There are three convenient ways to graphically summarize an element’s redox properties:

- Latimer diagram
- Frost diagram
- Pourbaix diagram

Latimer Diagram (for Oxygen)

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

Frost Diagram

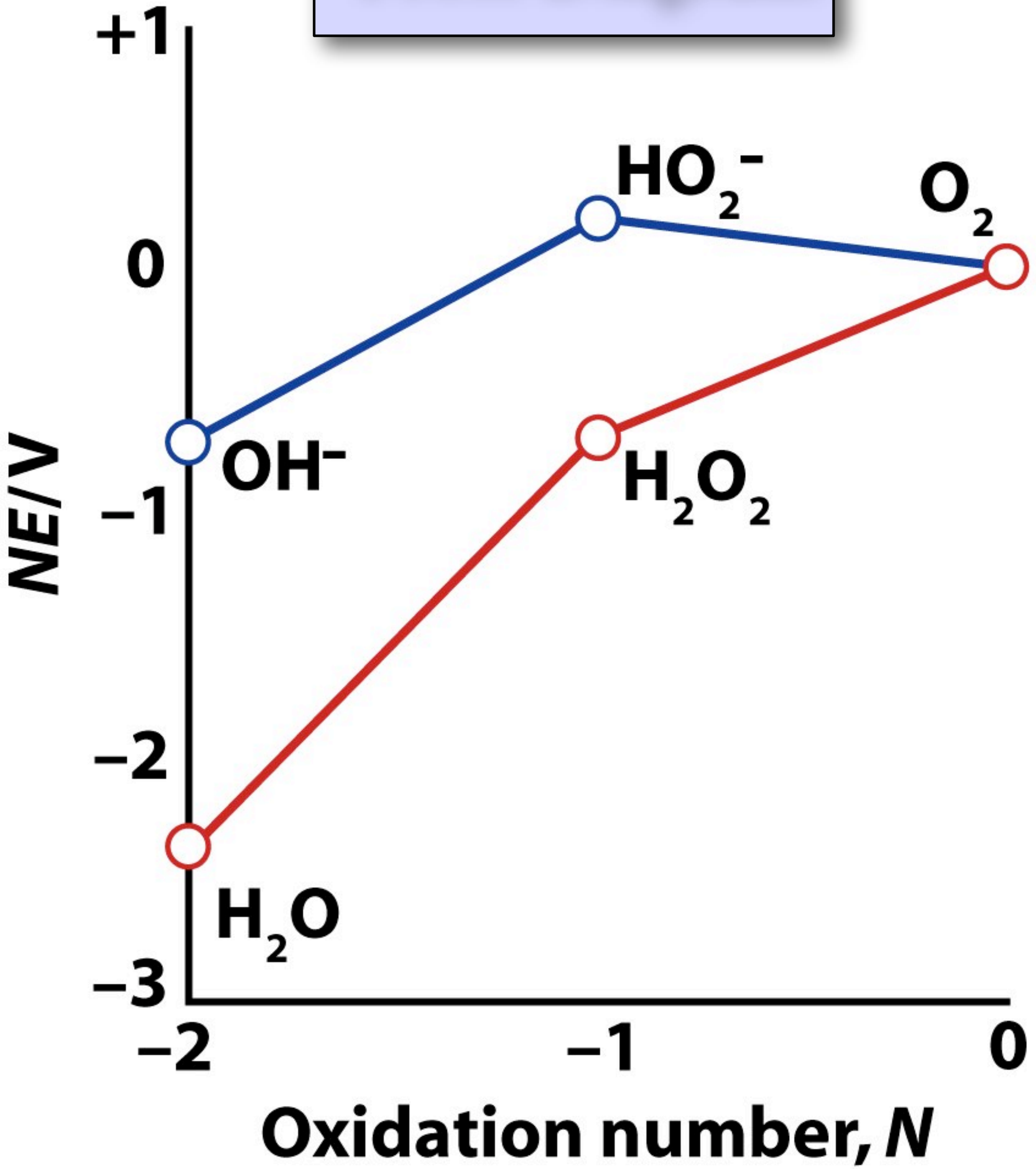

Fig 5.7

Pourbaix Diagram

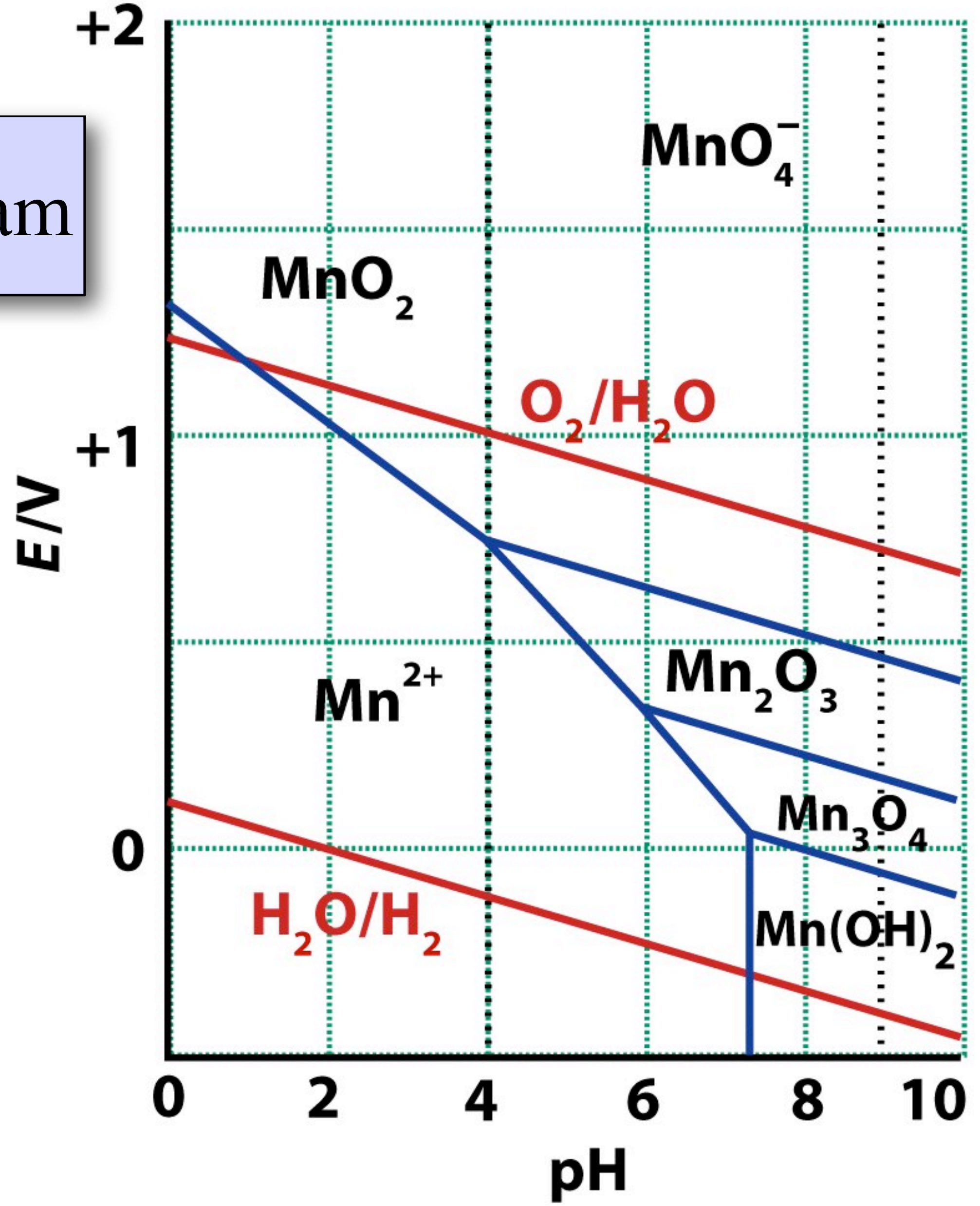

Fig 5.13

Figure 5-13

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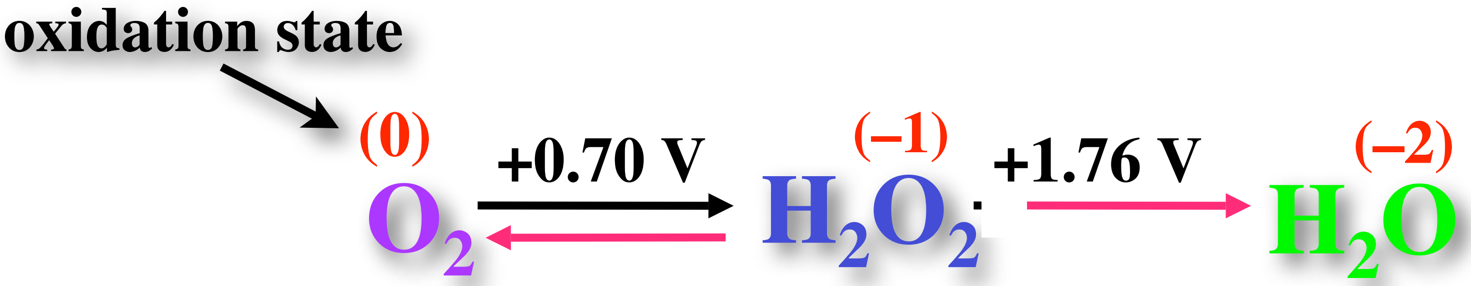
Latimer Diagrams

- written with the most oxidized species on the left, and the most reduced species on the right

- you can determine whether a species in an **intermediate** oxidation state will **disproportionate**, ie, convert to the more **oxidized species** to its right and the more **reduced species** to its left, by comparing the redox potential for its formation *vs.* the redox potential for its reduction



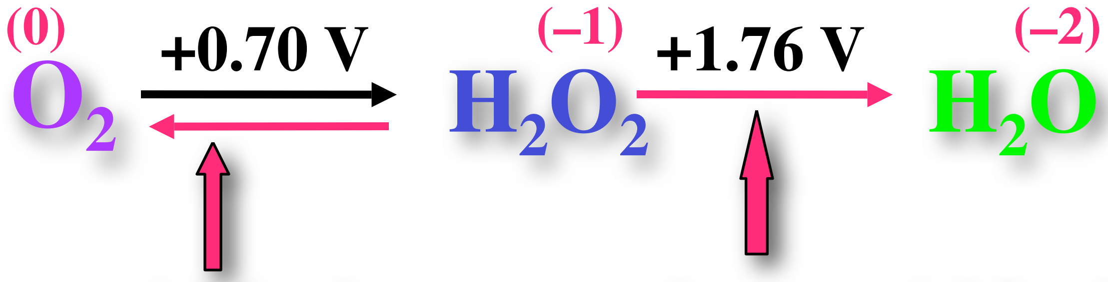
oxidation state

$$\overset{(0)}{O_2} \overset{+0.70\ V}{\rightleftarrows} \overset{(-1)}{H_2O_2} \xrightarrow{+1.76\ V} \overset{(-2)}{H_2O}$$

Latimer Diagrams

- you can determine whether a species in an **intermediate** oxidation state will **disproportionate**, ie, convert to the more **oxidized species** to its left and the more **reduced species** to its right, by comparing the redox potential for its formation *vs*. the redox potential for its reduction

example



$$\overset{(0)}{O_2} \underset{\longleftarrow}{\xrightarrow{+0.70\ V}} \overset{(-1)}{H_2O_2} \xrightarrow{+1.76\ V} \overset{(-2)}{H_2O}$$

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**

Disproportionation reaction:

$$H_2O_2 + \cancel{2e^-} + \cancel{2H^+} \longrightarrow 2\ H_2O$$ **reduction**

$$H_2O_2 \longrightarrow O_2 + \cancel{2e^-} + \cancel{2H^+}$$ **oxidation**

$$2\ H_2O_2 \longrightarrow O_2 + 2\ H_2O$$ **net rxn**

$$\begin{tikzcd} \overset{(0)}{O_2} \arrow[r, shift left, "\mathbf{+0.70\ V}"] & \overset{(-1)}{H_2O_2} \arrow[l, shift left, "\text{oxidation}"] \arrow[r, "\mathbf{+1.76\ V}", "\text{reduction}"'] & \overset{(-2)}{H_2O} \end{tikzcd}$$

Disproportionation reaction:

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

reduction

H_2O_2 acting as oxidant

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

oxidation

H_2O_2 acting as reductant

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

net rxn

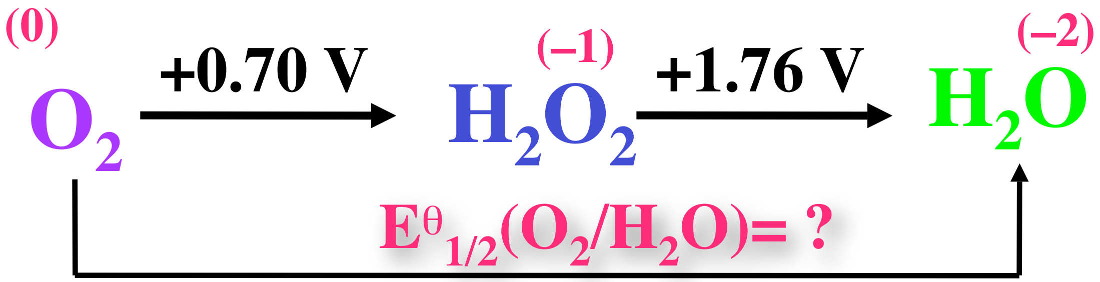
$$\Delta E = E^{\theta}(\text{oxidant}) - E^{\theta}\ (\text{reductant})$$

$$\Delta E = +1.76\ V - +0.70\ V = +1.06\ V$$

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

$$\overset{(0)}{O_2} \xrightarrow{+0.70\ V} \overset{(-1)}{H_2O_2} \xrightarrow{+1.76\ V} \overset{(-2)}{H_2O}$$

If we’re given

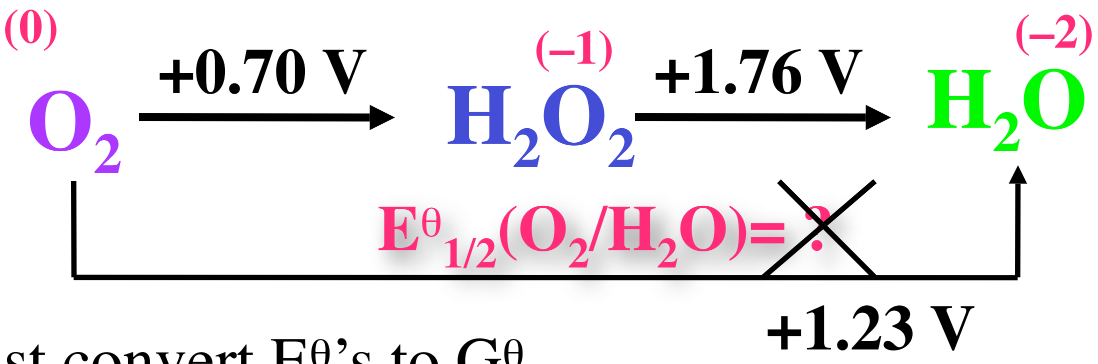


$$\overset{(0)}{O_2} \xrightarrow{+0.70\ V} H_2\overset{(-1)}{O_2} \xrightarrow{+1.76\ V} H_2\overset{(-2)}{O}$$

$E^{\theta}_{1/2}(O_2/H_2O) = ?$

Then, how do we calculate $E^{\theta}_{1/2}(O_2/H_2O) = ?$

- We don’t simply add E^{θ}’s, because E^{θ} is <u>not</u> a path–independent state function.
- G^{θ} on the other hand <u>is</u> a path–independent state function.
- So, we must first convert E^{θ}’s to G^{θ}



$$\overset{(0)}{O_2} \xrightarrow{+0.70\ V} \overset{(-1)}{H_2O_2} \xrightarrow{+1.76\ V} \overset{(-2)}{H_2O}$$

$E^{\theta}_{1/2}(O_2/H_2O) = \cancel{?}$

+1.23 V

We must convert Eθ's to Gθ

$$G^{\theta}(O_2/H_2O) = G^{\theta}(O_2/H_2O_2) + G^{\theta}(H_2O_2/H_2O)$$

$$-nFE^{\theta}(O_2/H_2O) = -nFE^{\theta}(O_2/H_2O_2) + -nFE^{\theta}(H_2O_2/H_2O)$$

$$4E^{\theta}(O_2/H_2O) = 2E^{\theta}(O_2/H_2O_2) + 2E^{\theta}(H_2O_2/H_2O)$$

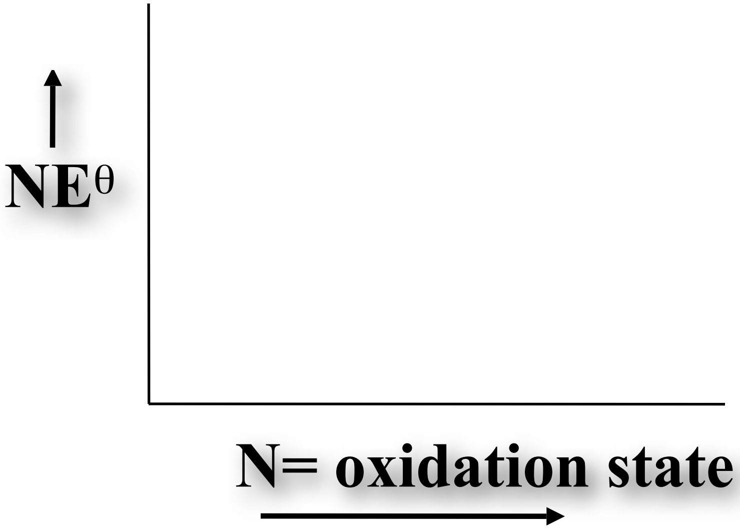
$$E^{\theta}(O_2/H_2O) = \frac{E^{\theta}(O_2/H_2O_2) + E^{\theta}(H_2O_2/H_2O)}{2}$$ ***= the average***

thus,

$$E^{\theta}(O_2/H_2O) = (+0.70\ V + +1.76\ V)/2 = +2.46/2 = +1.23$$

Frost Diagrams

- Graphically illustrate the stability of different oxidation states <u>relative to</u> its <u>elemental form</u> (ie, relative to **oxidation state= 0**)



NE^{θ}

N= oxidation state

Nitrogen Frost Diagram

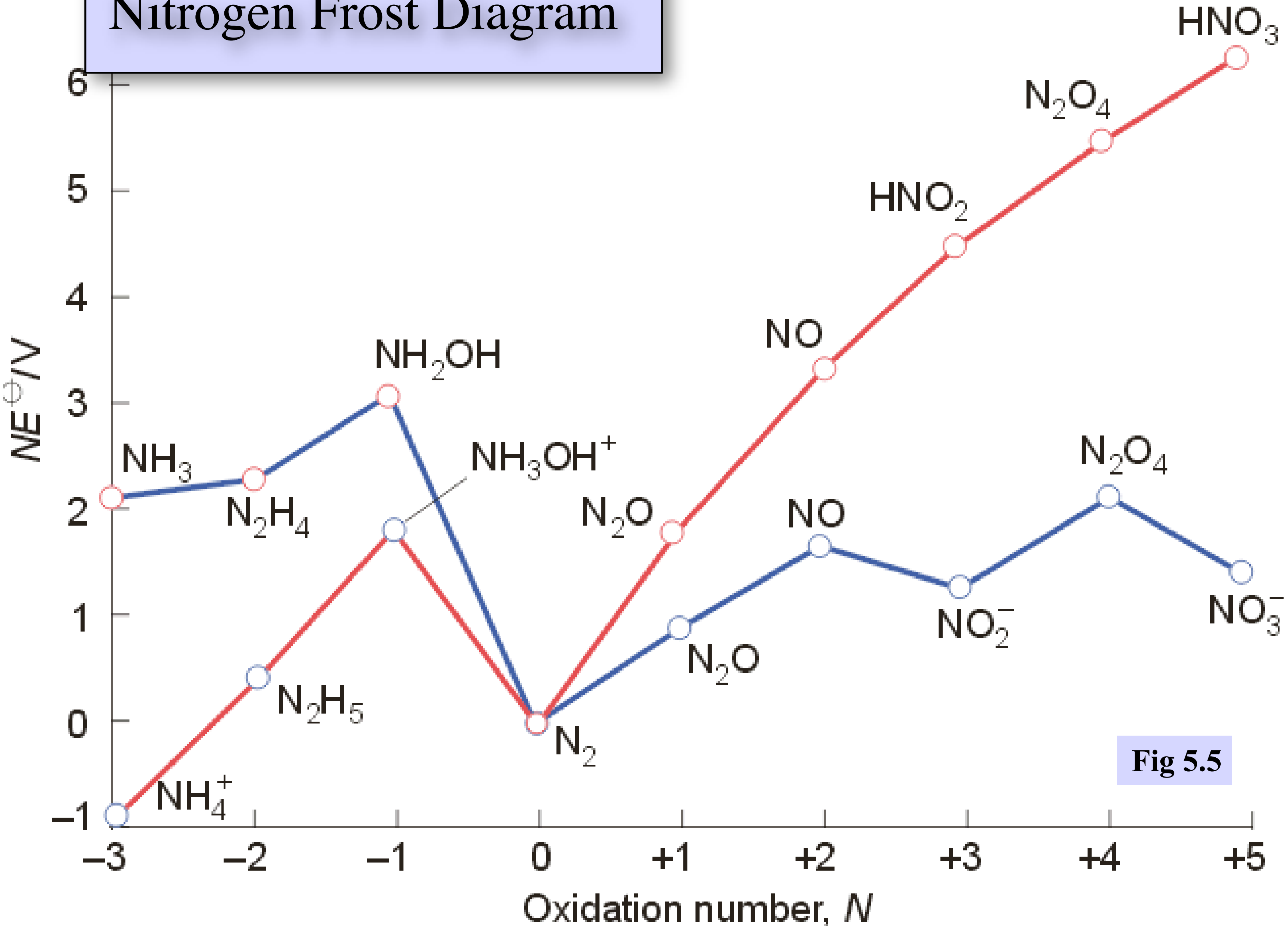
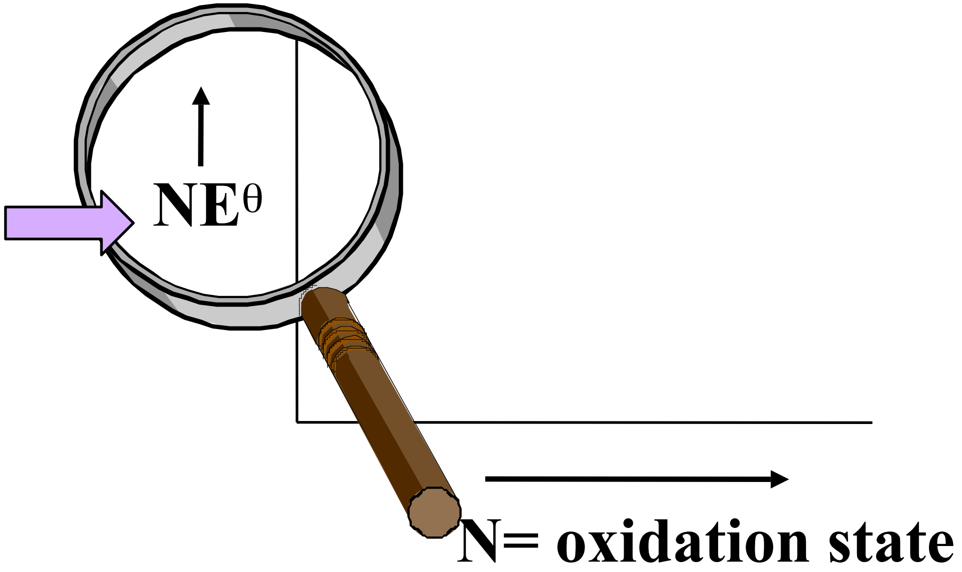


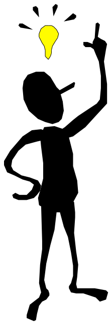
Fig 5.5

Frost Diagrams

note the similarity between this term

and $n\Delta E^{\theta} = -\Delta G^{\theta}/F$





……except it contains NE^{θ} instead of $n\Delta E^{\theta}$

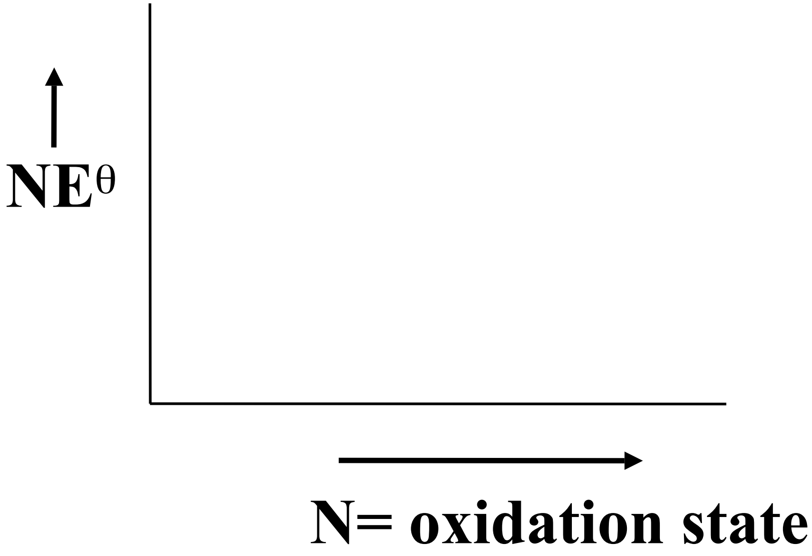
oxidation state

# of electrons

However perhaps this is not that different after all…………….

oxidation state= # electrons required to reduce or oxidize a compound to its elemental form, *ie* N_2 in this case.

Frost Diagrams



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

  (ie, $NE^{\theta} = -G^{\theta}/F$)

Frost Diagrams

so, the position of a nitrogen compound on this graph gives us its stability relative
to N_2

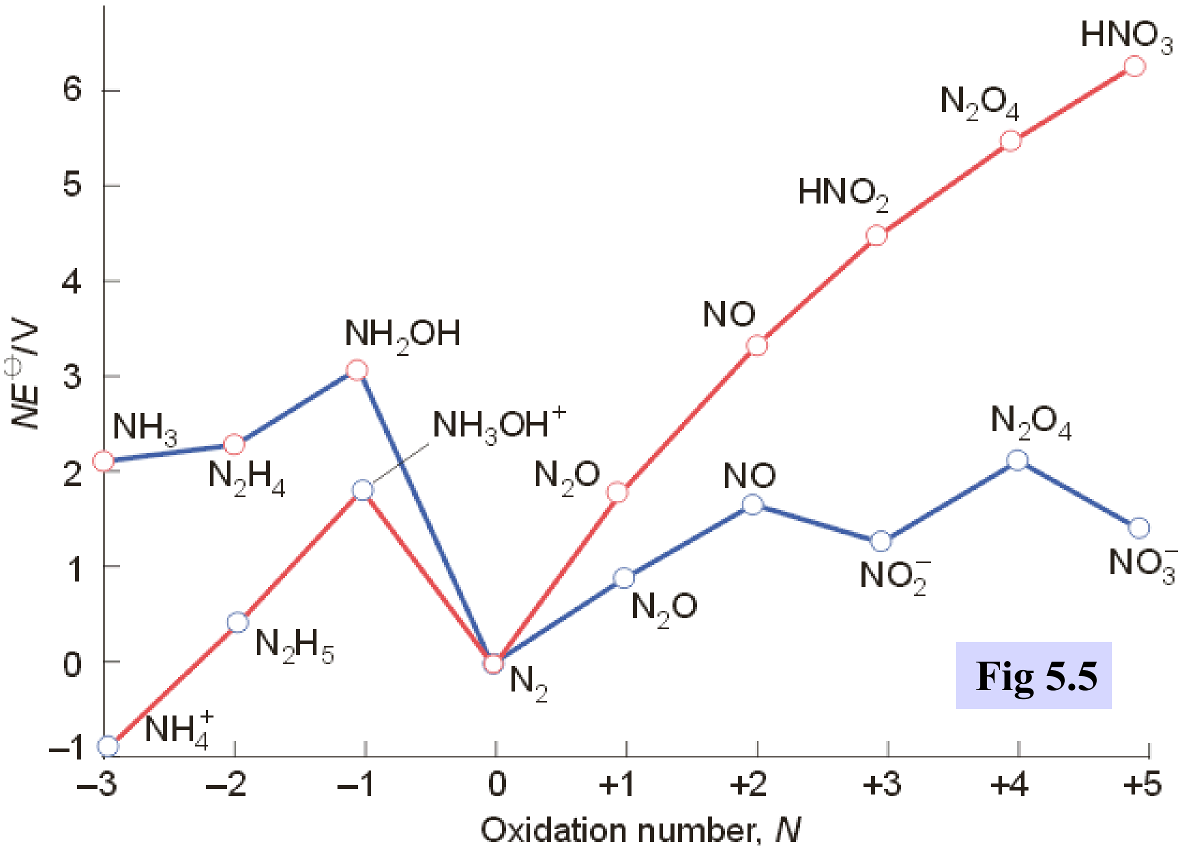


Fig 5.5

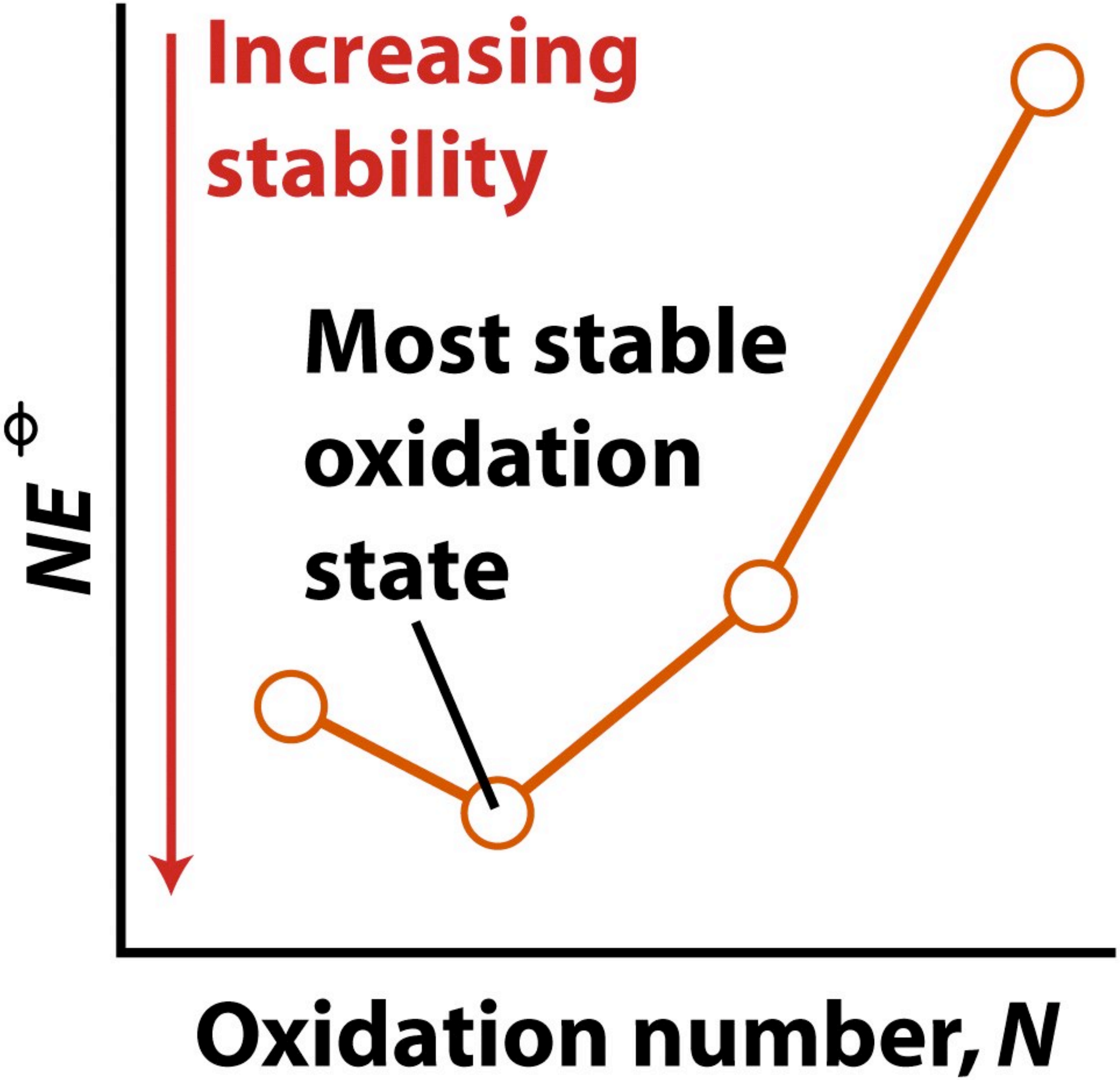


Fig 5.6

Figure 5-6
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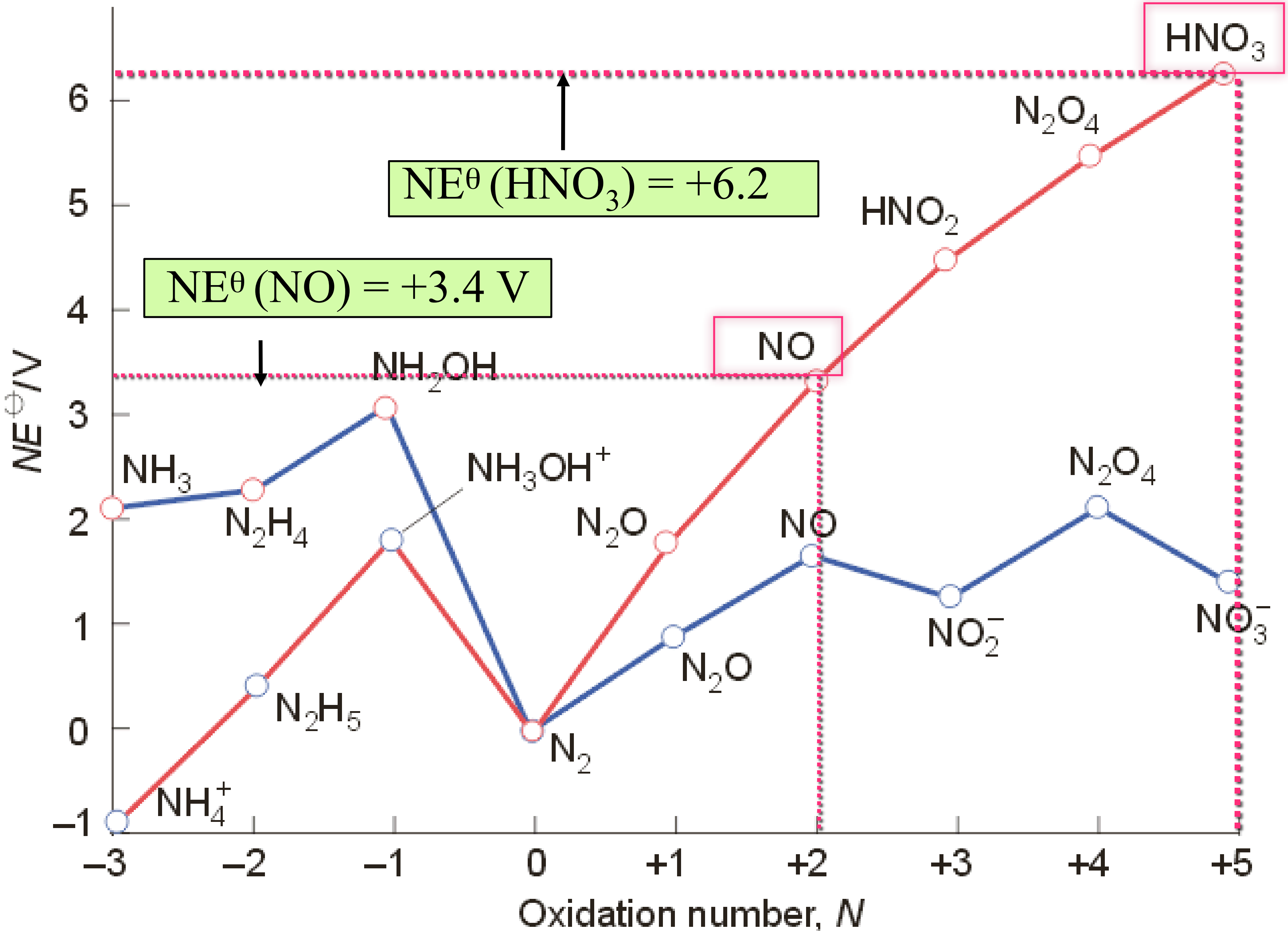
We can use a Frost Diagram to determine a number of things about a given compound……….

For example



$NE^{\theta}(HNO_3) = +6.2$

$NE^{\theta}(NO) = +3.4$ V

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

$N = +2$

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

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

The slope of the lines connecting species on a Frost diagram is equal to the redox potential for the rxn converting the species on the right to the species on the left

How so?

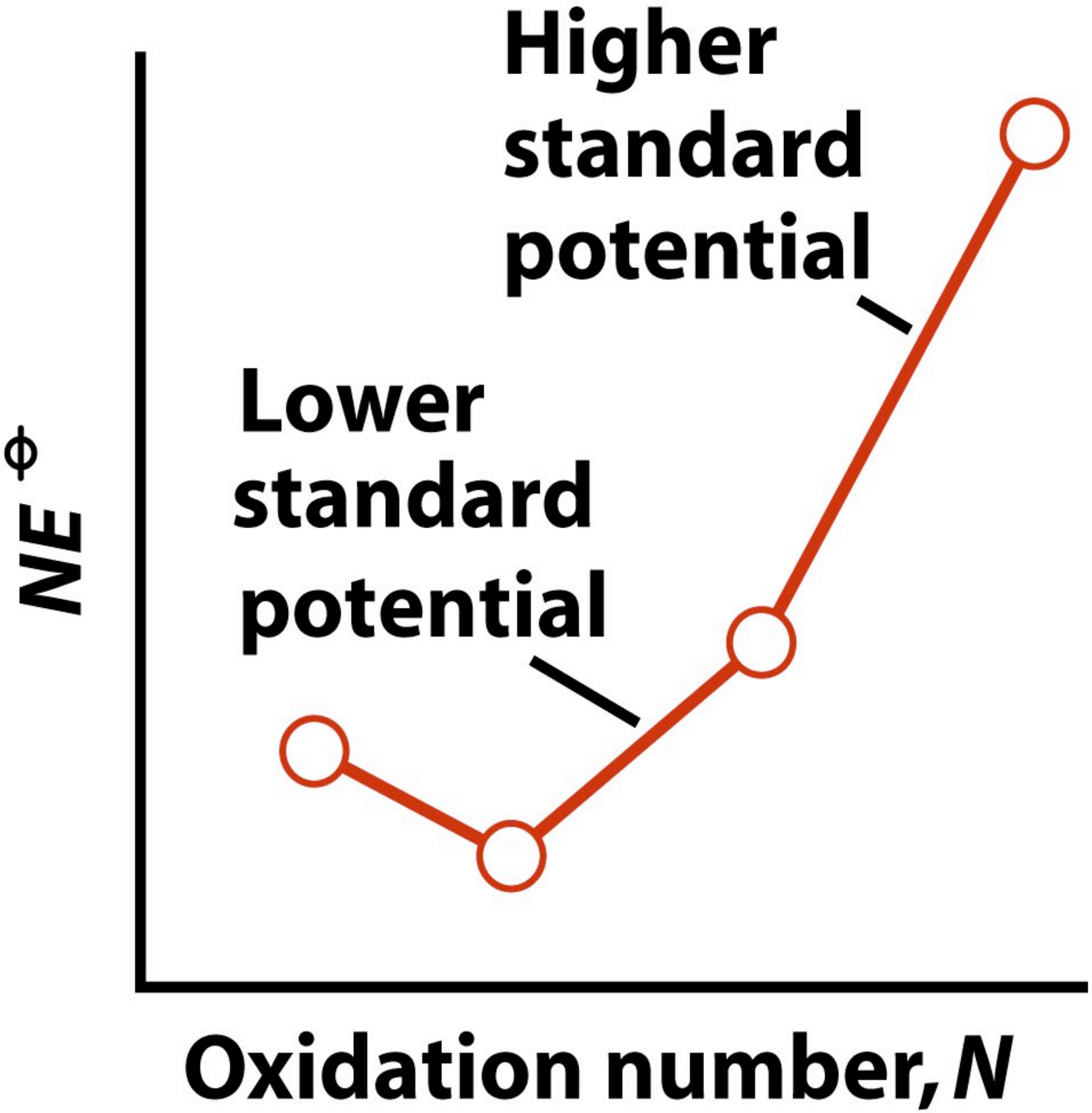


Figure 5-9a

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Frost Diagram

example