\longrightarrow Cd(s)$	−0.40
$Fe^{2+}(aq) + 2e^-$	$\longrightarrow Fe(s)$	−0.45
$Zn^{2+}(aq) + 2e^-$	$\longrightarrow Zn(s)$	−0.76
$2H_2O(l) + 2e^-$	$\longrightarrow H_2(g) + 2OH^-(aq)$	−0.83
$Al^{3+}(aq) + 3e^-$	$\longrightarrow Al(s)$	−1.66
$Mg^{2+}(aq) + 2e^-$	$\longrightarrow Mg(s)$	−2.37
$Na^+(aq) + e^-$	$\longrightarrow Na(s)$	−2.71
$Li^+(aq) + e^-$	$\longrightarrow Li(s)$	−3.04

Weaker oxidizing agent | Stronger reducing agent

Diagrammatic presentation of potential data

Latimer Diagram

Frost Diagram

Latimer Diagram

*** Written with the most oxidized species on the left, and the most reduced species on the right.**

*** Oxidation number decrease from left to right and the E^0 values are written above the line joining the species involved in the couple.**

$$A^{+5} \xrightarrow{w} B^{+3} \xrightarrow{x} C^{+1} \xrightarrow{y} D^{0} \xrightarrow{z} E^{-2}$$

TABLE 18.1 Standard Reduction Potentials at 25°C

	Reduction Half-Reaction		$E°$ (V)	
Stronger oxidizing agent	$F_2(g) + 2e^-$	$\longrightarrow 2F\ (aq)$	2.87	Weaker reducing agent
	$H_2O_2(aq) + 2H^+(aq) + 2e^-$	$\longrightarrow 2H_2O(l)$	1.78	
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	$\boxed{Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq)}$		$\boxed{1.36}$	
	$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^-$	$\longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$	1.33	
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	$Ag^+(aq) + e^-$	$\longrightarrow Ag(s)$	0.80	
	$Fe^{3+}(aq) + e^-$	$\longrightarrow Fe^{2+}(aq)$	0.77	
	$O_2(g) + 2H^+(aq) + 2e^-$	$\longrightarrow H_2O_2(aq)$	0.70	
	$I_2(s) + 2e^-$	$\longrightarrow 2I^-(aq)$	0.54	
	$O_2(g) + 2H_2O(l) + 4e^-$	$\longrightarrow 4OH^-(aq)$	0.40	
	$Cu^{2+}(aq) + 2e^-$	$\longrightarrow Cu(s)$	0.34	
	$Sn^{4+}(aq) + 2e^-$	$\longrightarrow Sn^{2+}(aq)$	0.15	
	$2H^+(aq) + 2e^-$	$\longrightarrow H_2(g)$	0	
	$Pb^{2+}(aq) + 2e^-$	$\longrightarrow Pb(s)$	−0.13	
	$Ni^{2+}(aq) + 2e^-$	$\longrightarrow Ni(s)$	−0.26	
	$Cd^{2+}(aq) + 2e^-$	$\longrightarrow Cd(s)$	−0.40	
	$Fe^{2+}(aq) + 2e^-$	$\longrightarrow Fe(s)$	−0.45	
	$Zn^{2+}(aq) + 2e^-$	$\longrightarrow Zn(s)$	−0.76	
	$2H_2O(l) + 2e^-$	$\longrightarrow H_2(g) + 2OH^-(aq)$	−0.83	
	$Al^{3+}(aq) + 3e^-$	$\longrightarrow Al(s)$	−1.66	
	$Mg^{2+}(aq) + 2e^-$	$\longrightarrow Mg(s)$	−2.37	
	$Na^+(aq) + e^-$	$\longrightarrow Na(s)$	−2.71	
Weaker oxidizing agent	$Li^+(aq) + e^-$	$\longrightarrow Li(s)$	−3.04	Stronger reducing agent

Latimer diagram for chlorine in acidic solution

$$\underset{+7}{ClO_4^-} \xrightarrow{+1.2} \underset{+5}{ClO_3^-} \xrightarrow{+1.18} \underset{+3}{HClO_2} \xrightarrow{+1.65} \underset{+1}{HClO} \xrightarrow{+1.63} \underset{0}{Cl_2} \xrightarrow{+1.36} \underset{-1}{Cl^-}$$

$$ClO_4^- \xrightarrow{+1.2} ClO_3^-$$

$$ClO_4^-(aq) + 2H^+(aq) + 2e^- \longrightarrow ClO_3^-(aq) + H_2O(l) \qquad E^\circ = 1.20\,V$$

$$HClO \xrightarrow{+1.63} Cl_2$$

$$2\,HClO(aq) + 2\,H^+(aq) + 2\,e^- \longrightarrow Cl_2(g) + 2\,H_2O(l) \quad E^0 = +1.63\,V$$

Latimer diagram for chlorine in basic solution

$$\underset{+7}{ClO_4^-} \xrightarrow{+1.2} \underset{+5}{ClO_3^-} \xrightarrow{+1.18} \underset{+3}{HClO_2} \xrightarrow{+1.65} \underset{+1}{HClO} \xrightarrow{+1.63} \underset{0}{Cl_2} \xrightarrow{+1.36} \underset{-1}{Cl^-}$$

$$\begin{tikzcd}
ClO_4^- \arrow[r, "+0.37"] & ClO_3^- \arrow[r, "+0.3"] & ClO_2^- \arrow[r, "+0.68"] & ClO^- \arrow[r, "+0.42"] \arrow[rr, bend right, "+0.89"'] & Cl_2 \arrow[r, "+1.36"] & Cl^-
\end{tikzcd}$$

$$ClO^- \xrightarrow{+0.42} Cl_2$$

$$ClO^- (aq) + 2H_2O(l) + 2e^- \longrightarrow Cl_2(g) + OH^-(aq) \qquad E^0 = 0.42\ V$$

What happens when Fe(s) react with H^+?

Iron +2 and +3

$\Delta G = -nFE$

$Fe^{2+} + 2e \longrightarrow Fe$ -0.440 $-2 \times F \times -0.44$ V

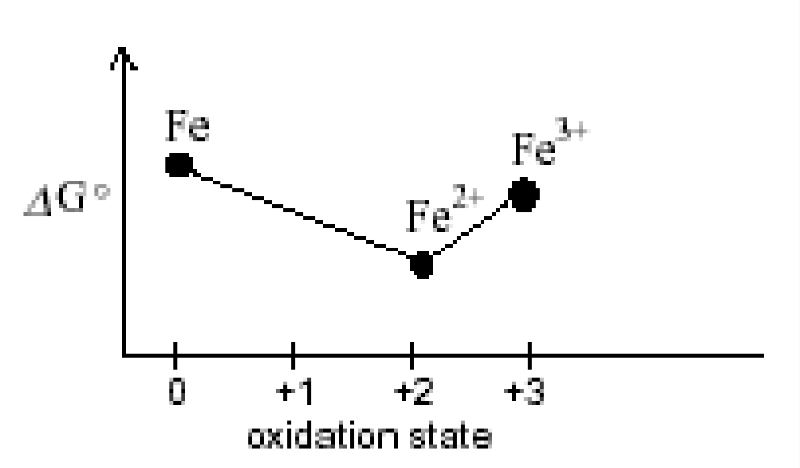
$Fe^{3+} + e \longrightarrow Fe^{2+}$ +0.77 $-1 \times F \times +0.771$

$Fe^{3+} + 3e \longrightarrow Fe$ $+ 0.109$ F

$= -3 \times F \times -0.036$

$Fe \xrightarrow{+0.036} Fe^{3+}$

$Fe \xrightarrow{+0.44} Fe^{2+}$



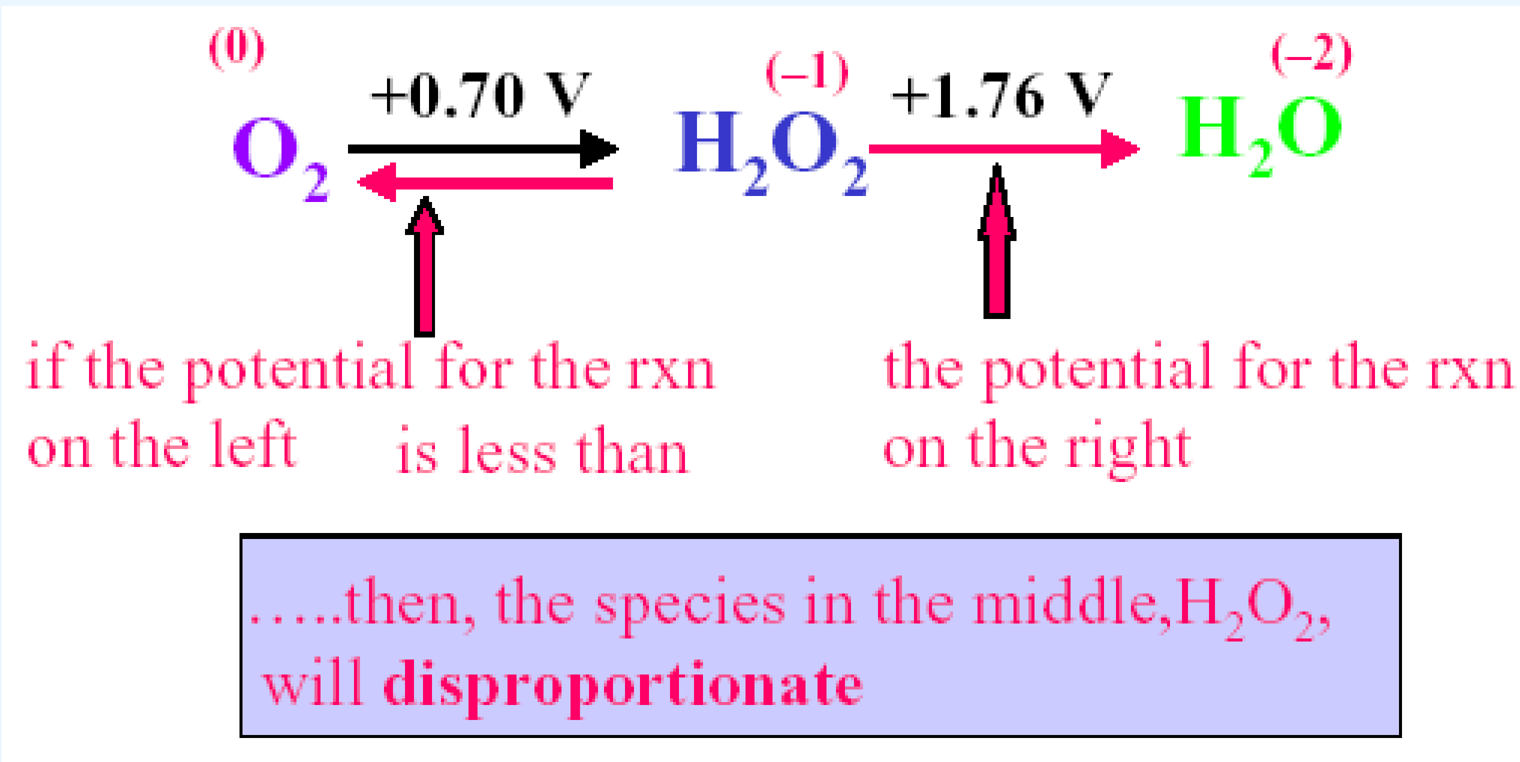
-0.036

$Fe^{3+} \xrightarrow{+0.77} Fe^{2+} \xrightarrow{-0.44} Fe$

Disproportionation

the potential on the left of a species is less positive than that on the right- the species can oxidize and reduce itself, a process known as ***disproportionation***.

$$M_{(s)} \xleftarrow{E^0} 2M^+_{(aq)} \xrightarrow{E^{0'}} M^{2+}_{(aq)}$$



Is it spontaneous?

$$H_2O_2 + 2e^- + 2H^+ \xrightarrow{+1.76\ V} 2\ H_2O$$

reduction

H_2O_2 acting as <u>oxidant</u>

$$H_2O_2 \xrightarrow{+0.70\ V} O_2 + 2e^- + 2H^+$$

oxidation

H_2O_2 acting as <u>reductant</u>

$$2\ H_2O_2 \xrightarrow{\Delta E = \ ?} O_2 + 2\ H_2O$$

net rxn

$$\Delta E = E^{\theta}(\text{oxidant}) - E^{\theta}\ (\text{reductant})$$

$$\Delta E = \ +1.76\ V - +0.70\ V = \ +1.\ 06\ V$$

thus, $\Delta G < 0$ for the disproportionation rxn

Yes the reaction is spontaneous

Another example…

$$2\ Cu^{+}(aq) \longrightarrow Cu^{2+}(aq) + Cu(s)$$

$$Cu^{+}(aq) + e^{-} \longrightarrow Cu(s) \qquad E^{0} = +\ 0.52\ V$$

$$Cu^{2+}(aq) + e^{-} \longrightarrow Cu^{+}(aq) \qquad E^{0} = =0.16\ V$$

Cu(I) undergo disproportionation in aqueous solution

Comproportionation reaction

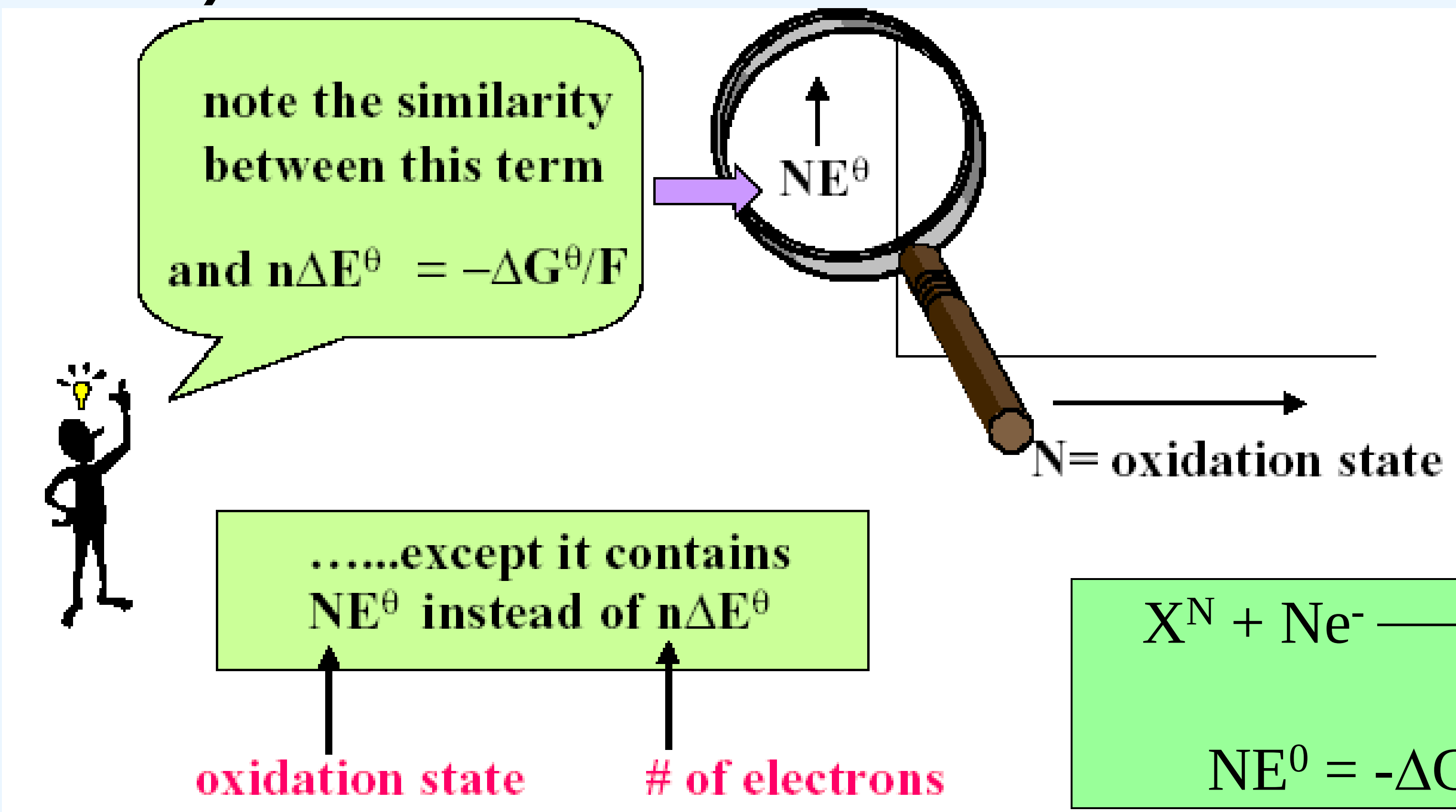
Reverse of disproportionation

$$Ag^{2+}(aq) + Ag(s) \longrightarrow 2Ag^{+}(aq) \qquad E^{0} = +\,1.18\ V$$

…we will study this in detail under Frost diagram

Frost Diagram

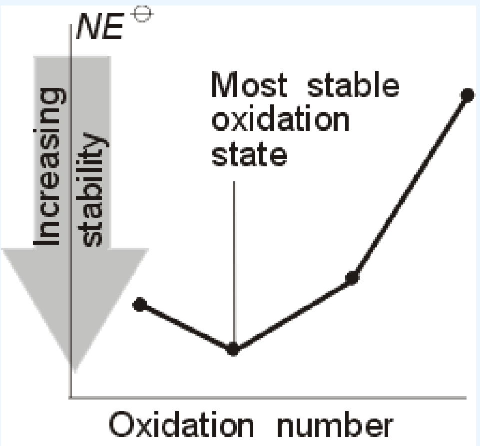
Graphically illustration of the stability of different oxidation states relative to its elemental form (ie, relative to oxidation state= 0)



$$X^N + Ne^- \longrightarrow X^0$$

$$NE^0 = -\Delta G^0/F$$

Important information provided by Frost diagram:



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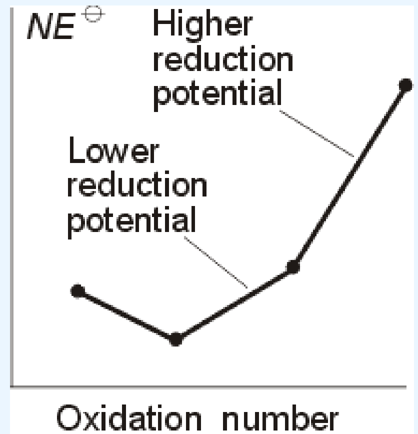

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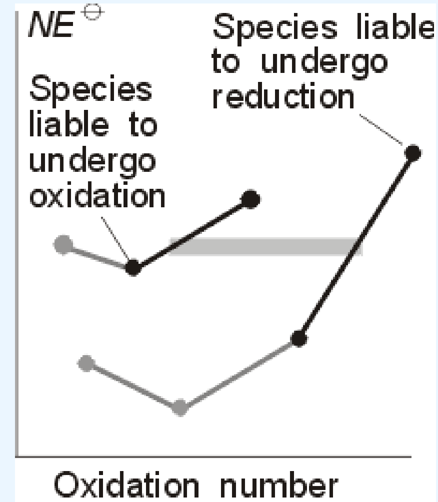

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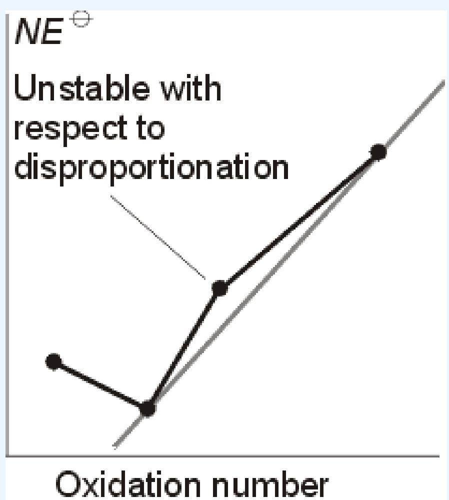

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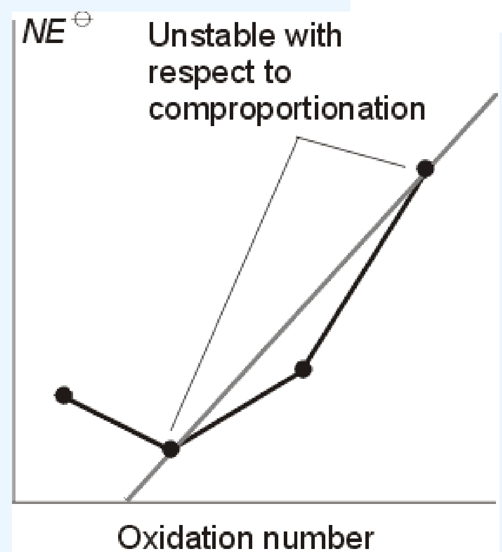
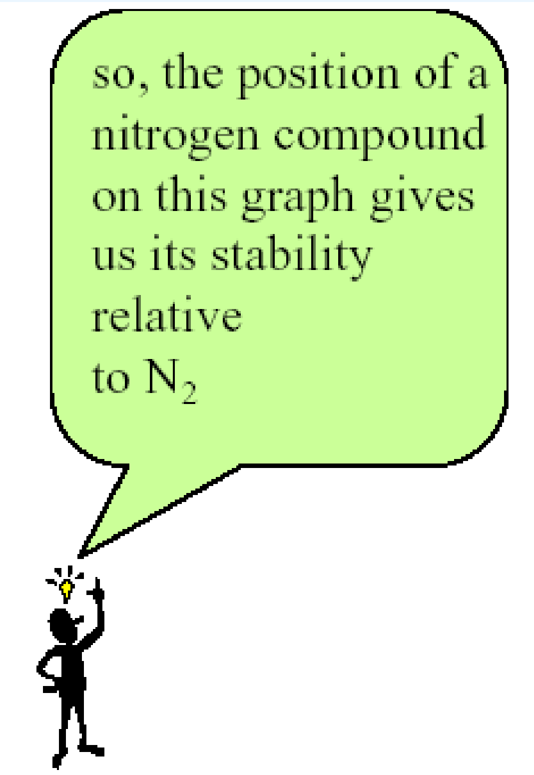
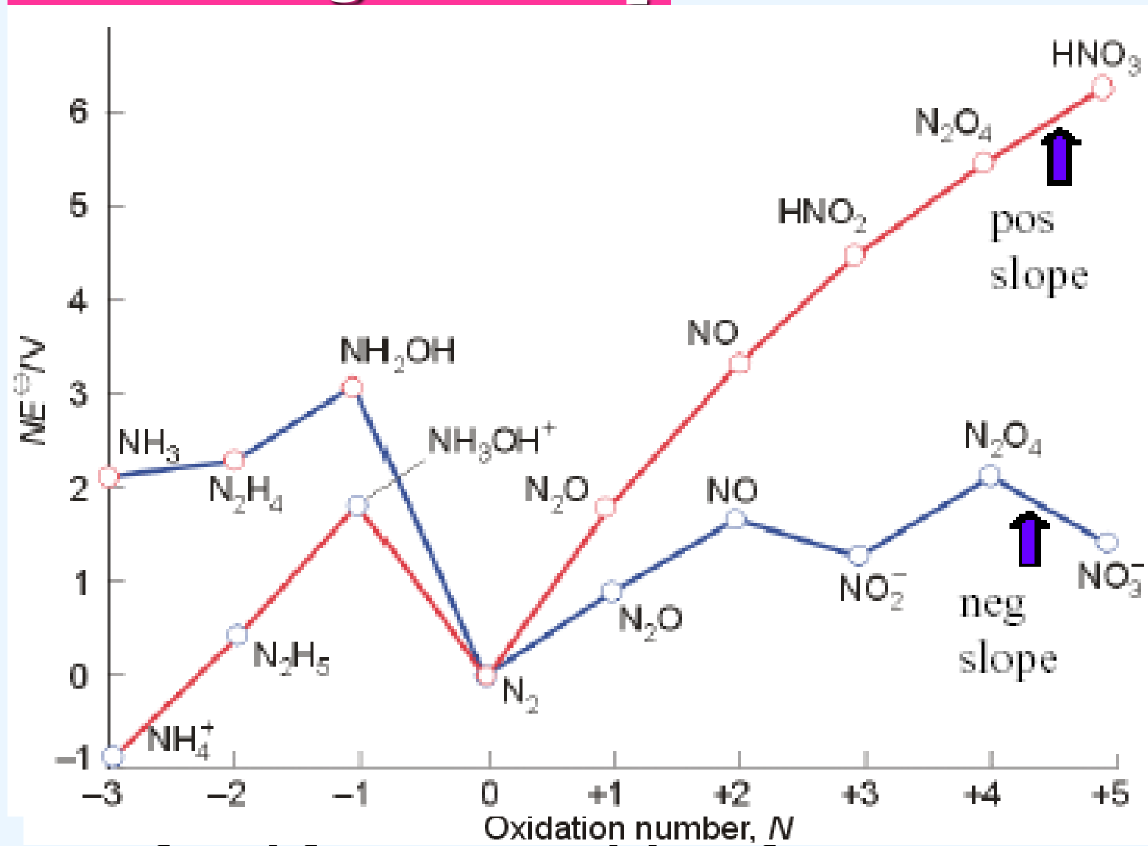


6

Frost Diagram – N_2



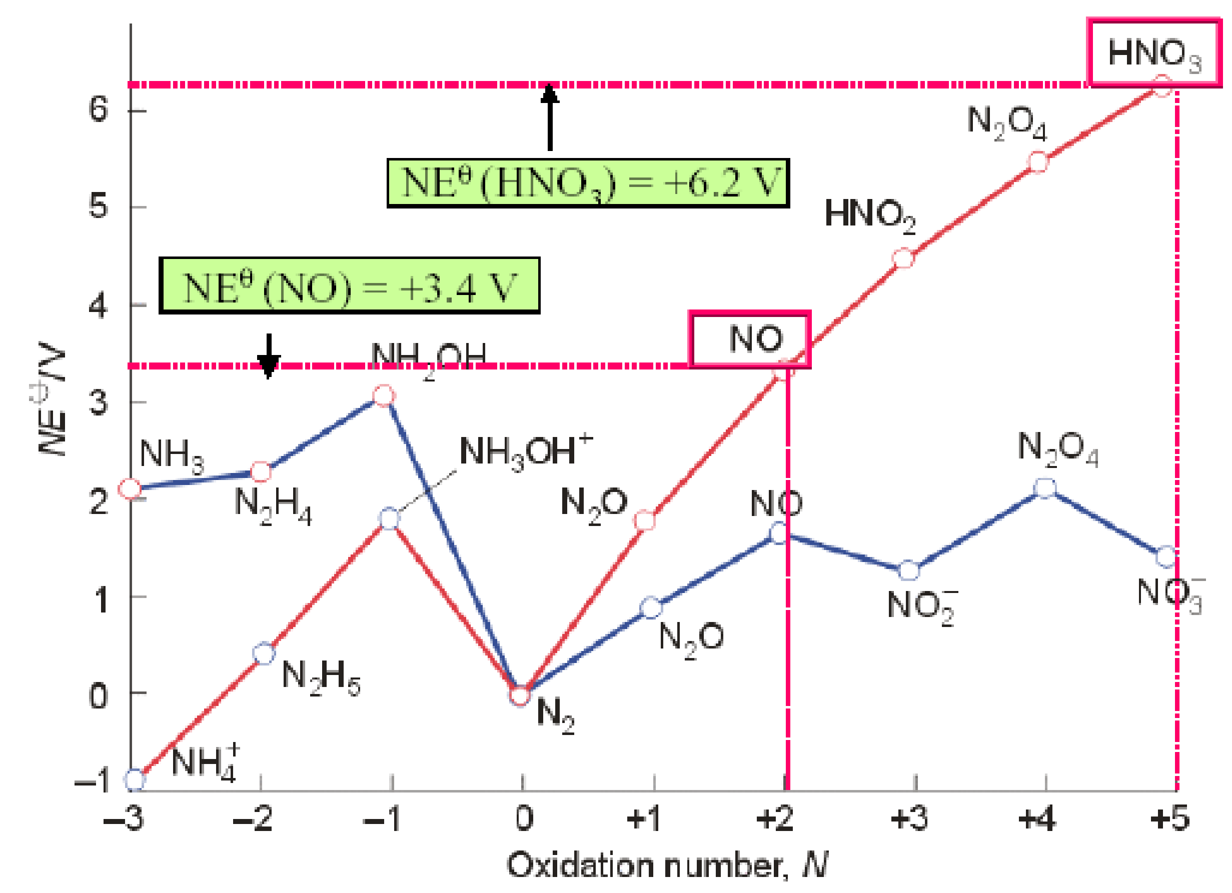


The oxidizing agent - couple with more positive slope - more positive E

The reducing agent - couple with less positive slope

If the line has –ive slope- higher lying species – reducing agent

If the line has +ive slope – higher lying species – oxidiing agent



$$2\,HNO_3 + 10e^- + 10H^+ \longrightarrow N_2 + 6H_2O$$

$\boxed{E^\theta = +1.24\ V}$

$$2\,NO + 4e^- + 4H^+ \longrightarrow N_2 + 2H_2O$$

$\boxed{E^\theta = +1.7\ V}$

NO – Stronger oxidant than HNO_3

From the position of HNO_3 ((+5, +6.2) and NO (+2, +3.4) on the nitrogen Frost diagram we can determine the reduction potential for the **half reactions** below:

$$2\,HNO_3 + 10e^- + 10H^+ \longrightarrow N_2 + 6H_2O$$

$NE^\theta = +6.2$ V *from graph y-value*

$N = +5$ *from graph x-value*

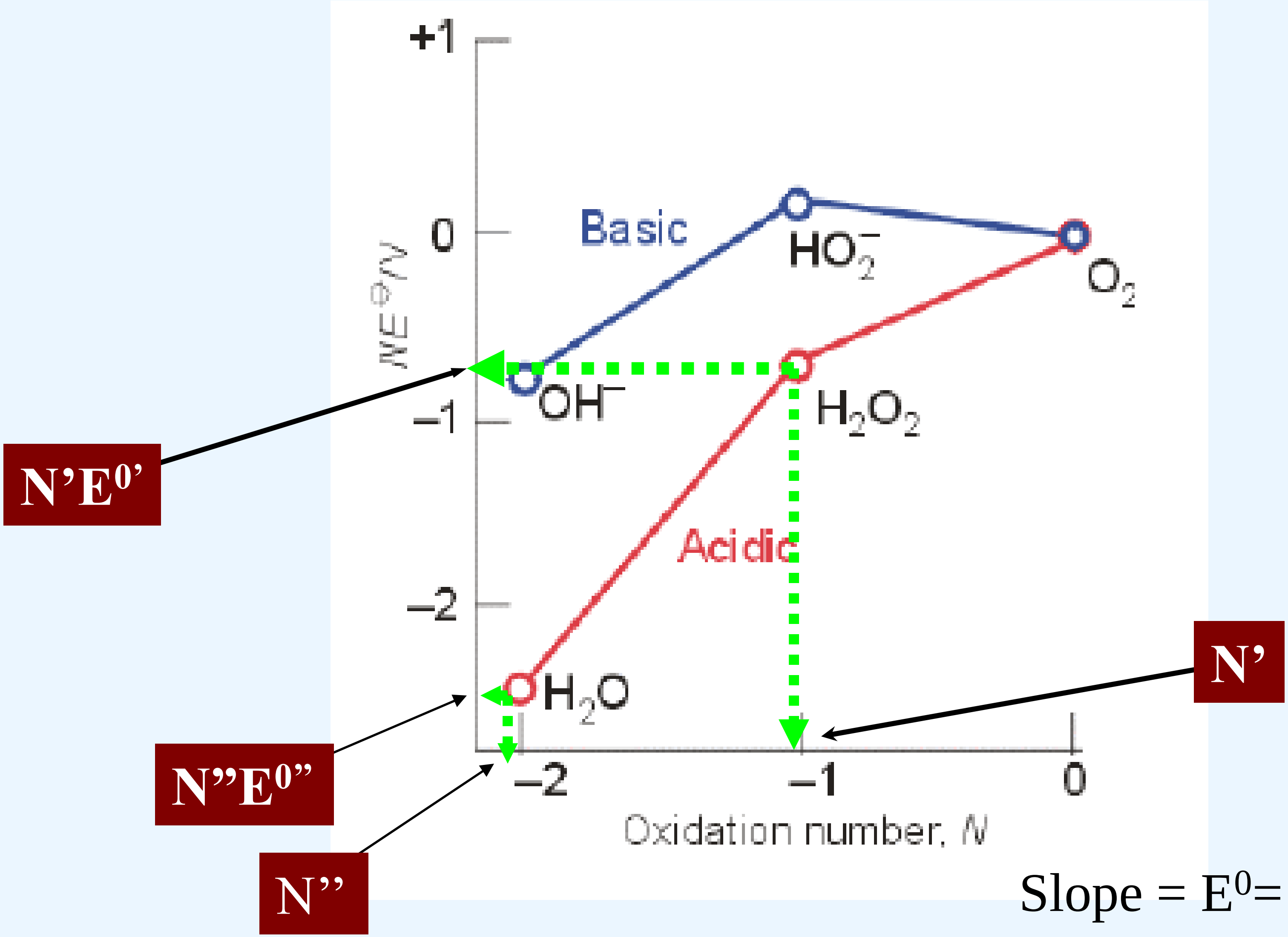
$$\boxed{E^\theta = +1.24\ V}$$

$$2\,NO + 4e^- + 4H^+ \longrightarrow N_2 + 2H_2O$$

$NE^\theta = +3.4$ V

$N = +2$

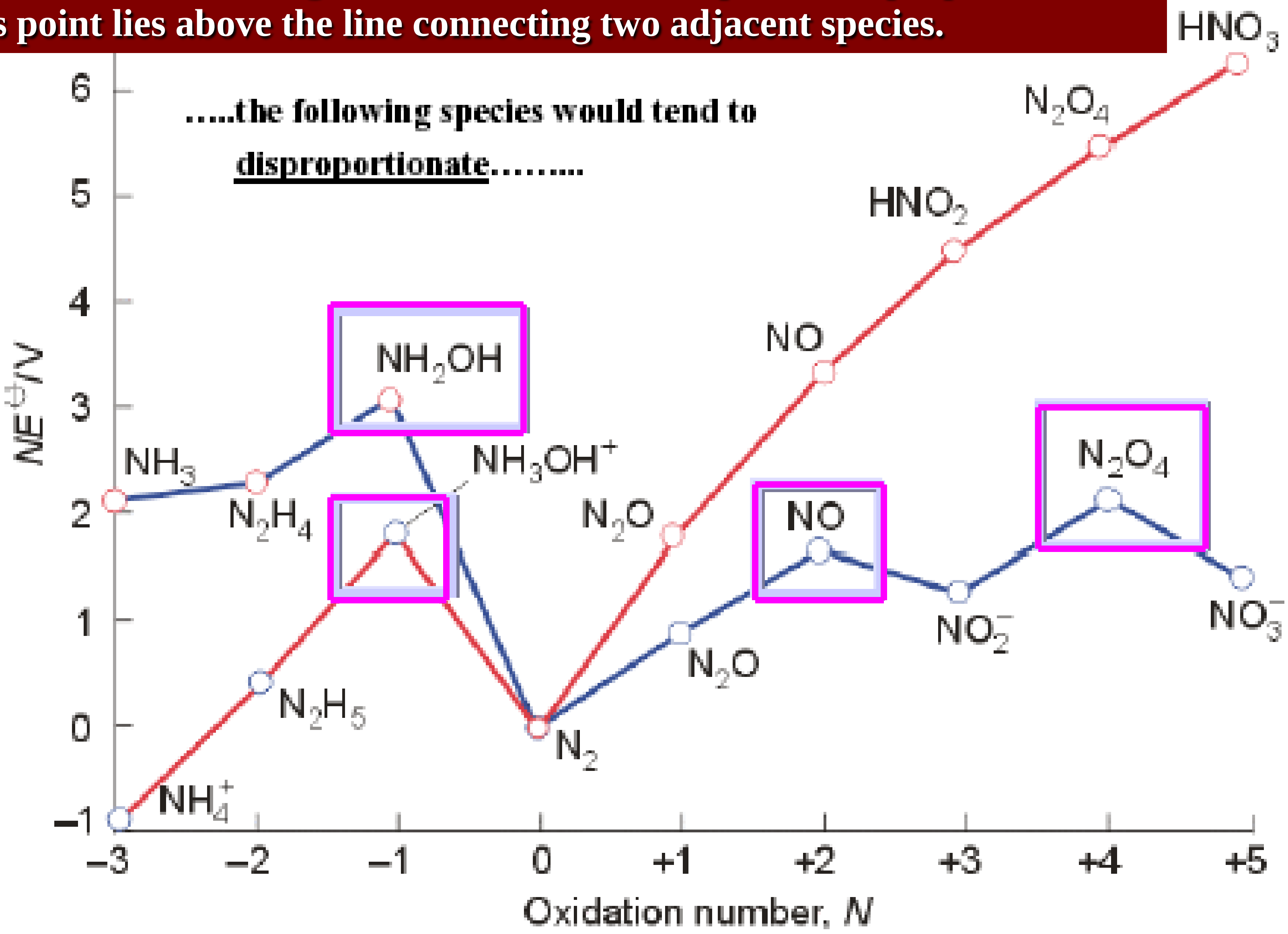
$$\boxed{E^\theta = +1.7\ V}$$



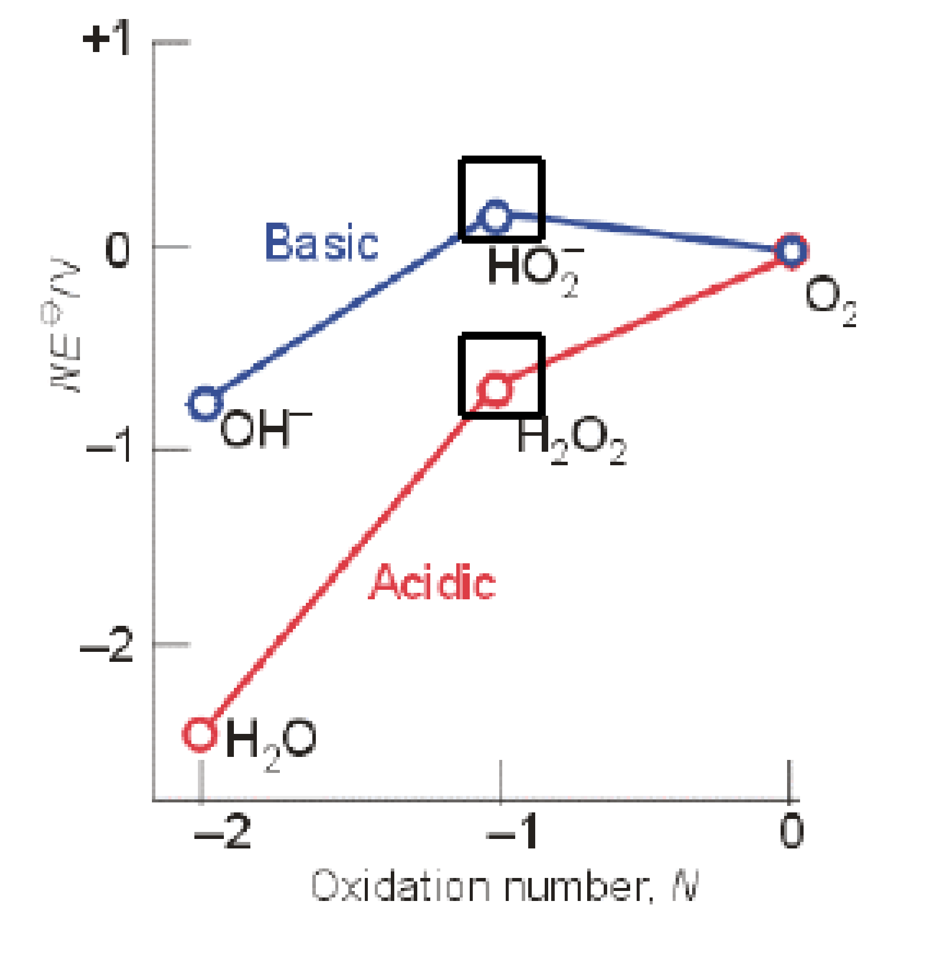
$$\text{Slope} = E^0 = \frac{N'E^{0'} - N''E^{0''}}{N' - N''}$$

Slope of the line joining any two points is equal to the std potential of the couple.

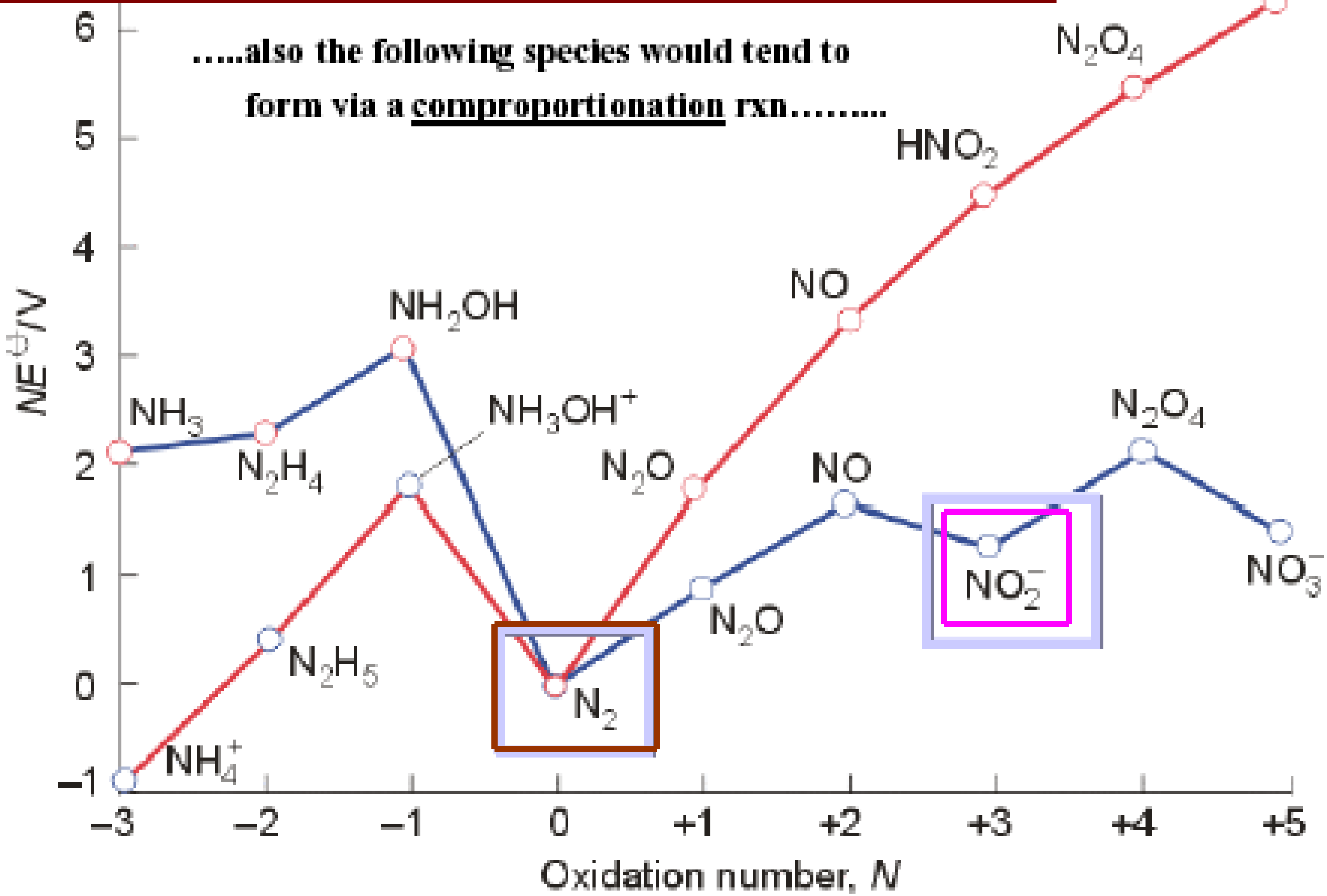
A species in a Frost diagram is unstable with respect to disproportionation if its point lies above the line connecting two adjacent species.



Disproportionation…. another example



Comproportionation is spontaneous if the intermediate species lies below the straight line joining the two reactant species.



Comproportionation Reactions:

A higher oxidation state species combines with a lower oxidation state species to afford an intermediate oxidation state species

$$\overset{+2}{NO} + \overset{+4}{N_2O_4} \longrightarrow \overset{+3}{NO_2^-}$$

Not balanced

Half reactions:

$$\overset{+4}{N_2O_4} \cancel{+ 2e^-} \longrightarrow 2\,\overset{+3}{NO_2^-}$$

(reduction rxn)

$$2\,\overset{+2}{NO} + 4OH^- \longrightarrow 2(\overset{+3}{NO_2^-} \cancel{+ e^-}) + 2\,H_2O$$

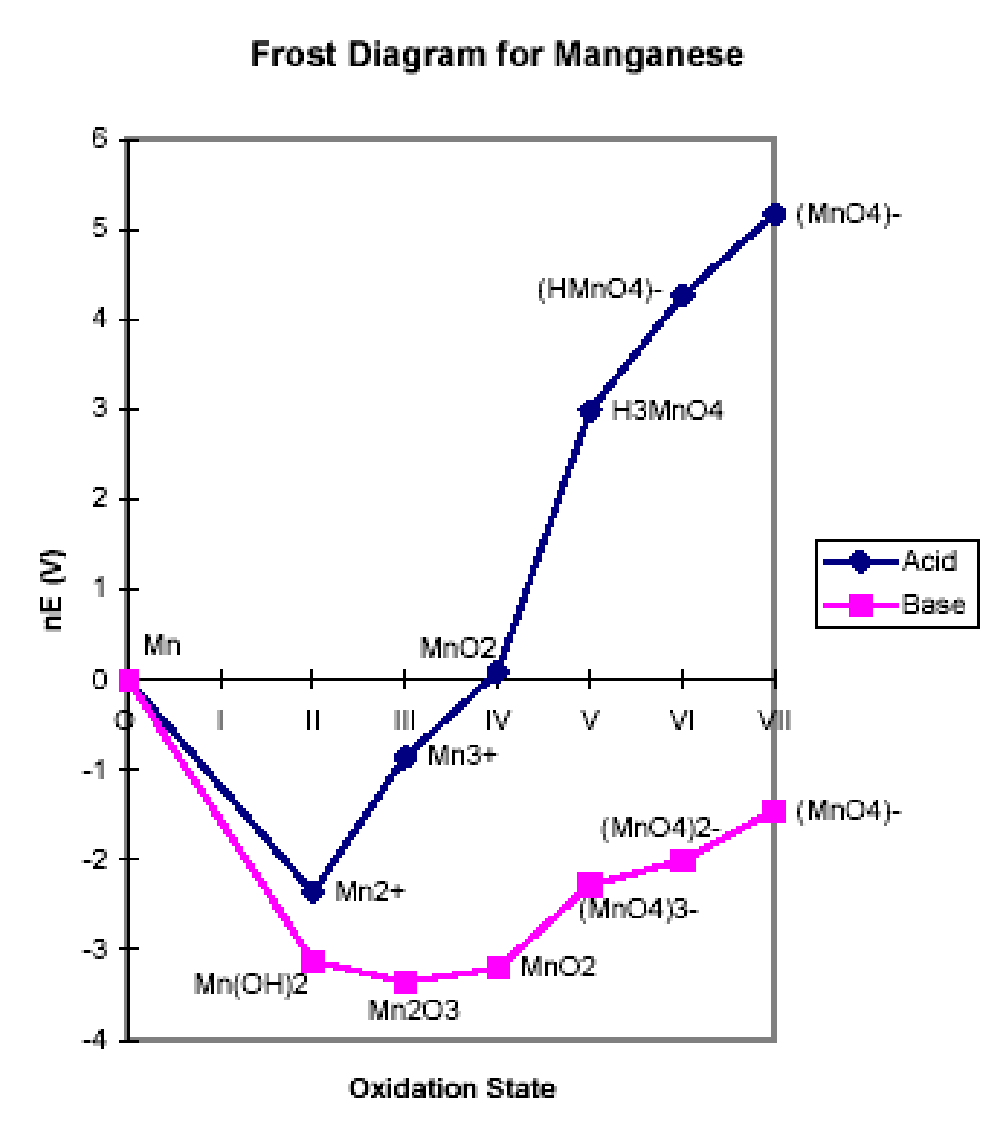
(oxidation rxn)

Net rxn:

$$2NO + N_2O_4 + 4OH^- \longrightarrow 4\,NO_2^- + 2\,H_2O$$

balanced

Comproportionation another example…



In acidic solution…

Mn and MnO_2

↓

Mn^{2+}

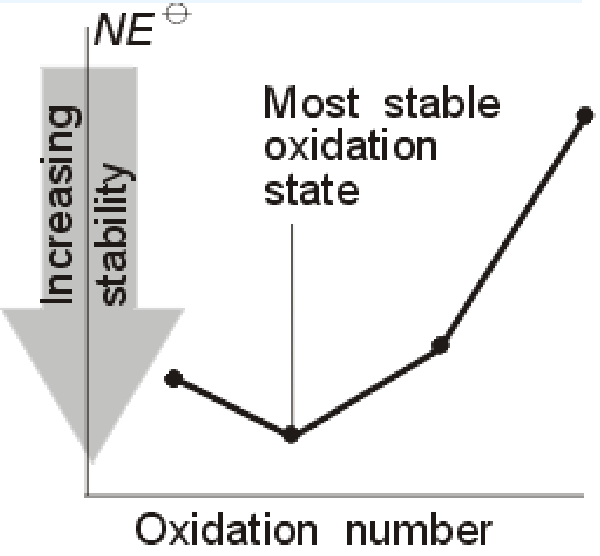
Rate of the reaction hindered insolubility?

In basic solution…

MnO_2 and $Mn(OH)_2$

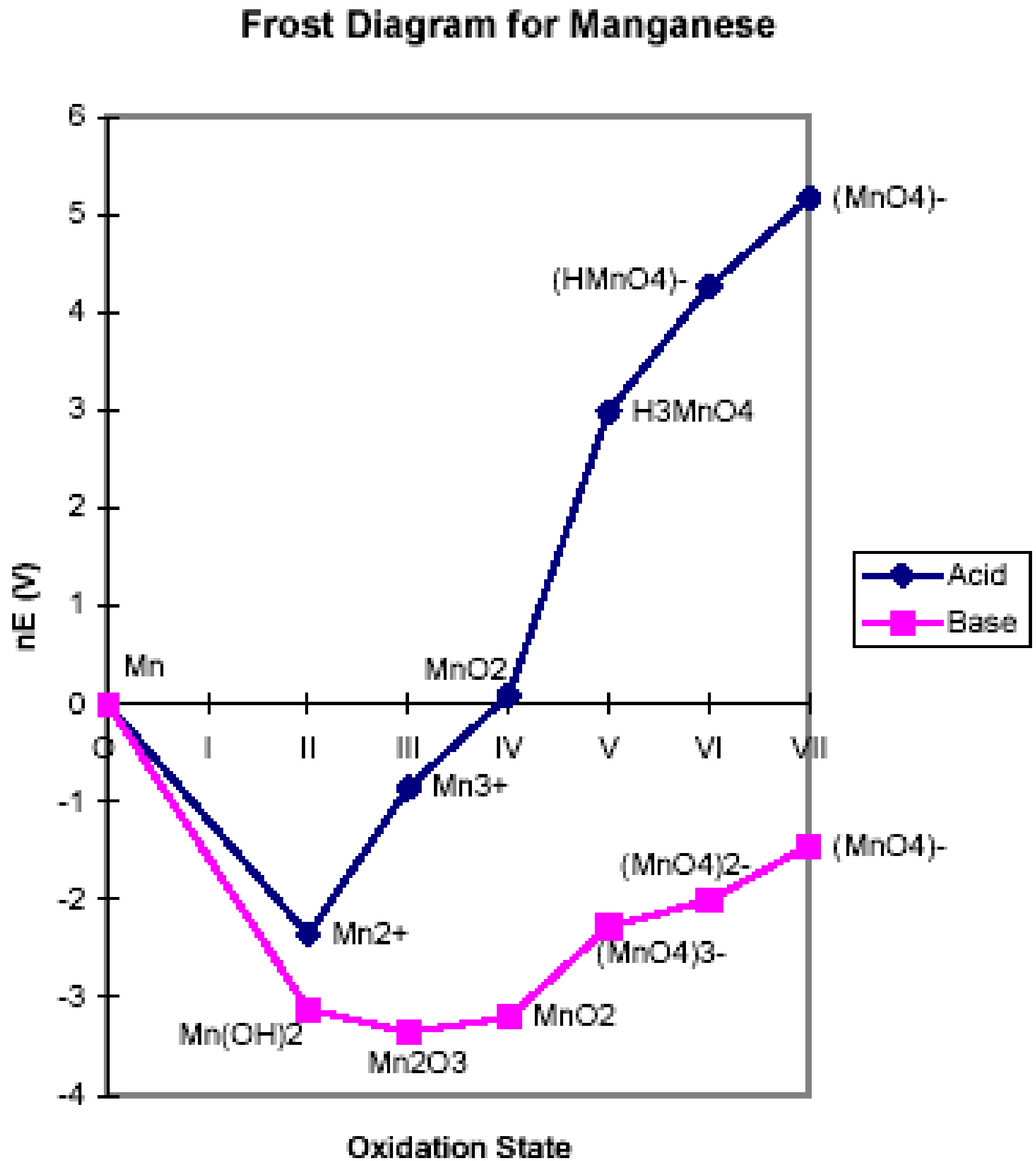
↓

Mn_2O_3



$NE^{\ominus}$
Increasing stability
Most stable oxidation state
Oxidation number

1



Frost Diagram for Manganese
nE (V)
6
5
4
3
2
1
0
-1
-2
-3
-4
0
I
II
III
IV
V
VI
VII
Mn
Mn2+
Mn3+
MnO2
H3MnO4
(HMnO4)-
(MnO4)-
Mn(OH)2
Mn2O3
MnO2
(MnO4)3-
(MnO4)2-
(MnO4)-
Acid
Base
Oxidation State

From the Frost diagram for Mn….

*** Thermodynamic stability is found at the bottom of the diagram.**
Mn (II) is the most stable species.

*** A species located on a convex curve can undergo disproportionation**

example: $MnO_4^{3-} \longrightarrow MnO_2$ ***and*** MnO_4^{2-} ***(in basic solution)***

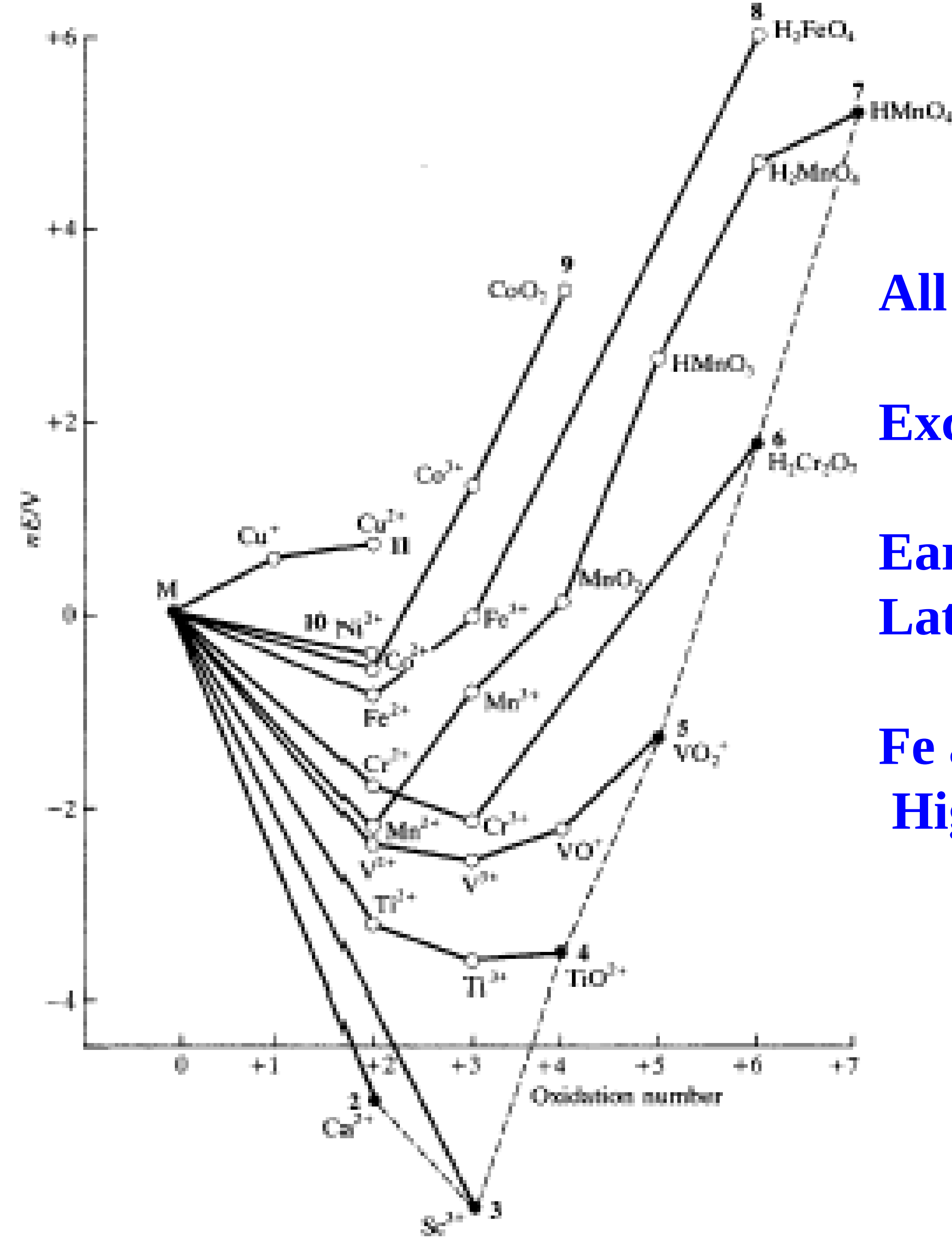
•Any species located on the upper right side of the diagram will be a strong oxidizing agent. **MnO_4^- - strong oxidizing agent.**

•Any species located on the upper left side of the diagram will be a reducing agent. Mn - moderate reducing agent.

* Although it is thermodynamically favorable for permanganate ion to be reduced to Mn(II) ion, the reaction is slow except in the presence of a catalyst. Thus, solutions of permanganate can be stored and used in the laboratory.

* Changes in pH may change the relative stabilities of the species. The potential of any process involving the hydrogen ion will change with pH because the concentration of this species is changing.

* Under basic conditions aqueous Mn^{2+} does not exist. Instead Insoluble $Mn(OH)_2$ forms.



All metals are good reducing agents

Exception: Cu

Early transition elements: +3 state
Latter +2 state

Fe and Mn – many oxidation states
High oxidation state:
Strong oxidizing agents

Group 6