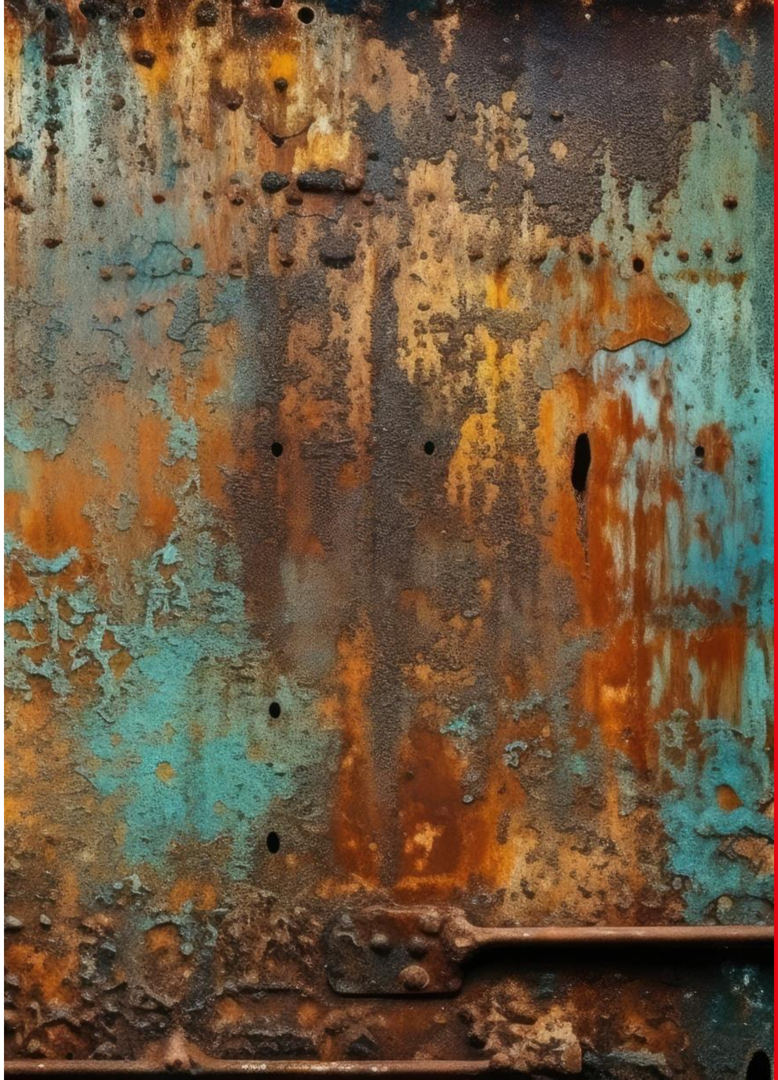

# Redox reactions in the environment

ENV-200

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# Exercise 1: Reduction potentials

1. Can $NOM_{red}$ react with $O_2$ to form $NOM_{ox}$ and $H_2O$? Yes.
2. Can $NOM_{red}$ react with $Fe^{2+}$ to form $NOM_{ox}$ and $Fe^0$? No.

Remember: $\Delta G = -n F E$
- $\Delta G > 0$: reaction not feasible
- $\Delta G < 0$: reaction is feasible (but may be kinetically limited)

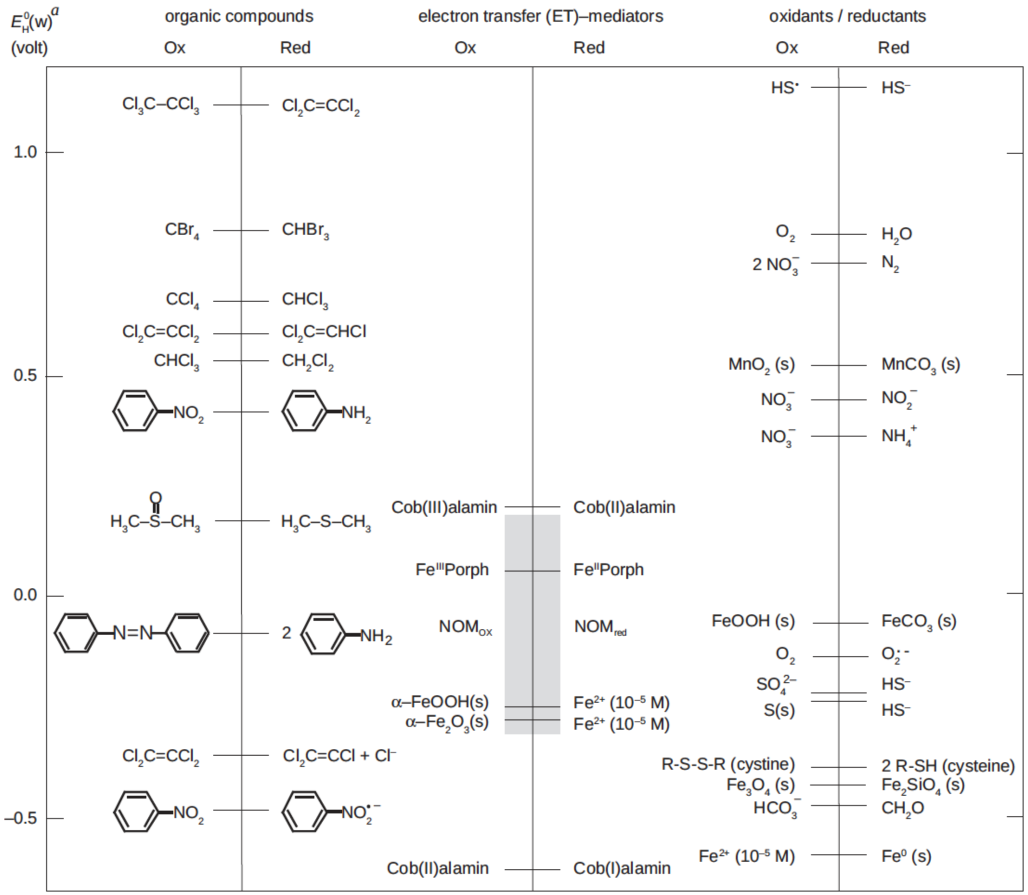


*Figure 23.3 in Environmental Organic Chemistry, by Schwarzenbach, Gschwend, Imboden (Edition 3, Wiley).*



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# Exercise 2: Nitrogen redox reactions

Determine the pe-pH relationship for the two equations below. The final equations should be in the form of pe = x + ypH.

| Redox couple | Reaction | log(K) |
| --- | --- | --- |
| N(V) / N(III) | $NO_2^- + H_2O = NO_3^- + 2H^+ + 2e^-$ | -28.57 |
| N(V) / N(0) | $N_2 + 6H_2O = 2\ NO_3^- + 12H^+ + 10e^-$ | -207.08 |

# Exercise 2: Solution

For each N redox reaction, the law of mass action gives the pe-pH relationship. So, for the first reaction

$NO_2^- + H_2O = NO_3^- + 2H^+ + 2e^-$ $\qquad$ $\log(K) = -28.57$

$\log(K) = -28.57 = \log([NO_3^-]) - 2pH - 2pe - \log([NO_2^-])$

i.e.,

$pe = 14.285 + \frac{1}{2}\log([NO_3^-]) - \frac{1}{2}\log([NO_2^-]) - pH$

Similarly, for the other equation:

$N_2 + 6H_2O = 2NO_3^- + 12H^+ + 10e^-$ $\qquad$ $\log(K) = -207.08$

$pe = 20.708 - 6/5pH + 1/5\log([NO_3^-]) - 1/10\log([P_{N2}])$

# Construction of pe-pH diagram for N species





We do the same for the remaining equations in the table:

$2NH_4^+ = N_2 + 8H^+ + 6e^-$ $\log(K) = -31.074$

$pe = 5.179 – 1/3 \log([NH_4^+]) – 4/3 pH + 1/6 \log([P_{N2}])$

and

$NH_4^+ = NH_3 + H^+$ $\log(K) = -9.252$

$pH = 9.252 – \log([NH_4^+]) + \log([NH_3])$

Note that we are ignoring $NO_2^-$ for now as it is metastable.

# Exercise 3: Interpreting pe-pH relationships

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We now have the following relationships:

N(V)/N(III)

$$pe = 14.285 + \tfrac{1}{2}\log([NO_3^-]) - \tfrac{1}{2}\log([NO_2^-]) - pH$$

N(V)/N(0)

$$pe = 20.708 - 6/5pH + 1/5\log([NO_3^-]) - 1/10\log([P_{N2}])$$

N(0)/N(-III)

$$pe = 5.179 - 1/3\log([NH_4^+]) - 4/3pH + 1/6\log([P_{N2}])$$

$NH_4^+/NH_3$ dissociation

$$pH = 9.252 - \log([NH_4^+]) + \log([NH_3])$$

When plotted on a pe-pH diagram, how will these relationships look? Assume that all N species have unit activities.

# Exercise 3: Solution



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N(V)/N(III)

$$pe = 14.285 + \frac{1}{2}\log([NO_3^-]) - \frac{1}{2}\log([NO_2^-]) - pH$$

pe varies with pH

N(V)/N(0)

$$pe = 20.708 - 6/5pH + 1/5\log([NO_3^-]) - 1/10\log([P_{N2}])$$

pe varies with pH

N(0)/N(-III)

$$pe = 5.179 - 1/3\log([NH_4^+]) - 4/3pH + 1/6\log([P_{N2}])$$

pe varies with pH

$NH_4^+/NH_3$ dissociation

$$pH = 9.252 - \log([NH_4^+]) + \log([NH_3])$$

Vertical line on pe-pH diagram

If all N species have unit activities, they disappear from the above equations. Then it is easily seen that the N(V)/N(0) line occurs at high pe, with the N(0)/N(-III) line below it. The pH line is vertical at the value 9.252. $NH_4^+$ lies to the left of this line and $NH_3$ to the right.

# Construction of pe-pH diagram for N species

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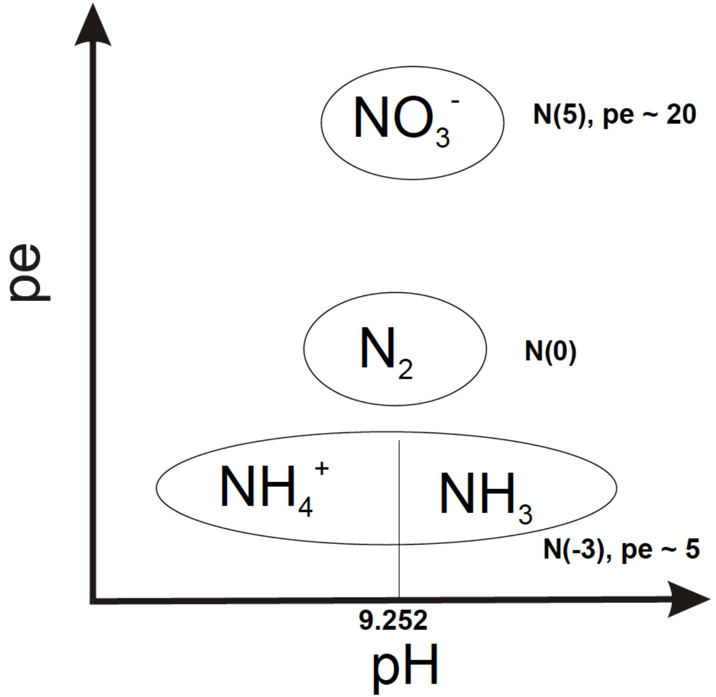
More oxidized species at high pe

More reduced species at low pe




More protonated species at low pH

Less protonated species at high pH

# Construction of pe-pH diagram for N species



Now we want to draw lines between the species in the figure below to delineate the pe-pH range in which they dominate.

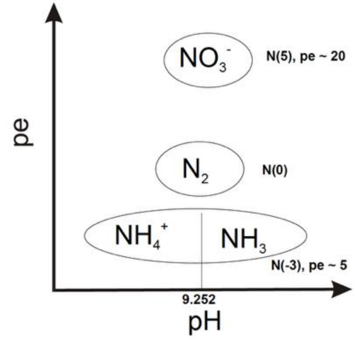
Each of the derived pe-pH equations defines a straight line

By choosing appropriate values for the activities of the various species involved, the stability diagram can be completed The stability diagram will vary according to the activities selected!

Choose equal activities, unless there are other “typical” values that would be more appropriate

For N: $[P_{N2}]$, $[NO_3^-]$, $[NH_4^+]$ and $[NH_3]$ must be selected

- $[P_{N2}]$ Atmospheric pressure of $N_2$ is 0.77
- $[NO_3^-]$ Assume polluted groundwater, activity ~$10^{-3}$
- $[NH_4^+]$ Take same value as $[NO_3^-]$
- $[NH_3]$ Take same value as $[NO_3^-]$



# Construction of pe-pH diagram for N species

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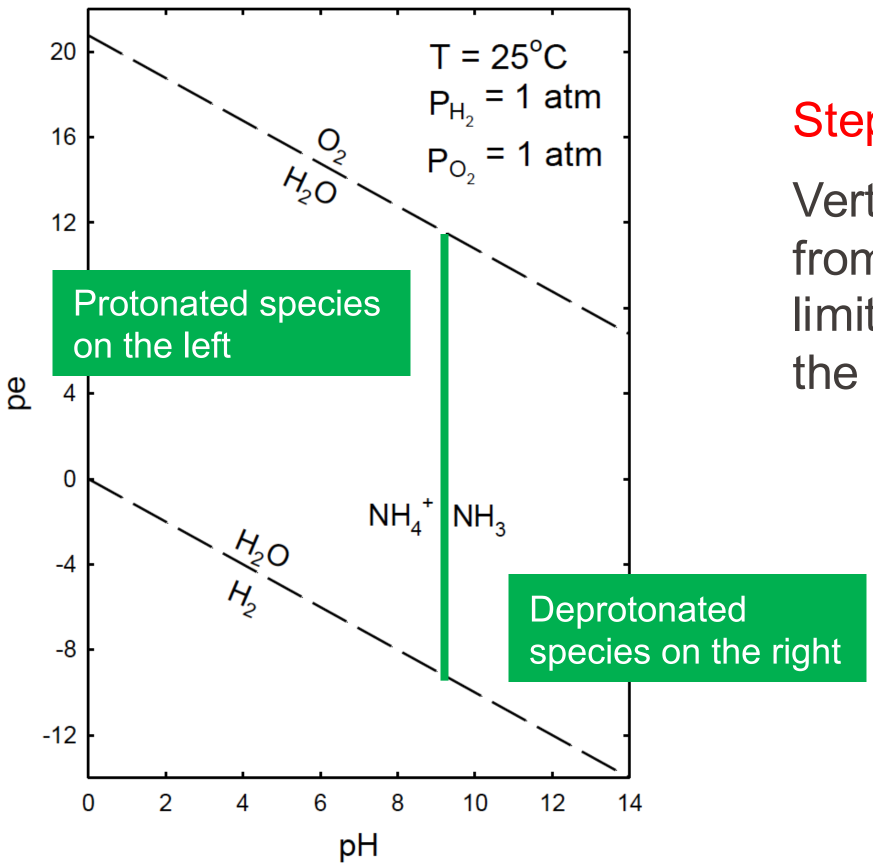


## Step 1: add $NH_4^+$ / $NH_3$ boundary

Vertical line at pH = 9.25 is plotted from upper to lower water stability limit since it is not yet known where the other lines will intersect it.

# Construction of pe-pH diagram for N species

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## Step 2: add $N_2(g)$ / $NH_4^+$ boundary

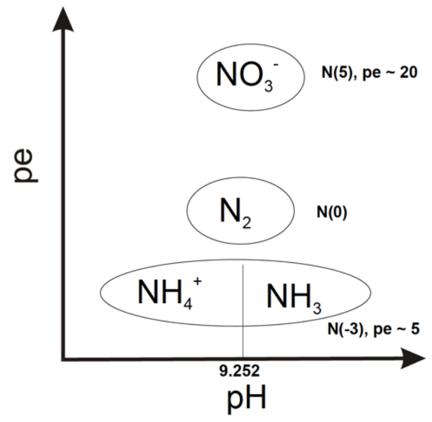
Recall:

N(0)/N(-III)

$$pe = 5.179 - 1/3\log([NH_4^+]) - 4/3pH + 1/6\log([P_{N2}])$$

with $[NH_4^+] = 10^{-3}$ and $\log([P_{N2}]) = \log(0.77)$:

$$pe = 6.16 - 4/3pH$$



# Construction of pe-pH diagram for N species



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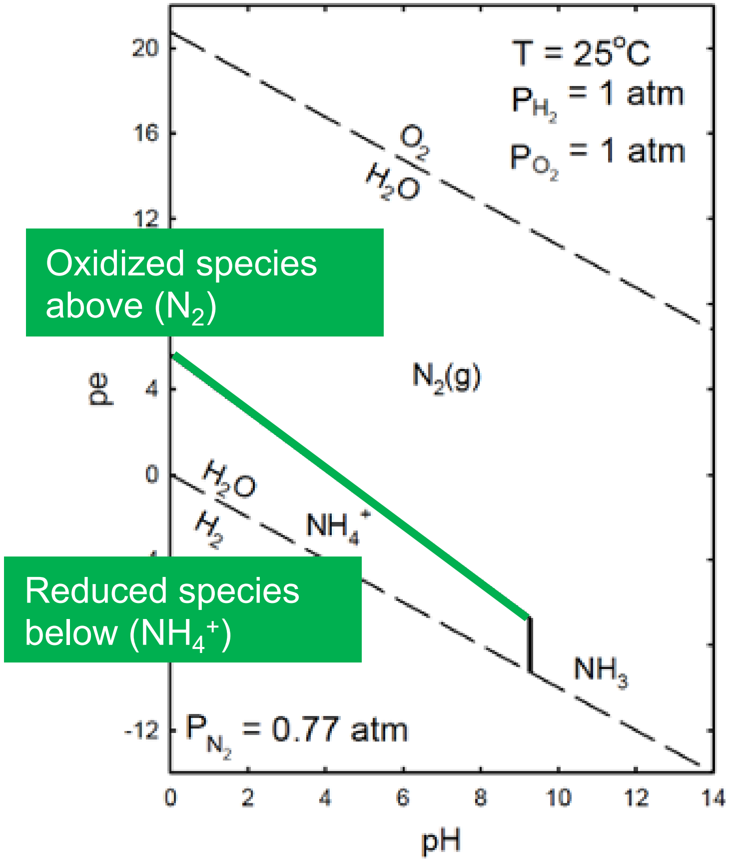


## Step 2: add $N_2$(g) / $NH_4^+$ boundary

$$pe = 6.16 - 4/3pH$$

The $N_2$(g) / $NH_4^+$ boundary intersects the $NH_4^+$ / $NH_3$ boundary at pe = -6.18 and pH = 9.252. The $NH_4^+$ field is now enclosed.

This means: $NH_4^+$ is never the dominant species at pe values above the green line, as it will oxidize to $N_2$. It also never dominates to the right of the verticle line, as it will deprotonate.

# Construction of pe-pH diagram for N species



## Step 3: add $N_2(g)$ / $NH_3$ boundary

Recall:

N(0)/N(-III)

$$pe = 5.179 – 1/3\log([NH_4^+]) – 4/3pH + 1/6\log([P_{N2}])$$

$NH_4^+/NH_3$ dissociation

$$pH = 9.252 - \log([NH_4^+]) + \log([NH_3])$$

Eliminate $\log([NH_4^+])$ from the first eq. using the second eq:

$$pe = 2.095 – 1/3\log([NH_3]) – pH + 1/6\log([P_{N2}])$$

With $[NH_3] = 10^{-3}$ and $N_2$ partial pressure of 0.77 atm this becomes

$$pe = 3.076 – pH \text{ (valid for pH > 9.252)}$$

Slope with pH changes from -4/3 to -1

# Construction of pe-pH diagram for N species



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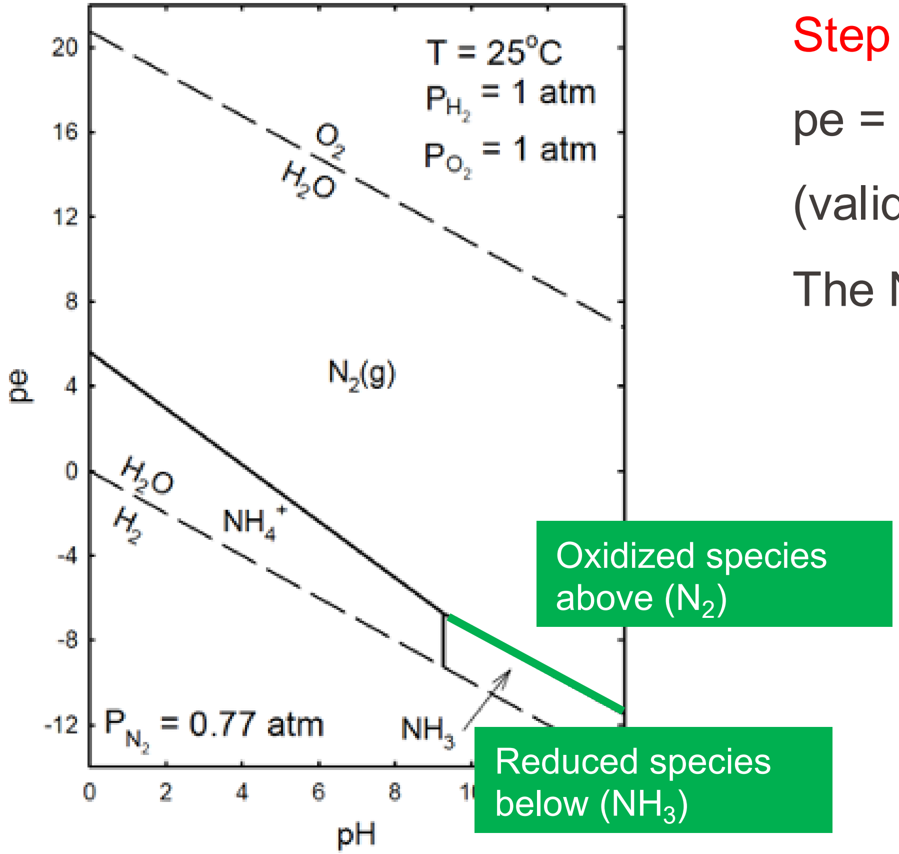



Step 3: add $N_2$(g) / $NH_3$ boundary

pe = 3.076 – pH

(valid for pH > 9.252)

The $NH_3$ field is enclosed.

# Construction of pe-pH diagram for N species

## Step 4: add $N_2(g)$ / $NO_3^-$ boundary

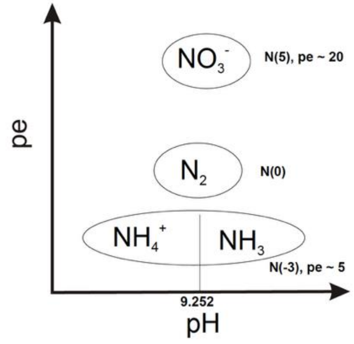
Recall:

N(V)/N(0)

$$pe = 20.708 - 6/5pH + 1/5\log([NO_3^-]) - 1/10\log([P_{N2}])$$

With $[NO_3^-] = 10^{-3}$ and $N_2$ partial pressure of 0.77 atm this becomes

$$pe = 21.32 - 6/5pH$$



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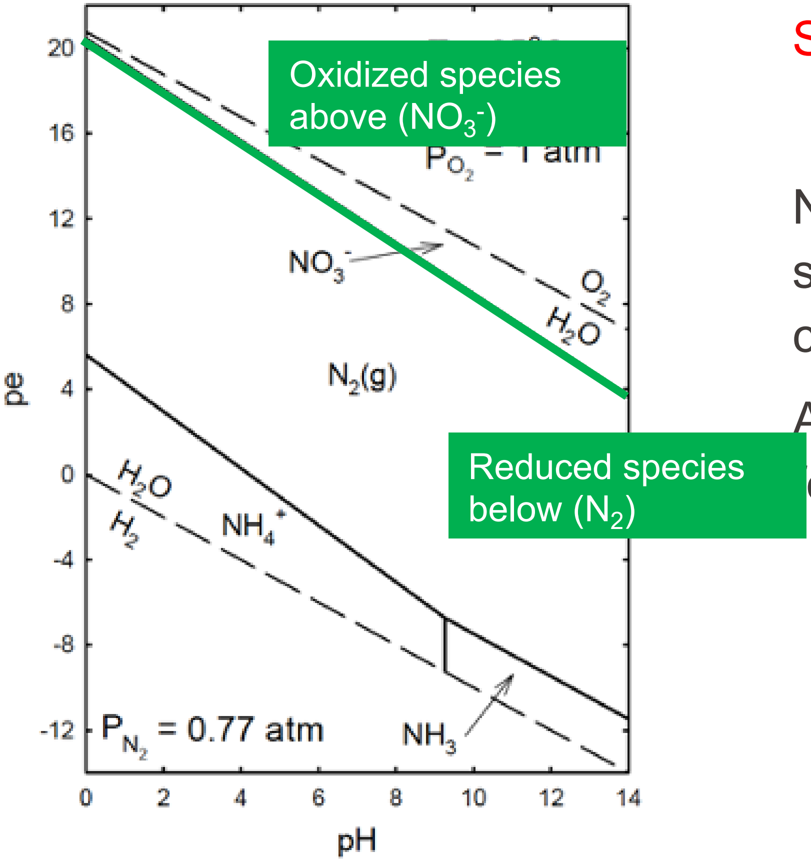
# Construction of pe-pH diagram for N species




## Step 4: add $N_2(g)$ / $NO_3^-$ boundary

$$pe = 21.32 - 6/5pH$$

$NO_3^-$ should be present in significant quantities only in waters containing free oxygen.

Ammonium ions and ammonia are found under reducing conditions.