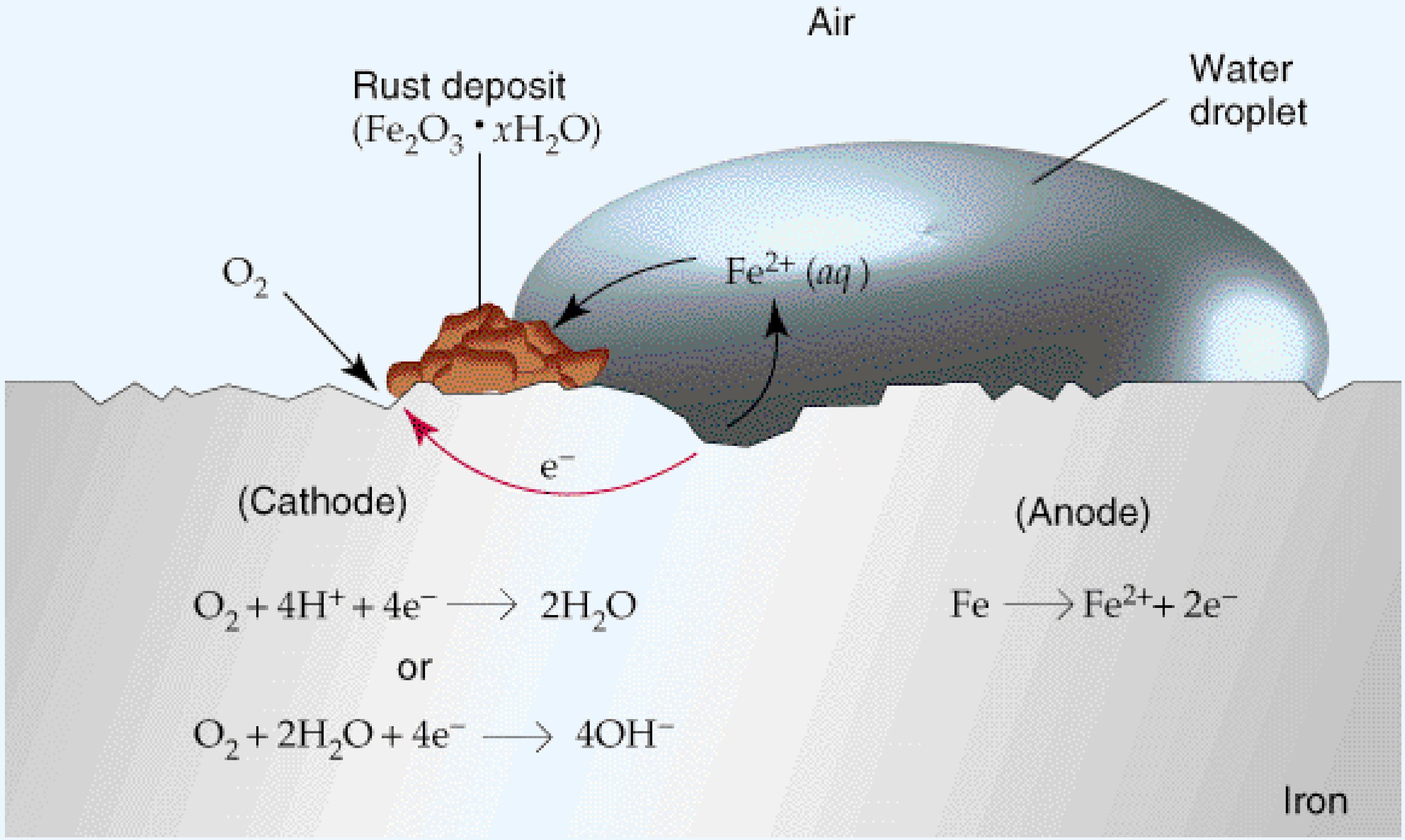
Oxidation-Reduction

Latimer Diagram

Frost Diagram

Environment

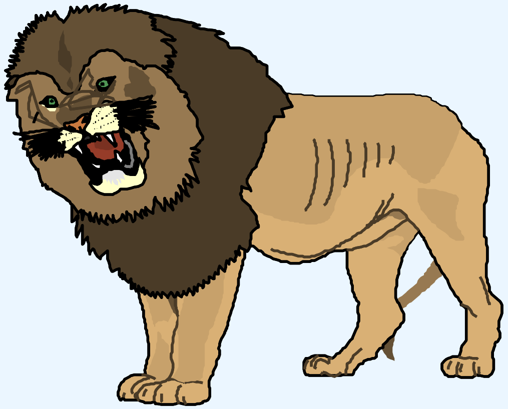


What is Redox?

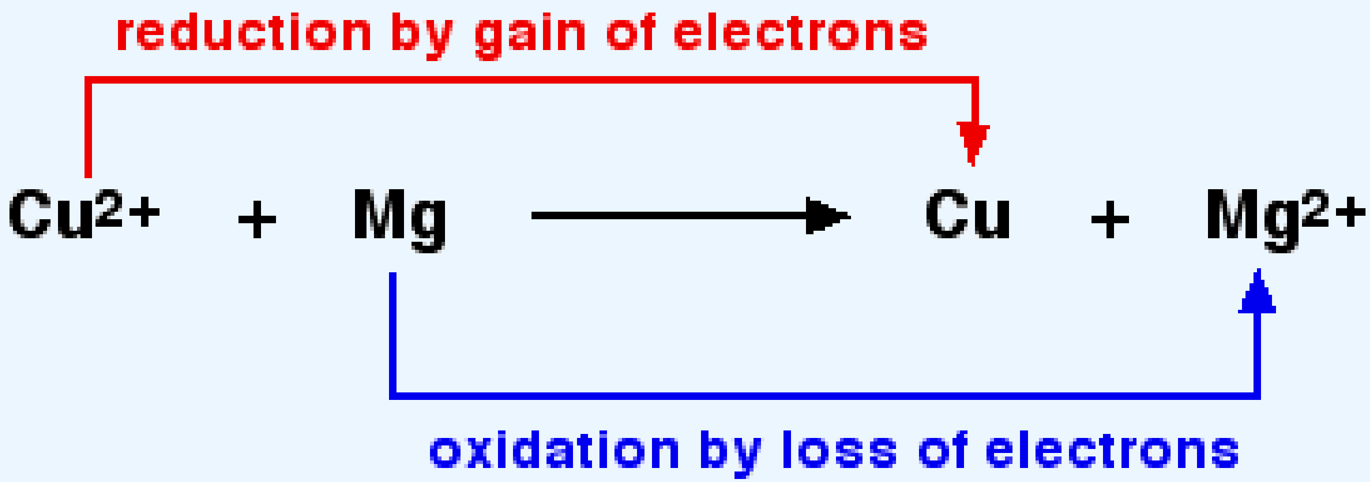
- REDOX stands for REDuction/OXidation

LEO says GER!

- **L**oss **E**lectrons = **O**xidation
- **G**ain **E**lectrons = **R**eduction



Redox reactions - transfer of electrons between species.



All the redox reactions have two parts:

Oxidation

Reduction

Balancing Redox Equation

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**

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

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

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

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

(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

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.**

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

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

Iron **+2 and +3**

$\Delta G = -nFE$

$$Fe^{2+} + 2e \longrightarrow Fe \qquad -0.440 \qquad -2 \times F \times -0.44 = 0.88\ V$$

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

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

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

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

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

$$Fe^{3+} \xrightarrow{+0.77} Fe^{2+} \xrightarrow{-0.44} Fe \qquad \text{overall } E^0$$

$E^0 = -0.036$

Example 1 : How to extract E^0 for nonadjacent oxidation state?

$$\underset{+7}{ClO_4^-} \xrightarrow{+1.2} \underset{+5}{ClO_3^-} \xrightarrow{+1.18} \underset{+3}{HClO_2} \xrightarrow{+1.65} \overbrace{\underbrace{\underset{+1}{HClO} \xrightarrow{+1.63} \underset{0}{Cl_2}}_{1} \underbrace{\xrightarrow{+1.36} \underset{-1}{Cl^-}}_{2}}^{E^0 = ?}$$

Identify the two redox couples

Worked Example to extract E^0 for nonadjacent oxidation state….

Identify the two redox couples

Find out the oxidation state of chlorine

Write the balanced equation for the first couple

$HClO(aq) + H^+(aq) + e \longrightarrow \frac{1}{2} Cl_2(g) + H_2O(l)$ +1.63 V

Write the balanced equation for the **second couple**

$\frac{1}{2} Cl_2(g) + e \longrightarrow Cl^- (l)$ +1.36 V

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

$$-\upsilon FE = -\upsilon' FE' - \upsilon'' FE''$$

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

E = 1.5 V

H.W. 1 Latimer diagram for chlorine in basic solution:

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

$\boxed{+?9}$

Find out the E^0

Disproportionation

Element is simultaneously oxidized and reduced.

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

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

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

'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*'.

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

$$ClO^- \underset{}{\overset{+0.42}{\rightleftarrows}} Cl_2 \xrightarrow{+1.36} Cl^-$$

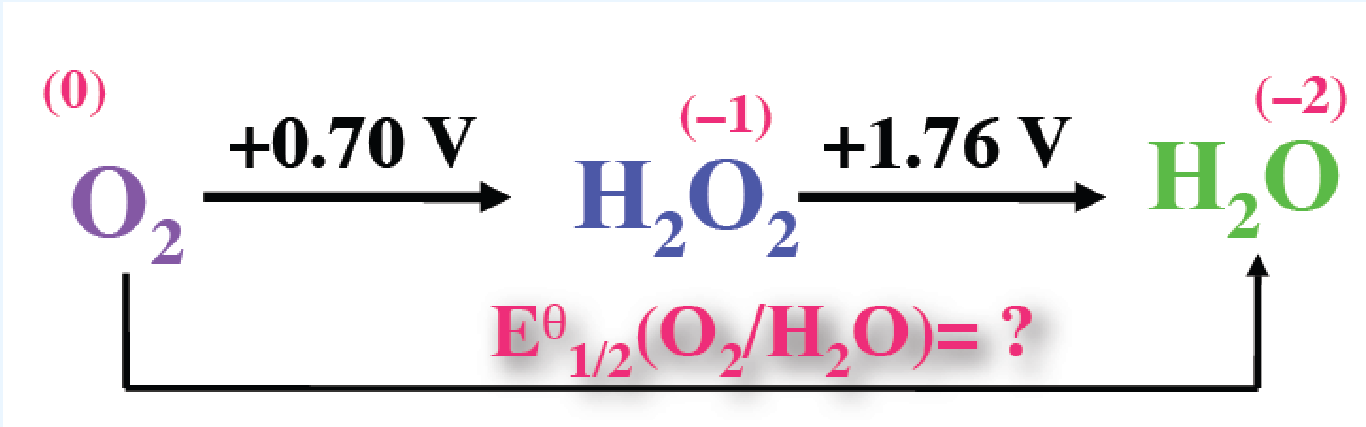
$Cl_2(g) + 2\ e^- \longrightarrow 2Cl^-(aq)$ +1.36

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

$$\Delta E = E^0\ (Cl_2/Cl^-) - E^0\ (ClO^-/Cl_2) = 1.36 - +0.42 = 0.94$$

Reaction is spontaneous

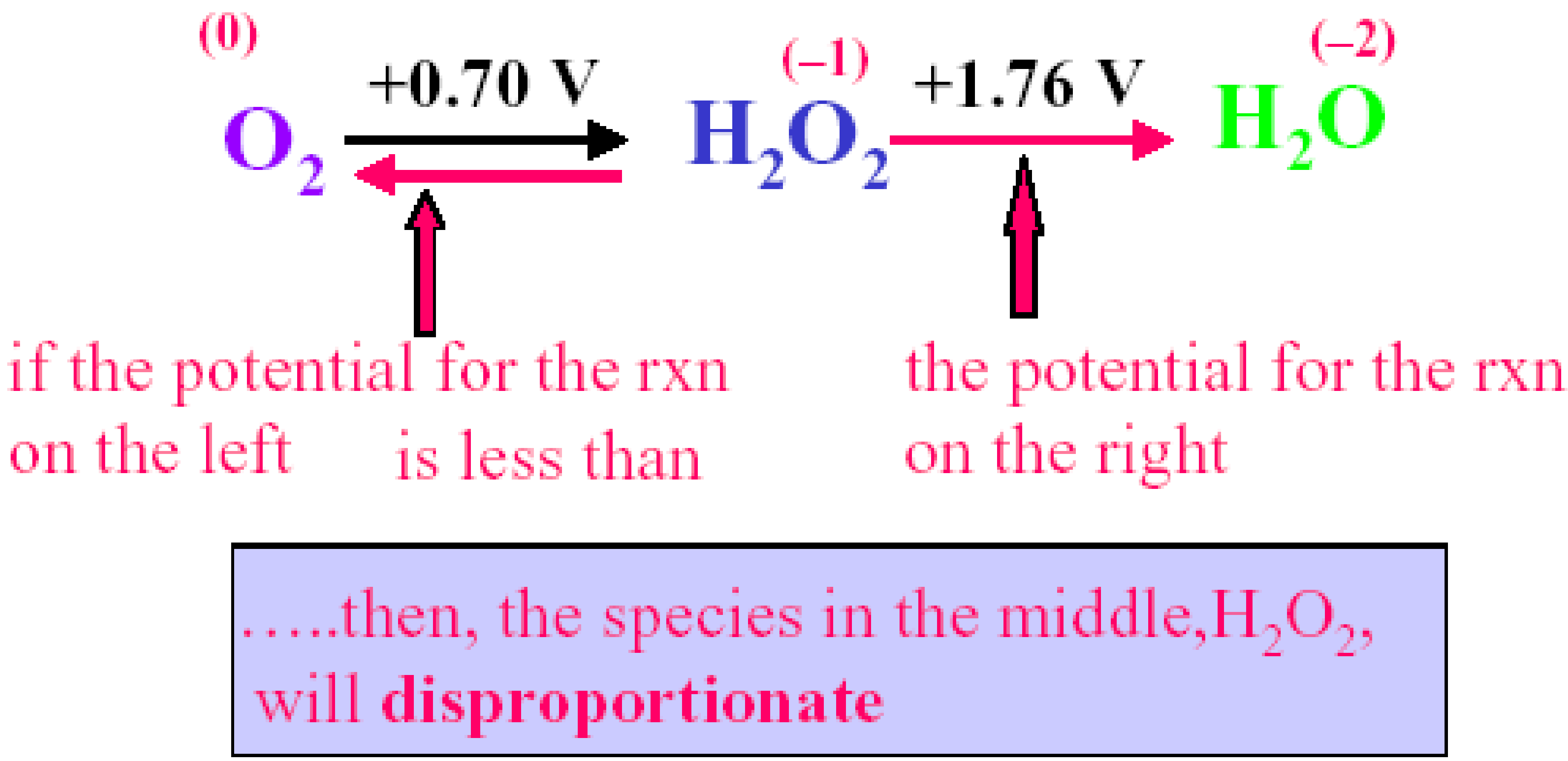
H.W. 2: Latimer diagram for Oxygen



1.23 V

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***.



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

Comproportionation reaction

Reverse of disproportionation

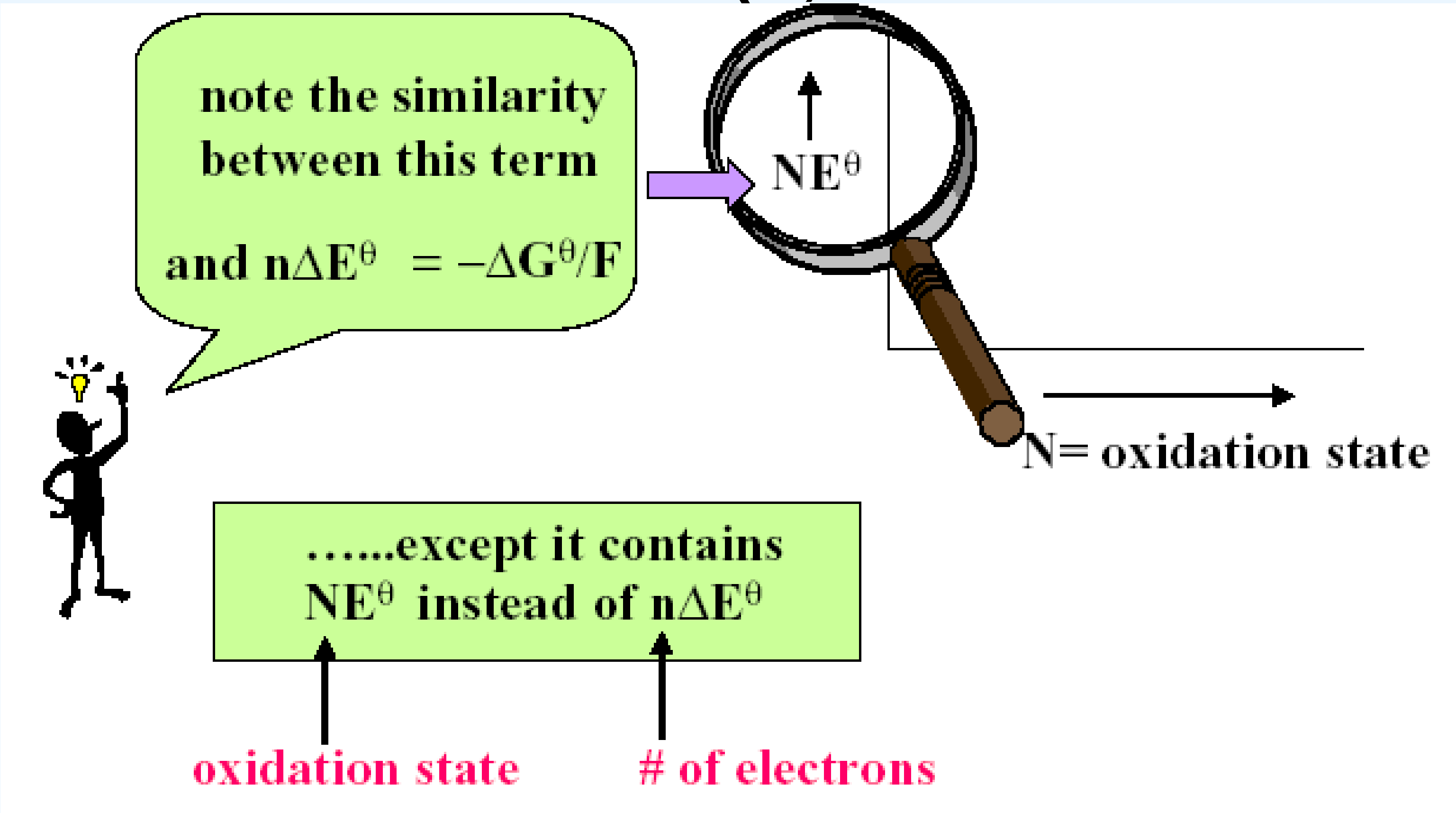
$$Ag^{2+}(aq) + Ag(s) \longrightarrow 2Ag^{+}(aq) \qquad E^0 = +1.18\ V$$

…we will study this in detail under Frost diagram

Frost Diagram

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

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

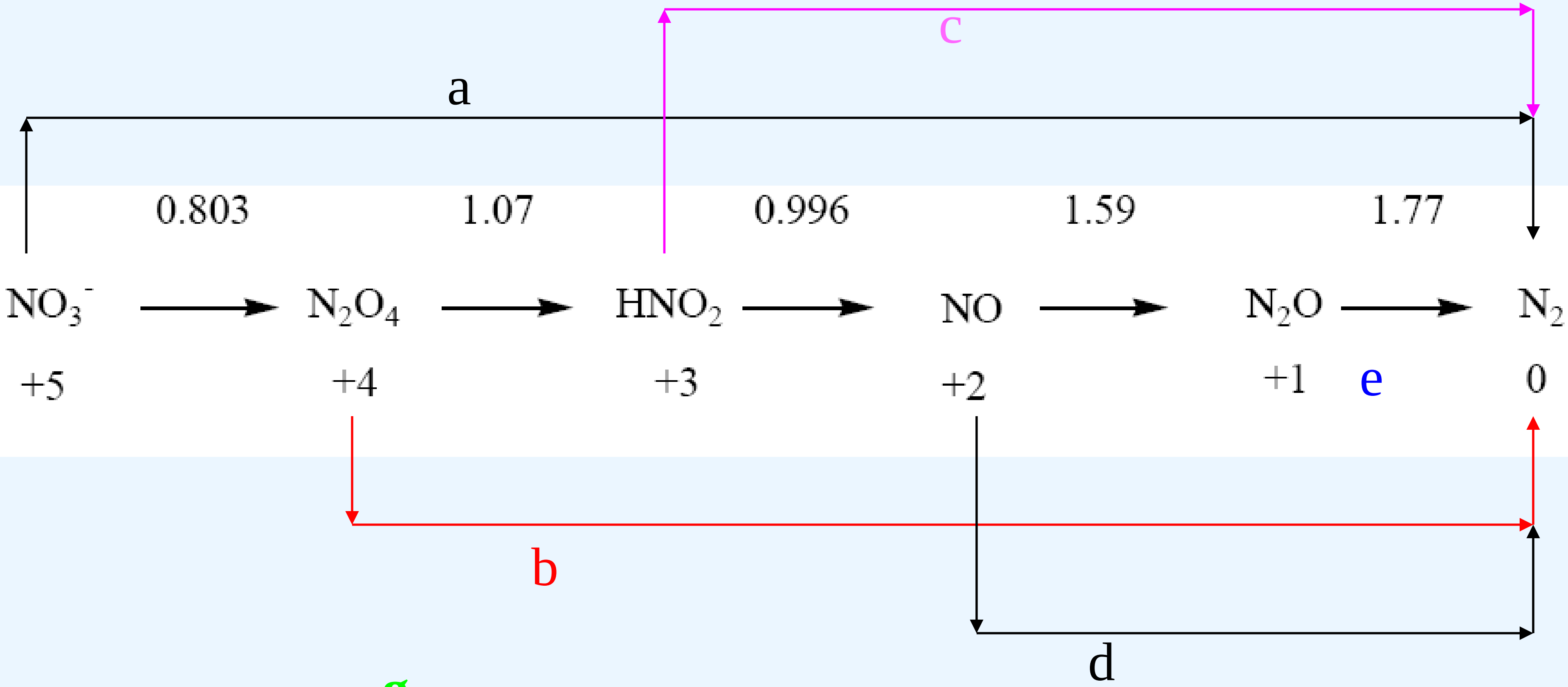
$$NE^{0} = -G^{0}/F$$

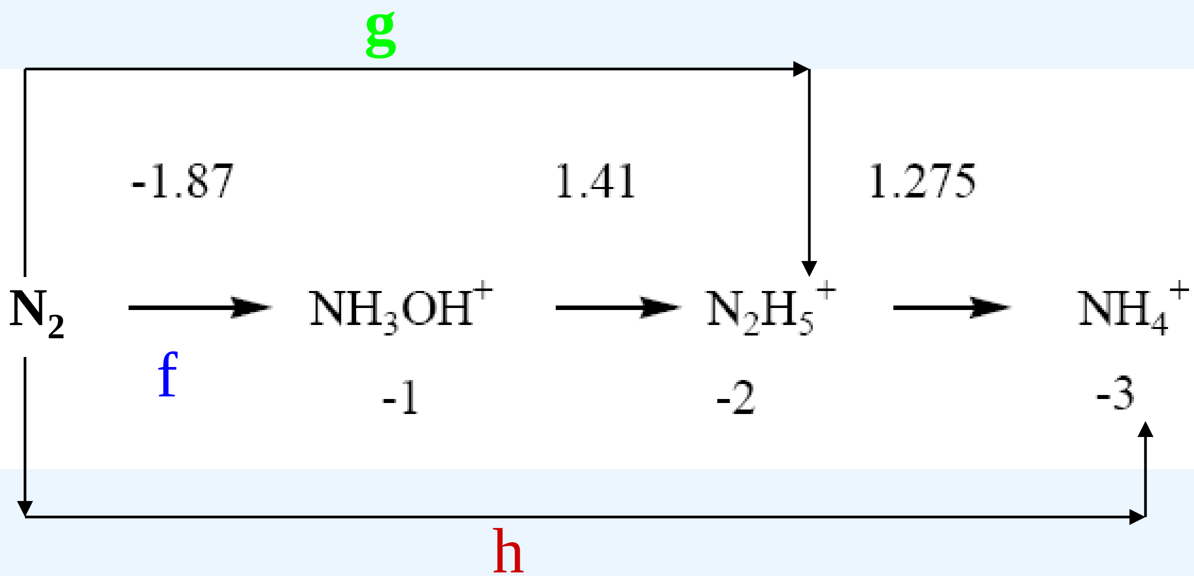
Look at the Latimer diagram of nitrogen in acidic solution

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

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

NO_3^-	+5	a
N_2O_4	+4	b
HNO_2	+3	c
NO	+2	d
N_2O	+1	e
N_2	0	
NH_3OH^+	-1	f
$N_2H_5^+$	-2	g
NH_4^+	-3	h





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

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

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

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

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

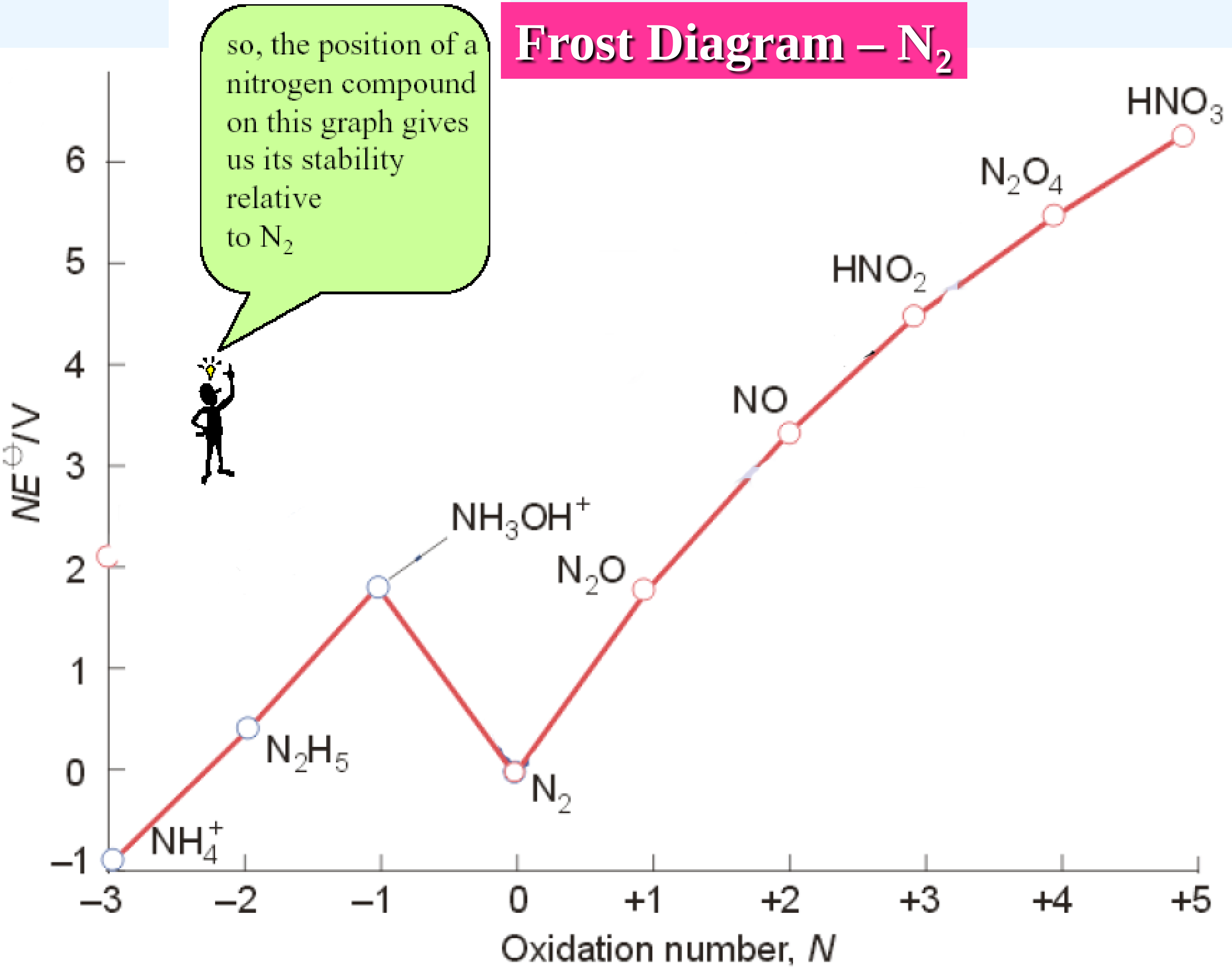
f $\frac{1}{2} N_2 + 2H^+ + H_2O + e^- \longrightarrow NH_3OH^+$ $E^0 = -1.87V$

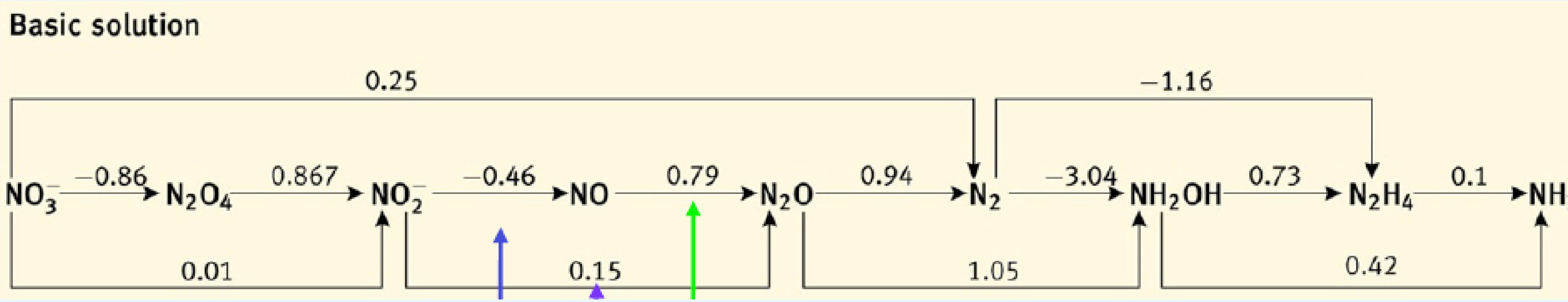
g $\frac{1}{2} N_2 + 5/2\ H^+ + 2e^- \longrightarrow \frac{1}{2} N_2H_5^+$ $E^0 = -0.23V$

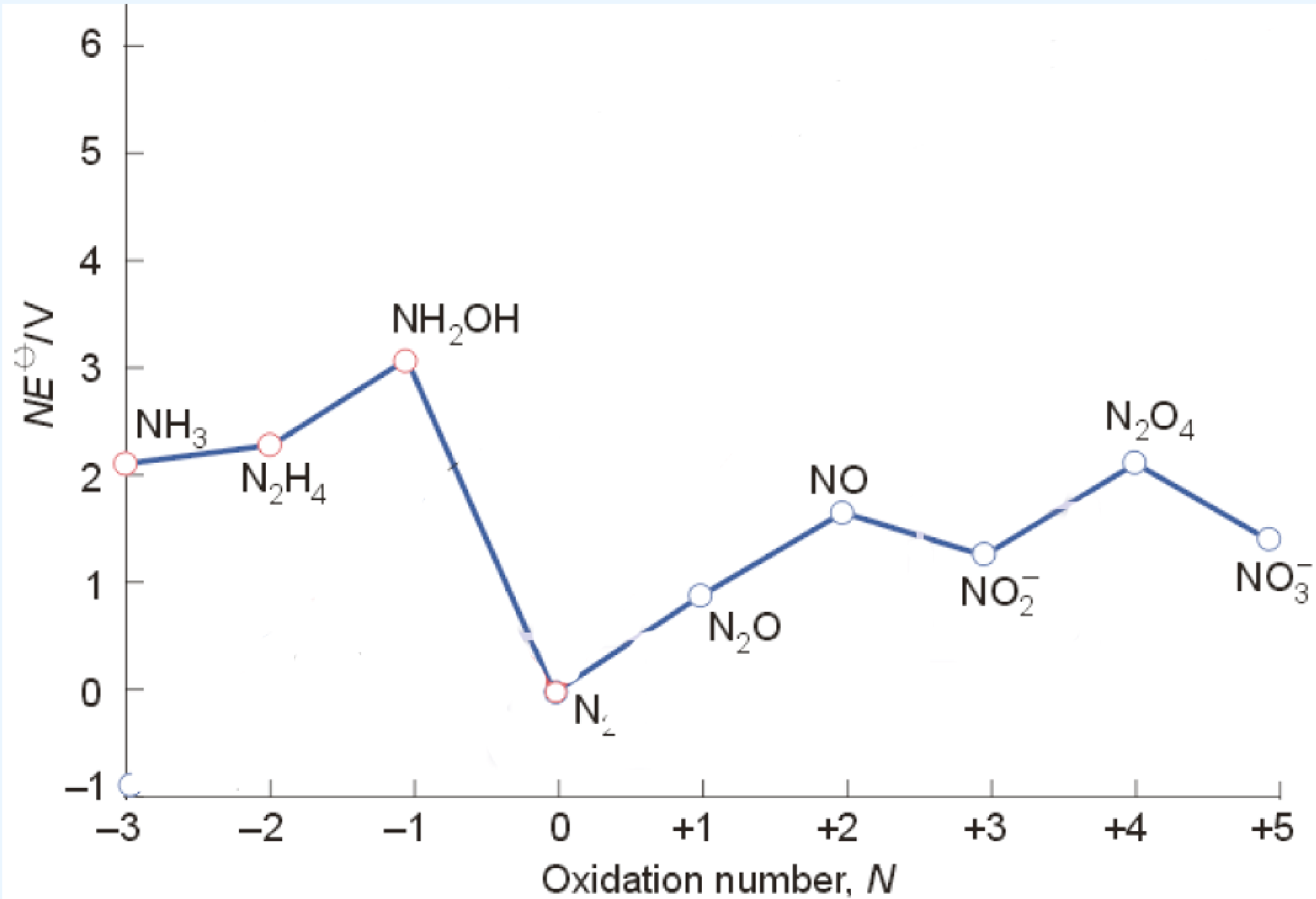
h $\frac{1}{2} N_2 + 4H^+ + 3e^- \longrightarrow NH_4^+$ $E^0 = 0.27V$

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 1.35, 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)

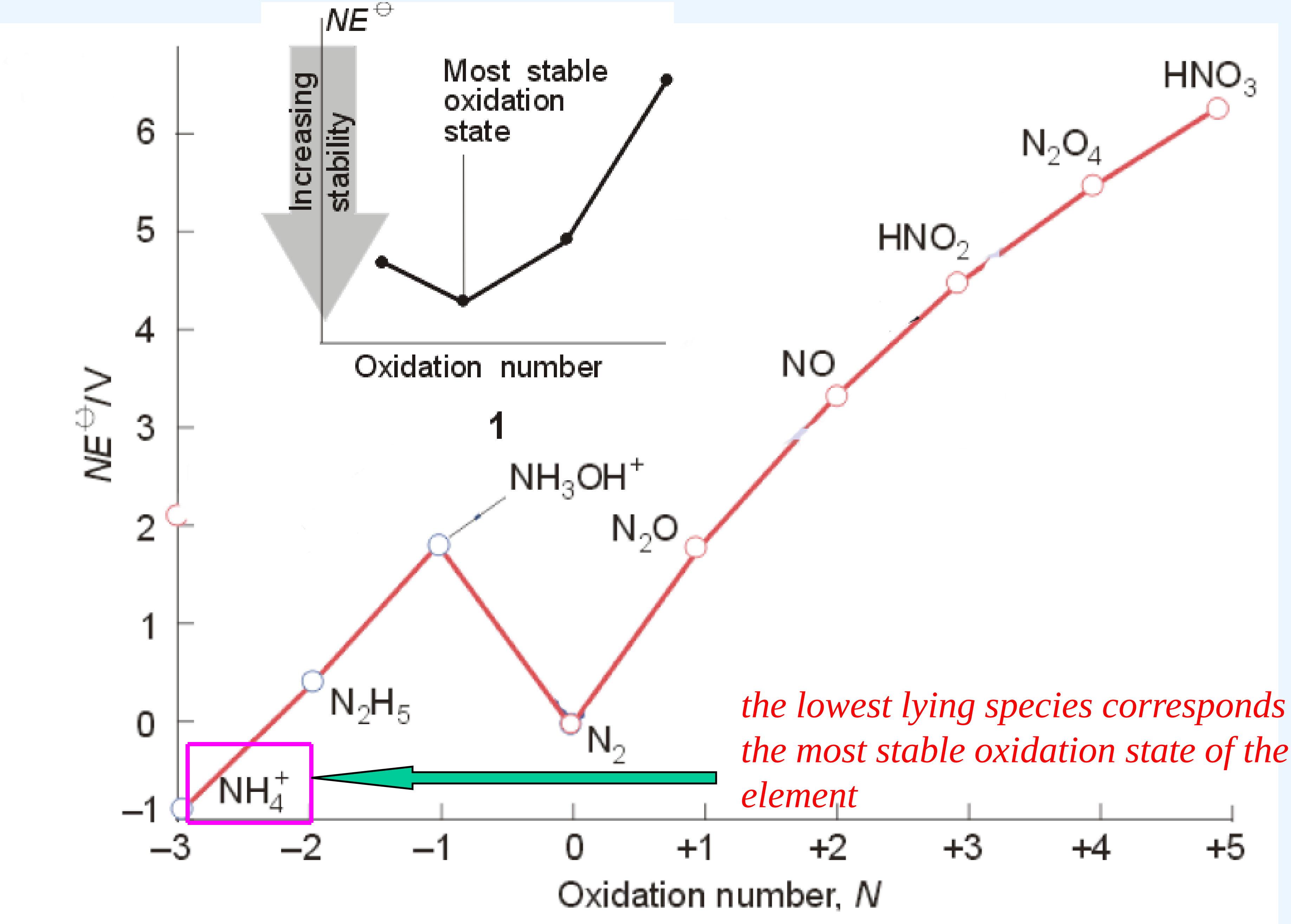
Frost Diagram – N_2




Basic solution
0.25
−1.16
NO_3^-
−0.86
N_2O_4
0.867
NO_2^-
−0.46
NO
0.79
N_2O
0.94
N_2
−3.04
NH_2OH
0.73
N_2H_4
0.1
NH_3
0.01
0.15
1.05
0.42

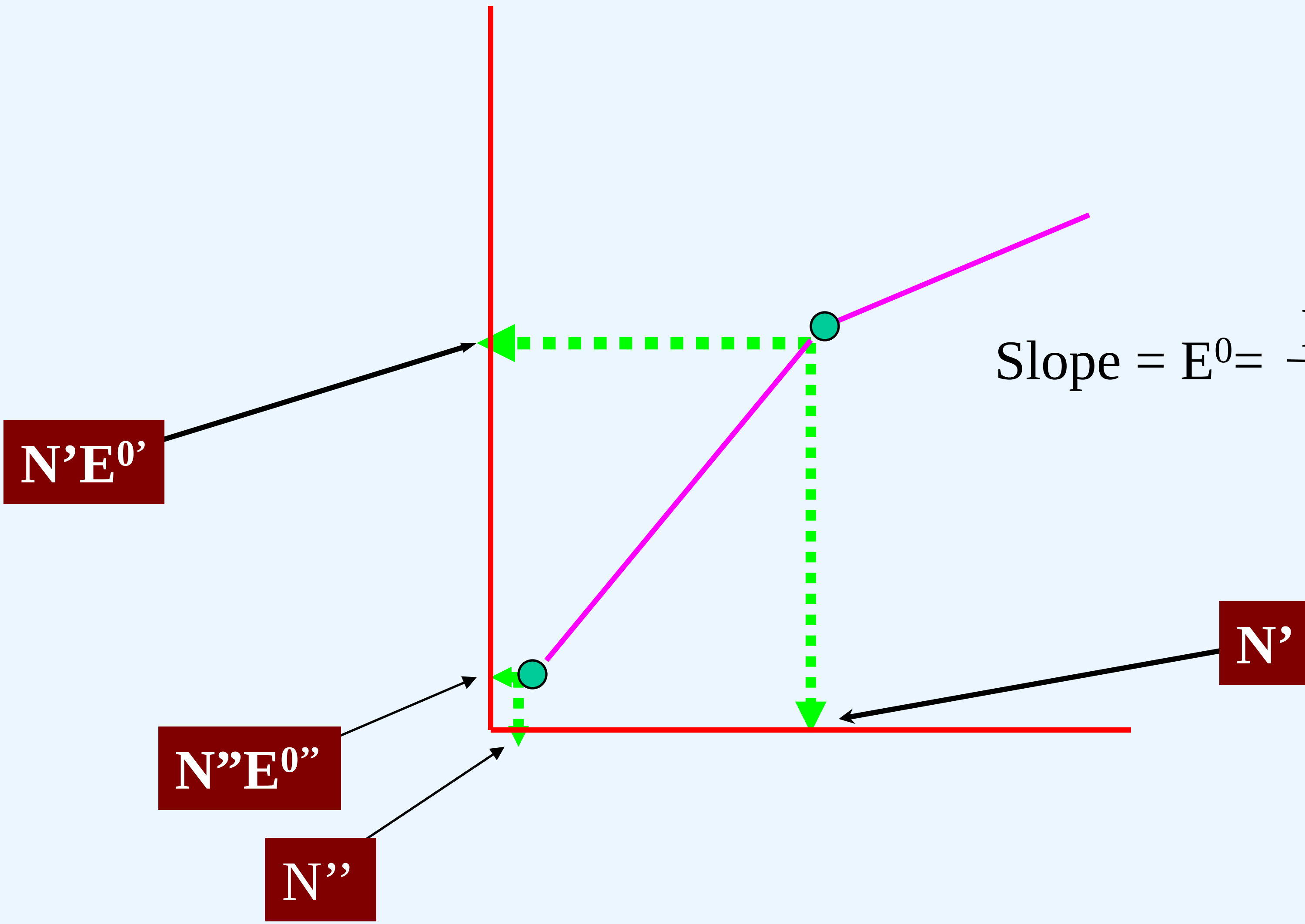

$NE^{\ominus}/V$
Oxidation number, N
NH_3
N_2H_4
NH_2OH
N_2
N_2O
NO
NO_2^-
N_2O_4
NO_3^-

What do we really get from the Frost diagram?



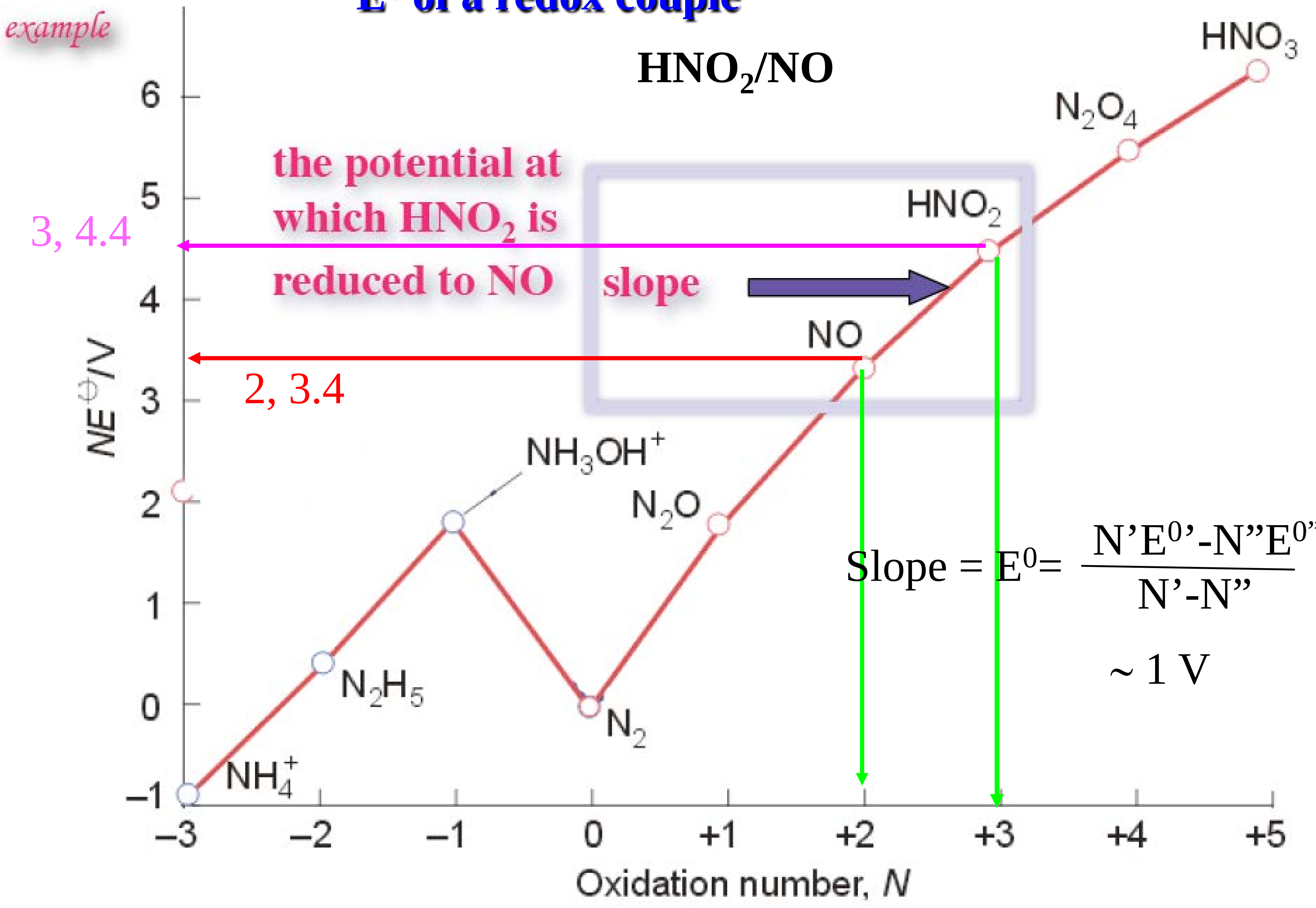
the lowest lying species corresponds to the most stable oxidation state of the element

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



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

E^0 of a redox couple



Oxidizing agent? Reducing agent?

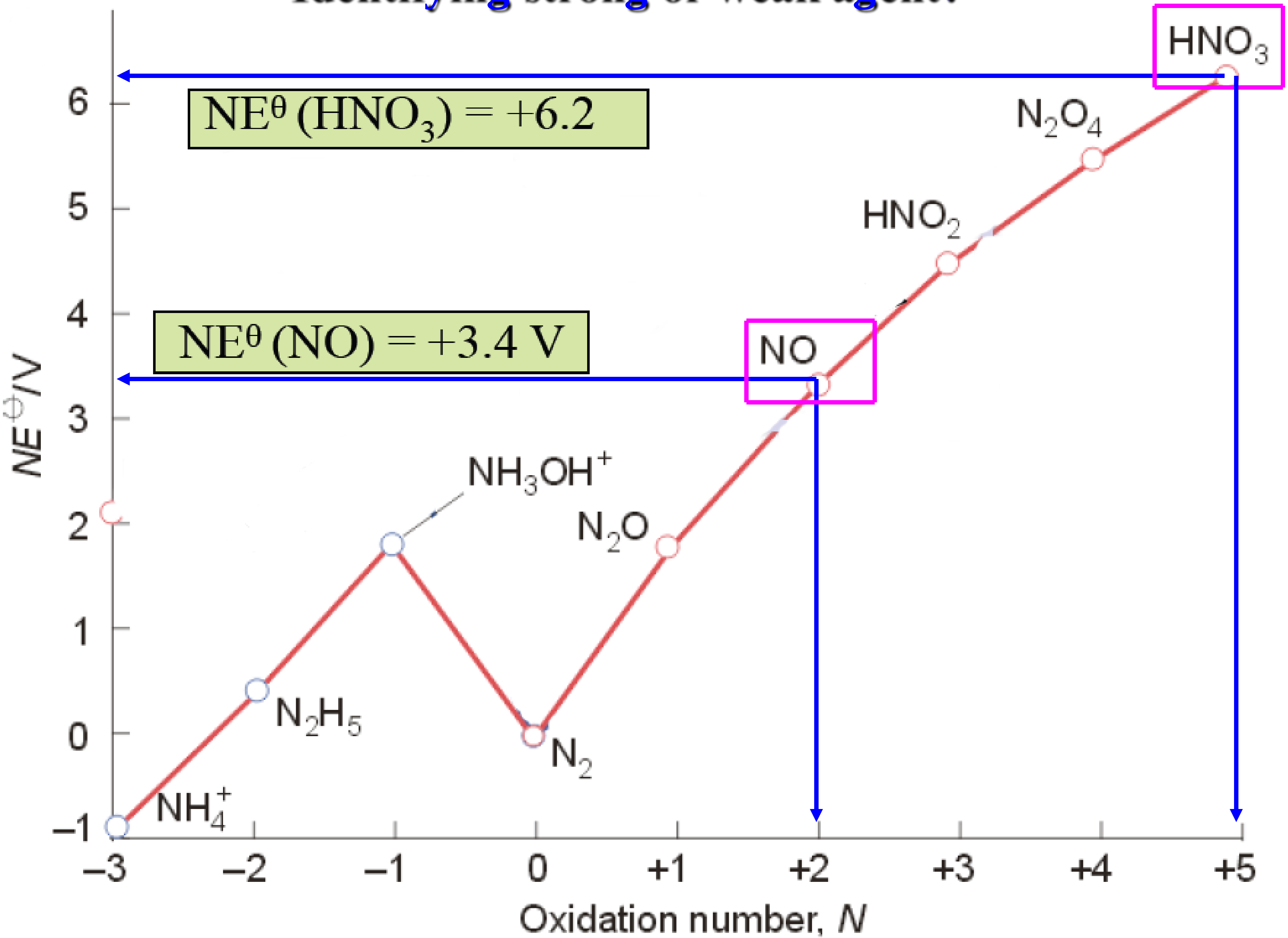
The oxidizing agent - couple with more positive slope - more positive E

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*

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

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

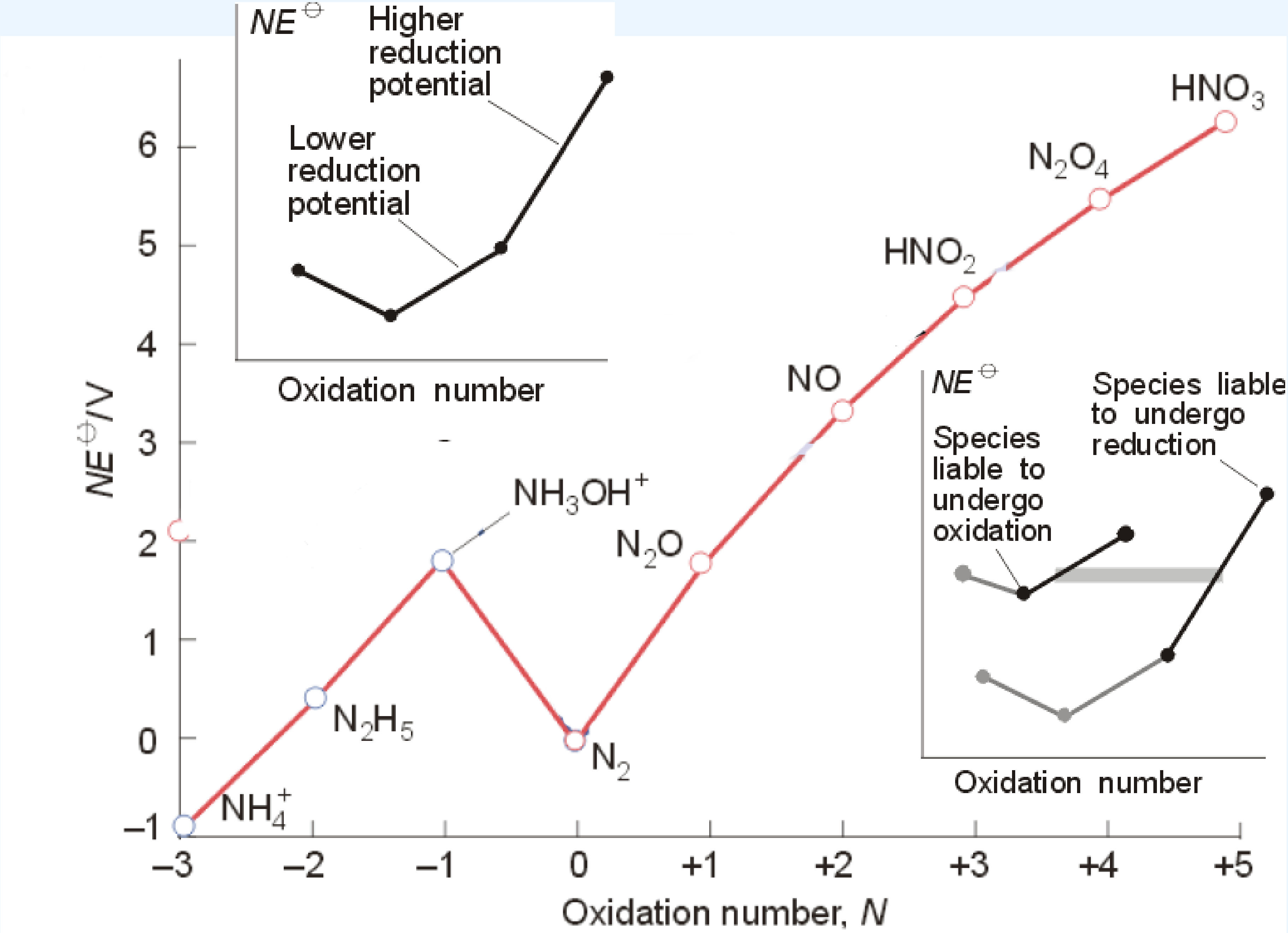
$NE^\theta = +3.4$ V

$N = +2$

NO – Strong oxidant than HNO_3

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

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

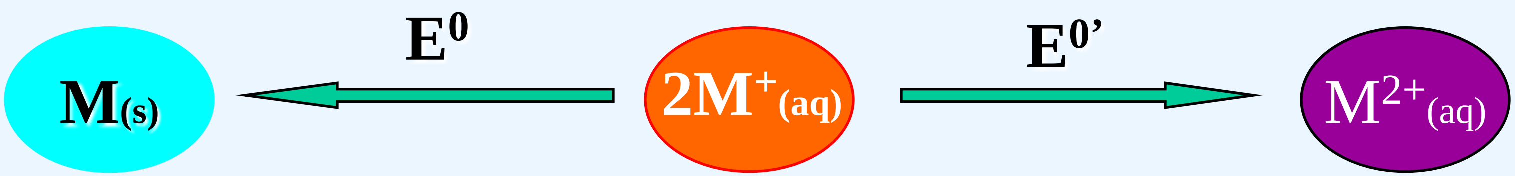


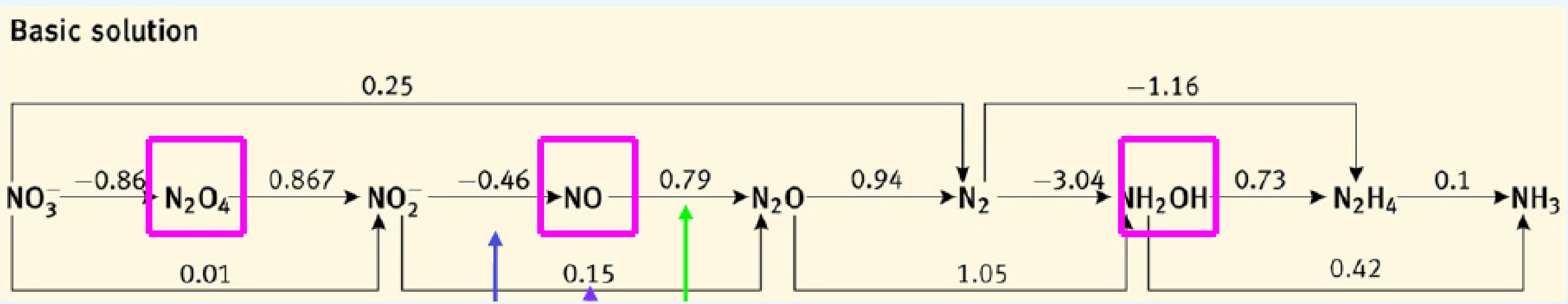
$NE^{\ominus}$
Higher reduction potential
Lower reduction potential
Oxidation number
$NE^{\ominus}$
Species liable to undergo reduction
Species liable to undergo oxidation
Oxidation number
HNO_3
N_2O_4
HNO_2
NO
N_2O
NH_3OH^+
N_2H_5
N_2
NH_4^+
$NE^{\ominus}/V$
6
5
4
3
2
1
0
–1
–3
–2
–1
0
+1
+2
+3
+4
+5
Oxidation number, N

Disproportionation

Element is simultaneously oxidized and reduced.

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

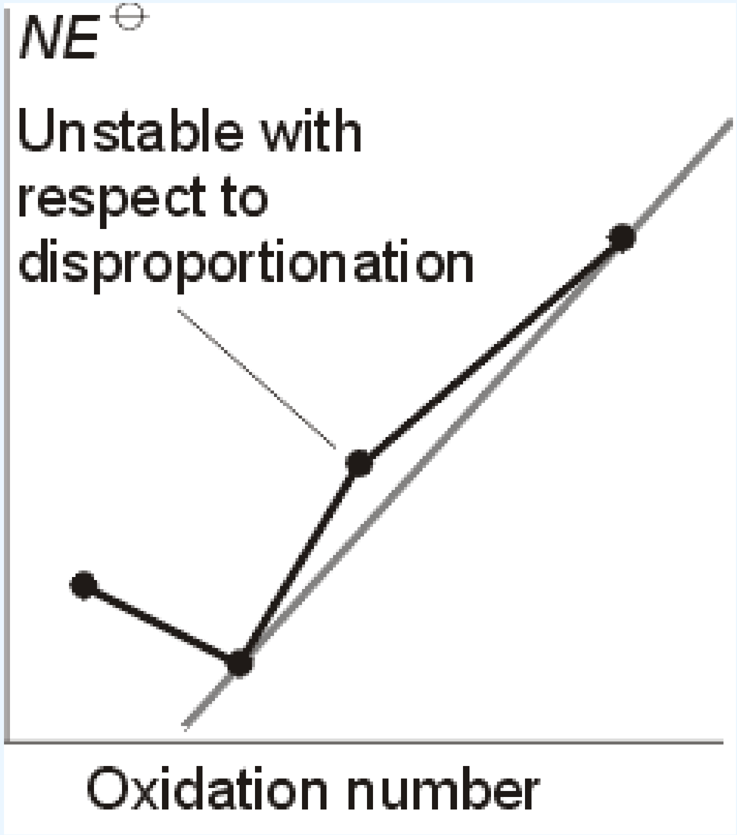




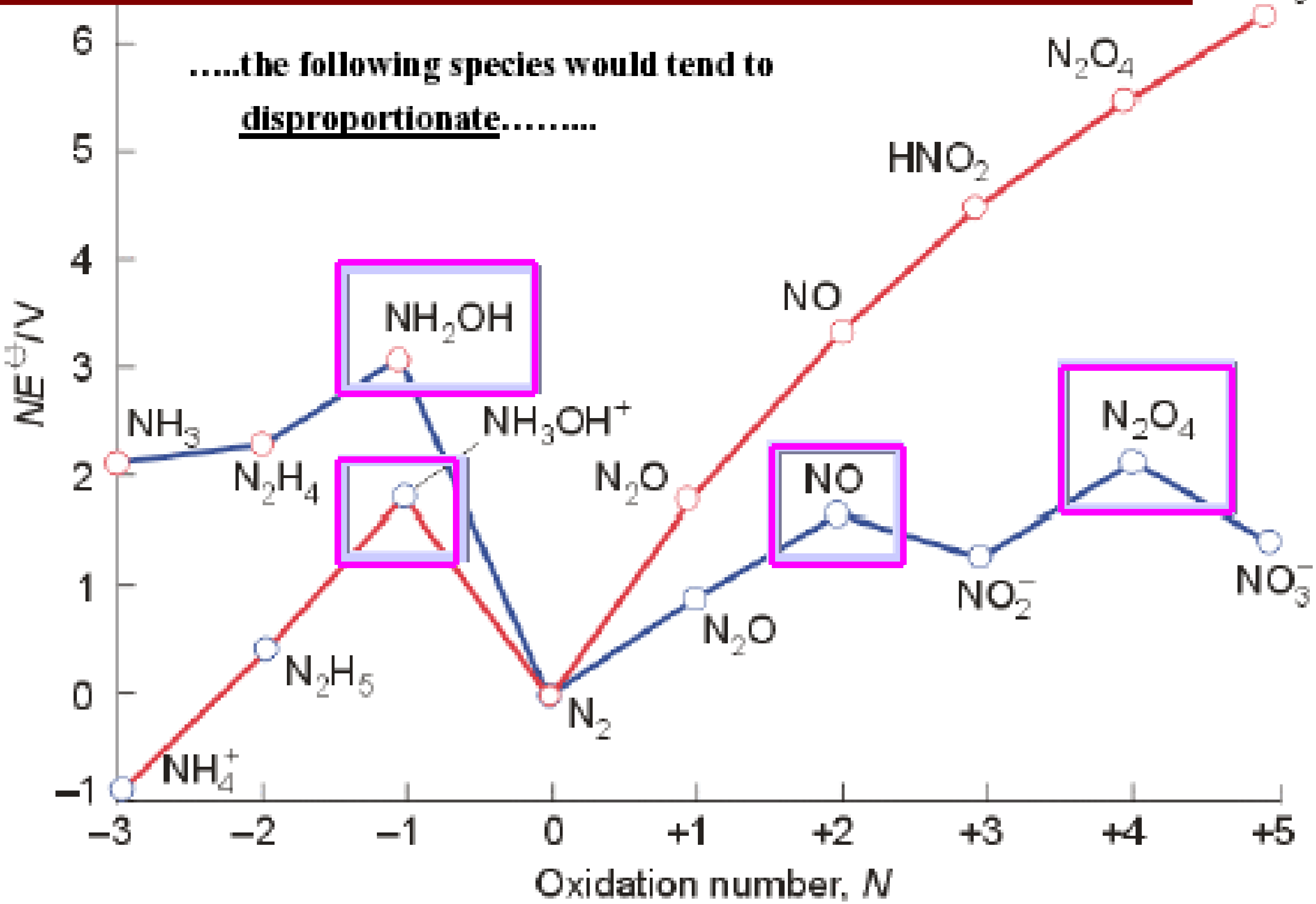
'the potential on the left of a species is less positive than that on the right- the species can oxidize and reduce itself, a process known as *disproportionation*'.

Disproportionation

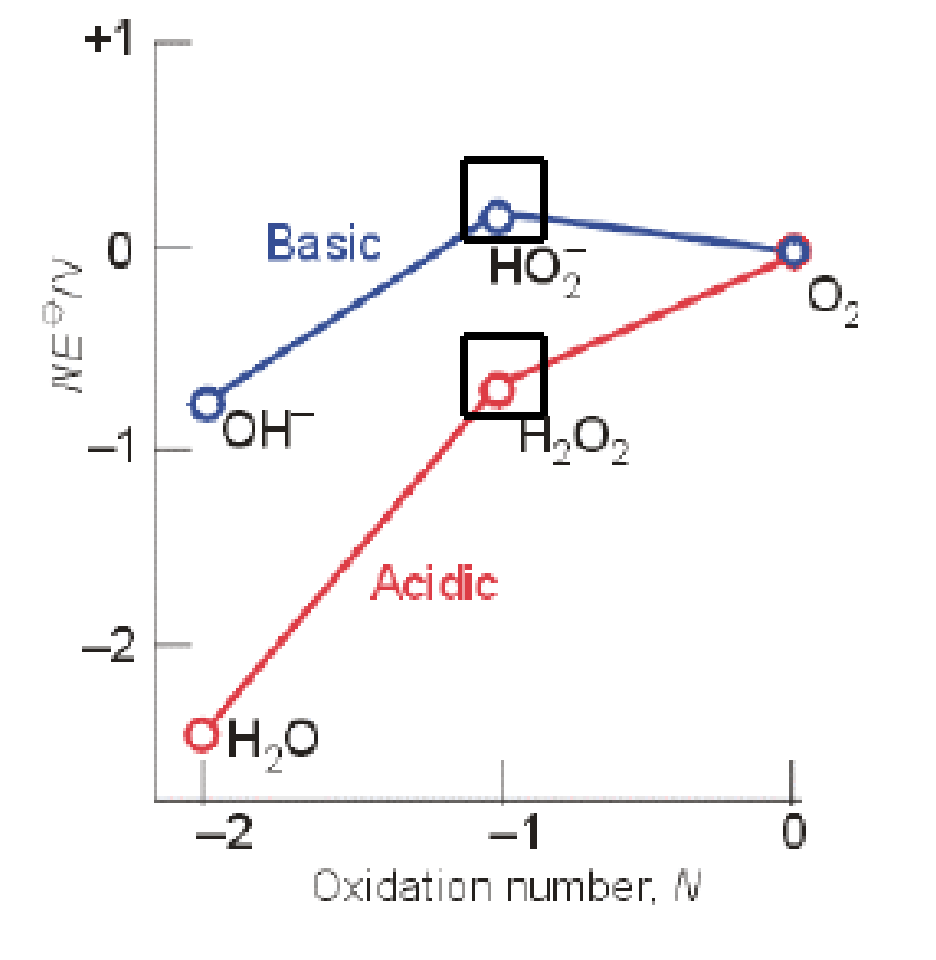
What Frost diagram tells about this reaction?



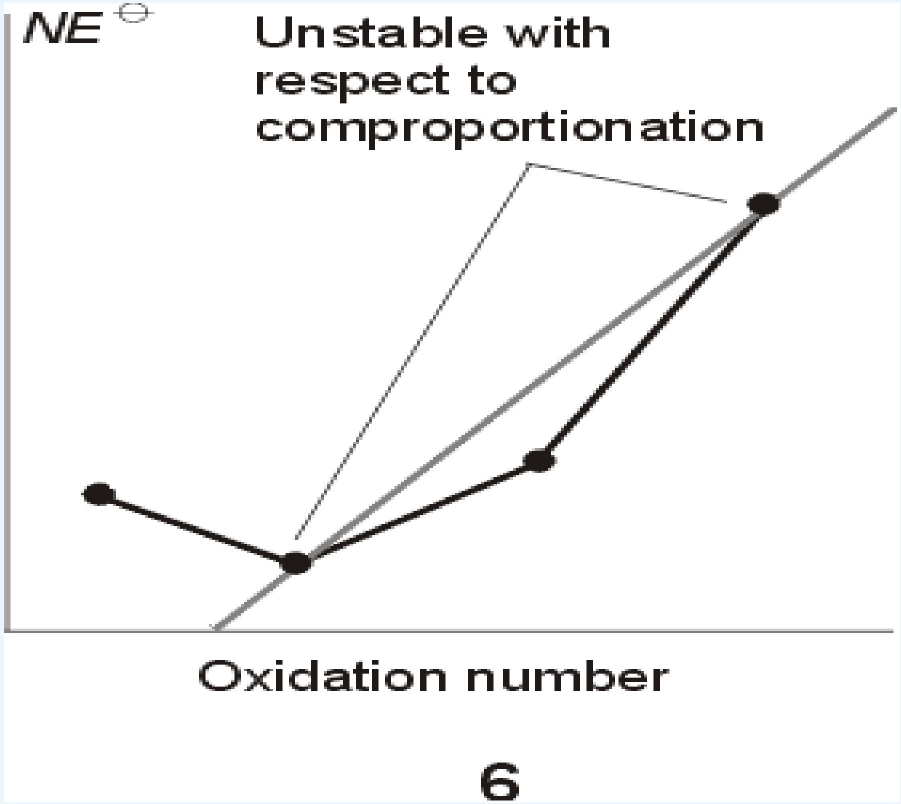
A species in a Frost diagram is unstable with respect to disproportionation if its point lies above the line connecting two adjacent species.



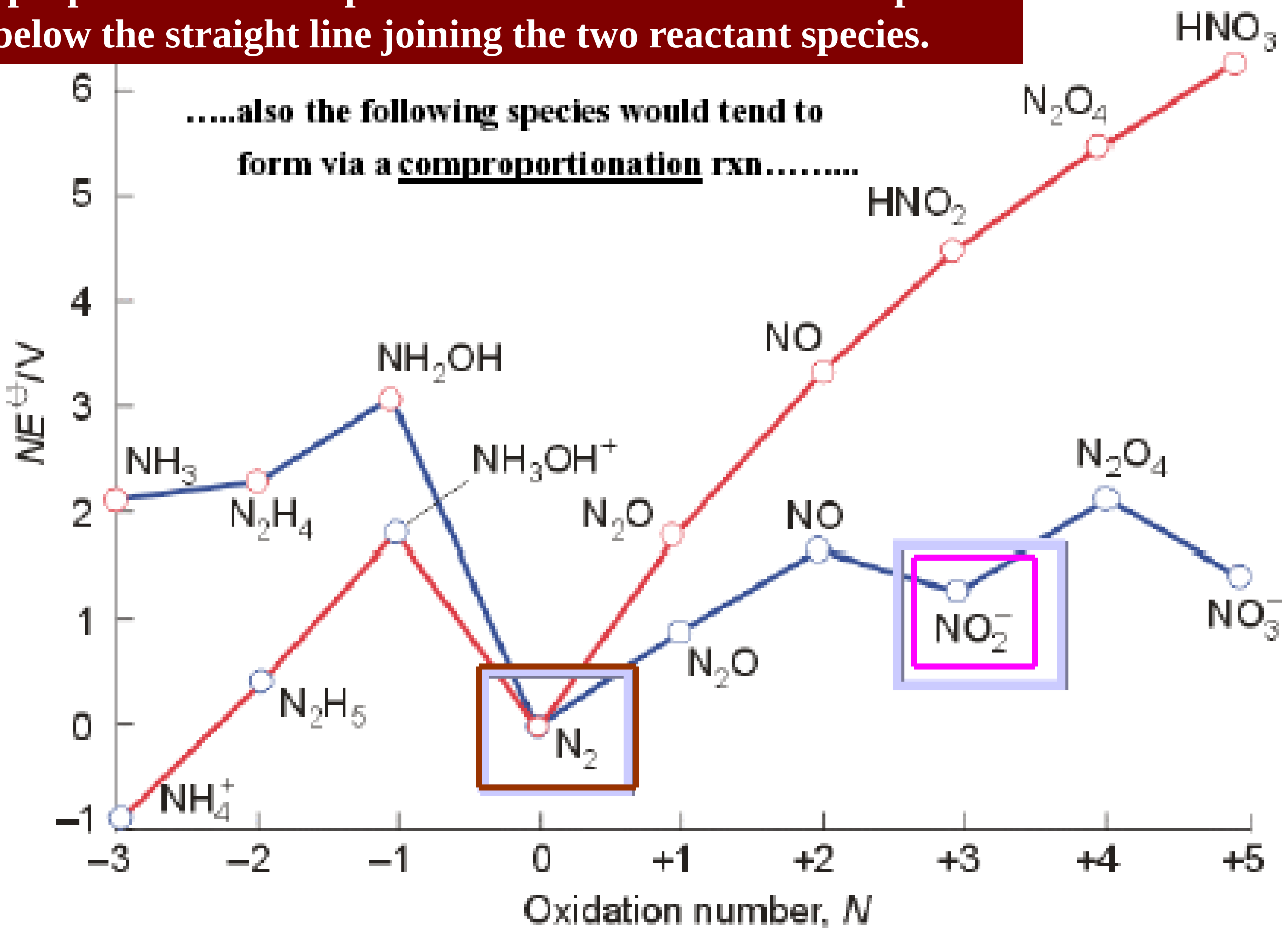
Disproportionation…. another example



Comproportionation reaction



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

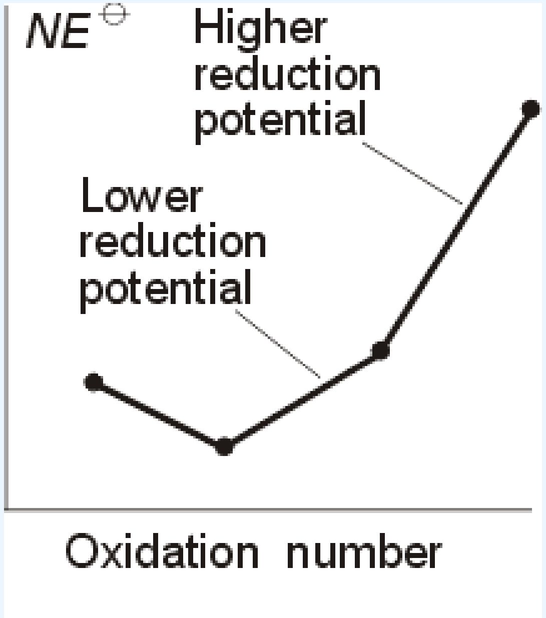
Half reactions:

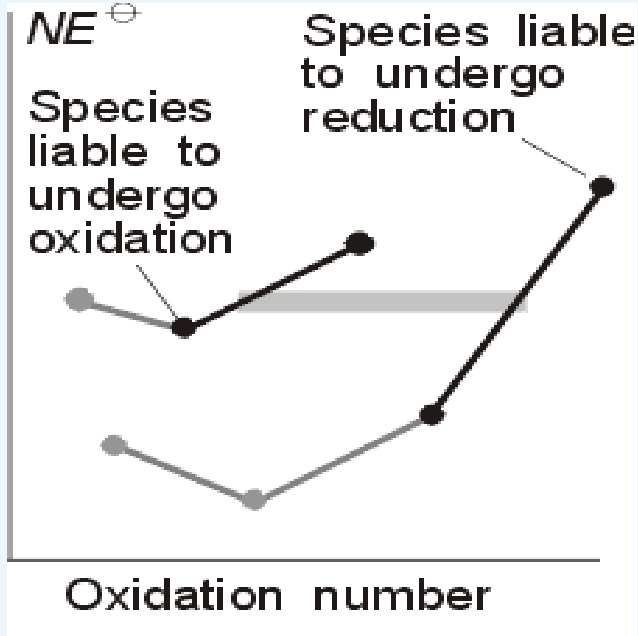
$$\overset{+4}{N_2O_4} \cancel{+ 2e^-} \longrightarrow 2\,\overset{+3}{NO_2^-}$$ *(reduction rxn)*

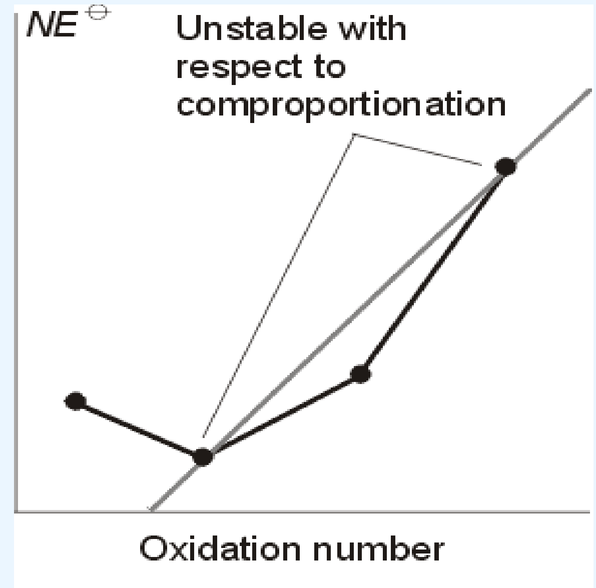
$$2\,\overset{+2}{NO} + 4OH^- \longrightarrow 2(\overset{+3}{NO_2^-} \cancel{+ e^-}) + 2\,H_2O$$ *(oxidation rxn)*

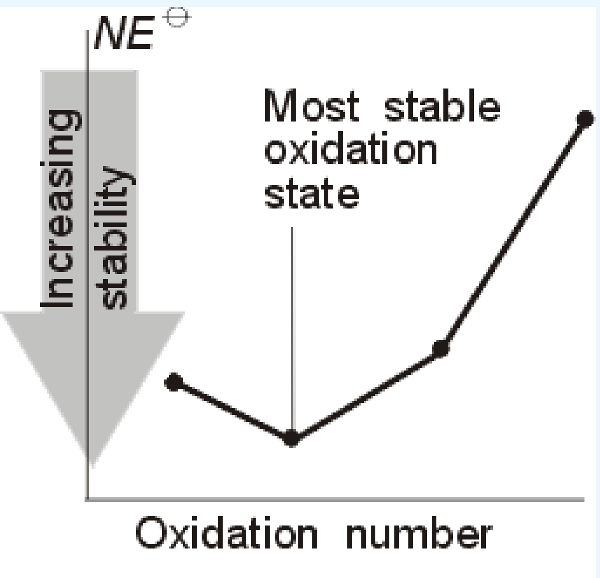
Net rxn: $$2NO + N_2O_4 + 4OH^- \longrightarrow 4\,NO_2^- + 2\,H_2O$$

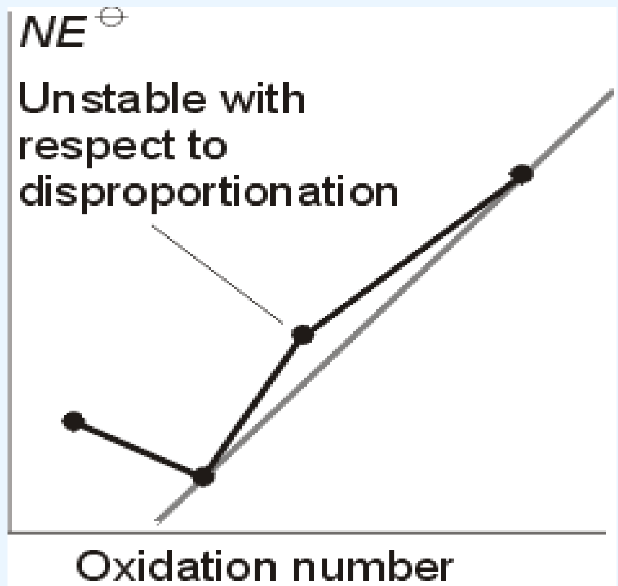
balanced


NE⊖
Higher reduction potential
Lower reduction potential
Oxidation number


NE⊖
Species liable to undergo reduction
Species liable to undergo oxidation
Oxidation number


NE⊖
Unstable with respect to comproportionation
Oxidation number


NE⊖
Increasing stability
Most stable oxidation state
Oxidation number


NE⊖
Unstable with respect to disproportionation
Oxidation number

H.W. 3: Draw Frost Diagram for the below:

+VII	+VI	+V	+IV	+III	+II	0

acidic solution

$$MnO_4^- \xrightarrow{0.90} HMnO_4^- \xrightarrow{1.28} (H_3MnO_4) \xrightarrow{2.9} MnO_2 \xrightarrow{0.95} Mn^{3+} \xrightarrow{1.5} Mn^{2+} \xrightarrow{-1.18} Mn$$

basic solution

$$MnO_4^- \xrightarrow{0.56} MnO_4^{2-} \xrightarrow{0.27} MnO_4^{3-} \xrightarrow{0.93} MnO_2 \xrightarrow{0.146} Mn_2O_3 \xrightarrow{-0.234} Mn(OH)_2 \xrightarrow{-1.56} Mn$$

Identify the most stable species, strong oxidizing agent and reducing agent in each case.