

Inorganic Chemistry (CY11001)

Oxidation-Reduction/Redox Chemistry

Books to Refer:

Inorganic Chemistry by Shriver & Atkins

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Biology

Selected Biologically Important Redox Couples

Redox Couple	E'_0 (Volts) ^a
Ferredoxin(Fe^{3+}) + e^- \longrightarrow ferredoxin (Fe^{2+})	-0.42
$\text{NAD(P)}^+ + \text{H}^+ + 2e^- \longrightarrow \text{NAD(P)H}$	-0.32
$\text{S} + 2\text{H}^+ + 2e^- \longrightarrow \text{H}_2\text{S}$	-0.274
Acetaldehyde + $2\text{H}^+ + 2e^- \longrightarrow$ ethanol	-0.197
Pyruvate ⁻ + $2\text{H}^+ + 2e^- \longrightarrow$ lactate ²⁻	-0.185
$\text{FAD} + 2\text{H}^+ + 2e^- \longrightarrow \text{FADH}_2$	-0.18 ^b
Oxaloacetate ²⁻ + $2\text{H}^+ + 2e^- \longrightarrow$ malate ²⁻	-0.166
Fumarate ²⁻ + $2\text{H}^+ + 2e^- \longrightarrow$ succinate ²⁻	0.031
Cytochrome <i>b</i> (Fe^{3+}) + $e^- \longrightarrow$ cytochrome <i>b</i> (Fe^{2+})	0.075
Ubiquinone + $2\text{H}^+ + 2e^- \longrightarrow$ ubiquinol	0.10
Cytochrome <i>c</i> (Fe^{3+}) + $e^- \longrightarrow$ cytochrome <i>c</i> (Fe^{2+})	0.254
Cytochrome <i>a</i> (Fe^{3+}) + $e^- \longrightarrow$ cytochrome <i>a</i> (Fe^{2+})	0.29
Cytochrome <i>a</i> ₃ (Fe^{3+}) + $e^- \longrightarrow$ cytochrome <i>a</i> ₃ (Fe^{2+})	0.35
$\text{NO}_3^- + 2\text{H}^+ + 2e^- \longrightarrow \text{NO}_2^- + \text{H}_2\text{O}$	0.421
$\text{NO}_2^- + 8\text{H}^+ + 6e^- \longrightarrow \text{NH}_4^+ + 2\text{H}_2\text{O}$	0.44
$\text{Fe}^{3+} + e^- \longrightarrow \text{Fe}^{2+}$	0.771 ^c
$\text{O}_2 + 4\text{H}^+ + 4e^- \longrightarrow 2\text{H}_2\text{O}$	0.815

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

^bThe value for FAD/FADH₂ applies to the free cofactor because it can vary considerably when bound to an apoenzyme.

^cThe value for free Fe, not Fe complexed with proteins (e.g., cytochromes).

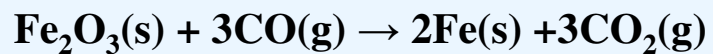
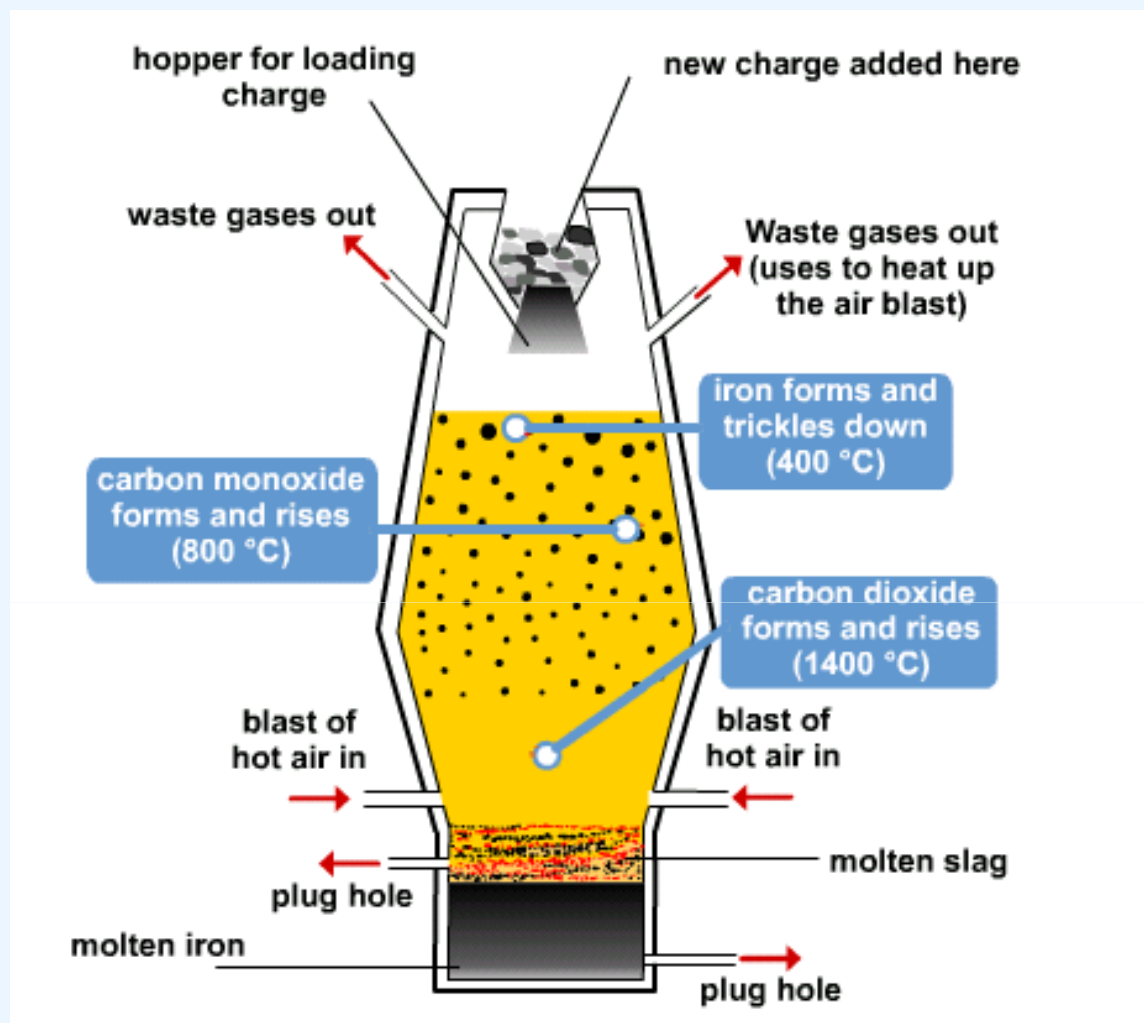
Just for your info

Industry

Extraction of metals

Dry & wet batteries

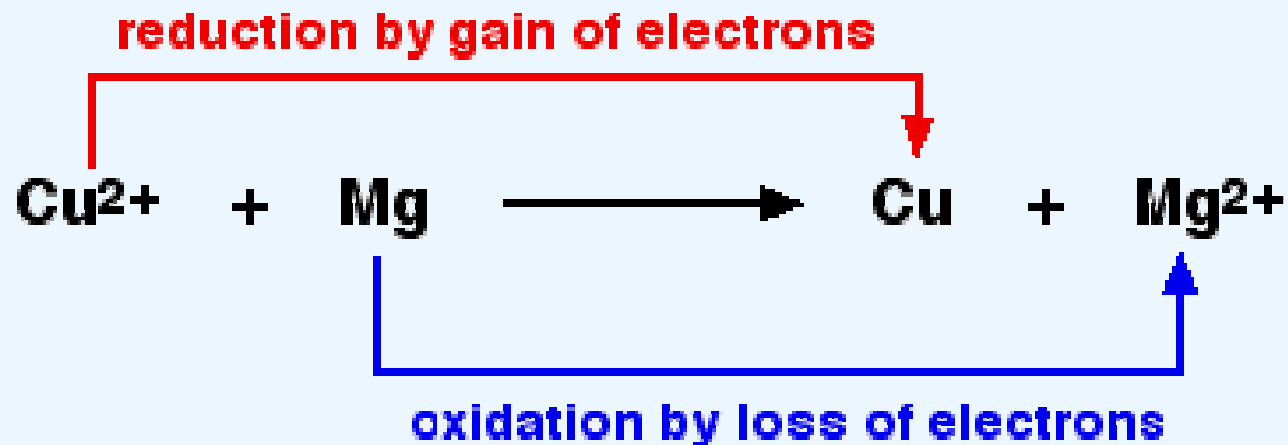
Fe
Na
Al



hematite

Just for your info

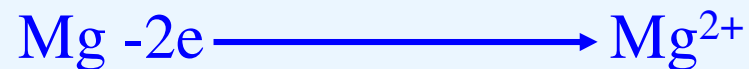
Redox reactions - transfer of electrons between species.



All the redox reactions have two parts (half reactions):

Oxidation (ON increases)

Reduction (ON decreases)

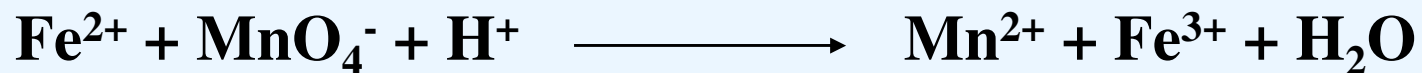


Mg: reducing agent: **reduces others but get oxidized itself**
Cu²⁺: oxidizing agent: **oxidizes others but get reduced itself**

ON= oxidation no



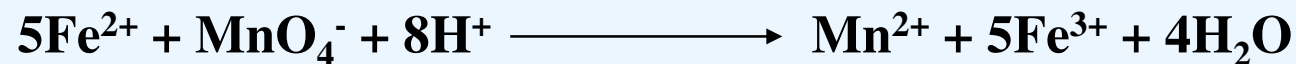
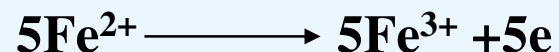
Balancing Redox Equations



1. Determine the elements that get oxidized and reduced.
2. Split the equation into half-reactions.
3. Balance all atoms in each half-reaction, except H and O.
4. Balance O atoms using H_2O .
5. 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: $\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$

Example

Do it by yourself

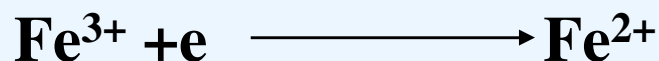


Standard oxidation/ reduction/ redox potential

- The emf which determines the tendency or power of any atom towards e loss or gain under standard conditions is called std oxd or std red potential.
- Std condition: Ions in unit activity, Metal are solid, Gas at 1 atm/25 °C
- Algebraic sum of the std oxd & std red potentials are called std redox potential

Std H Electrodes: The electrodes whose potential is arbitrarily assumed and with respect to which the potential of all other electrodes are determined : $2 \text{H}^+(\text{aq}) + 2 \text{e}^- = \text{H}_2(\text{g})$ $E^0_{\text{H}^+ / 1/2\text{H}_2} = 0.0 \text{ V}$



International convention: std reduction potential



$$E^0_{\text{Fe}^{3+}/\text{Fe}^{2+}} = 0.77 \text{ V} \text{ OR}$$
$$E^0 (\text{Fe}^{3+}, \text{Fe}^{2+}) = 0.77 \text{ V}$$

TABLE 18.1

Standard Reduction Potentials at 25°C

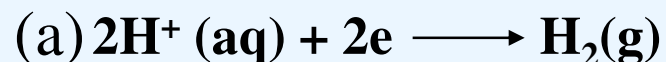
	Reduction Half-Reaction	E° (V)	
 <p>Stronger oxidizing agent</p>	$F_2(g) + 2 e^- \longrightarrow 2 F(aq)$	2.87	<p>Weaker reducing agent</p> 
	$H_2O_2(aq) + 2 H^+(aq) + 2 e^- \longrightarrow 2 H_2O(l)$	1.78	
	$MnO_4^-(aq) + 8 H^+(aq) + 5 e^- \longrightarrow Mn^{2+}(aq) + 4 H_2O(l)$	1.51	
	$Cl_2(g) + 2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

Application of std reduction potential value

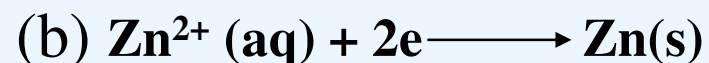
$$\Delta G^0 = - n F E^0$$

Spontaneous reaction: $\Delta G^0 < 0$, then E^0 must be > 0

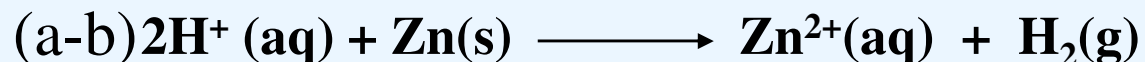
A reaction is favorable if $E^0 > 0$



$$E^0 (H^+, H_2) = 0.0 \text{ V}$$



$$E^0 (Zn^{2+}, Zn) = -0.76 \text{ V}$$



$$E^0_{\text{cell}} = +0.76 \text{ V}$$

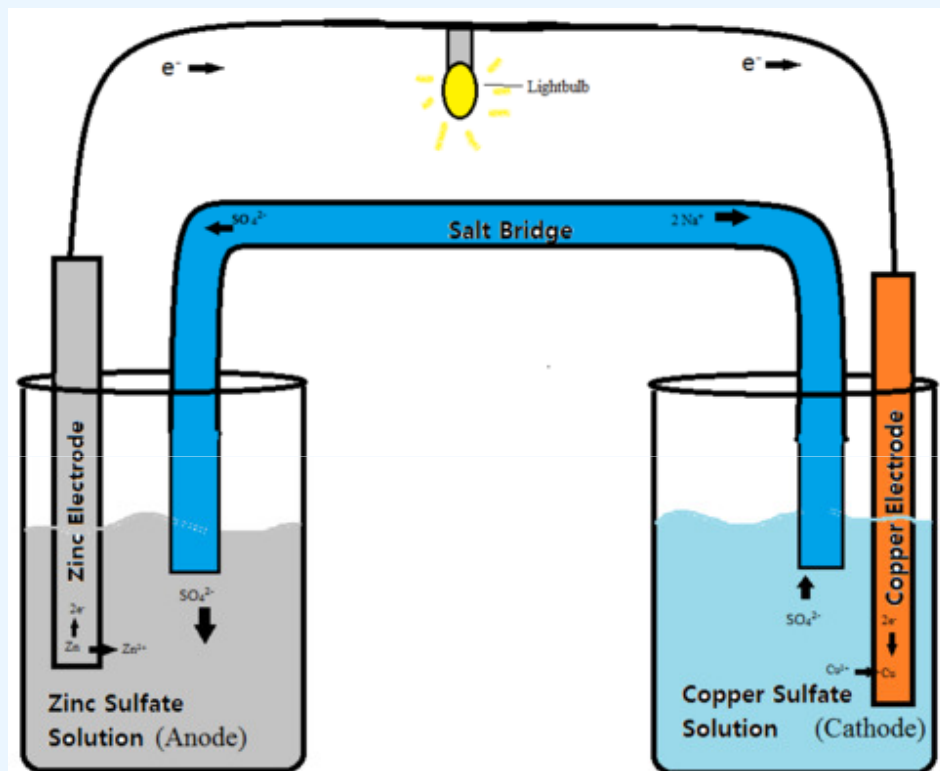
Reaction is favorable

High std reduction potential: Highly oxidizing agent

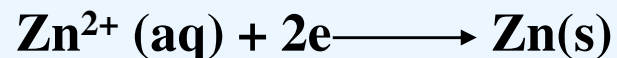
Note: this is full redox reaction: e are cancelled out

Galvanic Cell: a electrochemical cell

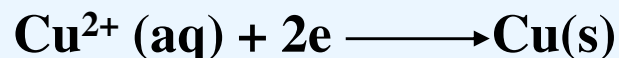
Electricity: by cost of redox reactions



Test Question: Predict if Ag will be oxidized when immersed In CuSO_4 solution.
 $E^0 (\text{Cu}^{2+}, \text{Cu}) = 0.34 \text{ V}$
 $E^0 (\text{Ag}^+, \text{Ag}) = 0.80 \text{ V}$



$$E^0 (\text{Zn}^{2+}, \text{Zn}) = -0.76 \text{ V}$$



$$E^0 (\text{Cu}^{2+}, \text{Cu}) = 0.34\text{V}$$



$$E^0_{\text{cell}} = 0.34 - (-0.76) = 1.10\text{V}$$

(high + ve value, spontaneous)

Diagrammatic presentation of potential data

Latimer Diagram (reduction potential diagram)

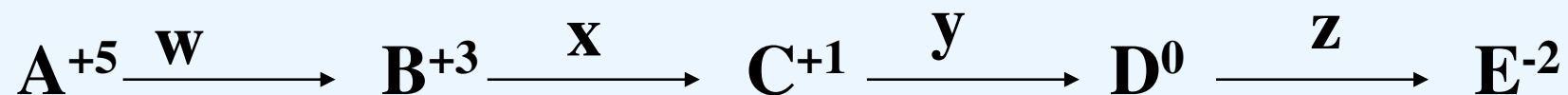
Frost Diagram (oxidation state diagram)

Latimer Diagram

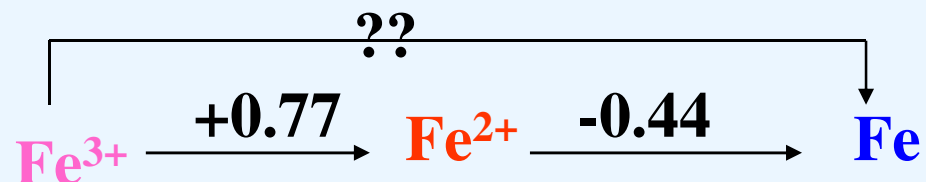
*The numerical value of std red pot (in v) is written over a horizontal line (or arrow) connecting species with the element in different OS

* 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.



What could be extracted from **Latimer Diagram...**

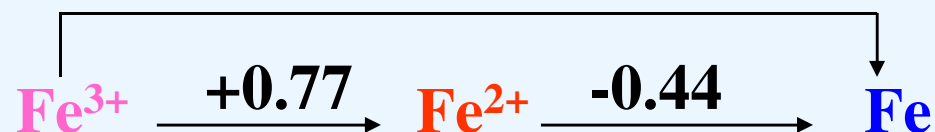


$$\Delta G = -nFE$$



$$\Rightarrow E^\circ_{\text{Fe}^{3+}/\text{Fe}} = -0.036$$

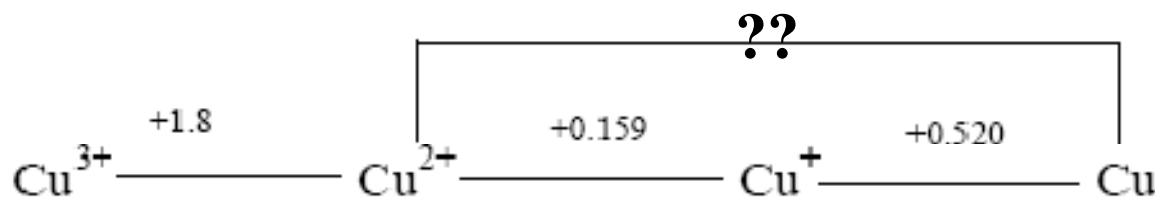
$$\mathbf{-0.036}$$



Note: this is HALF reaction: e are NOT cancelled out

What could be extracted from **Latimer Diagram**...

Reaction	Potential	$\Delta G = nFE$
$\text{Cu}^+ + \text{e}^- \rightarrow \text{Cu}$	+0.520 V	$-1 \times F \times 0.520$
$\text{Cu}^{2+} + \text{e}^- \rightarrow \text{Cu}^+$	+0.159 V	$-1 \times F \times 0.159$
$\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$	NOT 0.679!	$-2 \times F \times E^0 = -0.679F$

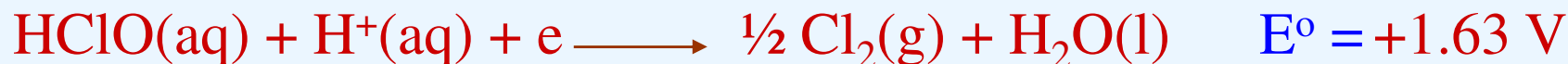
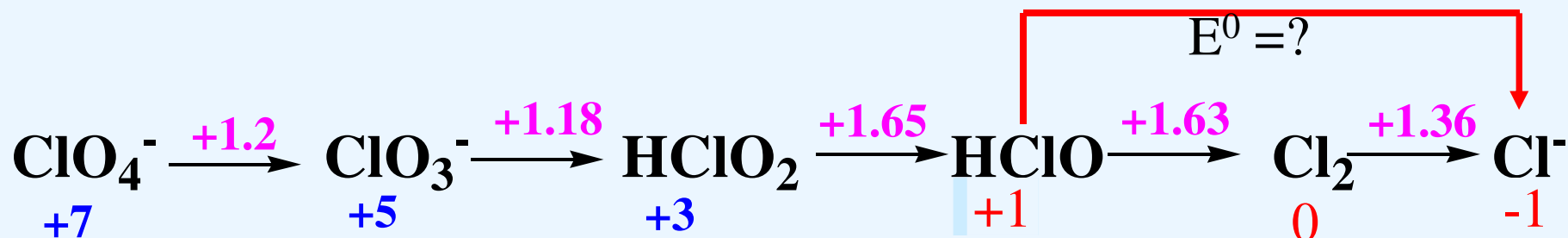


$$E^0_{\text{Cu}^{2+}/\text{Cu}} = 0.34 \text{ V}$$



No need to go to lab for EXPT

Latimer diagram for chlorine in acidic solution



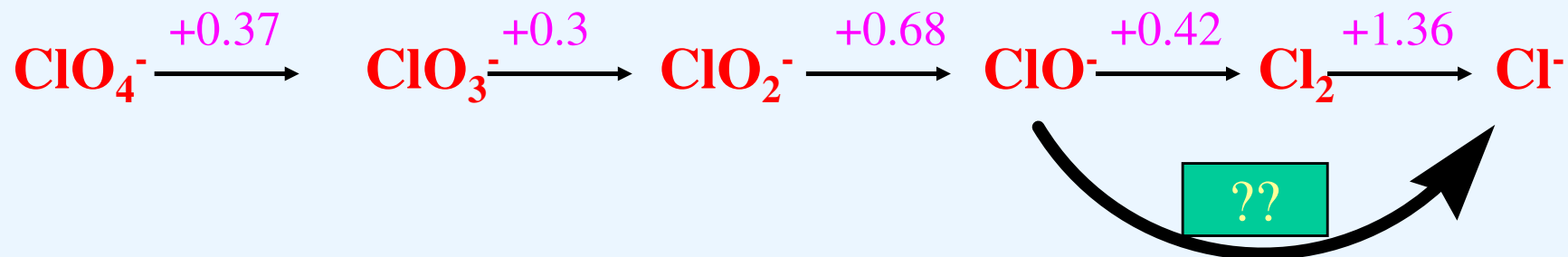
Simple formula

$$\begin{aligned}
 \Delta G &= \Delta G' + \Delta G'' \\
 -nFE &= -n'FE' - n''FE'' \\
 E &= \frac{n'E' + n''E''}{n'+n''}
 \end{aligned}$$

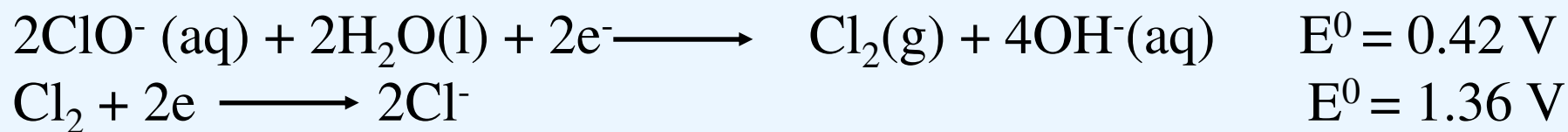
Write the balanced equation for the



Latimer diagram for chlorine in basic solution



Balance the half reactions...



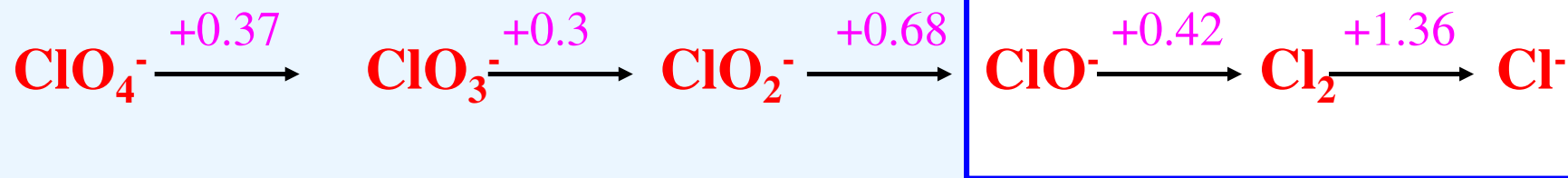
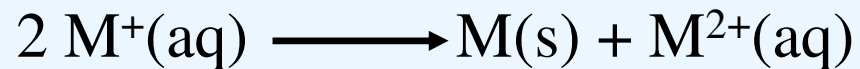
Why not $\frac{1}{2} \text{Cl}_2$ like before?
Try it out: same result



$$E^0 = +0.89$$

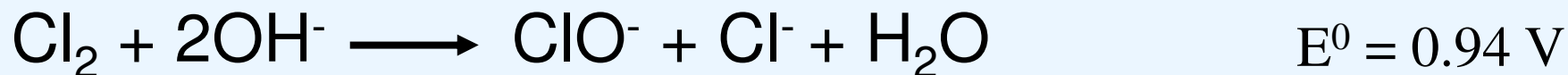
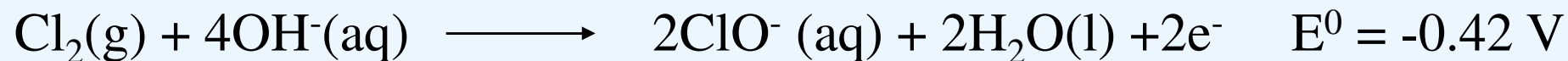
Disproportionation

Element is simultaneously oxidized and reduced.



‘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*’.

Continued.....

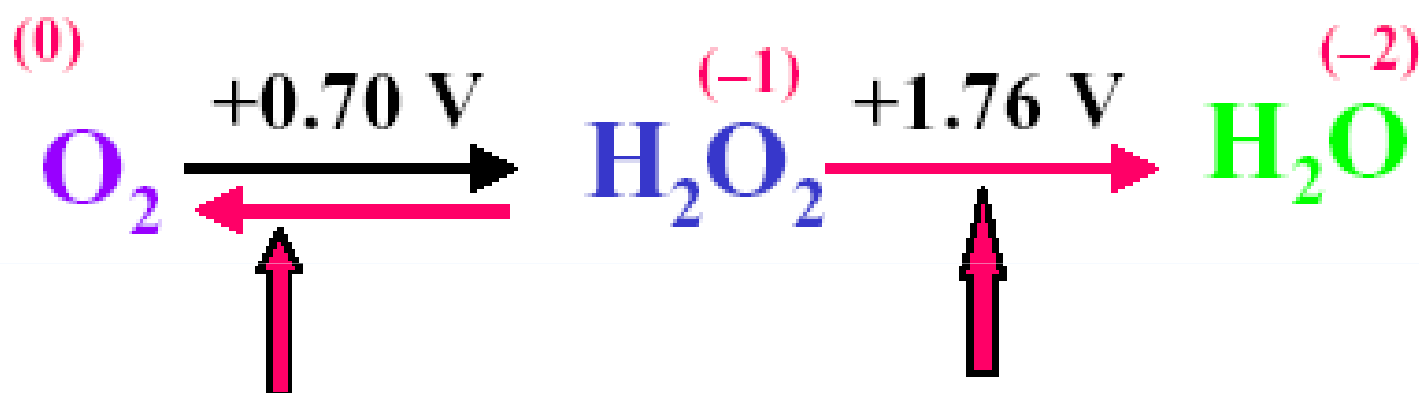


Full rkn

Reaction is spontaneous as E^0 is positive

Note: this is full redox reaction: e are cancelled out

Disproportionation

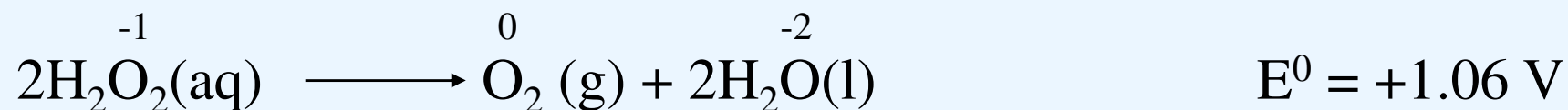
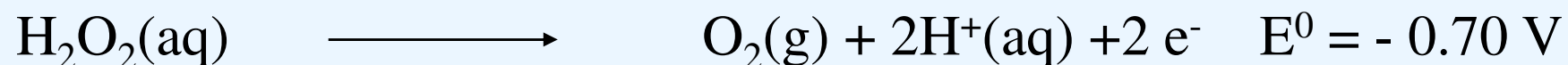


if the potential for the rxn
on the left is less than

the potential for the rxn
on the right

.....then, the species in the middle, H_2O_2 ,
will **disproportionate**

Is it spontaneous?



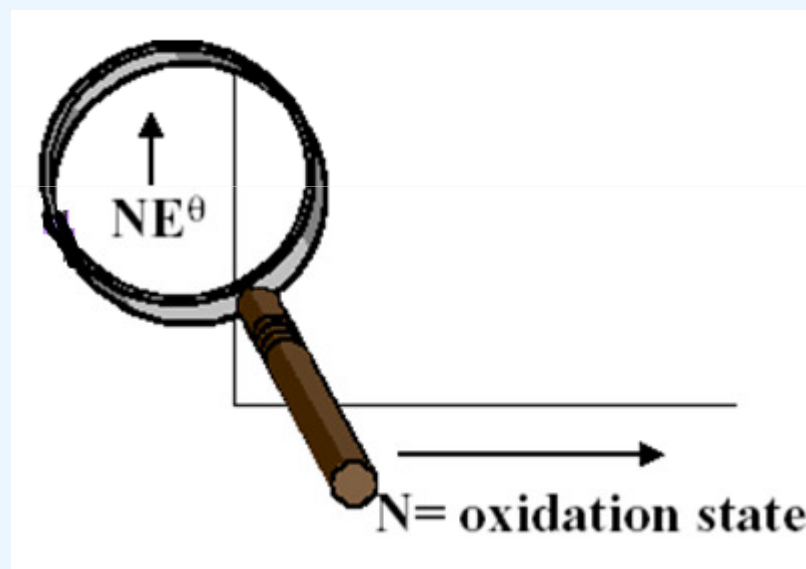
Yes the reaction is spontaneous

Auto-decomposition of H_2O_2 in lab

Frost Diagram

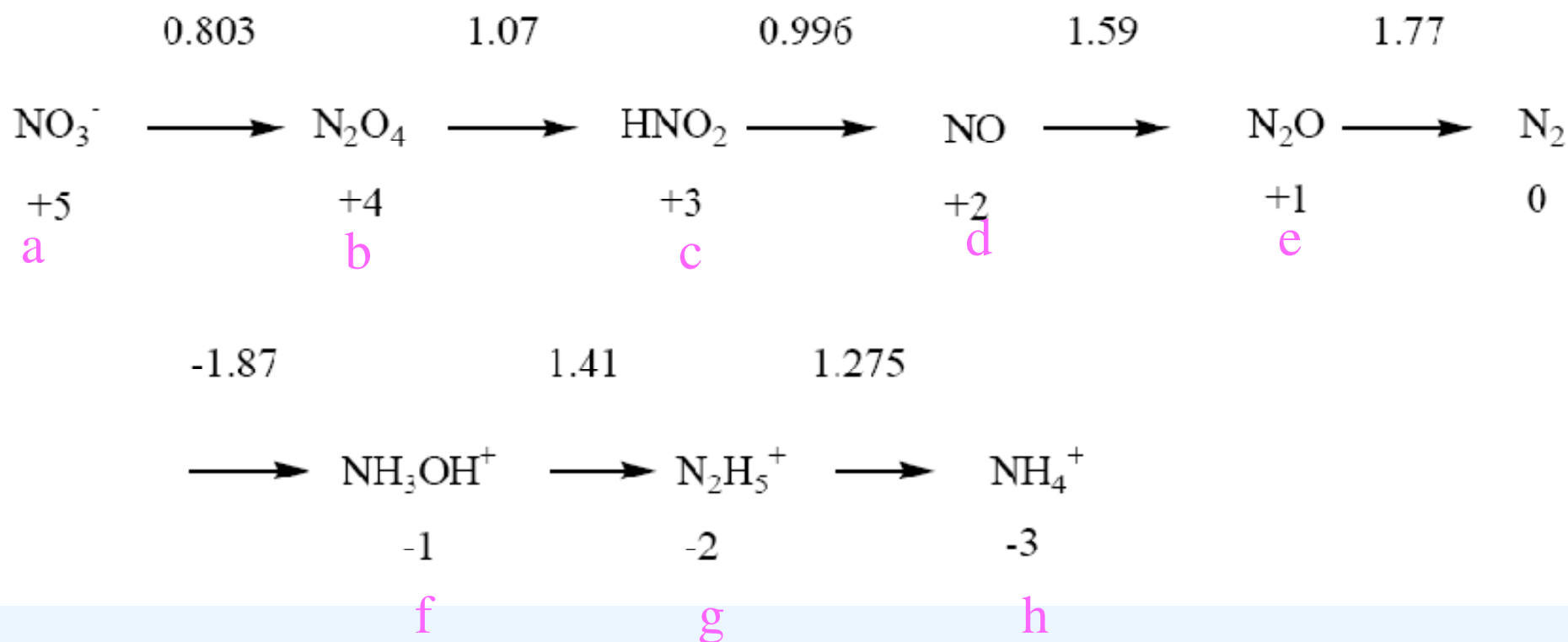
Arthur A. Frost

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

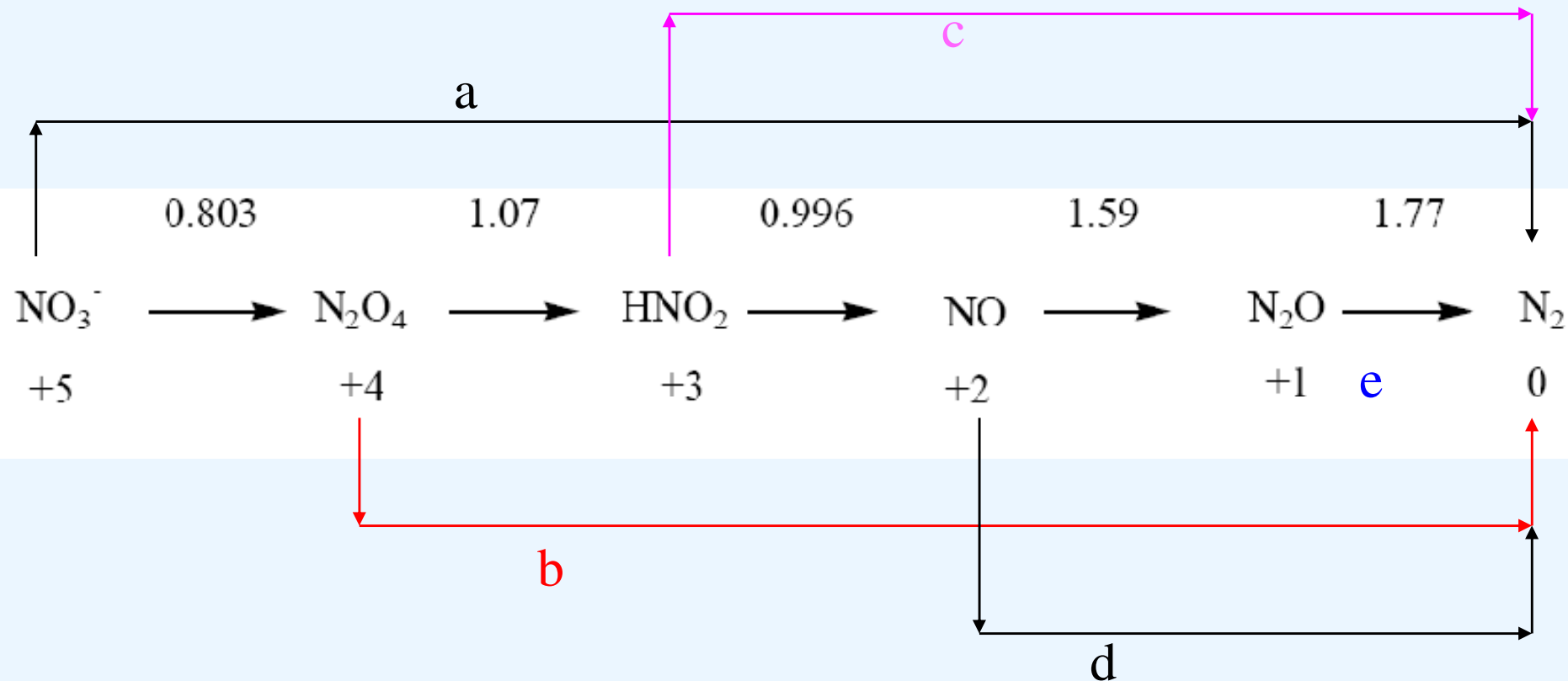


FD of an element X is a plot of NE^0 for the couple X^N/X^0 against the oxd no N , of the element.

Look at the Latimer diagram of **nitrogen** in **acidic solution**



From Latimer diagram, you can make the Frost Diagram

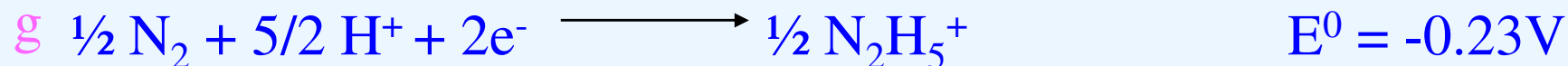
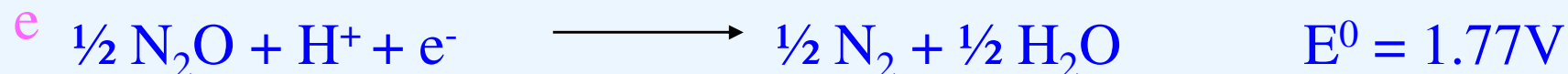
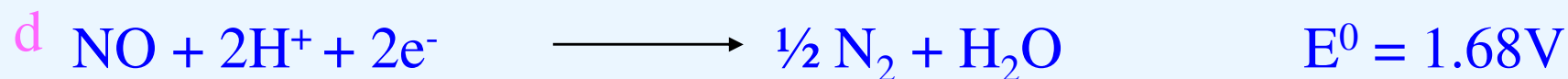
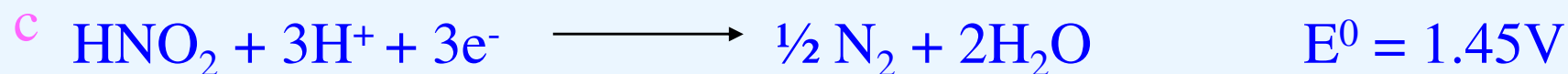
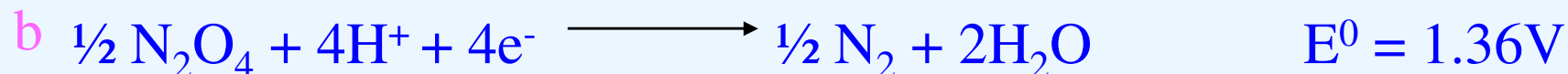
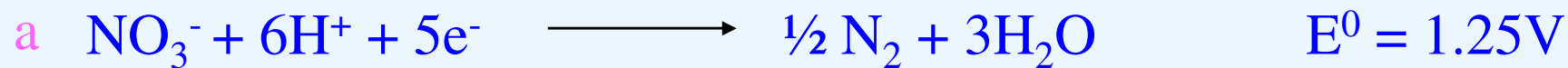


$$\Delta G = \Delta G' + \Delta G''$$

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

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

By using the equation in Latimer diagram we can calculate....



Oxidation state: species**N x E⁰, N**N(V): NO₃⁻

(5 x 1.25, 5)

N(IV): N₂O₄

(4 x 1.36, 4)

N(III): HNO₂

(3 x 1.35, 3)

N(II): NO

(2 x 1.68, 2)

N(I): N₂O

(1 x 1.77, 1)

N(0): N₂

(0, 0)

N(-I): NH₃OH⁺

[-1 x (-1.87), -1]

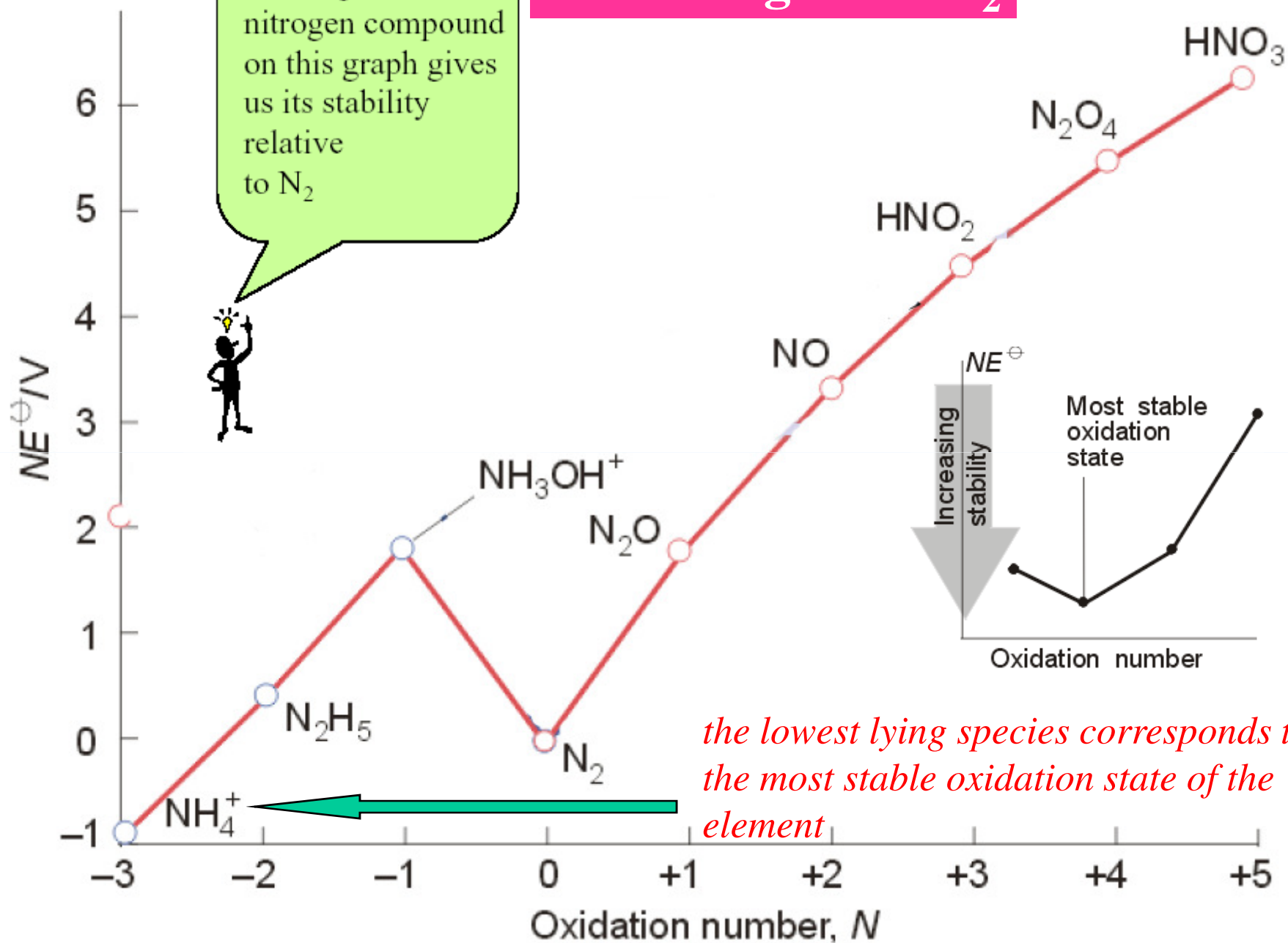
N(-II): N₂H₅⁺

[-2 x (-0.23), -2]

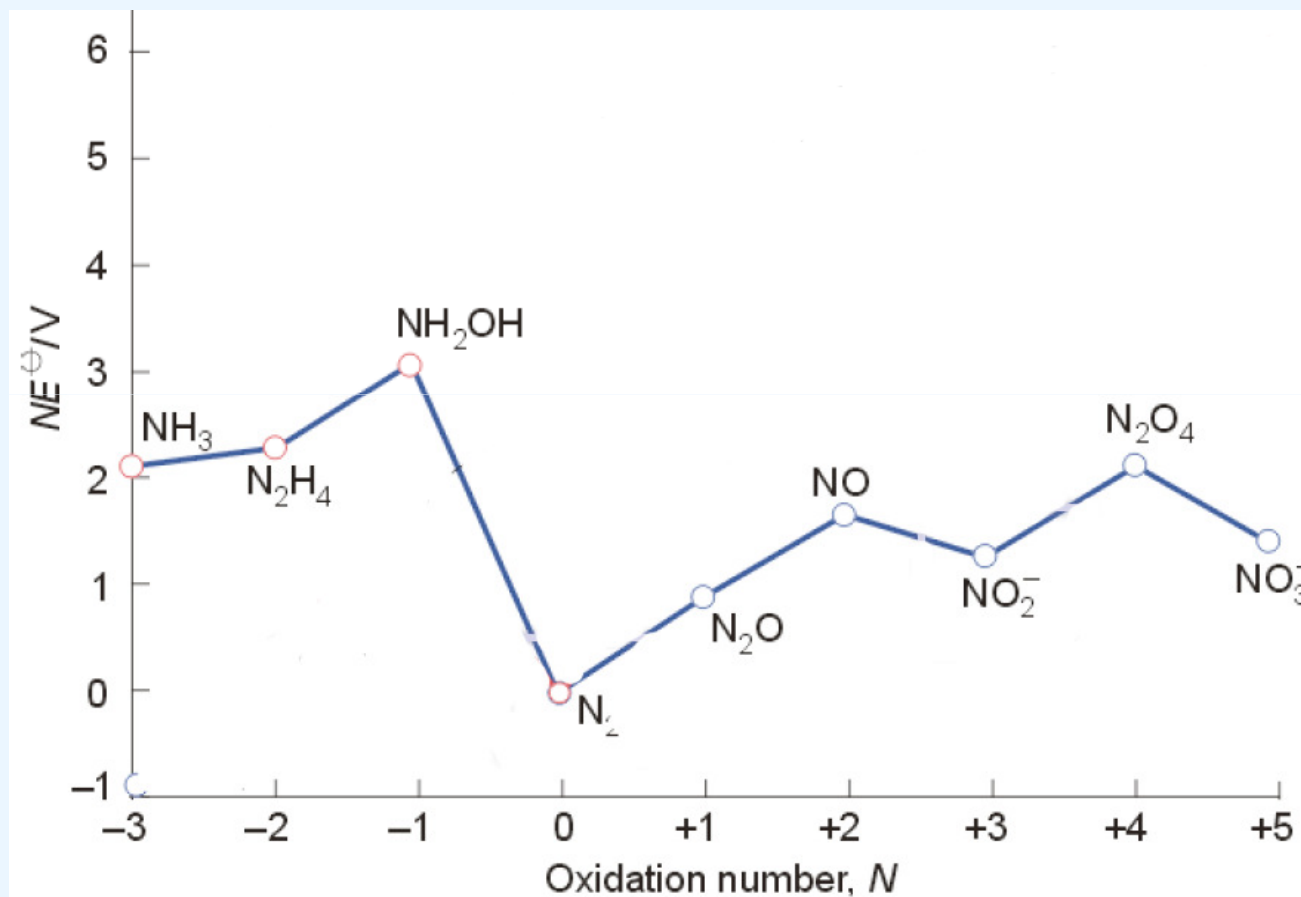
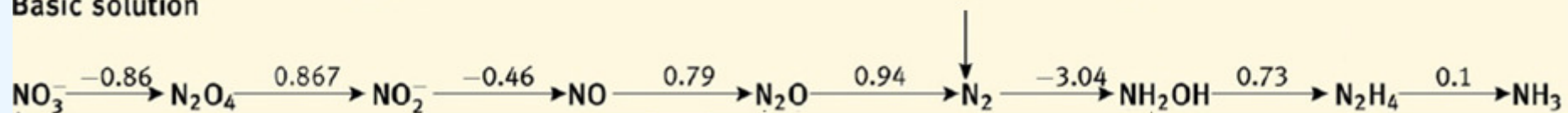
N(-III): NH₄⁺

(-3 x 0.27, -3)

Frost Diagram – N₂

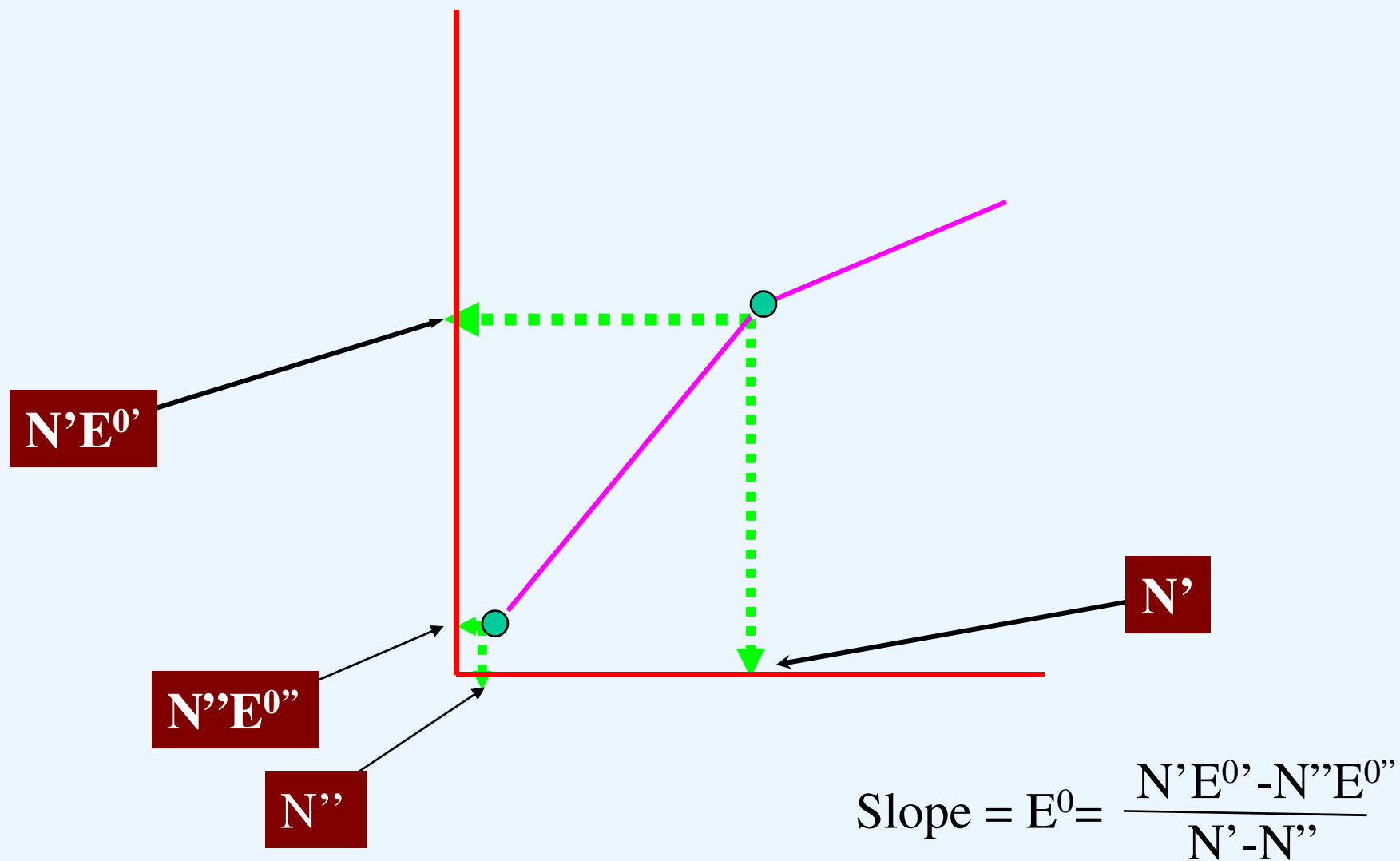


Basic solution



Conclusion: Higher oxides & oxo-acids are unstable in acidic sol but relatively stable in basic sol

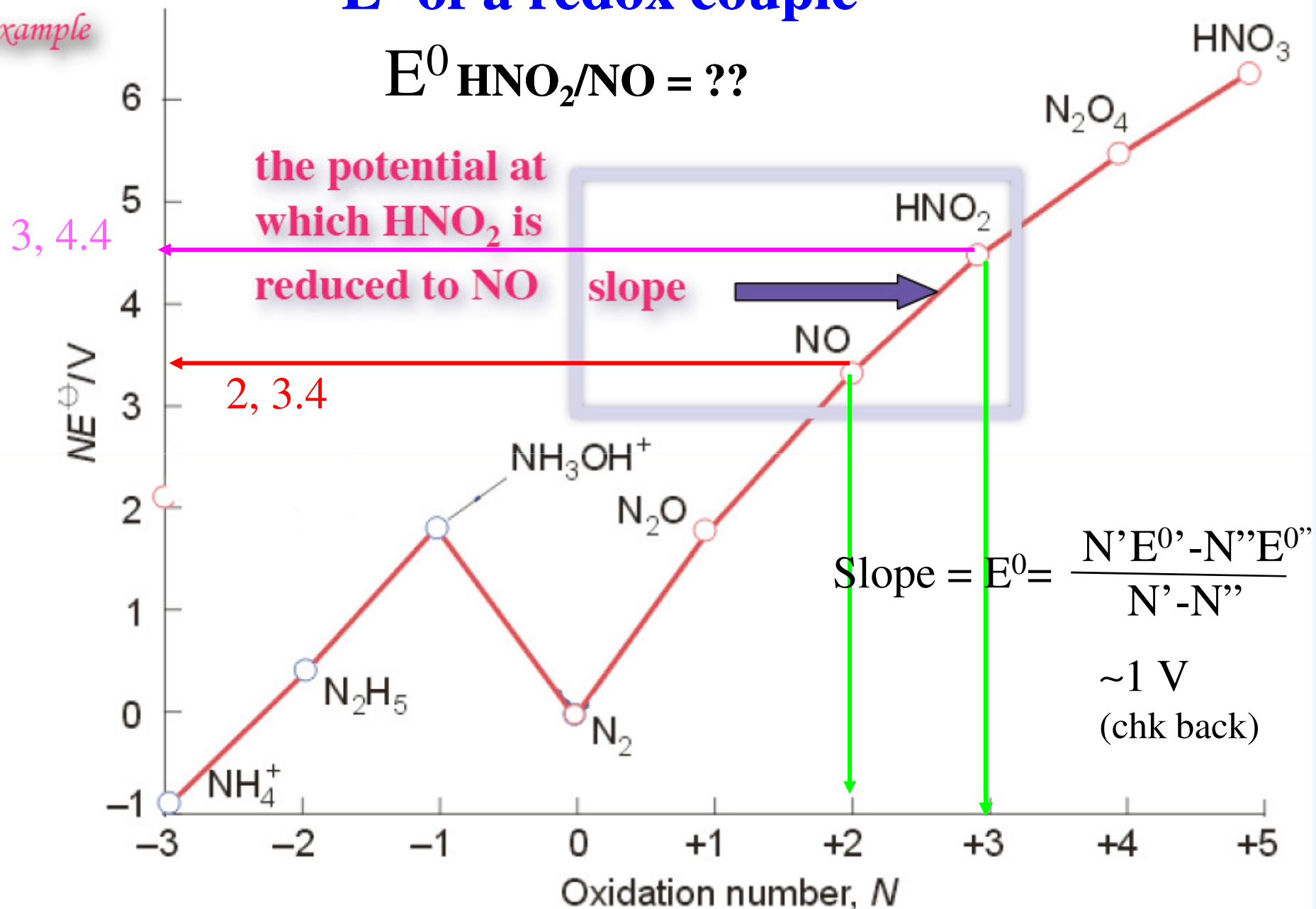
Slope of the line joining any two points is equal to the std potential of the couple.



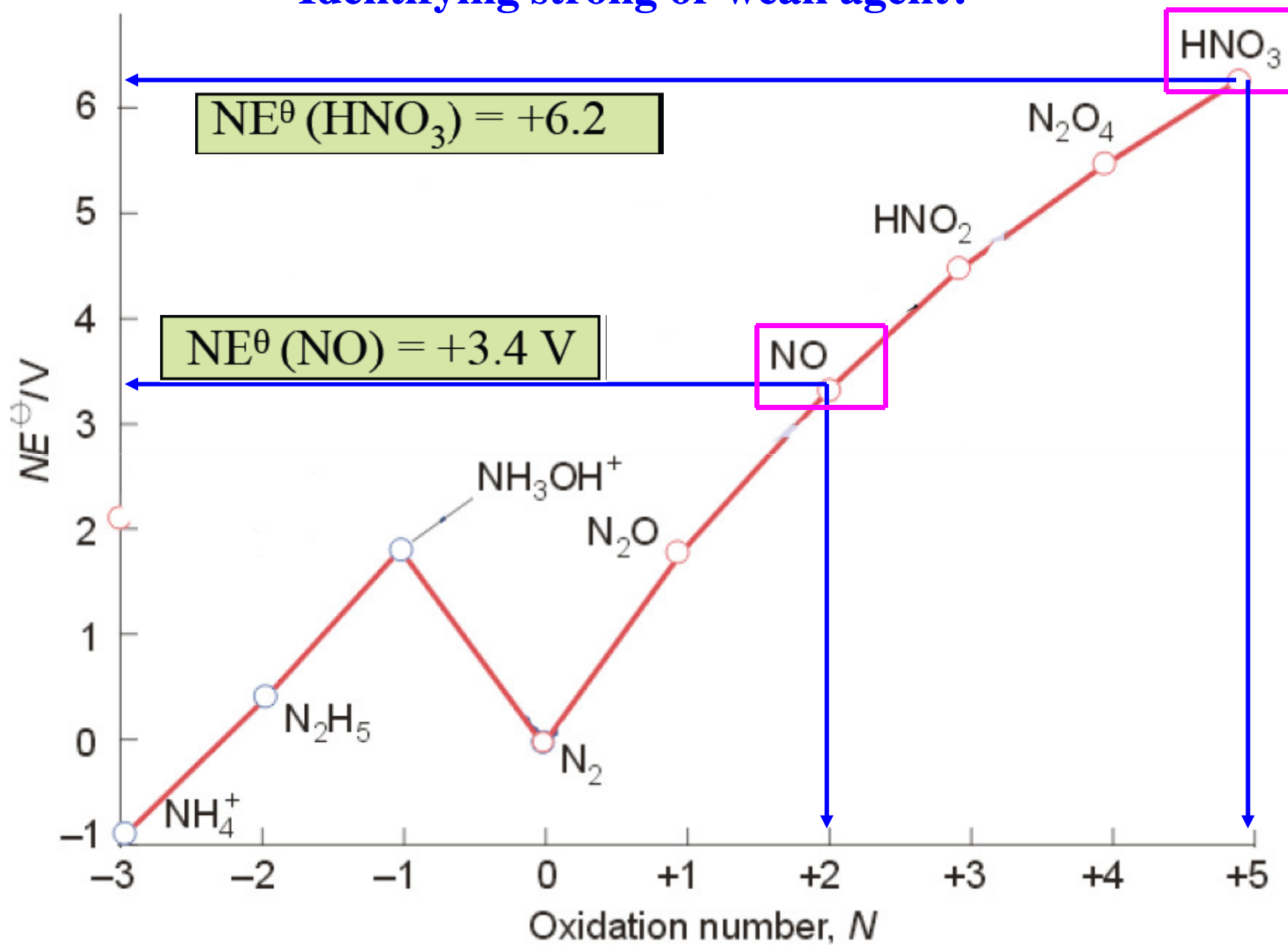
E^0 of a redox couple

$$E^0 \text{HNO}_2/\text{NO} = ??$$

example



Identifying strong or weak agent?



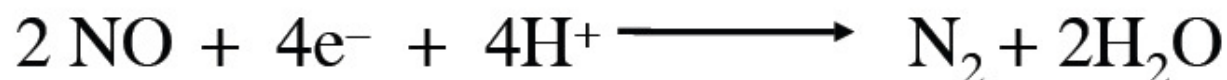
From the coordinates of HNO_3 (+5, +6.2) and NO (+2, +3.4) on the nitrogen Frost diagram we can determine the reduction potential for the half reactions below



$$\text{NE}^\theta = +6.2 \text{ V} \quad \text{from graph y-value}$$

$$\text{N} = +5 \quad \text{from graph x-value}$$

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



$$\text{NE}^\theta = +3.4 \text{ V}$$

$$\text{N} = +2$$

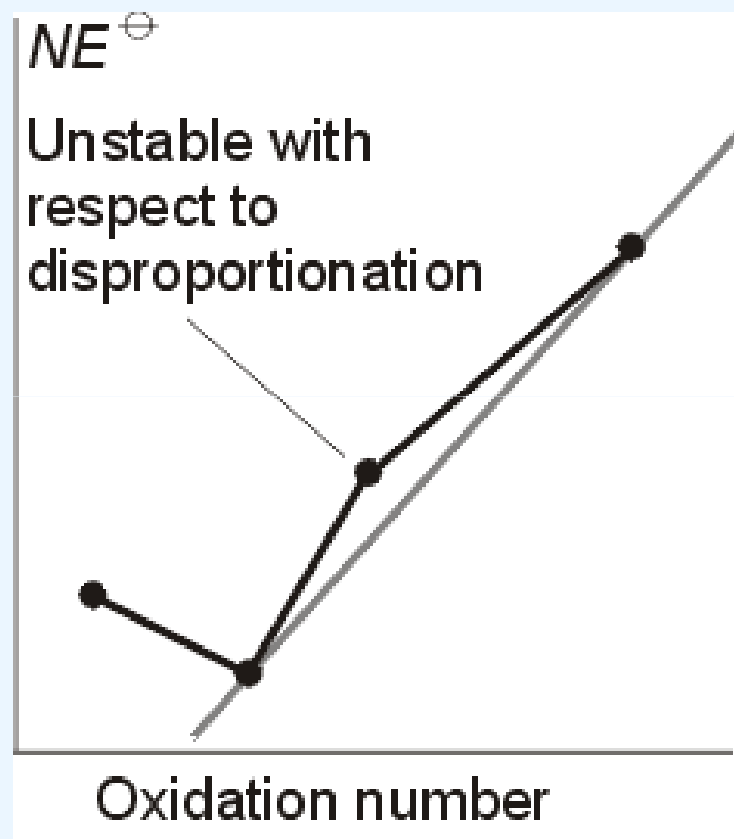
$$E^\theta = +1.70 \text{ V}$$

NO – Strong oxidant than HNO_3

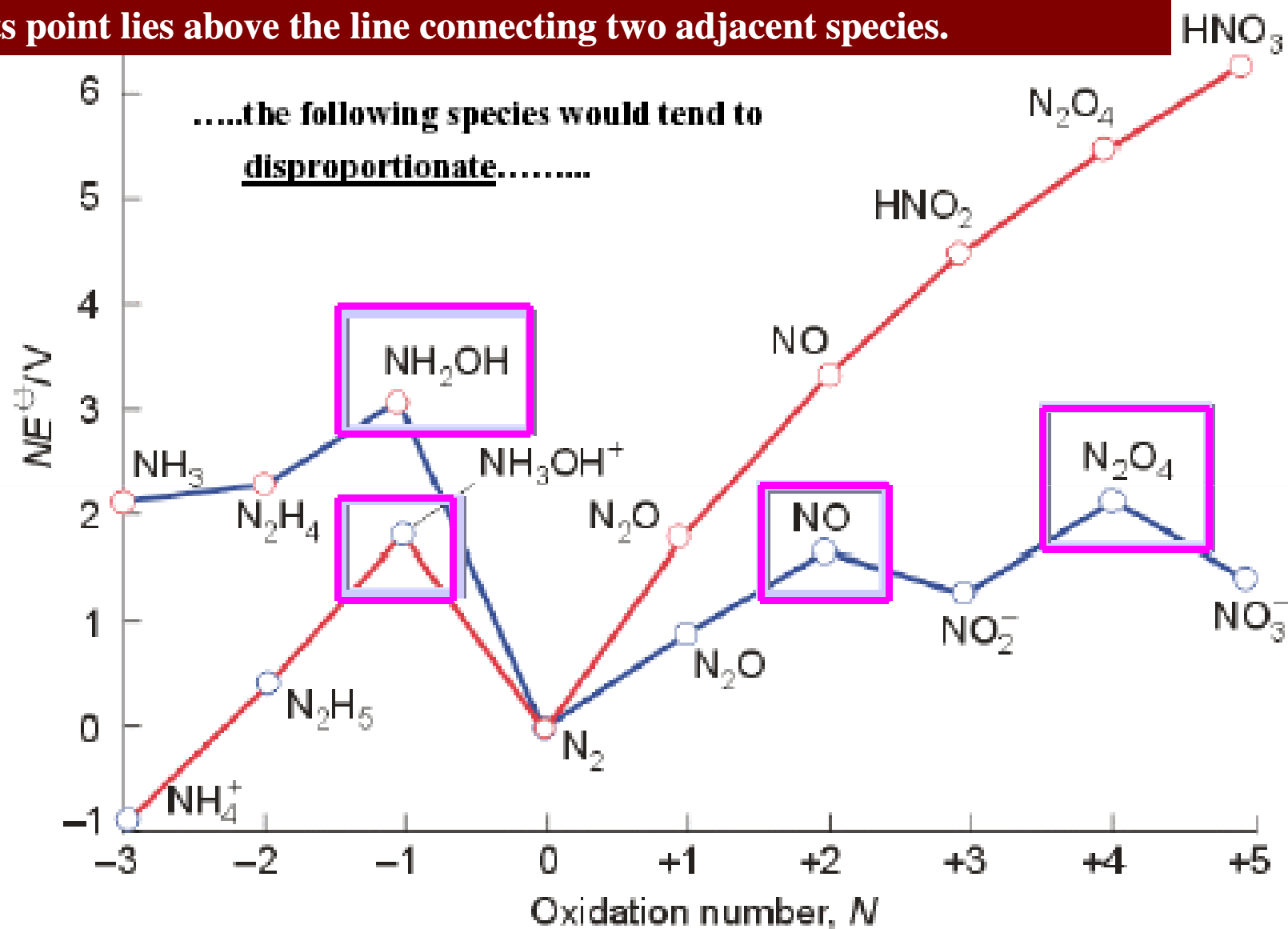
But, keep in mind that this potential only corresponds to the potential at which a given species converts to its elemental form

Disproportionation

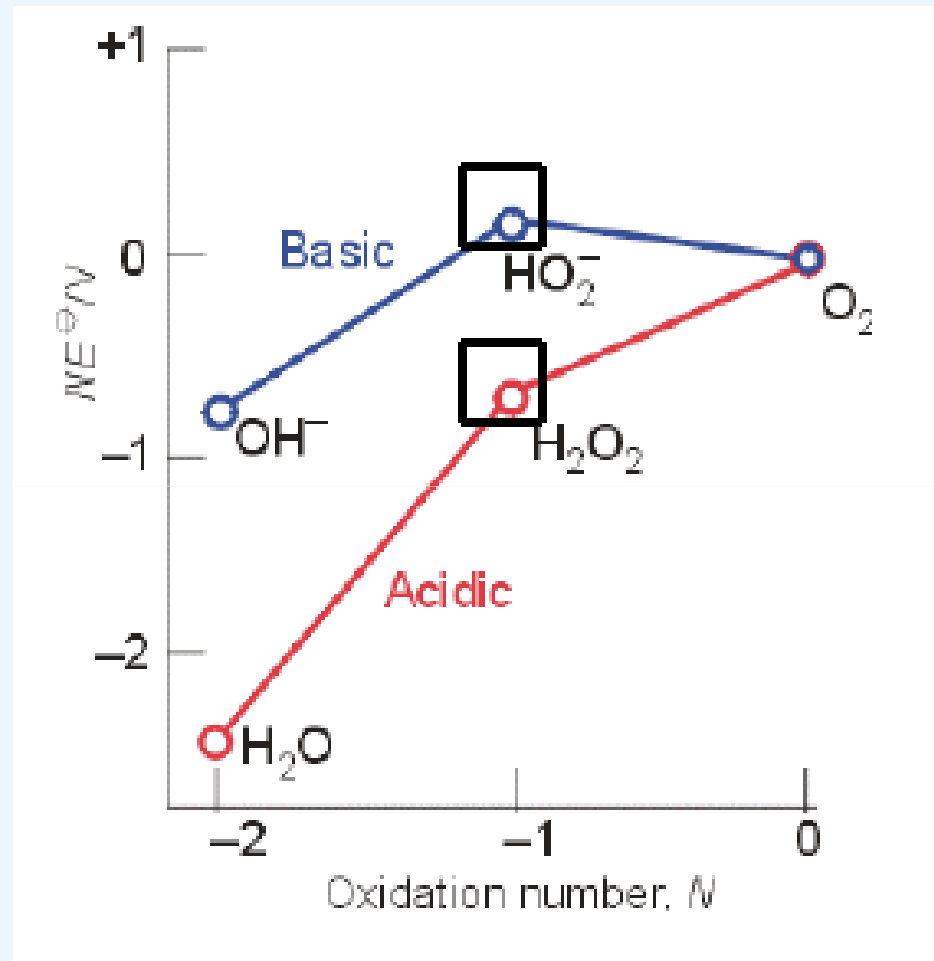
What Frost diagram tells about this reaction?



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

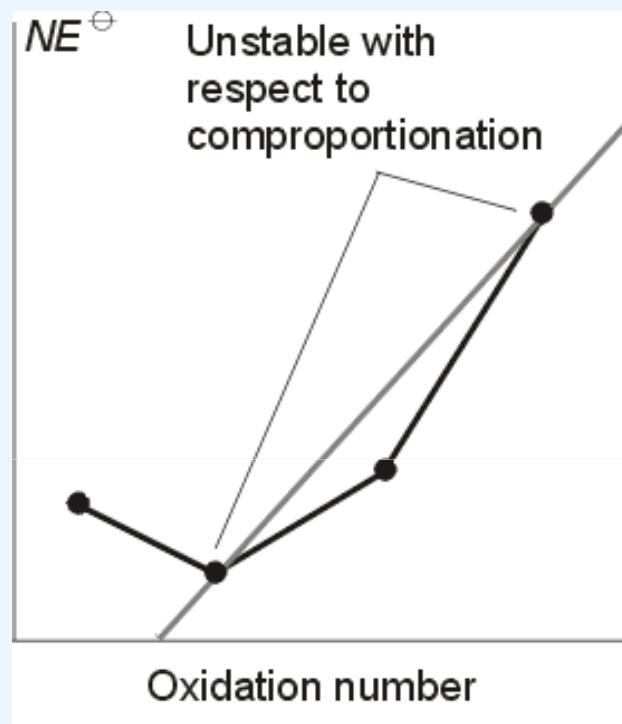


Disproportionation.... another example



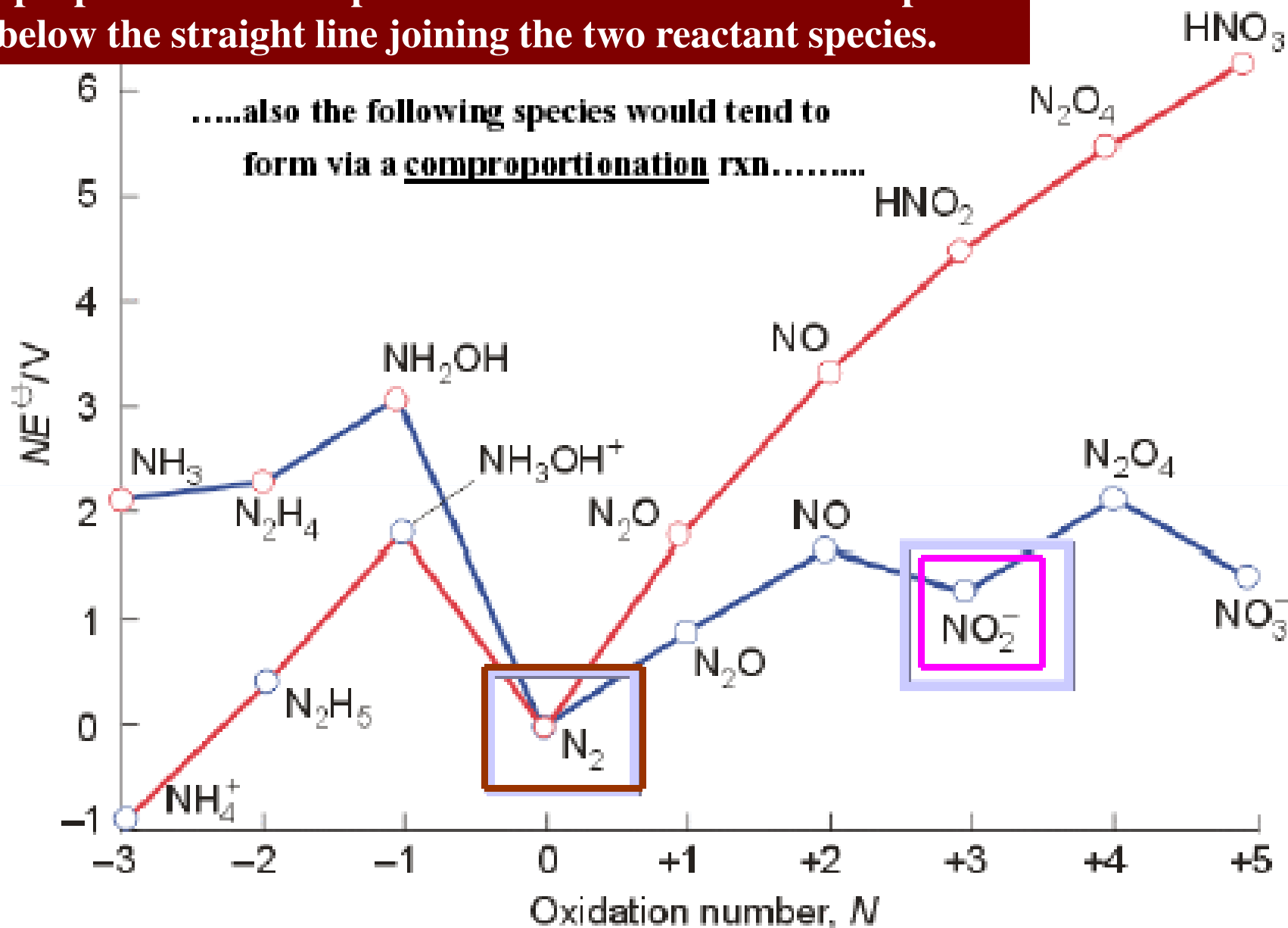
this is peroxide auto decomposition

Comproportionation reaction



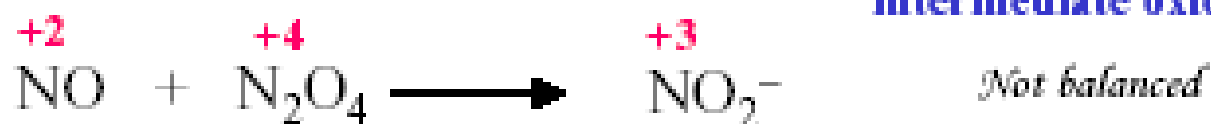
In comproportionation, the reverse of disproportionation, two species with the same element in different OS form a product in which the element is in intermediate OS

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

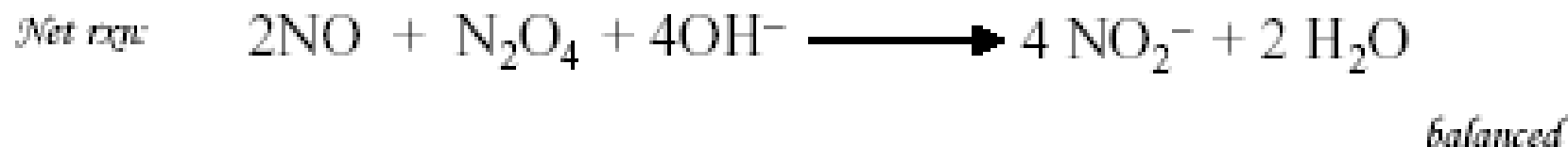


Comproportionation Reactions:

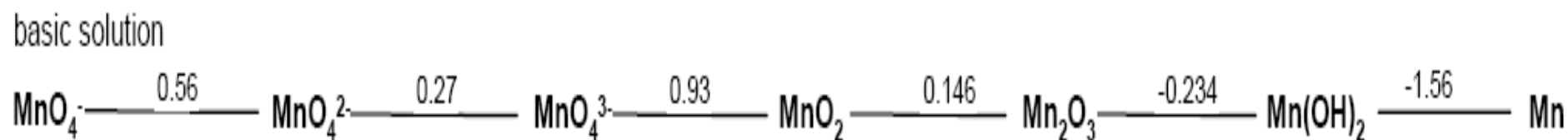
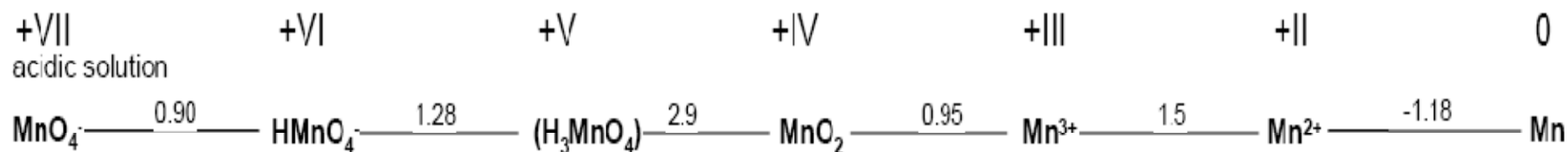
A higher oxidation state species combines with a lower oxidation state species to afford an intermediate oxidation state species



Half reactions:



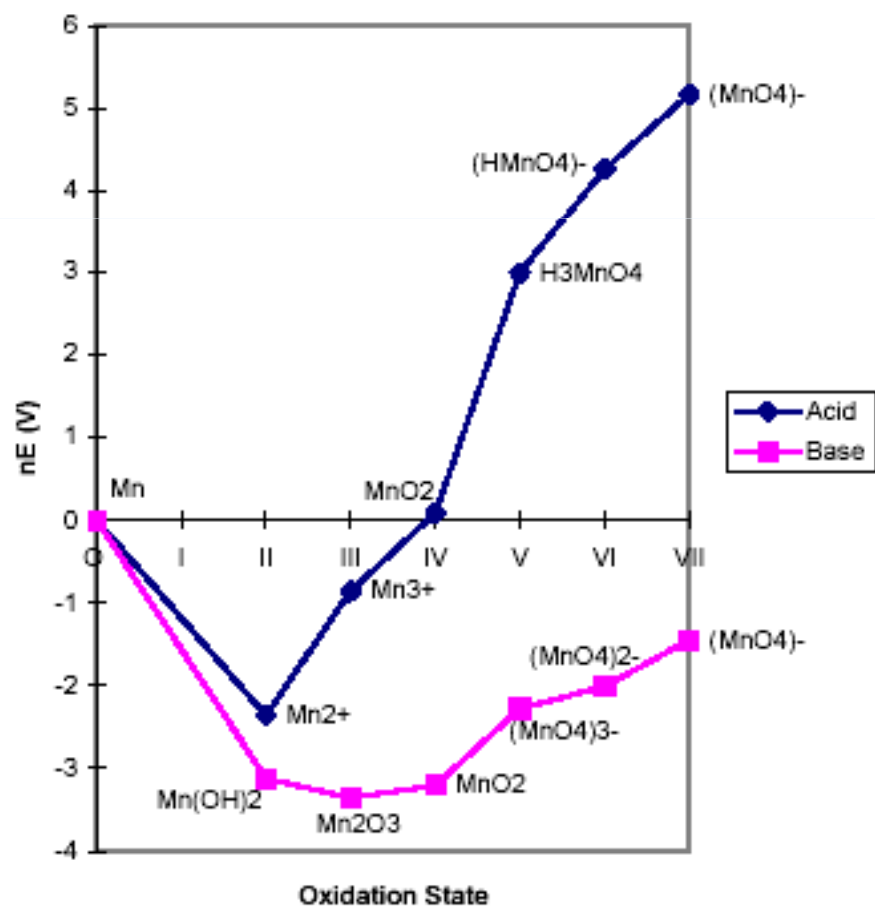
Construction of Frost diagram of Mn from the following Latimer diagram



Comproportionation: *In acidic solution...* $\text{Mn} + \text{Mn}^{3+} \longrightarrow \text{Mn}^{2+}$

In basic solution... $\text{MnO}_2 + \text{Mn(OH)}_2 \longrightarrow \text{Mn}_2\text{O}_3$

Frost Diagram for Manganese



From diagram comment on
Stability of Mn^{3+} in acidic sol

disproportionation

Mn^{3+} lies above the line joining MnO_2
& Mn^{2+}

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: $\text{MnO}_4^{3-} \longrightarrow \text{MnO}_2$ 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^- - oxidizing agent.**

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