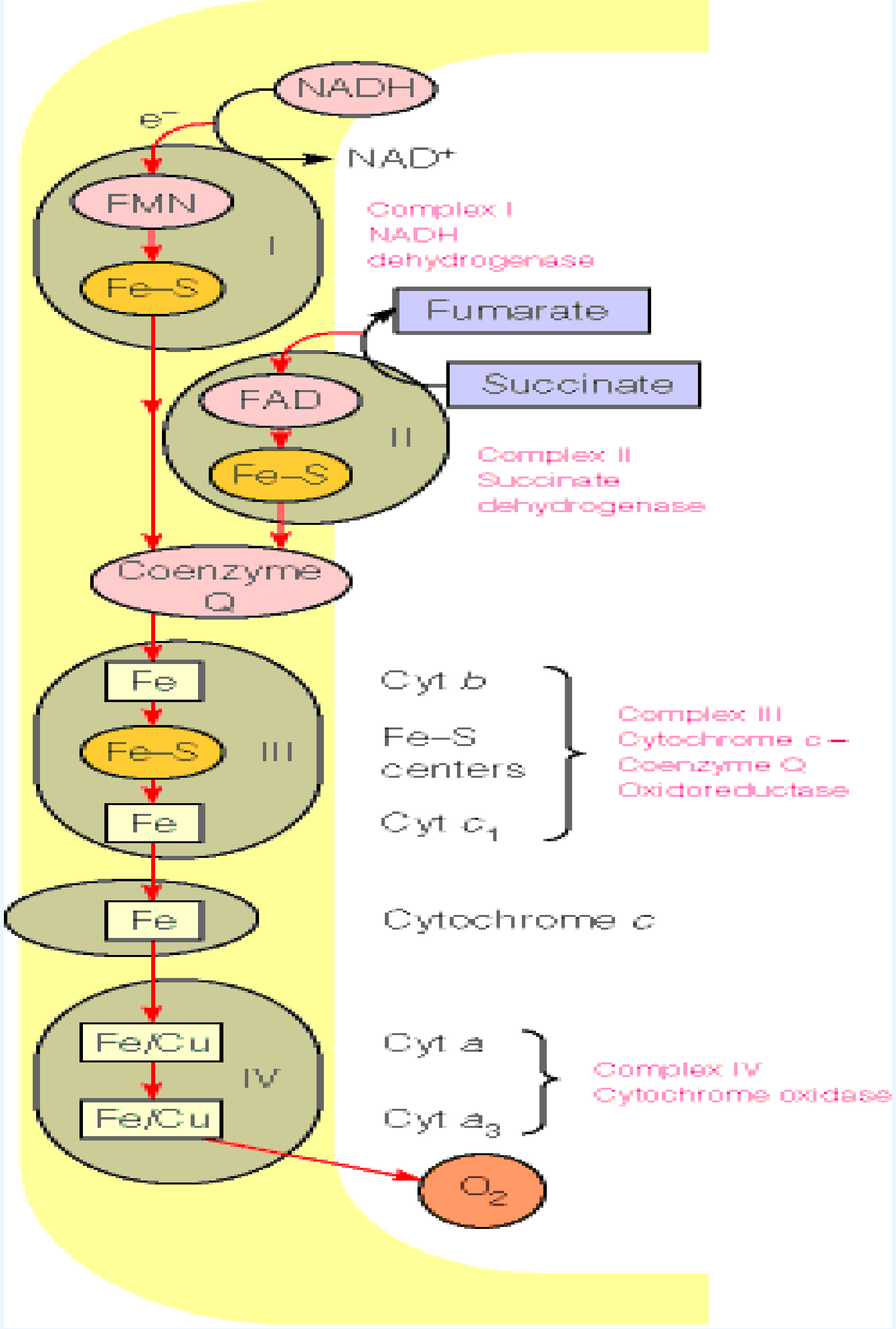
Redox Chemistry
Oxidation-Reduction

Biology

Industry

Environment

Biology


NADH
e⁻
NAD⁺
FMN
Fe–S
I
Complex I
NADH
dehydrogenase
Fumarate
Succinate
FAD
II
Fe–S
Complex II
Succinate
dehydrogenase
Coenzyme
Q
Fe
Fe–S
III
Fe
Cyt b
Fe–S
centers
Cyt c_1
Complex III
Cytochrome c –
Coenzyme Q
Oxidoreductase
Fe
Cytochrome c
Fe/Cu
IV
Fe/Cu
Cyt a
Cyt a_3
Complex IV
Cytochrome oxidase
O_2

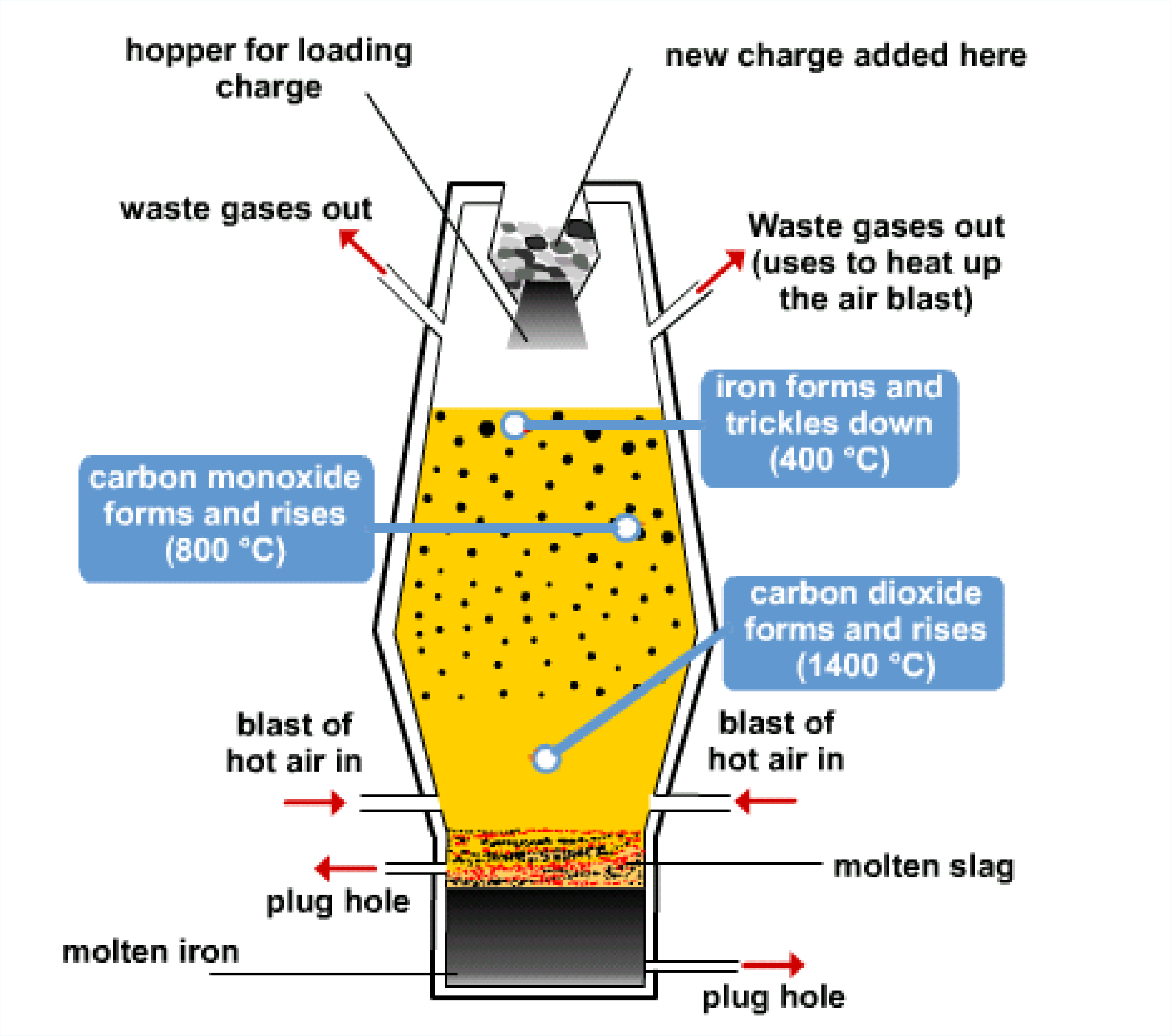
Biology

Selected Biologically Important Redox Couples

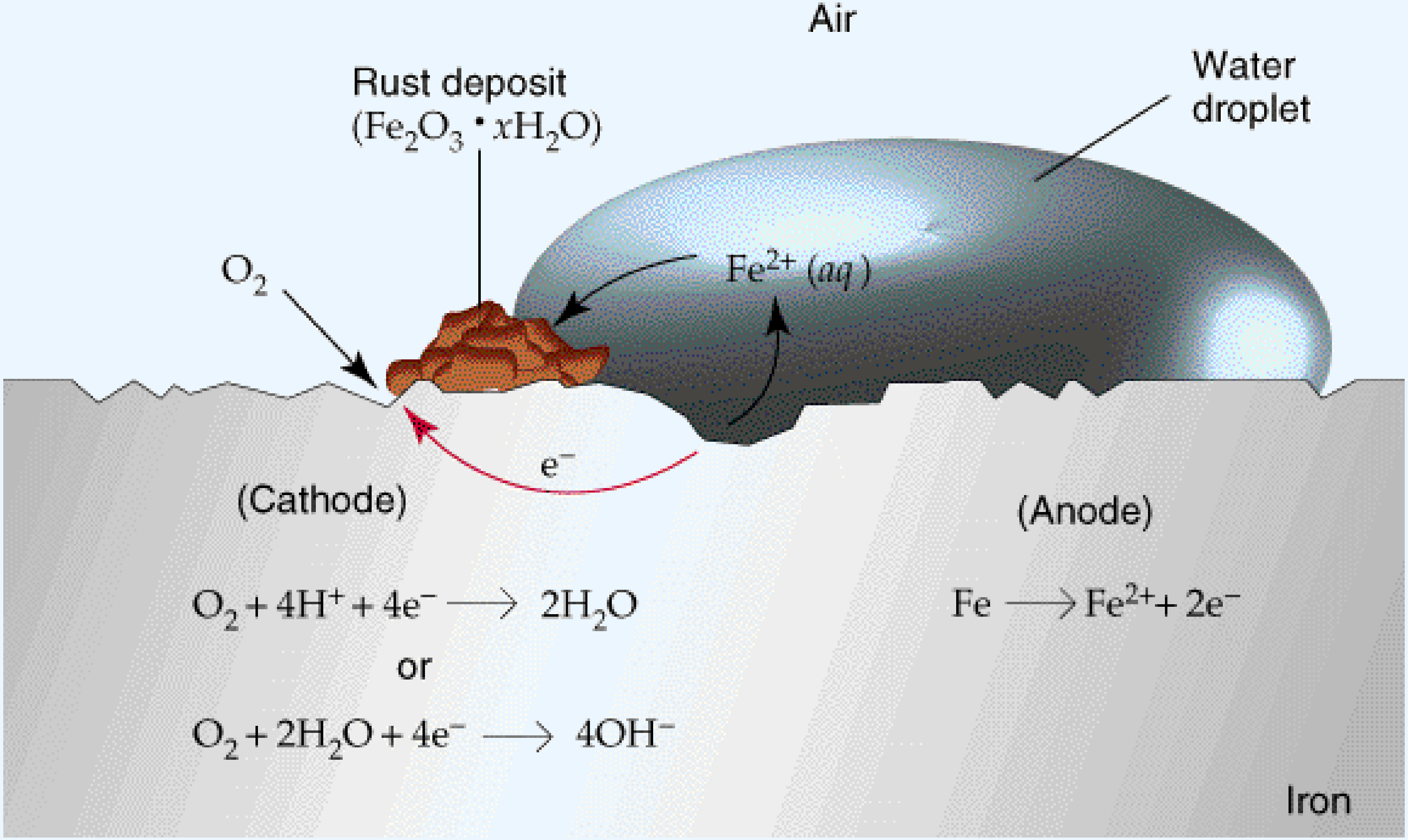
Redox Couple	E'_0 (Volts) [a]
$2H^+ + 2e^- \longrightarrow H_2$	0
Ferredoxin(Fe^{3+}) + $e^- \longrightarrow$ ferredoxin (Fe^{2+})	−0.42
$NAD(P)^+ + H^+ + 2e^- \longrightarrow NAD(P)H$	−0.32
$S + 2H^+ + 2e^- \longrightarrow H_2S$	−0.274
Acetaldehyde + $2H^+ + 2e^- \longrightarrow$ ethanol	−0.197
Pyruvate$^-$ + $2H^+ + 2e^- \longrightarrow$ lactate^{2-}	−0.185
$FAD + 2H^+ + 2e^- \longrightarrow FADH_2$	−0.18[b]
Oxaloacetate^{2-} + $2H^+ + 2e^- \longrightarrow$ malate^{2-}	−0.166
Fumarate^{2-} + $2H^+ + 2e^- \longrightarrow$ 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).

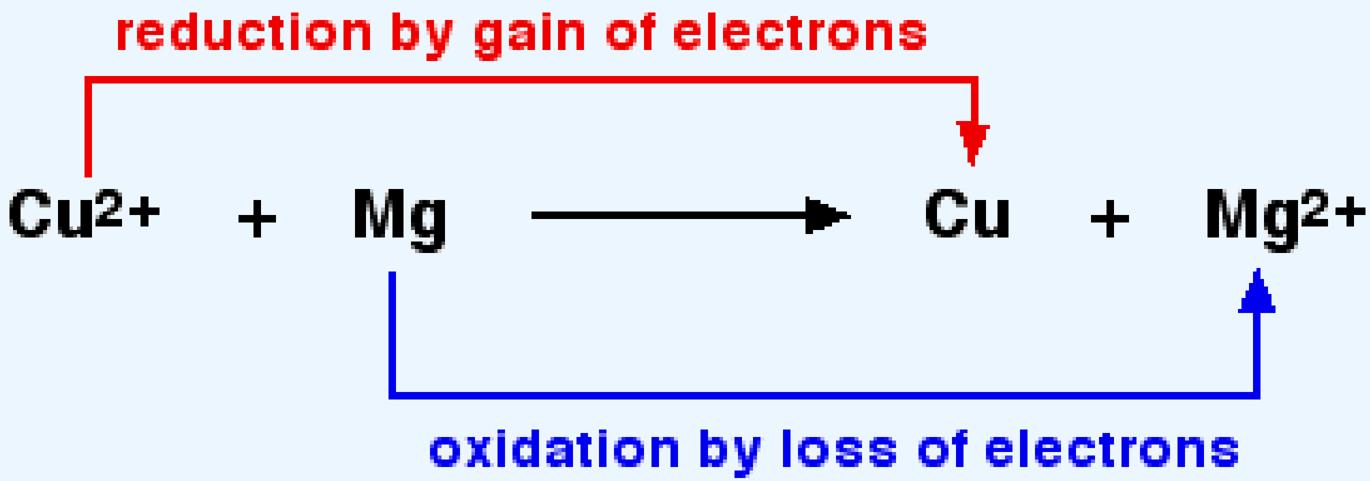
Industry **Extraction of elements** **Synthesis of different compounds**



Environment



Redox reactions - transfer of electrons between species.



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

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

$$\underset{(+7)}{MnO_4^-} \longrightarrow \underset{(+2)}{Mn^{2+}}$$ Reduction half reaction

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

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

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

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

Nernst Equation

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

$$Q = \frac{[Red_1]^{a'} [Ox_2]^{b'}}{[Ox_1]^{a} [Red_2]^{b}}$$

$$E = E^0 - \frac{RT}{nF} \ln Q$$

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

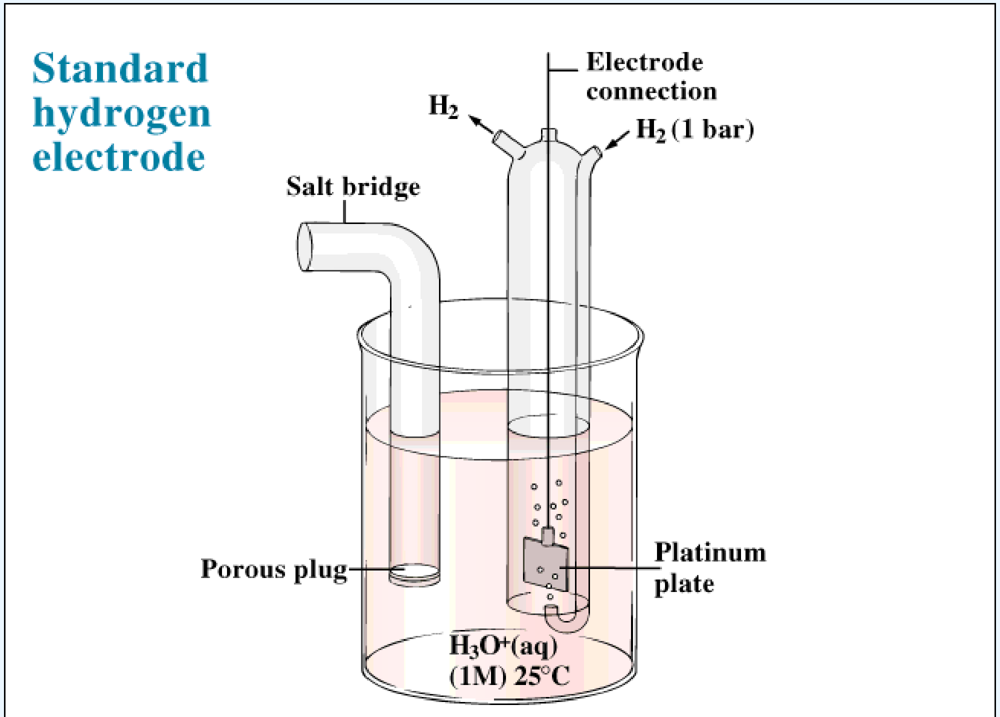
(b) $Zn^{2+} (aq) + 2e \longrightarrow Zn(s)$ $E^0 (Zn^{2+}, Zn) = -0.76$ V

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

Reaction is favorable

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.



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Hydrogen Half-Cell

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

reversible reaction

Galvanic Cell

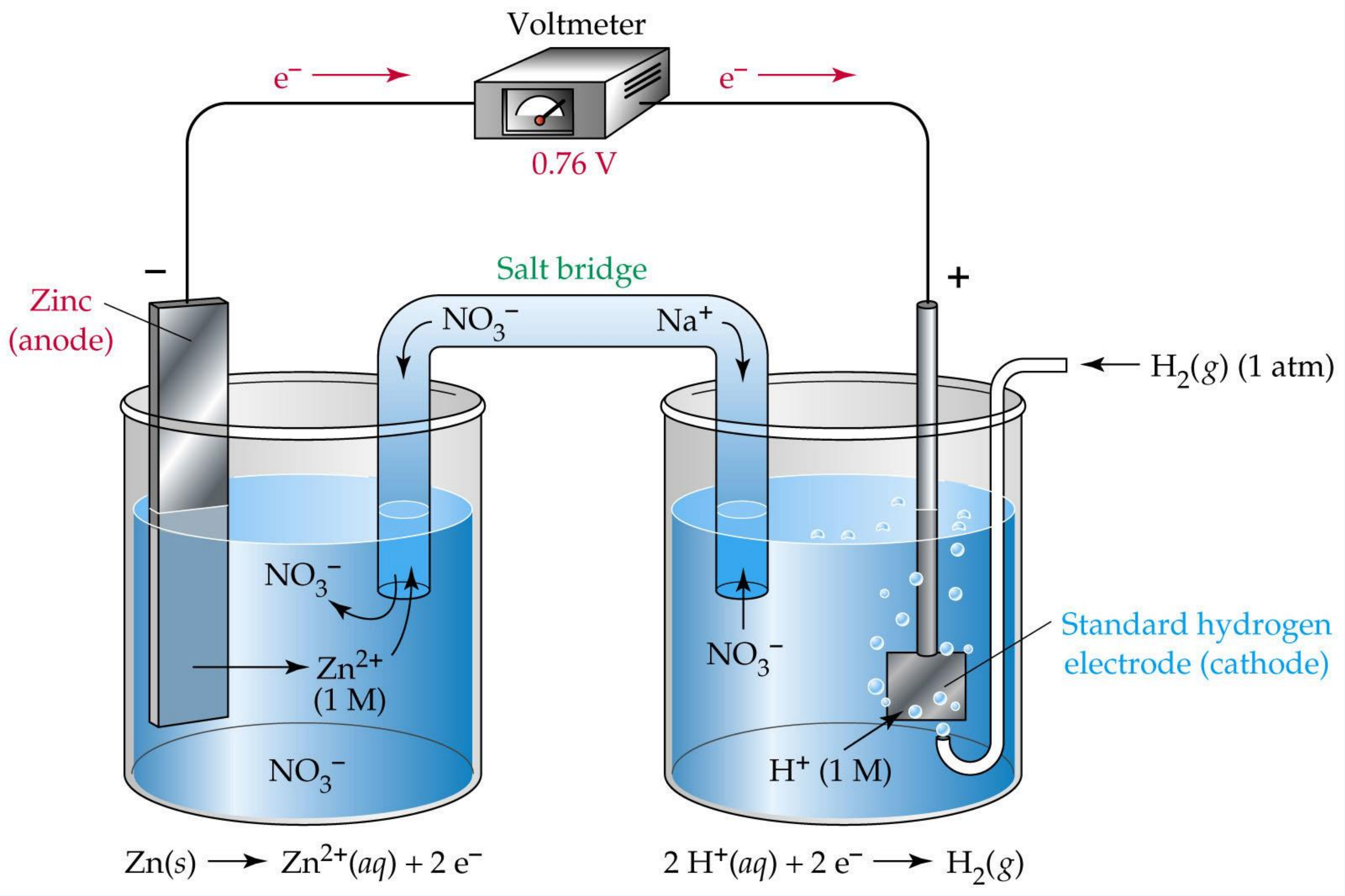

TABLE 18.1 Standard Reduction Potentials at 25°C

	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	
	$MnO_4^-(aq) + 8H^+(aq) + 5e^-$	$\longrightarrow Mn^{2+}(aq) + 4H_2O(l)$	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	
Weaker oxidizing agent	$Li^+(aq) + e^-$	$\longrightarrow Li(s)$	−3.04	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.

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

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Stronger oxidizing agent · Weaker reducing agent

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$Cu^{2+}(aq) + 2e^-$	$\longrightarrow Cu(s)$	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
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$Cd^{2+}(aq) + 2e^-$	$\longrightarrow Cd(s)$	−0.40
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$Al^{3+}(aq) + 3e^-$	$\longrightarrow Al(s)$	−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

Latimer diagram for chlorine in acidic solution

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

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

Can you balance the equation?

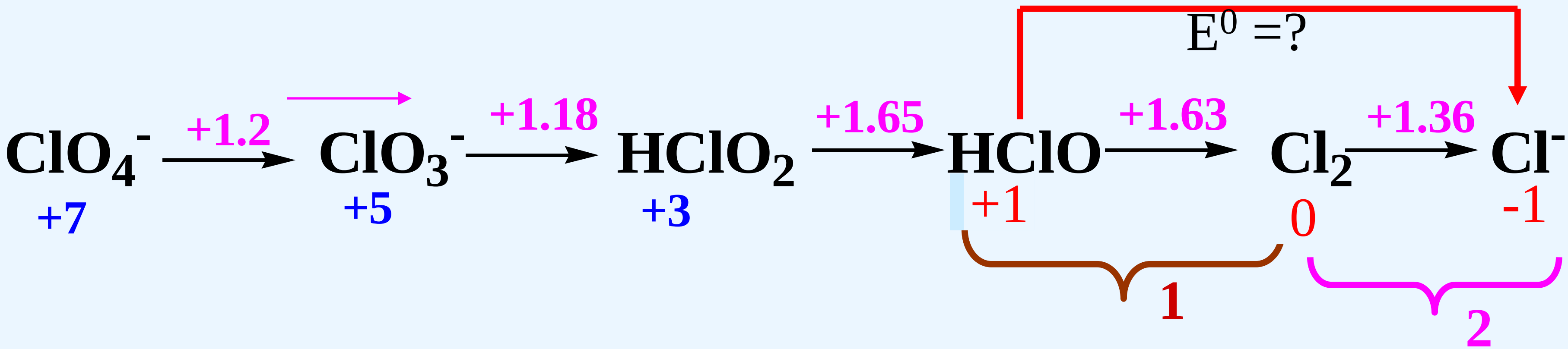
$$ClO_4^-(aq) + 2H^+(aq) + 2e^- \longrightarrow ClO_3^-(aq) + H_2O(l) \qquad E^\circ = 1.20\,V$$

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

balance the equation

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

How to extract E^0 for nonadjacent oxidation state?



Should not add their potentials, but make use of $\Delta G^0 = -\upsilon F E^0$

The overall ΔG^0 is the sum of the individual values.

So, $\Delta G^0(\mathrm{a+b}) = \Delta G^0(\mathrm{a}) + \Delta G^0(\mathrm{b})$

$-\upsilon F E^0(a+b) = -\upsilon(\mathrm{a}) F E^0(a) - \upsilon(\mathrm{b}) F E^0(b)$

$-F$ *cancel and* $\upsilon = \upsilon(a) + \upsilon(b)$

$E^0(a+b) = \upsilon(\mathrm{a})E^0(a) + \upsilon(\mathrm{b})E^0(b)/\upsilon(a) + \upsilon(b)$

$$E^0 = ?$$

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

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

$$Cl_2(g) + 2e^- \longrightarrow 2Cl^-(l) \qquad E^0 = +1.36\ V$$

$$2\ HClO(aq) + 2H^+(aq) + 4e^- \longrightarrow 2Cl^-\ (l) + 2\ H_2O(l)$$

$$E^0(a+b) = \upsilon(\mathrm{a})E^0(a) + \upsilon(\mathrm{b})E^0(b)/\upsilon(a) + \upsilon(b)$$

$$E^0 = (1)\ (1.63\ V) + (1)\ (1.36\ V)/1 + 1 = 1.50\ V$$

In basic aqueous solution

$$\begin{array}{ccccccccccc} ClO_4^- & \xrightarrow{+0.37} & ClO_3^- & \xrightarrow{+0.30} & ClO_2^- & \xrightarrow{+0.68} & ClO^- & \xrightarrow{+0.42} & Cl_2 & \xrightarrow{+1.36} & Cl^- \\ +7 & & +5 & & +3 & & +1 & & 0 & & -1 \end{array}$$

$$ClO_2^- \xrightarrow{E^0\ ?} Cl_2$$

$$ClO_2^-(aq) + H_2O\ (l) + 2e- \longrightarrow ClO^-(aq) + 2OH^-\ (aq)$$

$$ClO^-(aq) + H_2O\ (l) + e^- \longrightarrow 1/_2Cl_2(aq) + 2OH^-\ (aq)$$

$$ClO_2^-(aq) + 2\ H_2O\ (l) + 3e- \longrightarrow 1/_2Cl_2(aq) + 4\ OH^-\ (aq)$$

$$E^0(a+b) = \upsilon(\mathrm{a})E^0(a) + \upsilon(\mathrm{b})E^0(b)/\upsilon(a) + \upsilon(b)$$

$$E^0 = (2)\ (0.68\ \mathrm{V}) + (1)\ (0.42\ \mathrm{V})/3 = +0.59\ \mathrm{V}$$

Predicting a disproportionation reaction using the Latimer diagram

$$M^{2+}_{(aq)} \xrightarrow{E^0(L)} M^{+}_{(aq)} \xrightarrow{E^0(R)} M(0)_{(s)}$$

A species has a tendency to disproportionate into its two neighbors if the potential on the right of the species in a Latimer diagram is more positive than that on the left.

$E^0 = E^0(\text{R}) - E^0(\text{L})$ is positive if $E^0(\text{R}) > E^0(\text{L})$

$$Cu^{2+} \xrightarrow{+0.16\ V} Cu^{+} \xrightarrow{+0.52\ V} Cu$$

Yes, as the $E^0(\text{R}) > E^0(\text{L})$, Cu^+ will undergo a disproportionation reaction

Disproportionation

A redox reaction in which the oxidation number of an element is simultaneously raised and lowered – oxidized and reduced

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

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

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

$$Cu^{2+} \xrightarrow{+0.16\ V} Cu^{+} \xrightarrow{+0.52\ V} Cu$$

$E^{0}_{cell} = E^{0}(\text{cathode}) - E^{0}(\text{anode})$

$= 0.52\ V - 0.16\ V$

$= 0.36\ V$

$K = 1.3 \times 10^{6}$

Highly favorable

The more positive E^{0} is the cathode reaction – reduction takes place.
And the less positive E^{0} is the anode reaction – oxidation takes place.
So $E^{0} = E^{0}(\text{cathode}) - E^{0}(\text{anode})$
E^{0} should be positive for ΔG^{0} to be negative. $E^{0}_{cell} > 0$, then $\Delta_{r}G^{0} < 0$

$$ClO_4^- \xrightarrow{+0.37} ClO_3^- \xrightarrow{+0.3} ClO_2^- \xrightarrow{+0.68} \boxed{ClO^- \xrightarrow{+0.42} Cl_2 \xrightarrow{+1.36} Cl^-}$$

$Cl_2(g) + 2\,e^- \longrightarrow 2Cl^-(aq)$ +1.36

$2ClO^-\,(aq) + 2H_2O(l) + 2e^- \longrightarrow Cl_2(g) + 4OH^-(aq)$ +0.42

$Cl_2(g) + 4OH^-\,(aq) \longrightarrow 2ClO_2^-(aq) + 2H_2O\,(l) + 2e-$

$Cl_2(aq) + 2\,e^- \longrightarrow 2Cl^-\,(aq)$

$2Cl_2(aq) + 4\,OH^-\,(aq) \longrightarrow 2\,ClO_2^-(aq) + 2\,Cl^- + 2\,H_2O\,(l)$

$Cl_2(aq) + 2\,OH^-\,(aq) \longrightarrow ClO_2^-(aq) + Cl^- + H_2O\,(l)$

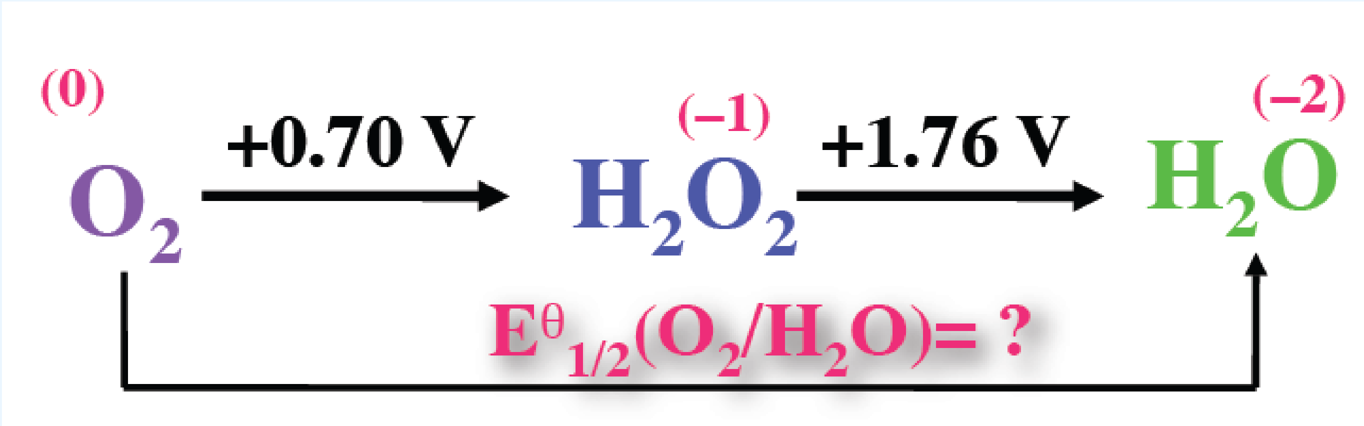
0 +1 -1

$$E^0 = E^0(R) - E^0(L)$$

$$E_{cell} = E^0\,(Cl^-/Cl_2) - E^0\,(Cl_2/ClO^-) = 1.36\text{ V} - 0.42\text{ V} = 0.94\text{ V}$$

Reaction is spontaneous

Latimer diagram for Oxygen



$2\,H^+(aq) + 2e^- + H_2O_2(aq) \longrightarrow 2\,H_2O(l)$ $\quad E^0 = +1.76$ V

$O_2(g) + 2\,H^+(aq) + 2e^- \longrightarrow H_2O_2(aq)$ $\quad E^0 = +0.70$ V

$$E^0 = E^0(\mathrm{R}) - E^0(\mathrm{L})$$
$$= 1.76\text{ V} - 0.70\text{ V}$$
$$= 1.06\text{ V}$$

is spontaneous and $K > 1$

$H_2O_2(aq) \longrightarrow O_2(g) + 2\,H^+(aq) + 2e^-$

$2\,H^+(aq) + 2e^- + H_2O_2(aq) \longrightarrow 2\,H_2O(l)$

$2H_2O_2(aq) \longrightarrow O_2(g) + 2H_2O(l)$

$E^0cell = +1.06$ V

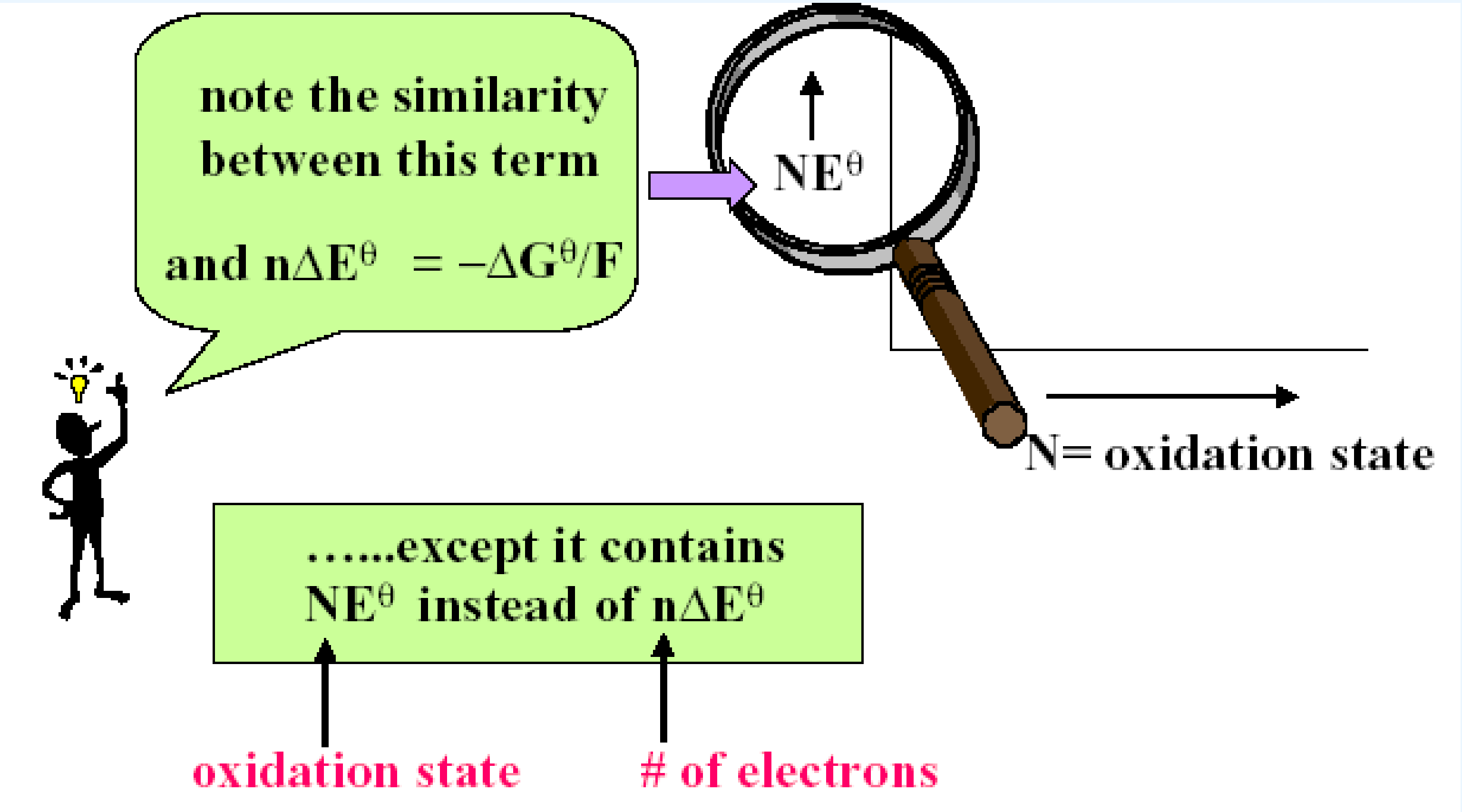
$E^0 = (1)\,(0.70\text{ V}) + (1)\,(1.76\text{ V})/2 = +1.23$ V

ΔG^0 is negative.

Frost Diagram

Arthur A. Frost

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



- so, NE^{θ} is proportional to the free energy of a compound in oxidation state "N" relative to its elemental form

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

$$NE^{0} = -G^{0}/F$$

Frost Diagrams

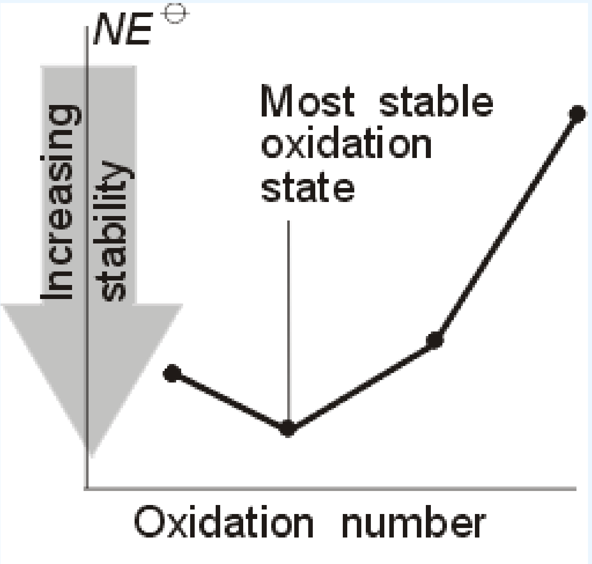
$$X(N) + Ne^- \rightarrow X(0)$$

It is a plot of NE^0 of the couple X(N)/X(0) against the oxidation number N, where N is the net number of electrons transferred from the oxidation state of zero in the element.

It is the plot of NE^0 versus ΔG^0

Since $\Delta G^0 = -\upsilon FE^0$; $\upsilon E^0 = -\Delta G^0/F$;

Then $NE^0 \propto \Delta G^0$



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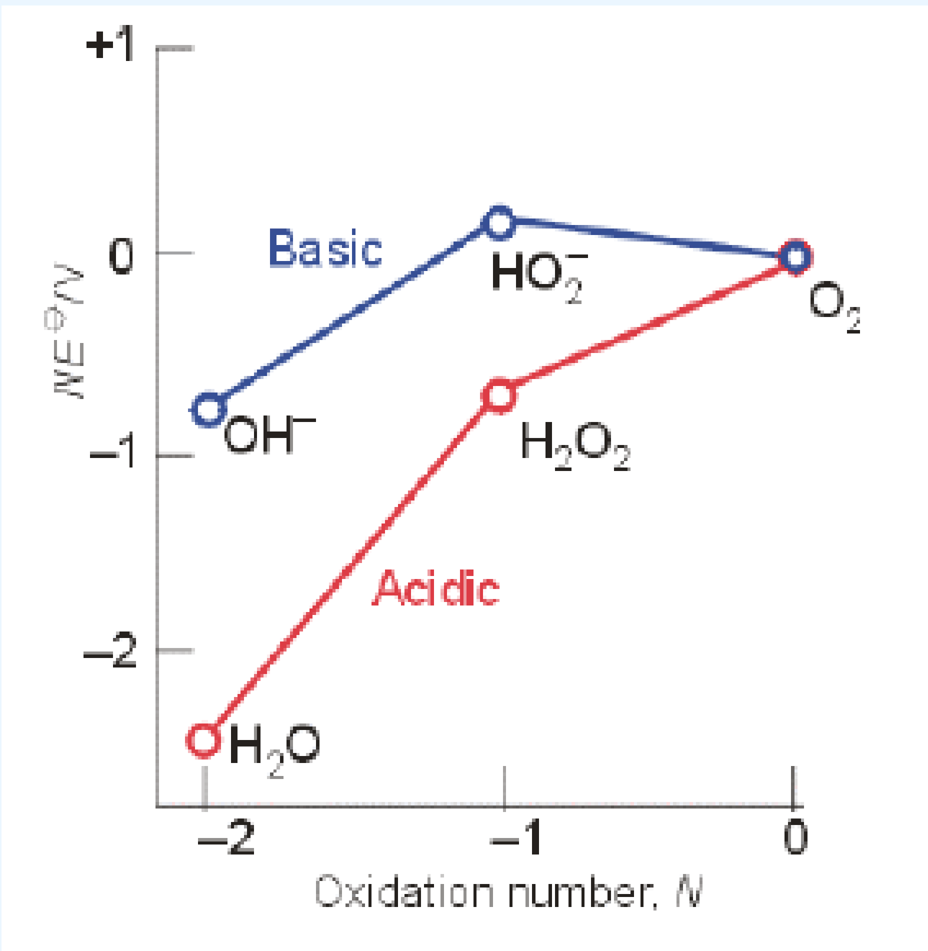
The Frost diagram for O_2

$$O_2 \xrightarrow{0.70\ \text{V}} H_2O_2 \xrightarrow{1.76\ \text{V}} H_2O$$

$E^0 = 1.23$ V

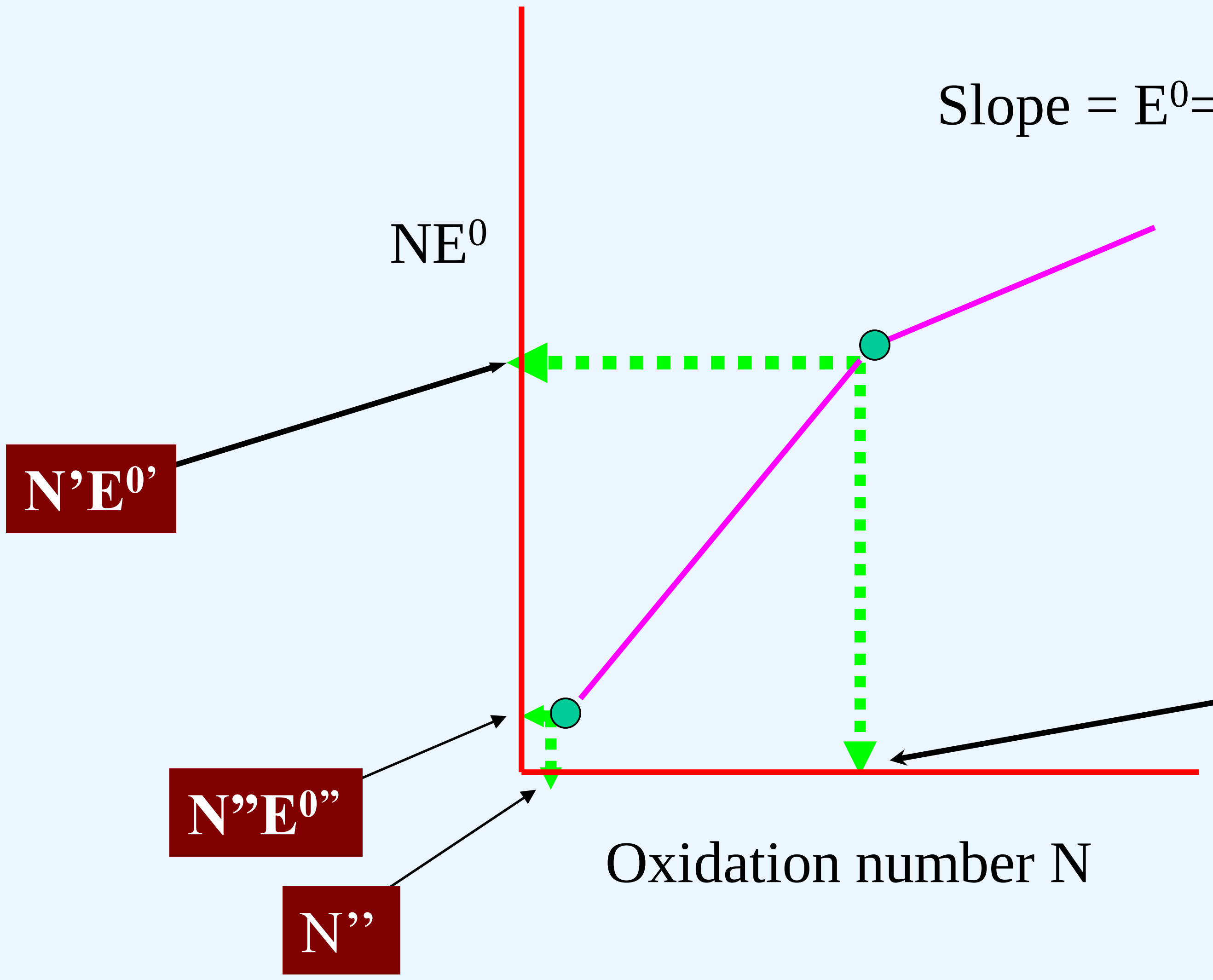


species	N	E^0	NE^0
O_2	0	0	0
H_2O_2	-1	0.70	-0.70
H_2O	-2	1.23	-2.46

Slope = -0.70-(-2.46)/-1-(-2)
= 1.76 V

the slope of a line connecting two species is the reduction potential for the redox couple

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



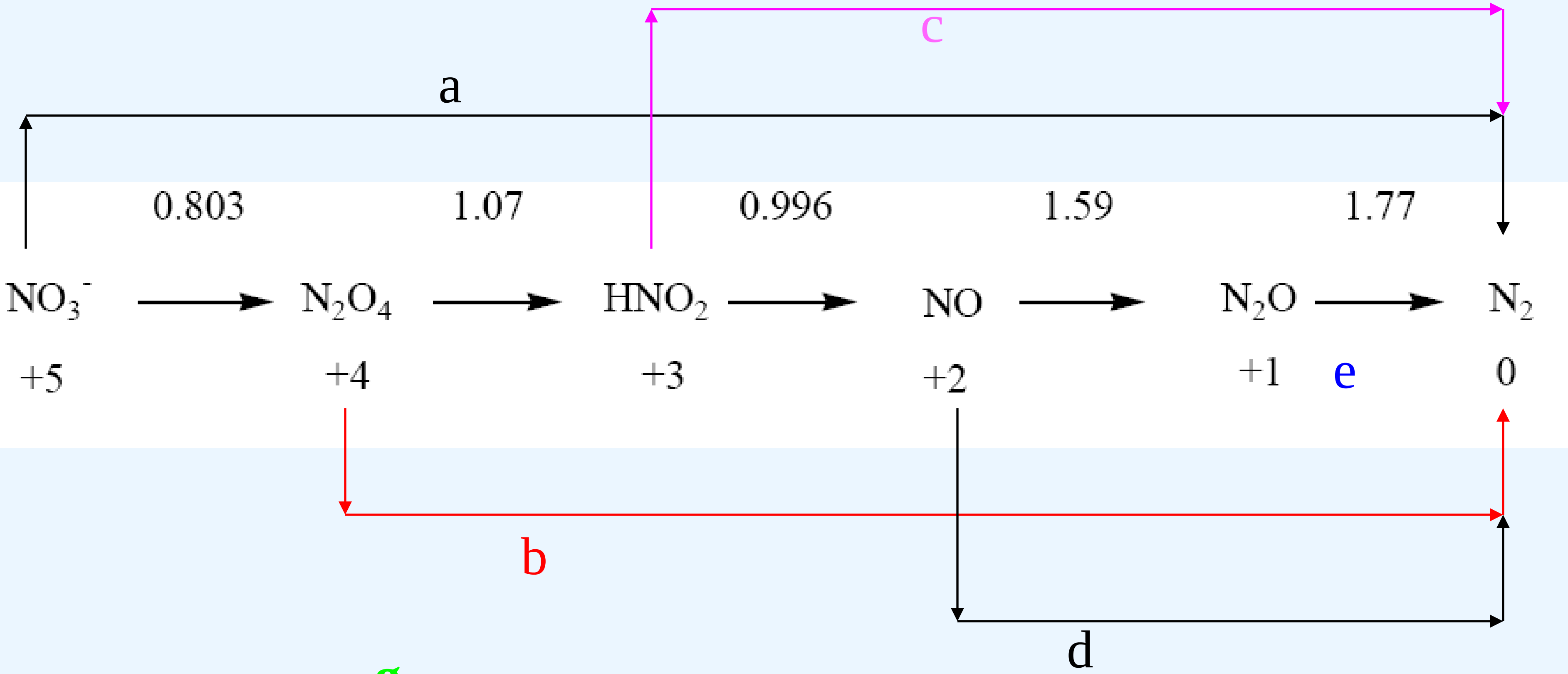
Look at the Latimer diagram of nitrogen in acidic solution

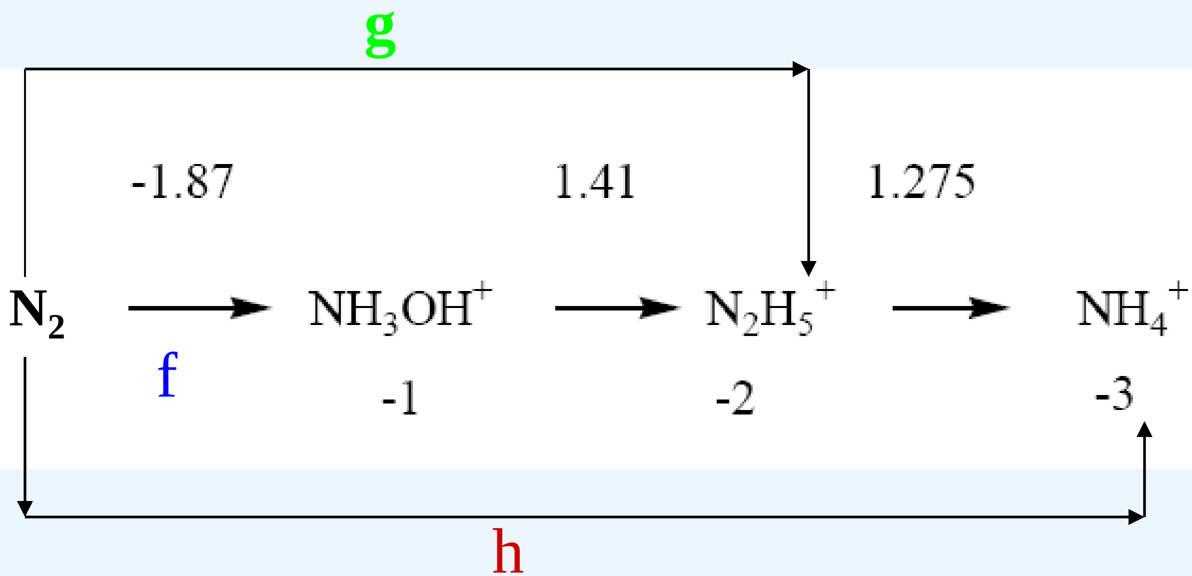
$$NO_3^- \xrightarrow{0.803} N_2O_4 \xrightarrow{1.07} HNO_2 \xrightarrow{0.996} NO \xrightarrow{1.59} N_2O \xrightarrow{1.77} N_2$$

NO_3^-	N_2O_4	HNO_2	NO	N_2O	N_2
+5	+4	+3	+2	+1	0
a	b	c	d	e	

$$\xrightarrow{-1.87} NH_3OH^+ \xrightarrow{1.41} N_2H_5^+ \xrightarrow{1.275} NH_4^+$$

NH_3OH^+	$N_2H_5^+$	NH_4^+
-1	-2	-3
f	g	h





$$\Delta G = \Delta G' + \Delta G''$$

$$-nFE = -n'FE' - n''FE''$$

$$E = \frac{n'E' + n''E''}{n' + n''}$$

a $NO_3^- + 6H^+ + 5e^- \longrightarrow \frac{1}{2} N_2 + 3H_2O$ $E^0 = 1.25V$

$E^0 = 1\times0.803 + 1\times1.07 + 1\times0.996 + 1\times1.59 + 1\times1.77/1+1+1+1+1 = 1.25$

b $\frac{1}{2} N_2O_4 + 4H^+ + 4e^- \longrightarrow \frac{1}{2} N_2 + 2H_2O$ $E^0 = 1.36V$

c $HNO_2 + 3H^+ + 3e^- \longrightarrow \frac{1}{2} N_2 + 2H_2O$ $E^0 = 1.45V$

d $NO + 2H^+ + 2e^- \longrightarrow \frac{1}{2} N_2 + H_2O$ $E^0 = 1.68V$

e $\frac{1}{2} N_2O + H^+ + e^- \longrightarrow \frac{1}{2} N_2 + \frac{1}{2} H_2O$ $E^0 = 1.77V$

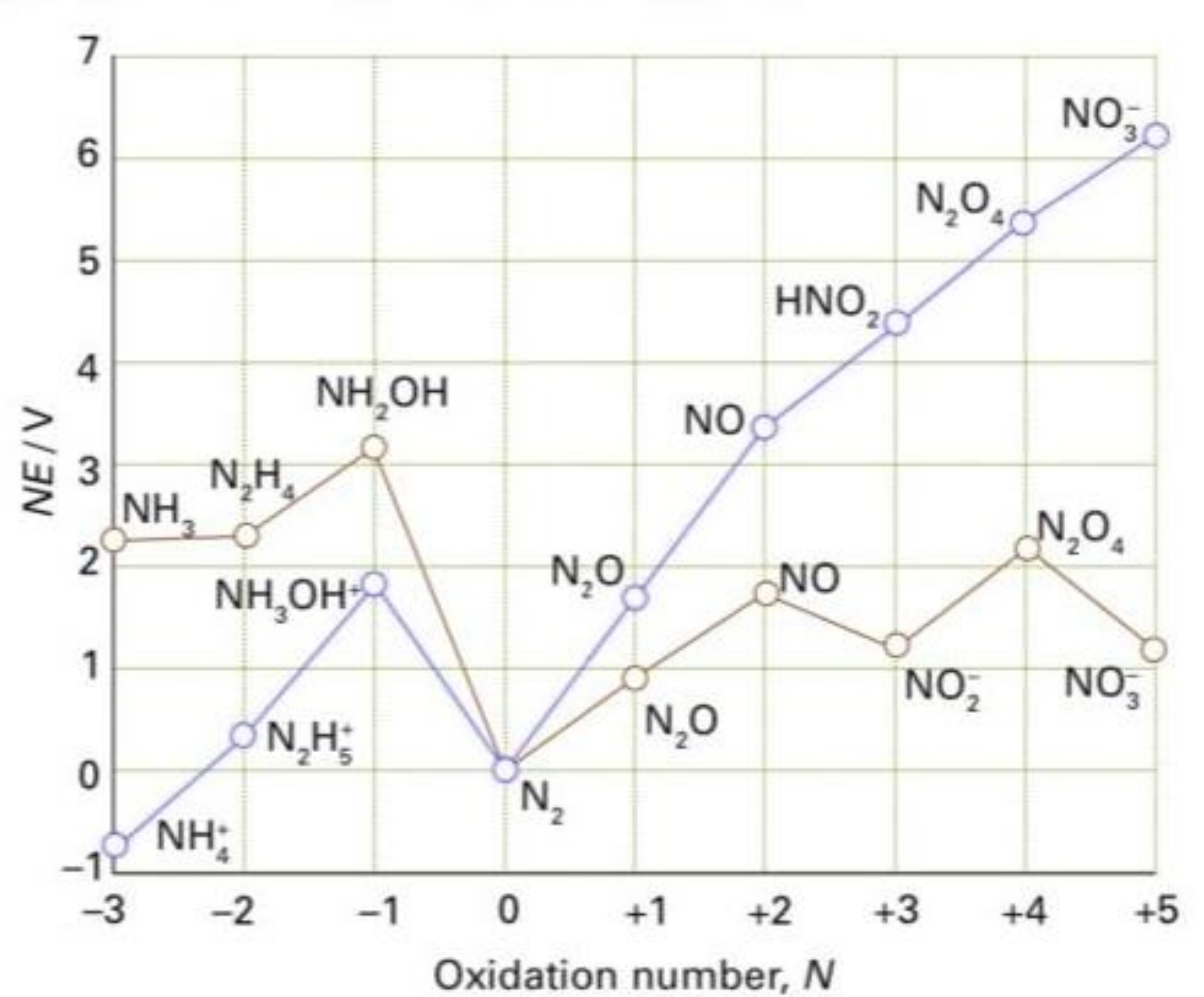
f $\frac{1}{2} N_2 + 2H^+ + H_2O + e^- \longrightarrow NH_3OH^+$ $E^0 = -1.87V$

g $\frac{1}{2} N_2 + 5/2\ H^+ + 2e^- \longrightarrow \frac{1}{2} N_2H_5^+$ $E^0 = -0.23V$

h $\frac{1}{2} N_2 + 4H^+ + 3e^-$ NH_4^+ $E^0 = 0.27V$

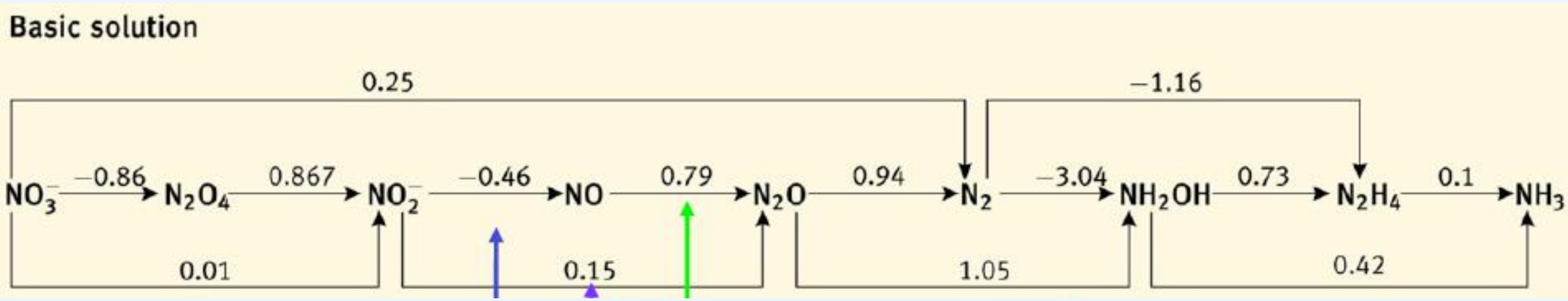
Oxidation state: species	NE^0, N
N(V): NO_3^-	(5 x 1.25, 5)
N(IV): N_2O_4	(4 x 1.36, 4)
N(III): HNO_2	(3 x 1.45, 3)
N(II): NO	(2 x 1.68, 2)
N(I): N_2O	(1 x 1.77, 1)
N(-I): NH_3OH^+	[-1 x (-1.87), -1]
N(-II): $N_2H_5^+$	[-2 x (-0.23), -2]
N(-III): NH_4^+	(-3 x 0.27, -3)

The Frost diagram for nitrogen

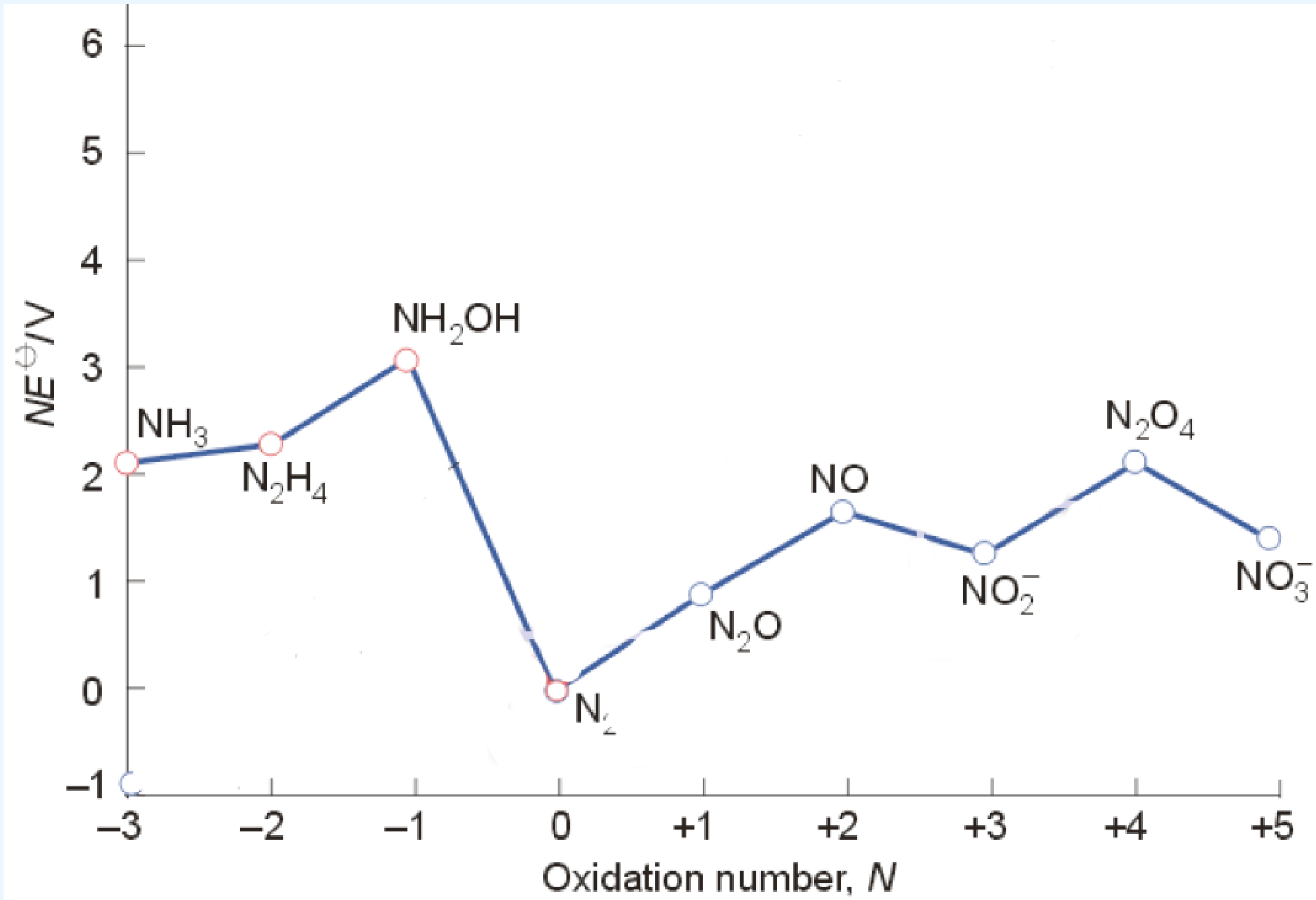


Blue line: acidic pH =0;

Grey line: pH = 14

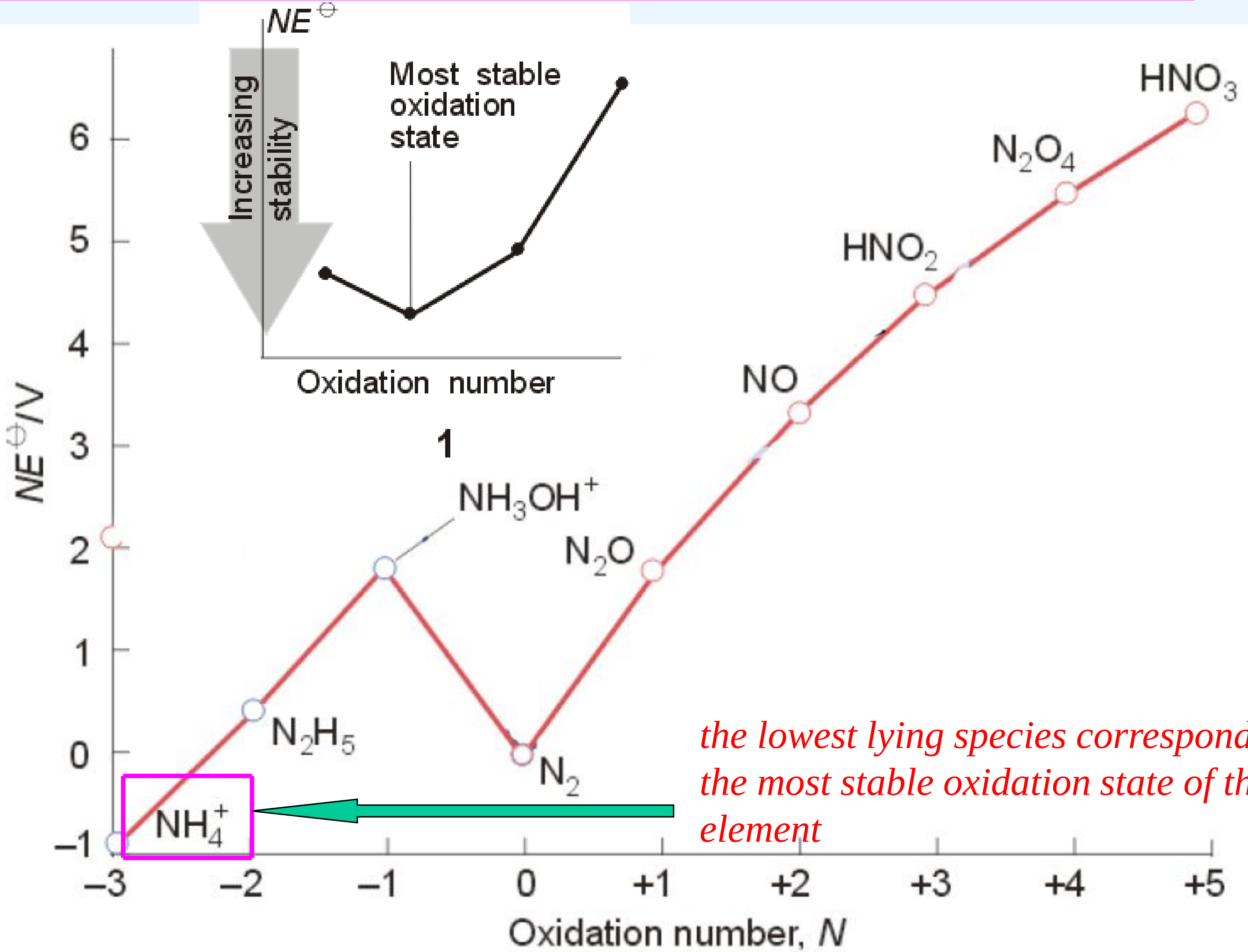


Basic solution
0.25
−1.16
NO3− −0.86 N2O4 0.867 NO2− −0.46 NO 0.79 N2O 0.94 N2 −3.04 NH2OH 0.73 N2H4 0.1 NH3
0.01
0.15
1.05
0.42



NE⊖/V
NH3
N2H4
NH2OH
N2
N2O
NO
NO2−
N2O4
NO3−
Oxidation number, N

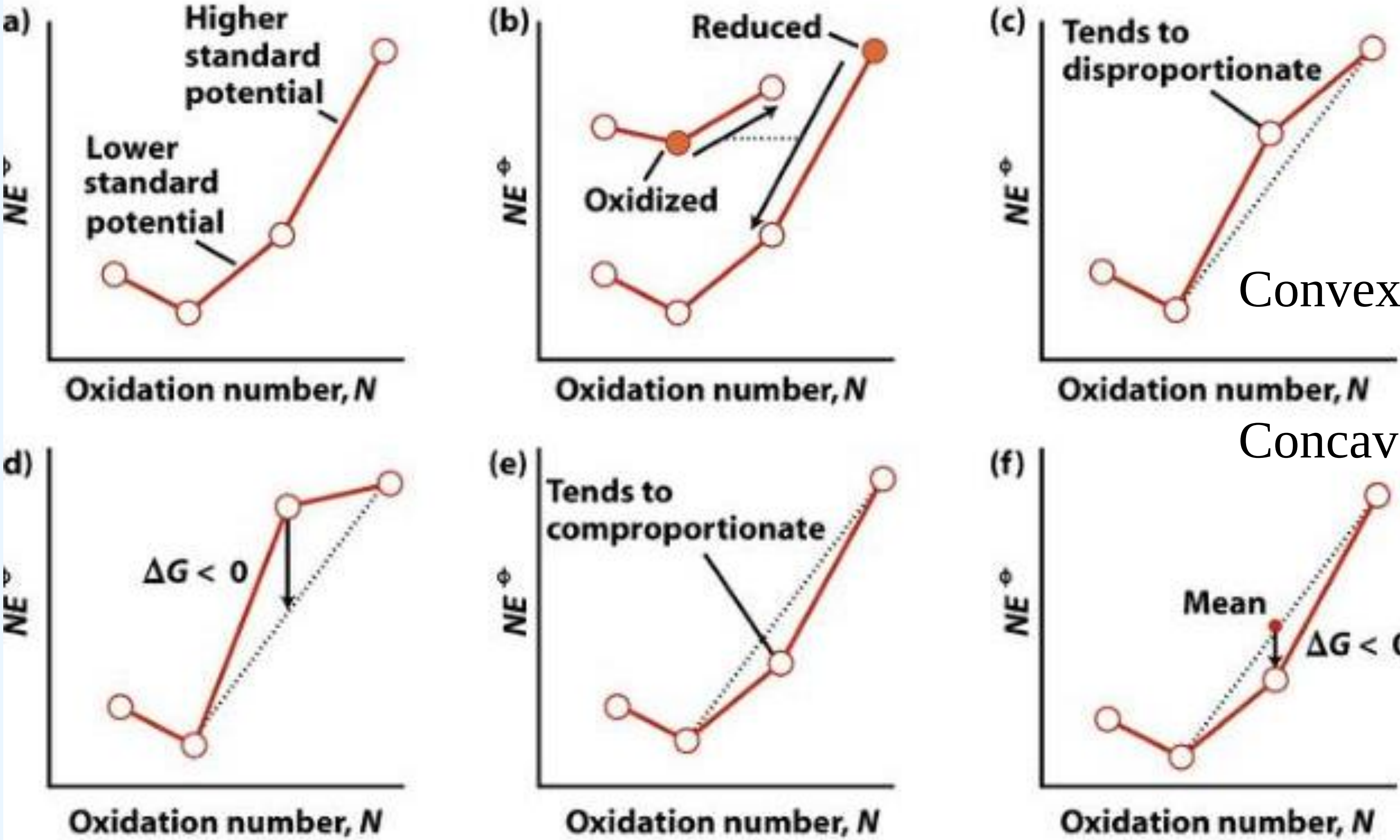
What do we really get from the Frost diagram?



the lowest lying species corresponds to the most stable oxidation state of the element

Frost diagrams

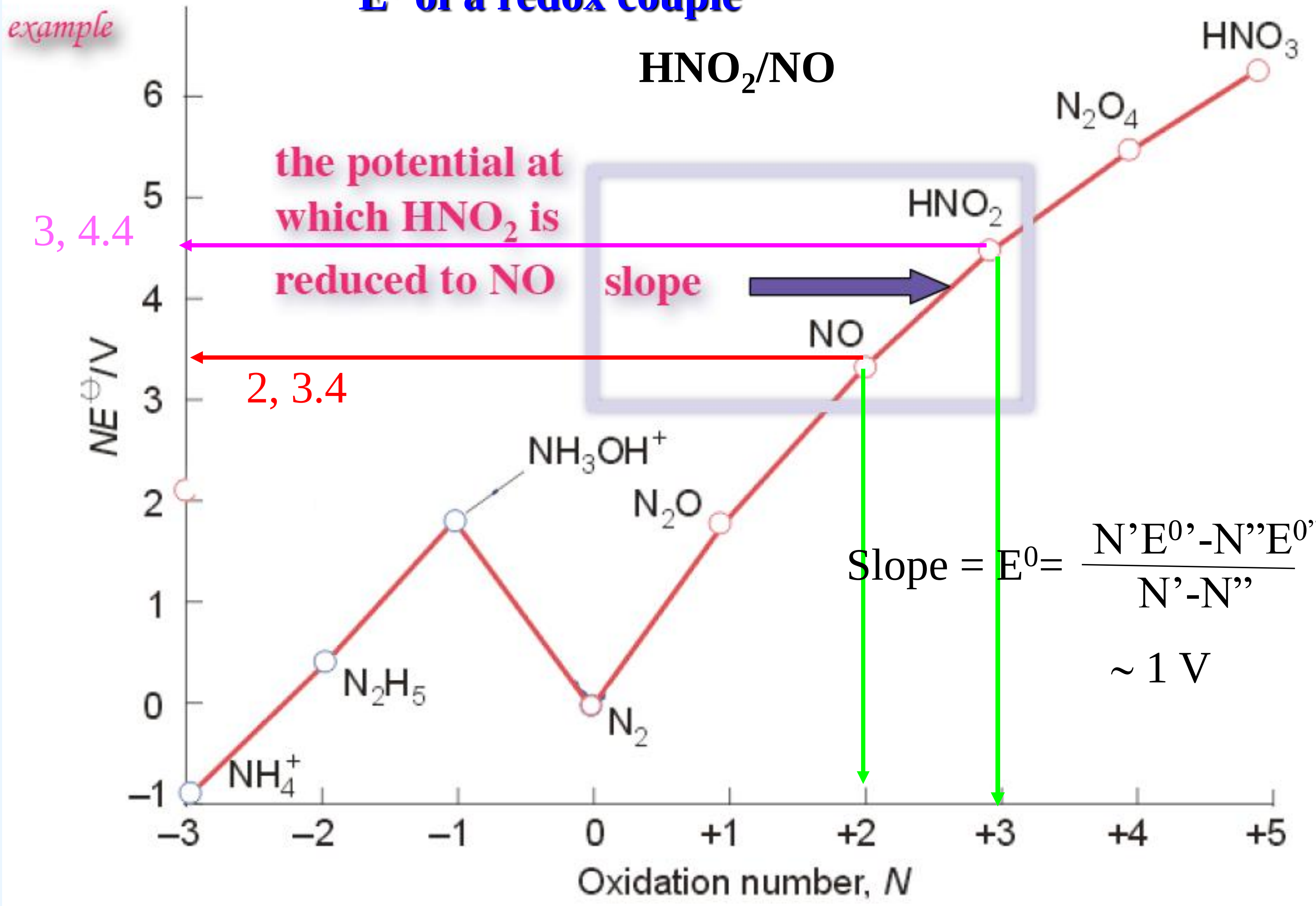
The steeper the slope, the higher
The potential



Convex curve

Concave curve

E^0 of a redox couple



$$NH_4^+(aq) + NO_3^-(aq) \longrightarrow N_2O\,(g) + 2H_2O(l)$$

-3 +5 +1

In solution, kinetically inhibited – does not occur;
In the solid state, spontaneous ΔG^0 = -168 kj/mol

Oxidizing agent? Reducing agent?

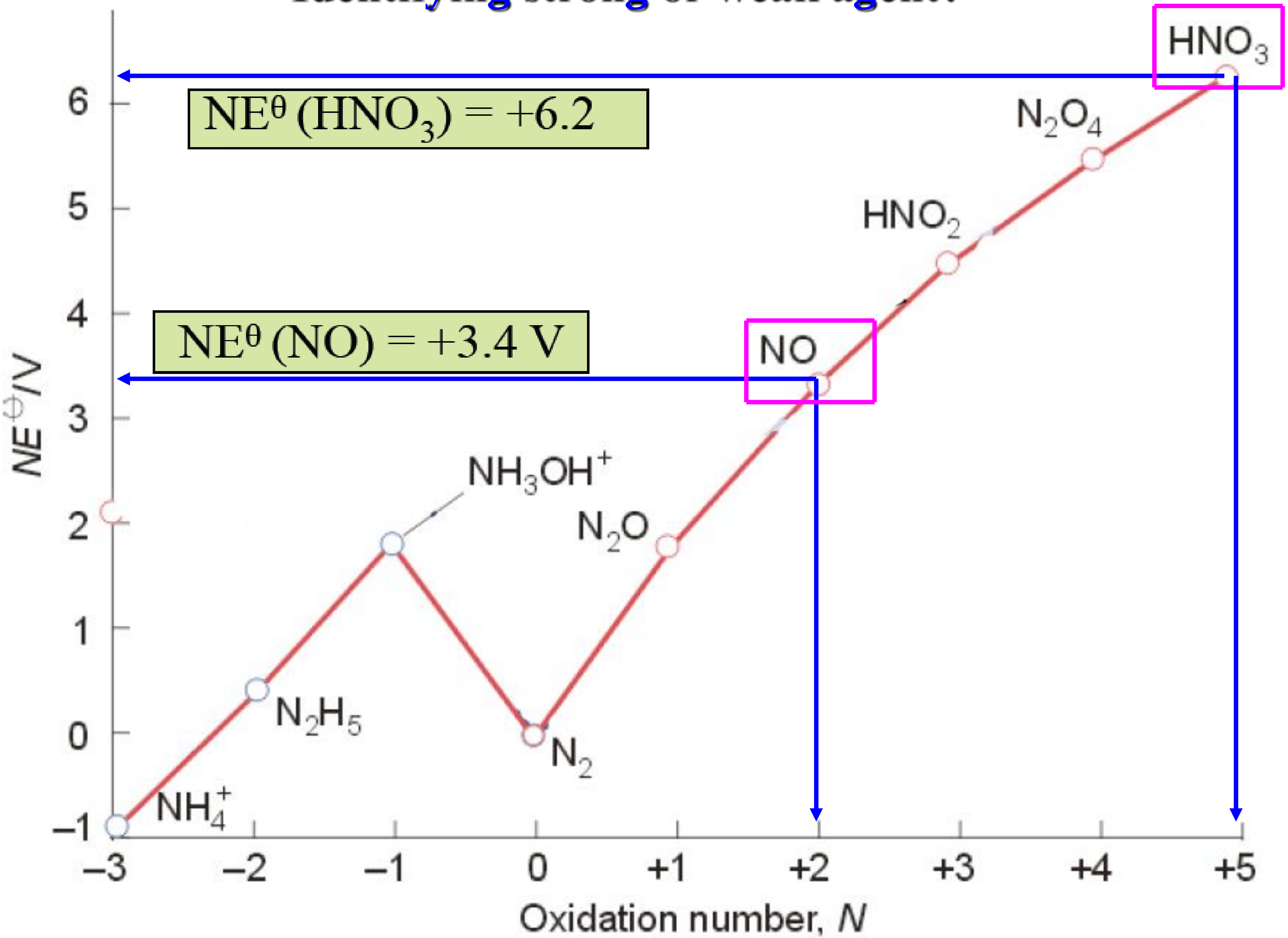
The oxidizing agent - couple with more positive slope - more positive E

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 – oxidizing agent

Identifying strong or weak agent?



From the coordinates 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

$N = +2$

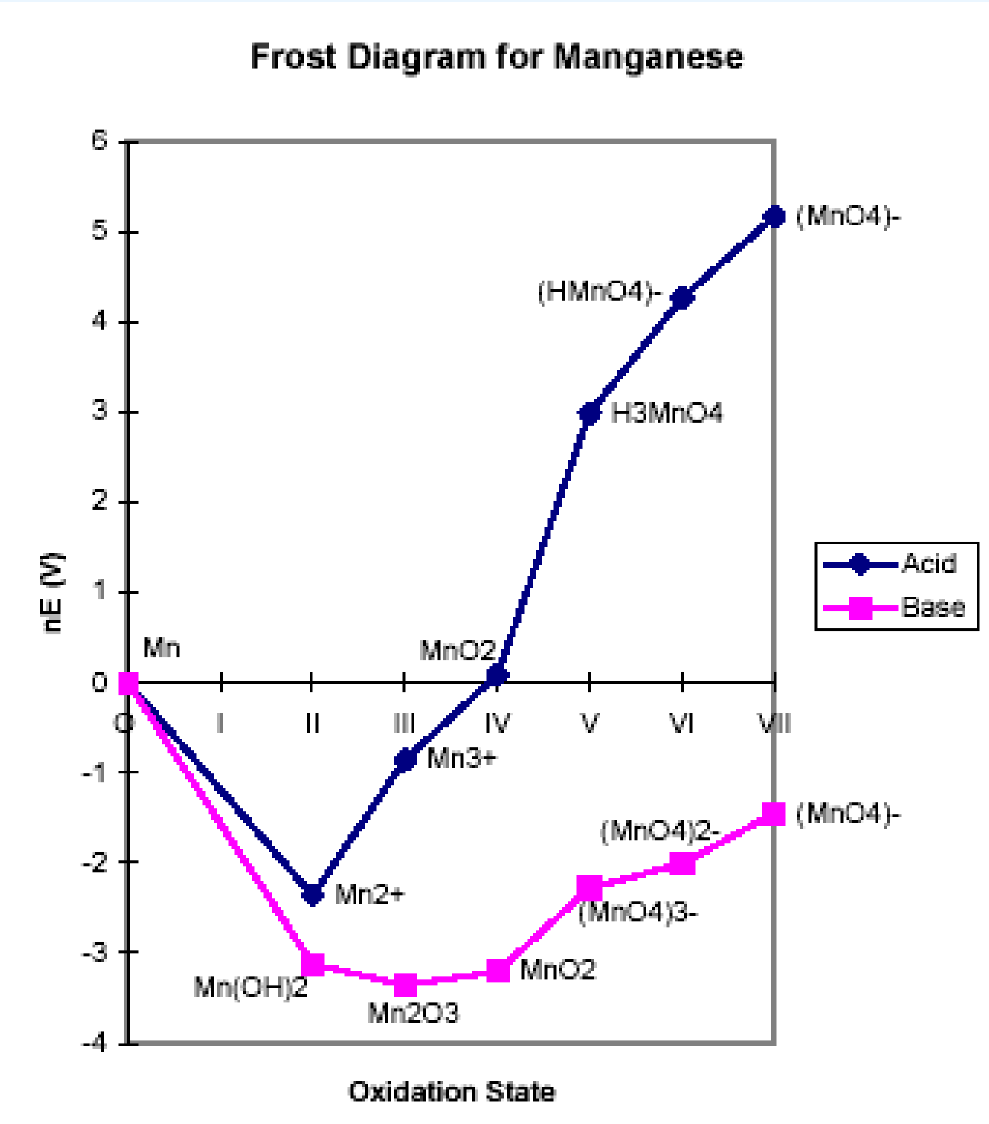
NO – Strong oxidant than HNO_3

$\boxed{E^\theta = +1.70\ V}$

But, keep in mind that this potential only corresponds to the potential at which a given species converts to its <u>elemental form</u>

Comproportionation

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



In acidic solution…

Mn and MnO_2

$\downarrow$

Mn^{2+}

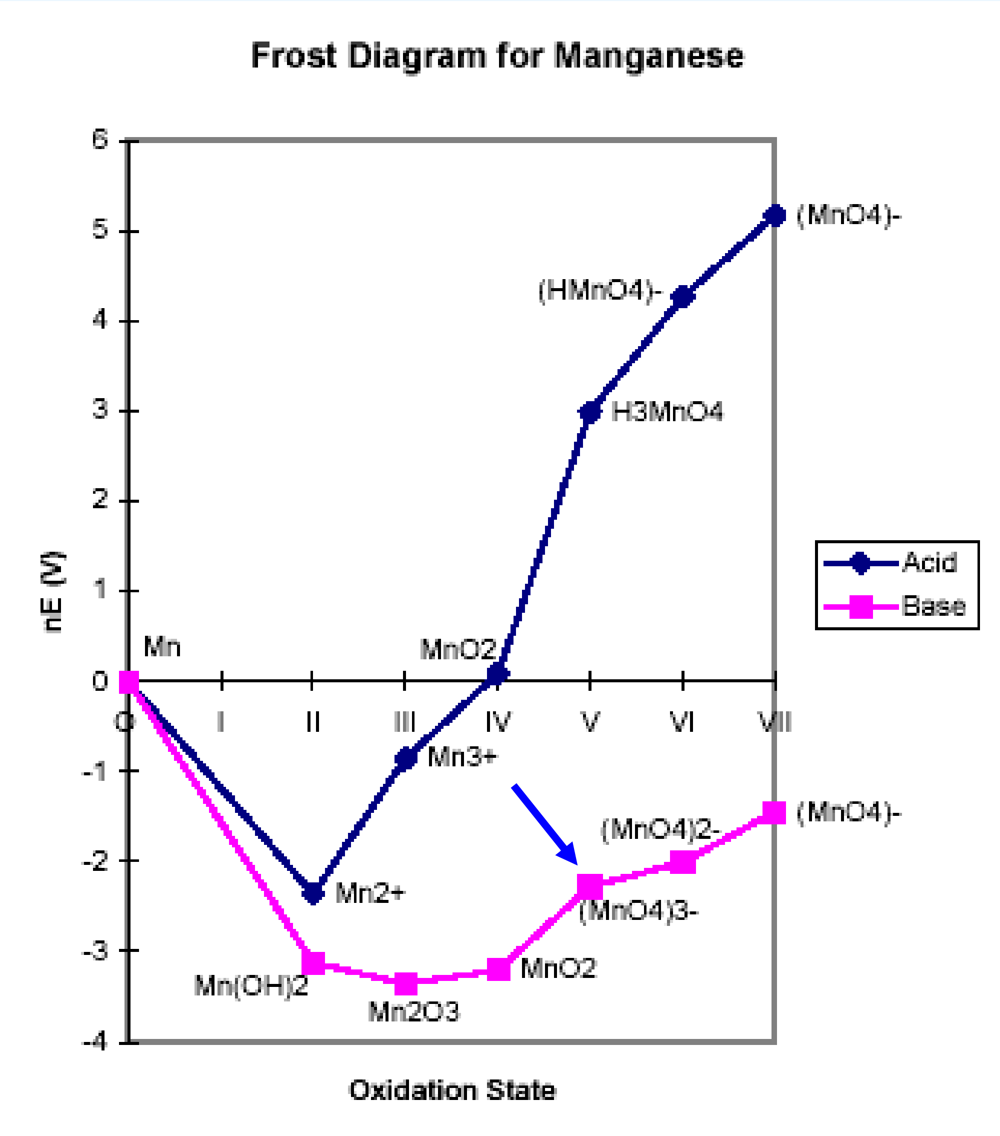
Rate of the reaction hindered insolubility?

In basic solution…

MnO_2 and $Mn(OH)_2$

$\downarrow$

Mn_2O_3



Disproportionation

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)***

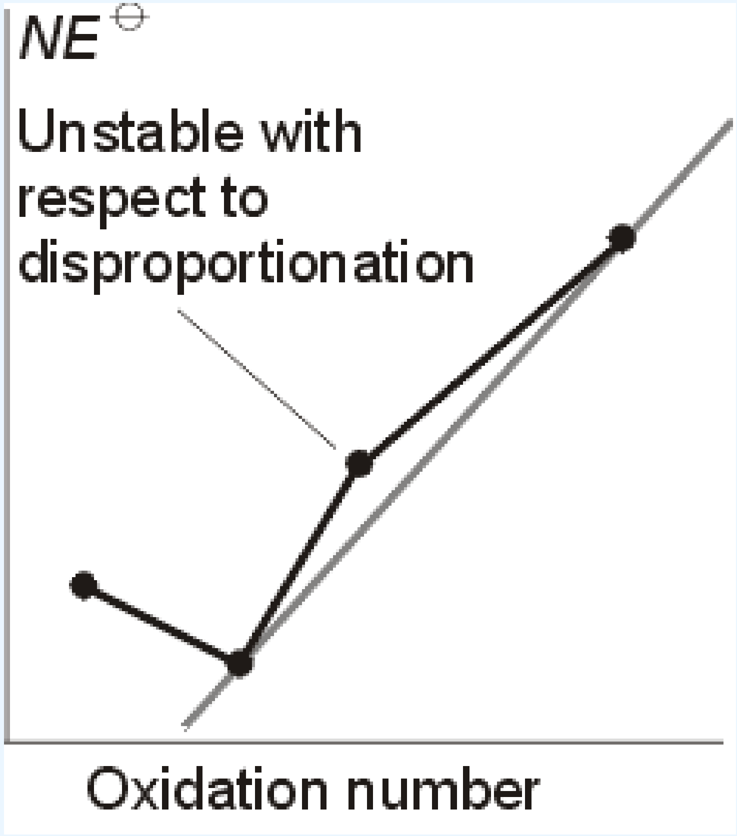
$$2\ MnO_4^{3-} + 2\ H_2O \rightarrow MnO_4^{2-} + MnO_2 + 4\ OH^-$$

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

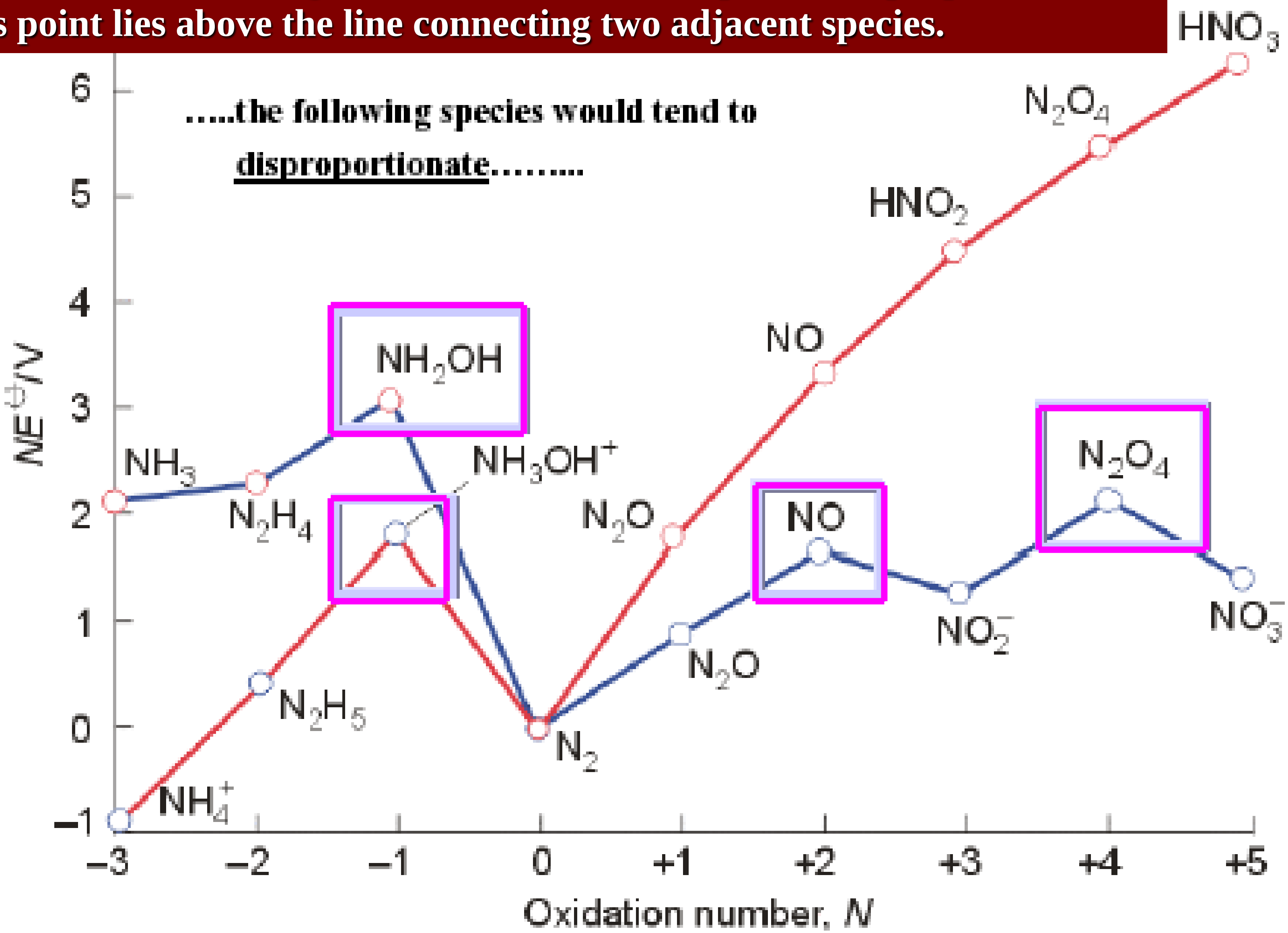
•Any species located on the upper left side of the diagram will be a reducing agent. **Mn - moderate reducing agent.**

Disproportionation

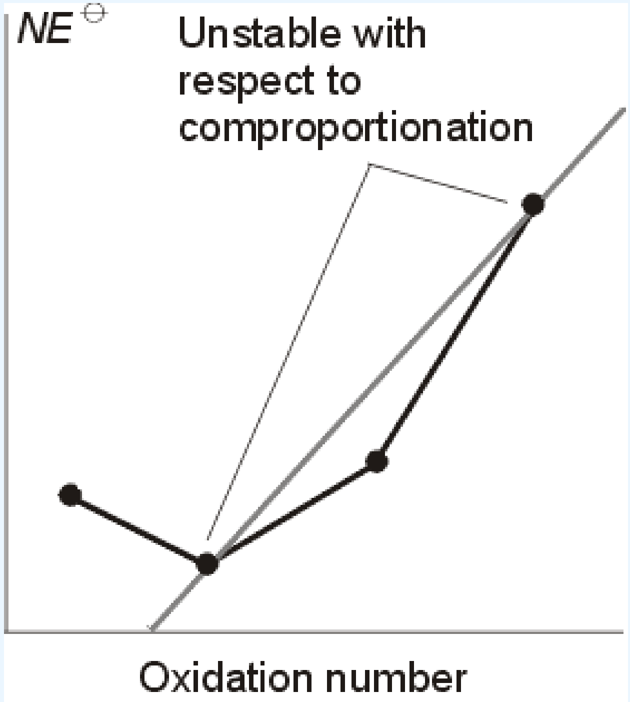
What Frost diagram tells about this reaction?



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



Comproportionation reaction



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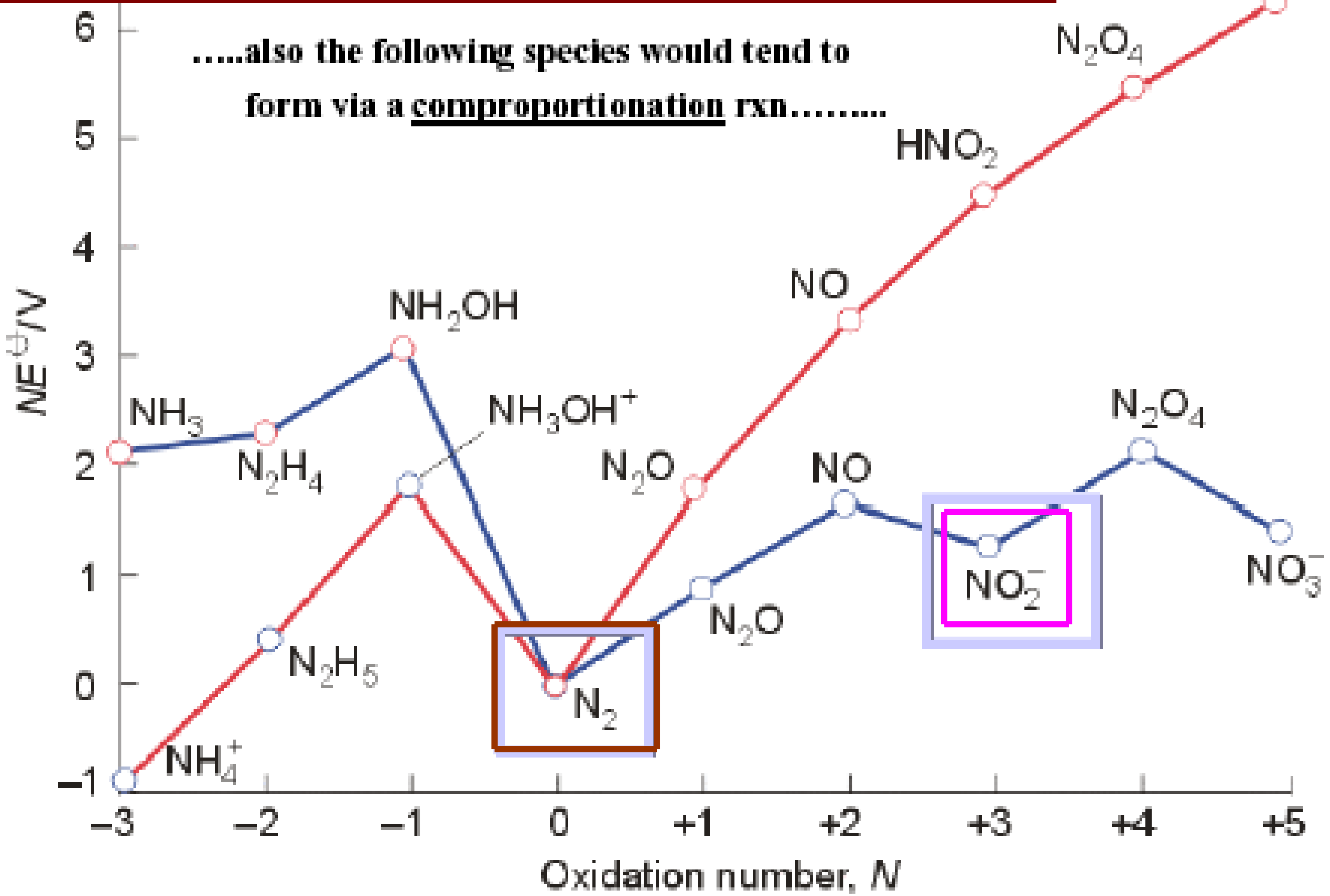
Comproportionation is spontaneous if the intermediate species lies below the straight line joining the two reactant species.



<u>Comproportionation Reactions:</u>

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

* 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.