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Correcting Frost Diagram Misconceptions Using Interactive Frost Diagrams

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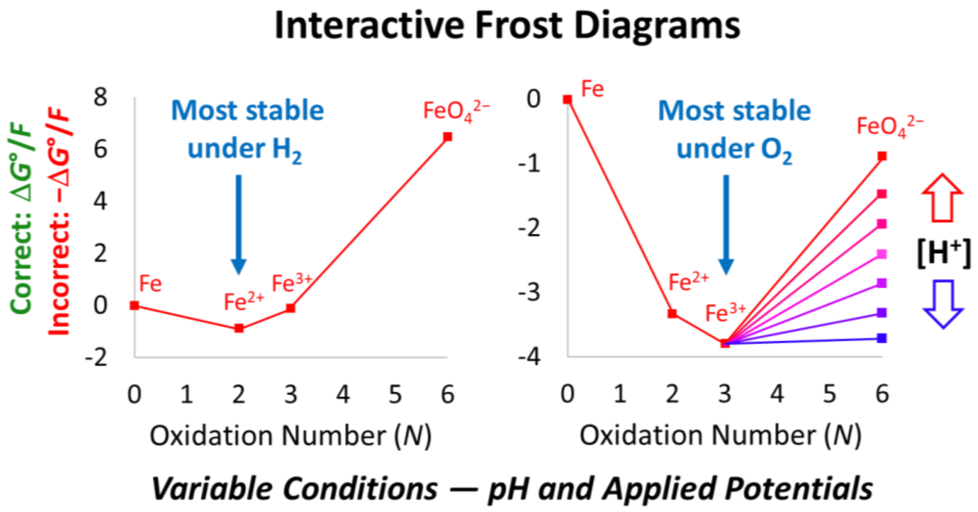
ABSTRACT

Frost diagrams provide convenient illustrations of the aqueous reduction potentials and thermodynamic tendencies of different oxidation states of an element. Undergraduate textbooks often describe the lowest point on a Frost diagram as the most stable oxidation state of the element, but this interpretation is incorrect because the thermodynamic stability of each oxidation state depends on the specific redox conditions in solution (i.e., the potential applied by the environment or an electrode). Further confusion is caused by the widespread use of different, contradictory conventions for labeling the y-axis of these diagrams as either n$E°$ or −n$E°$, among other possibilities. To aid in discussing and correcting these common mistakes, we introduce a series of interactive Frost diagrams that illustrate the conditional dependence of the relative stabilities of each oxidation state of an element. We include instructor's notes for using these interactive diagrams and a written activity for students to complete using these diagrams.

GRAPHICAL ABSTRACT



KEYWORDS

Undergraduate Instruction, Inorganic Chemistry, Redox, Frost Diagrams, Electrochemistry

Frost diagrams[1] provide a visual representation of reduction potentials and relative thermodynamic stabilities of different oxidation states of an element in aqueous conditions. In these diagrams (Figure 1), the oxidation number (*N*) of a common species (e.g., Fe^{2+}_{aq}) is plotted on the x-axis and its free energy (or a proportional value) relative to the $N = 0$ state is plotted on the y-axis. When the relative energy is provided as $\Delta G°/F$ (or $\Delta G/F$ if pH $\neq 0$ or 14), the slopes connecting each point correspond to the reduction potentials $E°$ (or E for pH $\neq 0$ or 14) connecting these oxidation states owing to the relationship $\Delta G° = -nFE°$. In this regard, Frost diagrams visually depict the electrode potentials tabulated in Latimer diagrams,[2] and both are often taught alongside other common redox diagrams such as Pourbaix diagrams.[3] Together, these graphs provide complementary depictions of the relationship between reduction potentials and the thermodynamics of redox processes. However, we have identified two notable points of confusion in common explanations of Frost diagrams.

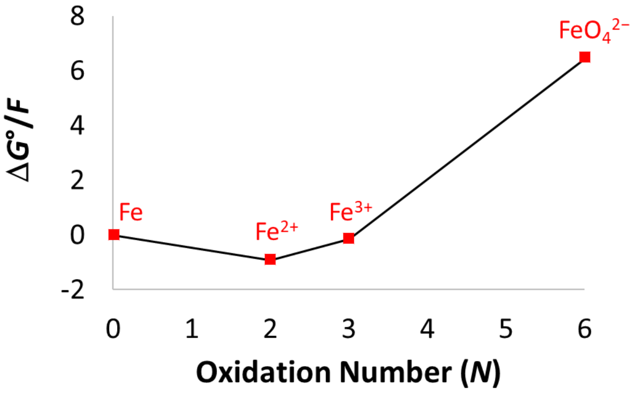


Figure 1. Frost diagrams for iron in pH = 0 solution.

Various textbooks and other resources utilize different, contradictory labels for the y-axis of Frost diagrams.[4-18] As originally intended by Frost,[1] the y-axis should be proportional to the free-energy change for conversion of the $N = 0$ oxidation state of an element to a higher or lower oxidation state. However, in providing the free energy in terms of electrode potentials, authors have chosen to label the y-axis as either $nE°$ or $-nE°$ to correspond to $\Delta G°/F$ (F = Faraday's constant). Either option can be considered correct depending on how n and $E°$ are defined, but the apparent contradiction has led some textbooks to incorrectly describe the y-axis as proportional to $-\Delta G°/F$,[6,12] which is unambiguously incorrect. We aim to highlight these contradictory conventions and suggest ways to avoid confusion over the correct quantitative relationship between free energy and reduction potentials.

A more substantial error concerns the interpretation of Frost diagrams. Many undergraduate textbooks instruct students to regard the lowest point on a Frost diagram as the most stable oxidation state of an element, but this statement is incorrect, as becomes apparent if the reference potential of each redox couple is changed. As illustrated in Figure 2, re-referencing the reduction potentials from the standard hydrogen electrode (SHE) to the O_2/H_2O redox couple alters which oxidation state is lowest on the diagram. Since reference potentials are arbitrary points for comparing different half reactions, this observation invalidates the notion that the lowest point represents the most stable oxidation state, at least not in an absolute sense. Instead, the lowest point in a typical Frost diagram represents the favored oxidation state of an element under conditions that apply a potential equal to that of the standard hydrogen electrode. We aim to clarify this misconception introduced by many textbooks and highlight how the correct interpretation adds greater utility to these diagrams since changing the reference potential provides a way to illustrate how the favored oxidation state changes based on the specific conditions present in solution. To aid this effort, we introduce interactive Frost diagrams in which the applied potential (E_{app}) and pH can be varied arbitrarily to illustrate how the favored oxidation state of an element changes.

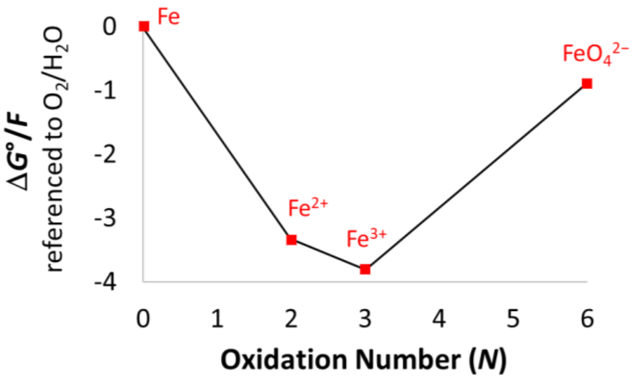


Figure 2. Frost diagram for iron at pH = 0 with reduction potentials referenced to O_2/H_2O couple.

CORRECTING MISCONCEPTIONS

Y-Axis Free Energy Label.

In the 1951 paper introducing Frost diagrams[1], Arthur Frost plotted free energy in electronvolts (eV) on the y-axis versus the oxidation number of an element on the x-axis. Organizing the data in this manner positions the thermodynamically favored oxidation state of an element (relative to H^+/H_2) as the lowest point on the diagram, thus adhering to the usual convention of depicting lower energy species beneath higher energy species. For instructive purposes, it has become common to label the y-axis in terms of electrode potentials and the number of electrons separating each oxidation state from the standard $N = 0$ state of an element. This labeling is proportional to free energy based on Equation 1, where n is the number of electrons involved in a redox process, $E°$ is the standard electrode potential in volts, and $\Delta G°/F$ is the standard free energy change in eV (note: $\Delta G/F$ and E apply when pH ≠ 0 or 14).

$$-nE^\circ = \Delta G^\circ/F \qquad (1)$$

Thus, it would seem that the y-axis of Frost diagrams should be labeled $-\mathrm{n}E^\circ$ to correspond to $\Delta G^\circ/F$, and this convention is common (Figure 3A).[15-18] However, this is only correct if E° is defined as the actual potential for the conversion of the $N = 0$ oxidation state to the other oxidation states in question, meaning that E° could be either a reduction potential (E°_{red}) or an oxidation potential (E°_{ox}, where $E^\circ_{\mathrm{ox}} = -E^\circ_{\mathrm{red}}$). This can create confusion since the IUPAC defines E° to refer specifically to standard reduction potentials (i.e., $E^\circ = E^\circ_{\mathrm{red}}$).

A common alternative convention labels the y-axis of Frost diagrams as $\mathrm{n}E^\circ$,[4-14,19] in which n equals the oxidation state along the x-axis and E° is exclusively a standard reduction potential. For oxidation states < 0, this convention reproduces the relationship of Eq 1 since the negative sign is introduced by the $N < 0$ value of the oxidation state. For oxidation states > 0, the use of $E^\circ = E^\circ_{\mathrm{red}}$ introduces the negative sign since the free energy change of an oxidative process should be calculated using the standard oxidation potential as E° in Eq1 and $E^\circ_{\mathrm{red}} = -E^\circ_{\mathrm{ox}}$. Thus, this convention correctly sets the proportionality of the y-axis to free energy but can produce confusion by representing $\Delta G^\circ/F$ as equal to $\mathrm{n}E^\circ$. Indeed, this confusion has led more than one textbook to incorrectly label the y-axis of Frost diagrams as representing $-\Delta G^\circ/F$ (Figure 3B), which cannot be justified regardless of how terms are defined.

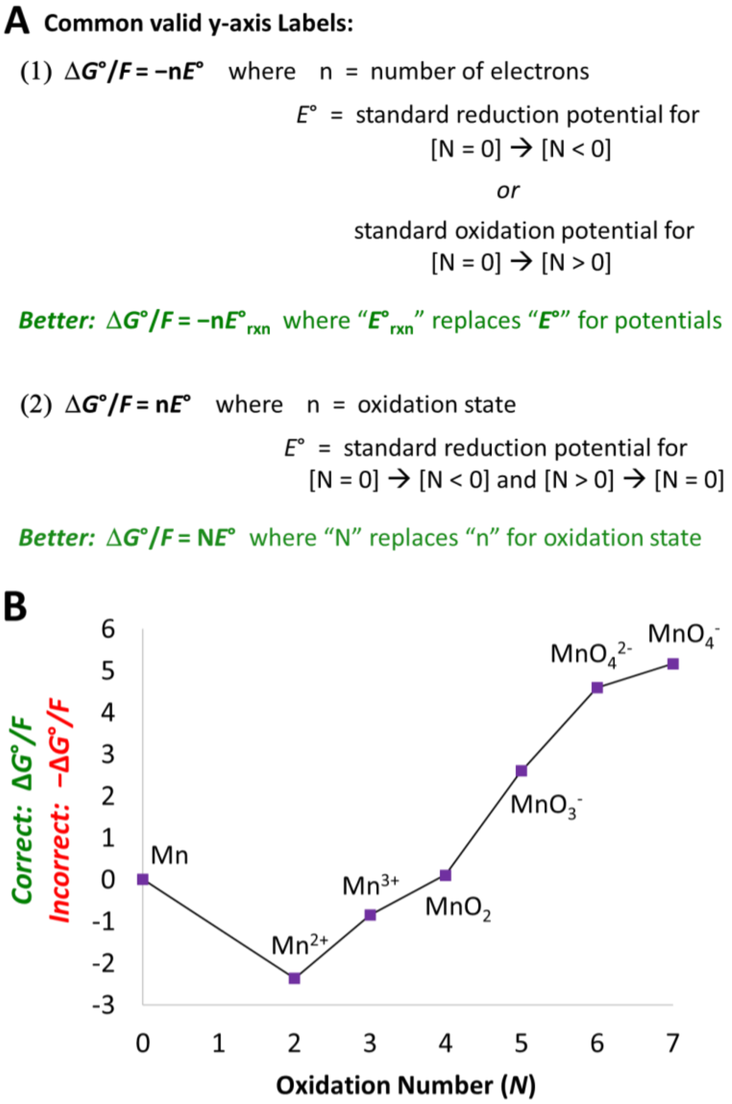


Figure 3. (A) Common conventions for labeling the y-axis of Frost diagrams and suggested clarifications. (B) Frost diagram for manganese with the correct energy label for the y-axis (green) and a common incorrect (red) y-axis label.

One common way of alleviating the above confusion is to use N to represent the oxidation state in the y-axis label $NE°$ to ensure that the signed oxidation state term is not confused with the unsigned term n that represents the number of electrons in Eq 1.[20] This solution has the advantage of simplicity since N in the y-axis label $NE°$ is also used to label the x-axis, and $E°$ represents only standard reduction potentials $E°_{red}$. However, we advocate for a different clarified y-axis label of $-nE°_{rxn}$ where n is the number of electrons as in Eq 1, and $E°_{rxn}$ is the reduction potential ($E°_{red}$) for movement to $N < 0$ oxidation states or the oxidation potential ($E°_{ox}$) for movement to $N > 0$ oxidation states. Though this solution is a little more complex, it serves to better reinforce the relationship between potentials and free energy described in Eq 1. Additionally, the use of $E°_{rxn}$ highlights that changes of an element's oxidation state must be accompanied by the opposite change of some other redox couple to provide a net redox reaction. In other words, $E°_{rxn}$ is a cell potential for a full redox reaction, as required to meaningfully compare energy changes. As discussed in the next section, this latter point is often overlooked in explanations of Frost diagrams since the H^+/H_2 couple is hidden by its role as the standard 0 V reference potential.

Conditional Stability of Oxidation States.

Many textbooks describe the lowest point on a Frost diagram as the most stable oxidation state of the element in water at pH = 0 (or for whichever pH the diagram was constructed), but this interpretation is incorrect, and a more nuanced explanation is needed: the lowest point corresponds to the thermodynamically favored species relative to the H^+/H_2 redox couple that is used as the $E° = 0$ V reference for tabulating standard electrode potentials. As explained by Frost, "a positive slope [connecting two oxidation states] means a tendency for the couple to oxidize H_2 to H^+ while a negative slope shows a tendency towards reduction [of H^+ to H_2]." In other words, the free energy change measured on the y-axis of a Frost diagram refers to an overall redox reaction in which the oxidation or reduction of the $N = 0$ state of an element is paired with the reduction of H^+ to H_2 or oxidation of H_2 to H^+, respectively (Figure 4). Textbooks rarely discuss this feature of the diagrams,

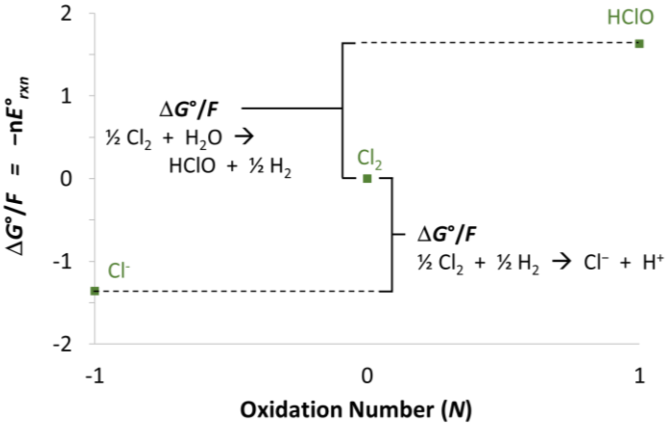


Figure 4. Partial Frost diagram for chlorine illustrating the full redox reactions connecting the oxidation states.

and many inaccurately describe the lowest point on a Frost diagram as the most stable oxidation state of an element. However, as revealed in comparing Figures 1 and 2, changing the reference potential gives rise to interchangeable lowest points, which reflect that the favored oxidation state is dependent on the specific redox conditions in solution (i.e., the potential applied by other redox-active species or by an electrode). Thus, the conclusion that the lowest point is the most stable is only conditionally true, and in fact, is meaningless in an absolute sense since half reactions must be paired with other half reactions to determine the overall thermodynamic driving force.

It is important to emphasize the significance of the reference redox couple used to construct Frost diagrams in order to reinforce that the free energy change of a redox process depends on a net reaction, not just the potentials of individual half reactions. Failing to emphasize this point causes confusion that extends beyond students in the classroom. We have seen this misconception in publications[21] from researchers in the field of electrochemistry, suggesting that textbooks are introducing a persistent misunderstanding. Labeling the y-axis $-nE°_{\mathrm{rxn}}$ helps resolve this misconception by emphasizing that the change in free energy involves a net redox process as noted in Frost's original paper. The term $E°_{\mathrm{rxn}}$ is also useful since it is nonspecific, allowing consideration of how Frost diagrams change under different applied potentials. The interactive diagrams introduced in the next section allow users to change the applied potential to immediately observe changes, which highlights how the favored oxidation state of an element is context dependent.

INTERACTIVE FROST DIAGRAMS

Textbooks often present Frost diagrams for different pH conditions to illustrate the effects of pH on redox processes (Figure 5A,B), but rarely are the effects of the applied potential noted in these diagrams. We present Frost diagrams for four elements (N, Cl, Fe, and Mn) in the form of Microsoft Excel spreadsheets in which the reduction potentials connecting each oxidation state are recalculated upon changing the applied potential or pH, thus providing an interactive visualization of how the thermodynamics of redox processes are affected (Figure 5C). Since the favored protonation state can depend on pH, both acidic and basic species are included to fully depict the effects of pH change in a single diagram. Lines connecting different oxidation states have been omitted for clarity to accommodate the inclusive range of aqueous species presented for each oxidation state. Since these interactive Frost diagrams are constructed using simple formulas for cell potentials and the pH dependence of reduction potentials, students can create additional examples as an advanced exercise (see the example problem set provided as supporting information).

The interactive diagrams illustrate that the most stable oxidation state of an element is conditional, while some properties, such as tendencies towards disproportionation and comproportionation are independent of potential (though can be dependent on pH). The interactive diagrams also illustrate the important general relationship between reduction potentials, applied potentials, and thermodynamic equilibria. For example, two oxidation states are equally favorable (i.e., the two points are at equal heights on the y-axis) at an applied potential equal to the reduction potential separating them, as illustrated for the $N = 0$ and $N = -3$ states in Figure 5C.

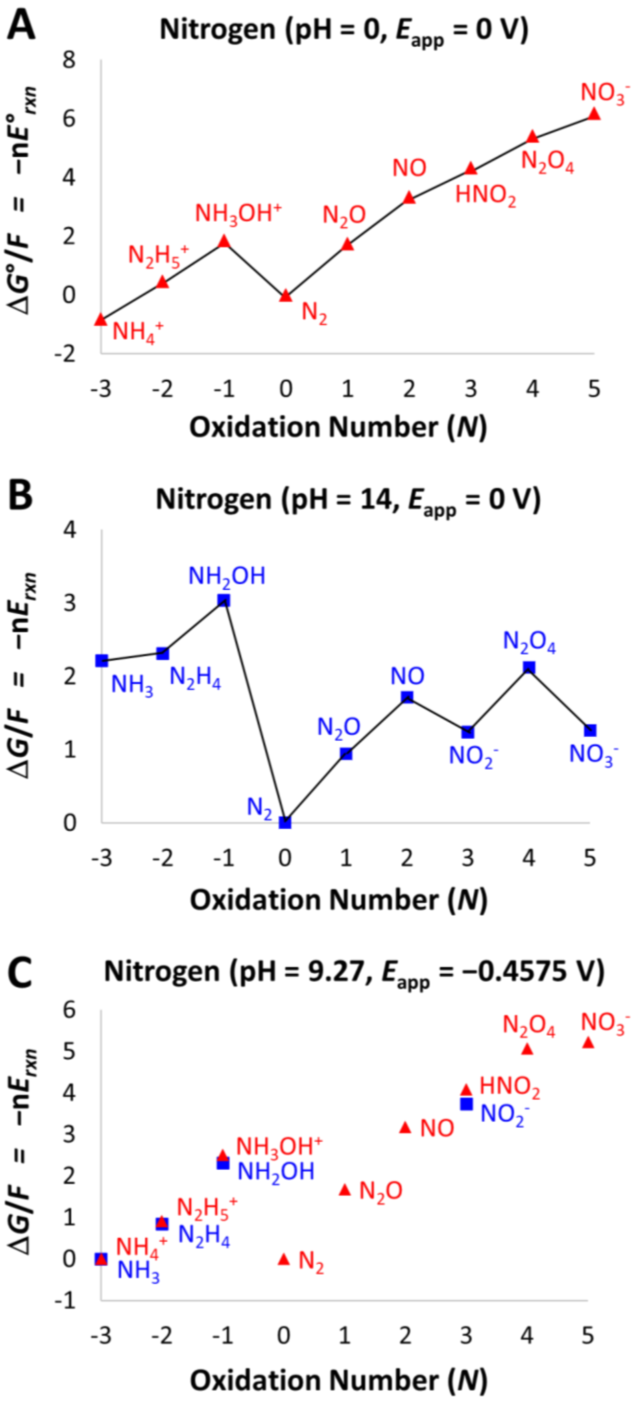
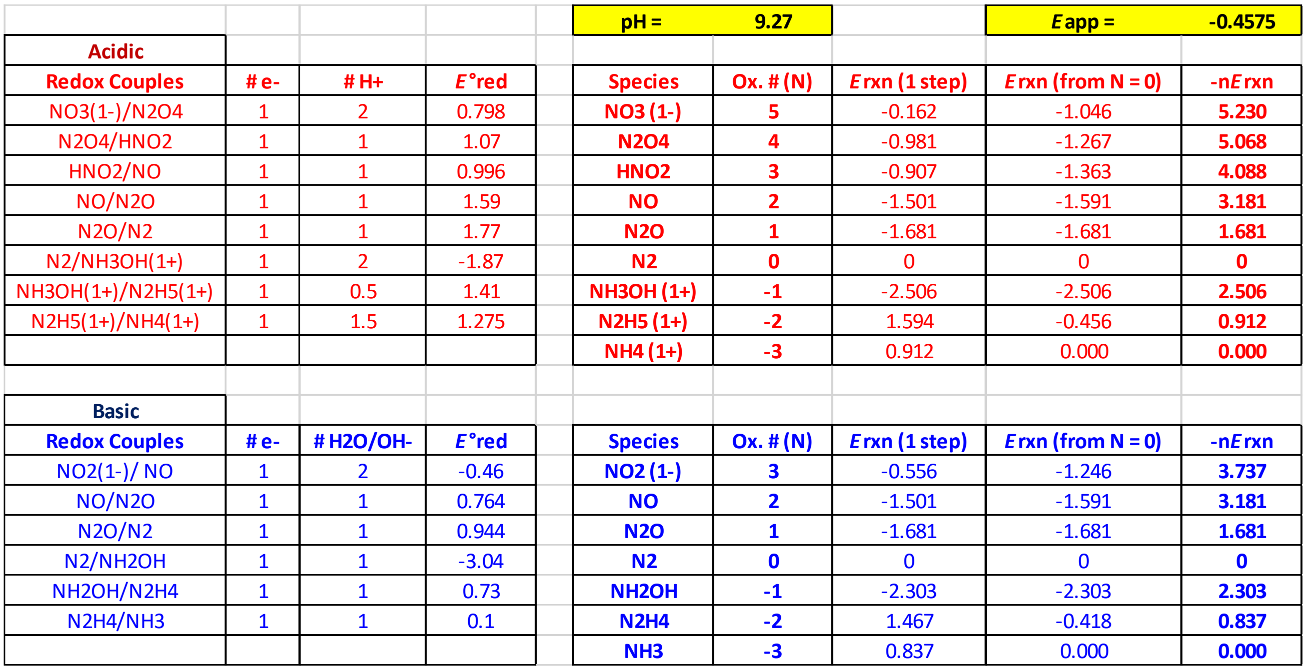


Figure 5. (A) Frost diagram for nitrogen at pH = 0. (B) Frost diagram for nitrogen modified to represent pH = 14 conditions. (C) A customized Frost diagram for nitrogen representing conditions (pH = 9.27, E_{app} = −0.4575 V vs. SHE) in which NH_4^+, NH_3, and N_2 are equal in energy.

Box 1: Using the Interactive Frost Diagrams

We provide interactive Frost Diagrams as a .xls file containing a sheet for each of four selected elements (nitrogen, chlorine, iron, manganese). There are tables on each sheet to represent acidic species (in red) and basic species (in blue). Redox couples and standard potentials from Latimer diagrams are tabulated to the left, while the righthand tables show individual species for each oxidation state along with E_{rxn} potentials and $-nE_{rxn}$ energies that are recalculated in response to changes in pH and applied potential (E_{app}). Cells for pH and E_{app} are highlighted in yellow. Users need only adjust these values since changes are propagated through the tables. The example shown here was used to calculate the Frost Diagram in Figure 5C in which N_2, NH_3, and NH_4^+ are equal in energy.



pH =	9.27	*E*app =	-0.4575

Acidic Redox Couples	# e-	# H+	*E*°red
NO3(1-)/N2O4	1	2	0.798
N2O4/HNO2	1	1	1.07
HNO2/NO	1	1	0.996
NO/N2O	1	1	1.59
N2O/N2	1	1	1.77
N2/NH3OH(1+)	1	2	-1.87
NH3OH(1+)/N2H5(1+)	1	0.5	1.41
N2H5(1+)/NH4(1+)	1	1.5	1.275

Species	Ox. # (N)	*E* rxn (1 step)	*E* rxn (from N = 0)	-n*E* rxn
NO3 (1-)	**5**	-0.162	-1.046	**5.230**
N2O4	**4**	-0.981	-1.267	**5.068**
HNO2	**3**	-0.907	-1.363	**4.088**
NO	**2**	-1.501	-1.591	**3.181**
N2O	**1**	-1.681	-1.681	**1.681**
N2	**0**	0	0	**0**
NH3OH (1+)	**-1**	-2.506	-2.506	**2.506**
N2H5 (1+)	**-2**	1.594	-0.456	**0.912**
NH4 (1+)	**-3**	0.912	0.000	**0.000**

Basic Redox Couples	# e-	# H2O/OH-	*E*°red
NO2(1-)/ NO	1	2	-0.46
NO/N2O	1	1	0.764
N2O/N2	1	1	0.944
N2/NH2OH	1	1	-3.04
NH2OH/N2H4	1	1	0.73
N2H4/NH3	1	1	0.1

Species	Ox. # (N)	*E* rxn (1 step)	*E* rxn (from N = 0)	-n*E* rxn
NO2 (1-)	**3**	-0.556	-1.246	**3.737**
NO	**2**	-1.501	-1.591	**3.181**
N2O	**1**	-1.681	-1.681	**1.681**
N2	**0**	0	0	**0**
NH2OH	**-1**	-2.303	-2.303	**2.303**
N2H4	**-2**	1.467	-0.418	**0.837**
NH3	**-3**	0.837	0.000	**0.000**

The interactive diagrams also allow the influence of pH on the thermodynamics of redox processes to be observed. Overlaying the diagrams derived from acidic and basic species allows users to to compare the free energies of different protonation states for weak acids at a desired pH. The overlaid diagrams show that protonated weak acids are favored at lower pH, while the conjugate bases become favorable as pH increases. If the pH is set to the pK_a of an acid in the diagram, the points for the acid and its conjugate base overlap (Figure 5C), illustrating that the acid and base are equal in energy at a pH matching the pK_a of the acid, similar to the observation that two oxidation states are equal in energy at a potential matching the reduction potential between the two oxidation states. Observing that pH and E_{app} both similarly affect the Frost diagrams illustrates that there is a similar thermodynamic relationship between reduction potentials and applied potentials as there is between pK_a and pH.

Connection to Pourbaix Diagrams.

Pedagogically, the interactive Frost diagrams are particularly useful when combined with Pourbaix diagrams (Figure 6) since students can cross-reference potentials and pH on a Pourbaix diagram with the Frost diagrams generated for those conditions. The lowest species depicted in the Frost diagram will correspond to the favored species indicated in the Pourbaix diagram for a given potential and pH. Furthermore, these Frost diagrams add nuance to the Pourbaix diagrams by illustrating how the equilibrium distribution between multiple species changes under different conditions, rather than just indicating the single most favorable species. For example, the Frost diagrams show that any points on a line separating two regions in the Pourbaix diagram represent conditions in which the two oxidation states and/or protonation states are equal in energy. Likewise, points in the Pourbaix diagram in which three lines intersect will show as having three equal energy species in the Frost diagram at that pH and potential.

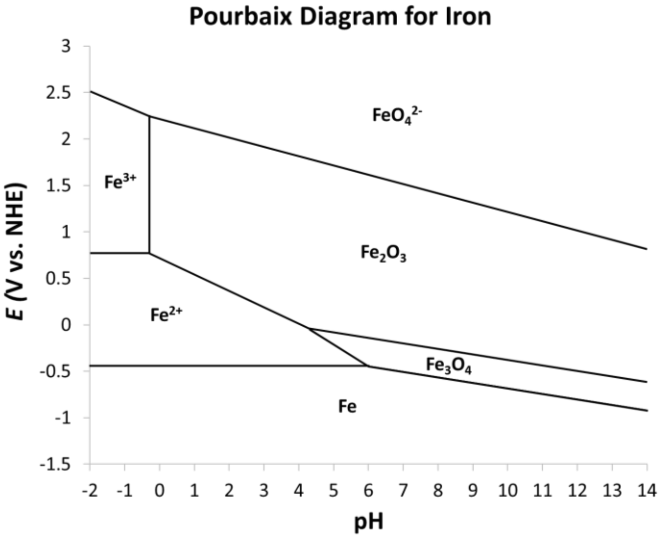


Figure 6. Pourbaix diagram for iron.[22-24]

CONCLUSIONS

We have identified two common errors regarding the labeling and interpretation of Frost diagrams that have been perpetuated by many textbooks and other resources. To aid in correcting these errors, we have developed a series of interactive Frost diagrams that illustrate the dependence of the relative free energies of oxidation states of an element on pH and the redox conditions in solution (i.e., the potential applied by an electrode or the environment). The y-axes of the interactive diagrams are labeled correctly to be proportional to the free energy of each oxidation state of the element under different applied potentials. Instructors can use these diagrams as pedagogical tools to complement Pourbaix diagrams while also reinforcing how reduction potentials relate to the concept of chemical equilibrium.

ASSOCIATED CONTENT

Supporting Information

Supporting Information available:

Notes for Instructors, Exercise Questions, and Answer Key (PDF, DOCX)

Interactive Frost Diagrams (XLS)

AUTHOR INFORMATION

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19. Interestingly, we have found one instance of a text that had labeled the y-axis $-nE°$ in its first edition (reference 16) but switched to $nE°$ in later editions (reference 9).

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22. The Pourbaix diagram for iron presented in Figure 6 and the interactive Frost diagram for iron provided as supporting information were constructed using reduction potentials tabulated in reference 23. These data produce a pH value (−0.28) separating the Fe^{3+} and Fe_2O_3 states that is much lower than commonly presented in Pourbaix diagrams for iron. This difference is likely because the data from reference 23 uses Fe^{3+} to refer specifically to $[Fe(OH_2)_6]^{3+}$, which exists only at very low pH, while other soluble Fe(III) species exist at higher pH before the precipitation of Fe_2O_3. In general, Fe(III) exhibits complex speciation in aqueous solution and as solid oxides, resulting in many acceptable variations of the Pourbaix diagram for iron. Reference 24 presents a Pourbaix diagram for iron that is consistent with the one we constructed.

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Supporting Information

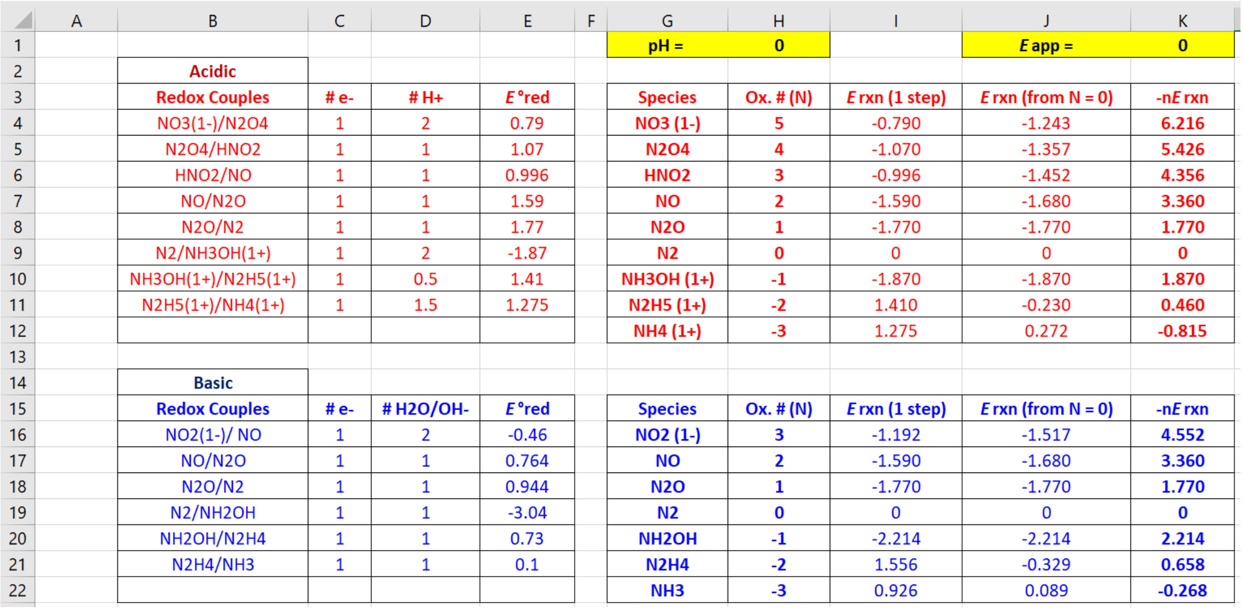
Table of Contents:

1) Notes for instructors.

The interactive Frost diagrams presented here are intended to add depth to undergraduate students' understanding and should be implemented after lessons on Latimer, Frost, and Pourbaix diagrams.

Diagram Attributes

Yellow Boxes – These are the only cells in the tables that should be changed. Enter the pH value in cell H1 and the applied potential (E_{app}) in cell K1.



	A	B	C	D	E	F	G	H	I	J	K
1							pH =	0		*E* app =	0
2		Acidic									
3		Redox Couples	# e-	# H+	*E*°red		Species	Ox. # (N)	*E* rxn (1 step)	*E* rxn (from N = 0)	-n*E* rxn
4		NO3(1-)/N2O4	1	2	0.79		NO3 (1-)	5	-0.790	-1.243	6.216
5		N2O4/HNO2	1	1	1.07		N2O4	4	-1.070	-1.357	5.426
6		HNO2/NO	1	1	0.996		HNO2	3	-0.996	-1.452	4.356
7		NO/N2O	1	1	1.59		NO	2	-1.590	-1.680	3.360
8		N2O/N2	1	1	1.77		N2O	1	-1.770	-1.770	1.770
9		N2/NH3OH(1+)	1	2	-1.87		N2	0	0	0	0
10		NH3OH(1+)/N2H5(1+)	1	0.5	1.41		NH3OH (1+)	-1	-1.870	-1.870	1.870
11		N2H5(1+)/NH4(1+)	1	1.5	1.275		N2H5 (1+)	-2	1.410	-0.230	0.460
12							NH4 (1+)	-3	1.275	0.272	-0.815
13											
14		Basic									
15		Redox Couples	# e-	# H2O/OH-	*E*°red		Species	Ox. # (N)	*E* rxn (1 step)	*E* rxn (from N = 0)	-n*E* rxn
16		NO2(1-)/ NO	1	2	-0.46		NO2 (1-)	3	-1.192	-1.517	4.552
17		NO/N2O	1	1	0.764		NO	2	-1.590	-1.680	3.360
18		N2O/N2	1	1	0.944		N2O	1	-1.770	-1.770	1.770
19		N2/NH2OH	1	1	-3.04		N2	0	0	0	0
20		NH2OH/N2H4	1	1	0.73		NH2OH	-1	-2.214	-2.214	2.214
21		N2H4/NH3	1	1	0.1		N2H4	-2	1.556	-0.329	0.658
22							NH3	-3	0.926	0.089	-0.268

Figure S1: Excerpt from Interactive Frost Diagram for Nitrogen showing only the data tables.

Tables – The upper pair of tables in red (Acidic) lists all the redox couples and species that are included in a typical Frost diagram for standard conditions (pH = 0). The lower tables in blue (Basic) lists the redox couples and species for pH = 14 Frost diagrams. Reduction potentials from Latimer diagrams are included for each redox couple and the tables are set up to recalculate the relative free energy ($-nE^\circ_{rxn}$) of each possible species when the pH or E_{app} values are changed, with the $N = 0$ states (Fe, Mn, Cl_2, N_2) set equal to 0 by definition. To avoid redundancy, the tables for basic conditions only include redox couples that differ from those found in acidic conditions. For example, NO_3^-/N_2O_4 is not included in the basic table in Figure S1 because NO_3^- and N_2O_4 represent the $N = 5$ and $N = 4$ states for the entire pH range of 0 – 14 in aqueous conditions.

Columns – There are several columns in the Acidic and Basic tables, some with fixed values and some with values that are altered by changing the pH or E_{app}. The columns for oxidation number (Ox. # (N)) and relative free energy ($-nE^\circ_{rxn}$) contain the data points which are used to construct the interactive Frost diagrams.

- **Redox Couples**: Lists the series of half reactions spanning the highest to lowest oxidation numbers of an element.
- **# e^-:** Number of electrons transferred in the specified half reaction.
- **# H^+:** Number of protons consumed in the specified half reaction in acidic conditions.
- **# H_2O/OH^-:** Number of hydroxide ions produced by deprotonating H_2O for the specified half-reaction under basic conditions.
- **$E°_{red}$:** Standard reduction potential of the given half reaction. The acidic tables list the standard reduction potentials for pH = 0 solutions and the basic tables for pH = 14.
- **Species:** Lists the individual species that are plotted in the Frost diagram to represent each oxidation number.
- **Ox # (*N*):** Oxidation numbers of the species that are plotted in the Frost diagrams.
- **E_{rxn} (1 step):** Calculates the actual potential at a specified pH and E_{app} for moving to a specific oxidation state from the next adjacent state closer to the $N = 0$ state. This value can be a reduction potential (E_{red}) when the oxidation state in question is < 0 or an oxidation potential (E_{ox}, where $E_{ox} = -E_{red}$) when moving to an oxidation state > 0.
- **E_{rxn} (from $N = 0$):** Calculates the actual potential under a specified pH and E_{app} for moving to a specific oxidation state from the $N = 0$ state. As for the 1 step potentials, this value can be either a reduction or oxidation potential.
- **$-nE_{rxn}$:** Calculates the free energy in electron volts of a given oxidation state relative to the $N = 0$ state under a specified pH and E_{app}. This value is plotted on the y-axis of the interactive Frost diagrams.

Features – The following are useful pedagogical features of the diagrams

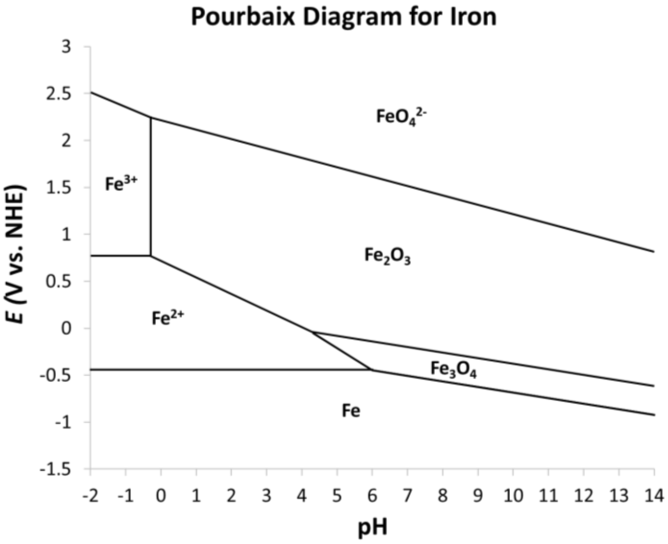
- Acid/base equilibrium – If the pH is set equal to the pKa of an acidic species in the upper table, then the corresponding conjugate base will have the same free energy in the lower table and the acid and base will overlap in the Frost diagram. This illustrates the relationship between pKa, pH, and equilibrium between an acid/base pair.

- Redox equilibrium – If the applied potential is set equal to the pH-adjusted reduction potential separating two oxidation states, then the oxidized and reduced species will have the same free energy and will be at equal heights in the Frost diagram. This illustrates that there is a similar relationship between reduction potentials, applied potentials, and equilibrium as there is between pKa, pH, and equilibrium.

- Connection to Pourbaix diagrams – Comparison of the interactive Frost diagrams with Pourbaix diagrams shows that the favored species in a Pourbaix diagram for a given pH and E_{app} corresponds to the lowest energy species in the Frost diagram for those conditions. The interactive Frost diagrams add detail to the Pourbaix diagram by depicting how favored/unfavored each species is at a given point within the Pourbaix diagram. Likewise, the Frost diagrams illustrate that lines and their intersecting points in Pourbaix diagrams represent conditions in which two or more species are at equal energy. Thus, the interactive Frost diagrams can be used to generate Pourbaix diagrams – the Pourbaix diagram for iron supplied in the *Suggested Exercise Questions* was generated in this manner.

2) Exercise Questions

Using the interactive Frost diagram Excel sheets and the Pourbaix diagram for iron that is provided here, answer the following questions.



1. Set pH and E_{app} equal to 0 in the Frost diagram for iron. This is the standard Frost diagram for Fe under 1.0 M H^+ and reducing conditions equal to the H^+/H_2 couple.

    a. What species is most favored under these conditions?

    b. Why is this species favored over the other species of the SAME oxidation state?

2. Select a single point on either the horizontal or vertical lines of the Pourbaix diagram and input the coordinates of this point into the yellow boxes for pH and E_{app} on the interactive Frost diagram.

    a. What do you observe on the Frost diagram?

    b. Write a balanced chemical equation describing your observation.

3. Select two species on the Pourbaix diagram that are separated by a diagonal line.

    a. Using the diagrams, find the slope of the diagonal line you have chosen (You may estimate based on the Pourbaix diagram and use the interactive Frost diagram to assist your estimate). What does this slope represent?

    b. Write balanced equations for the transformation you selected. Do the coefficients match the slope you estimated? Why or why not?

4. The Frost diagram depicts 7 distinct iron species but only 6 of these are represented in the Pourbaix diagram.

    a. Which species is missing?

    b. Can you input conditions into the Frost diagram to make the species from part (a) the most favorable? Why or why not?

5. Input the parameters pH = 4.31 and $E_{\text{app}} = –0.04287$ into the Frost diagram for iron.

    a. What do you observe on the Frost diagram?

    b. How is this depicted on the Pourbaix diagram?

6. The class of enzymes responsible for fixation of nitrogen (N_2) into ammonia (NH_3) are called nitrogenases. The generation of NH_3, a useful feedstock and fertilizer, from N_2 is of biological and industrial interest. A species of bacteria that fixes N_2 into NH_3 is *Azotobacter vinelandii*, which catalyzes the reduction of N_2 to NH_3 via a reaction *in vivo* with the approximate stoichiometry of:

$$\mathrm{N_2 + 8\,e^- + 8\,H^+ + 16\,MgATP \rightarrow 2\,NH_3 + H_2 + 16\,MgADP + 16\,P_i}$$

(note: P_i represents inorganic phosphate formed by ATP hydrolysis)

The active site of the nitrogenase in *Azotobacter vinelandii* has an effective pH of 7.4 and electrons are supplied at a potential (E_{app}) of –0.495 V.

    a. Using the interactive Frost diagram for nitrogen, determine if the applied potential is more reducing, less reducing, or equal to that which is thermodynamically required to convert N_2 to NH_3.

    b. If the applied potential is not equal to the thermodynamic potential, then what is the potential thermodynamically required for N_2 to NH_3 conversion at pH 7.4?

    c. *Azotobacter vinelandii* live in aerated soil. If the environmental potential is assumed to be that of the O_2/H_2O redox couple (+0.793 V at pH = 7.4), then what is the relative free energy in eV of NH_3 vs. N_2? Is NH_3 production a thermodynamically favorable process at this potential?

    d. What is the minimum energy that the bacteria must expend to convert one mole of N_2 into two moles of NH_3 under the soil conditions in which *Azotobacter vinelandii* lives? How does this compare with the amount of energy the bacteria releases from ATP hydrolysis in the equation provided above? (note: the hydrolysis of ATP to ADP provides 57 kJ/mol).

7. The following equations are commonly discussed in the context of efforts to electrochemically convert the greenhouse gas CO_2 to value-added chemicals and fuels.

$$CO_2 + e^- \rightarrow CO_2^{\bullet -} \qquad E° = -1.90\ V$$

$$CO_2 + 2\,H^+ + 2\,e^- \rightarrow CO_{(g)} + H_2O \qquad E° = -0.11\ V$$

$$CO_2 + 6\,H^+ + 6\,e^- \rightarrow CH_3OH_{(aq)} + H_2O \qquad E° = 0.03\ V$$

$$CO_2 + 8\,H^+ + 8\,e^- \rightarrow CH_{4(g)} + 2\,H_2O \qquad E° = 0.17\ V$$

$$CO_2 + 4\,H^+ + 4\,e^- \rightarrow C_{(s)} + 2\,H_2O \qquad E° = 0.21\ V$$

a. Assign formal oxidation numbers to carbon for all of the species in the above equations.

b. Construct an interactive Frost diagram for carbon that includes all the oxidation states you determined in part (a). To follow the format of the tables provided for nitrogen, chlorine, etc., you will need to determine the reduction potentials connecting nearest neighbor oxidation states. It is also possible (and less work) to reach the free energy values directly using the half reactions starting from CO_2. For this latter approach, determine the free energies relative to CO_2 and then convert these to the values relative to C.

c. Electrochemists studying how to convert CO_2 to the industrially useful gas CO typically want to employ the minimum reducing potential necessary in order to maximize electrical efficiency. Explain why $CO_2^{\bullet -}$ must be avoided as an intermediate in order to achieve such efficiency.

d. Presently, CO is produced industrially in a process known as steam reforming, following the equation:

$$CH_4 + H_2O \rightarrow CO + 3\,H_2$$

Use the interactive Frost diagram to determine whether this reaction is thermodynamically possible under standard conditions. What about at a pH of 7? (note: in practice this reaction is performed at very high temperatures and pressures, but this detail can be ignored for the question at hand)

3) Answer Key

1. Set pH and E_{app} equal to 0 in the Frost diagram for iron. This is the standard Frost diagram for Fe under 1.0 M H^+ and reducing conditions equal to the H^+/H_2 couple.

   a. What species is most favored under these conditions?

   Fe^{2+}

   b. Why is this species favored over the other species of the SAME oxidation state?

   The other available Fe(II) species is $Fe(OH)_2$. Since low oxidation state iron oxides and hydroxides are basic, the hydroxide anions can easily be protonated under strongly acidic conditions to dissolve $Fe(OH)_2$.

2. Select a single point on either the horizontal or vertical lines of the Pourbaix diagram and input the coordinates of this point into the yellow boxes for pH and E_{app} on the interactive Frost diagram.

   a. What do you observe on the Frost diagram?

   Two species at the same energy (Fe^{3+}/Fe_2O_3 or Fe^{3+}/Fe^{2+} or Fe^{2+}/Fe)

   b. Write a balanced chemical equation describing your observation.

   Possible answers:

$$Fe^{3+} + e^- \rightleftarrows Fe^{2+}$$

$$Fe^{2+} + 2\,e^- \rightleftarrows Fe$$

$$2\,Fe^{3+} + 3\,H_2O \rightleftarrows Fe_2O_3 + 3\,H^+$$

3. Select two species on the Pourbaix diagram that are separated by a diagonal line.

   a. Using the diagrams, find the slope of the diagonal line you have chosen (You may estimate based on the Pourbaix diagram and use the interactive Frost diagram to assist your estimate). What does this slope represent?

   Selected example: Fe_2O_3 and Fe^{2+}

   Slope = –0.177 V/pH

The slope represents the pH dependence of the reduction potential since the reduction of Fe_2O_3 requires H^+ as a reactant or OH^- as a product in order to provide an overall balanced equation. The slope is given by:

$$-0.059 \bullet \frac{\#\,protons}{electrons} \bullet \mathrm{pH}$$

The number of protons can be substituted with the number of OH^- produced for reactions under basic conditions.

b. Write balanced equations for the transformation you selected. Do the coefficients match the slope you estimated? Why or why not?

$$Fe_2O_3 + 2e^- + 3H_2O \rightleftarrows 2\,Fe^{2+} + 6OH^-$$

Yes, 6 OH^- over 2 e^- is 3, which matches the ratio predicted from slope in the Pourbaix diagram.

4. The Frost diagram depicts 7 distinct iron species but only 6 of these are represented in the Pourbaix diagram.

a. Which species is missing?

$Fe(OH)_2$

b. Can you input conditions into the Frost diagram to make the species from part (a) the most favorable? Why or why not?

No. Above pH 6.37 the $Fe(OH)_2$ state becomes favored relative to Fe^{2+}, but $Fe(OH)_2$ always remains at least slightly above the line connecting Fe_3O_4 to Fe. For example, at pH 6.37, the potential E_{ox} for oxidation of $Fe(OH)_2$ to Fe_3O_4 is 0.53 V while the potential E_{red} for reduction of $Fe(OH)_2$ to Fe is −0.44 V. Thus, disproportionation of $Fe(OH)_2$ to Fe and Fe_3O_4 is thermodynamically favored.

Note, however, that $Fe(OH)_2$ can still be formed by precipitation from Fe^{2+} solutions upon raising the pH.

5. Input the parameters pH = 4.31 and $E_{app} = –0.04287$ into the Frost diagram for iron.

a. What do you observe on the Frost diagram?

Three species Fe^{2+}, Fe_3O_4, and Fe_2O_3 are found at the same energy of −0.794 eV relative to the $N = 0$ state, making them mutually the most stable states for these conditions.

b. How is this depicted on the Pourbaix diagram?

The three equally stable states are represented by the point where the lines separating these states intersect.

6. The class of enzymes responsible for fixation of nitrogen (N_2) into ammonia (NH_3) are called nitrogenases. The generation of NH_3, a useful feedstock and fertilizer, from N_2 is of biological and industrial interest. A species of bacteria that fixes N_2 into NH_3 is *Azotobacter vinelandii*, which catalyzes the reduction of N_2 to NH_3 via a reaction *in vivo* with the approximate stoichiometry of:

$$N_2 + 8e^- + 8H^+ + 16MgATP \rightarrow 2NH_3 + H_2 + 16MgADP + 16P_i$$

(note: P_i represents inorganic phosphate formed by ATP hydrolysis)

The active site of the nitrogenase in *Azotobacter vinelandii* has an effective pH of 7.4 and electrons are supplied at a potential (E_{app}) of –0.495 V.

a. Using the interactive Frost diagram for nitrogen, determine if the applied potential is more reducing, less reducing, or equal to that which is thermodynamically required to convert N_2 to NH_3.

The potential is more reducing than required since NH_3 lies 0.443 eV lower than N_2 in the Frost diagram at an applied potential of −0.495 V and a pH of 7.4.

b. If the applied potential is not equal to the thermodynamic potential, then what is the potential thermodynamically required for N_2 to NH_3 conversion at a pH of 7.4?

Since a potential of −0.495 V places NH_3 at an energy of 0.443 eV lower than N_2, and 3 e^- are transferred, the excess potential is:

$(-0.443 \text{ eV})/(3\ e^-) = -0.1477$ V

Thus, the required potential is:

-0.495 V $- (-0.1477$ V$) = -0.3473$ V vs. SHE

Plugging this value in the interactive Frost Diagram as E_{app} sets N_2 and NH_3 equal in energy.

c. *Azotobacter vinelandii* live in aerated soil. If the environmental potential is assumed to be that of the O_2/H_2O redox couple (+0.793 V at pH = 7.4), then what is the relative free energy in eV of NH_3 vs. N_2? Is NH_3 production a thermodynamically favorable process at this potential?

Setting E_{app} to that of the O_2/H_2O potential and pH = 7.4 in the interactive Frost diagram reveals that NH_3 is +3.42 eV relative to N_2 (per nitrogen atom).

The formation of NH_3 is thermodynamically unfavorable since it is energetically uphill.

d. What is the minimum energy that the bacteria must expend to convert one mole of N_2 into two moles of NH_3 under the soil conditions in which *Azotobacter vinelandii* lives? How does this compare with the amount of energy the bacteria releases from ATP hydrolysis in the equation provided above? (The hydrolysis of one ATP to ADP provides 57 kJ/mol.)

The minimum required energy is provided by the difference between the potential in the soil and that of N_2/NH_3 interconversion multiplied by the number of electrons involved and Faraday's constant:

$$\Delta G = -nF(E_{\mathrm{N2/NH3}} - E_{\mathrm{soil}})$$

$$\begin{aligned} &= -(6)(F)(-0.347\ \mathrm{V} - 0.793\ \mathrm{V}) \\ &= -(6)(96485\ \mathrm{C})(-1.14\ \mathrm{V}) \\ &= 660{,}131\ \mathrm{J} \\ &= 660\ \mathrm{kJ} \end{aligned}$$

The energy released by ATP hydrolysis is simply:

$$\Delta G = -(16)(57\ \mathrm{kJ/mol}) = -912\ \mathrm{kJ}$$

Note that the above considerations do not account fully for the energy utilized to provide electrons at a potential of −0.495 V. The overall metabolic process is complex and requires a considerable expenditure of energy to generate reducing equivalents in addition to the ATP utilized directly by the enzyme.

7. The following equations (see Exercise Questions for the equations) are commonly discussed in the context of efforts to electrochemically convert the greenhouse gas CO_2 to value-added chemicals and fuels.

a. Assign formal oxidation numbers to carbon for all of the species in the above equations.

$CO_2 = +4$ $\quad CO_2^{\bullet-} = +3$ $\quad CO = +2$ $\quad C = 0$ $\quad CH_3OH = -2$ $\quad CH_4 = -4$

b. Construct an interactive Frost diagram for carbon that includes all the oxidation states you determined in part (a). To follow the format of the tables provided for nitrogen, chlorine, etc., you will need to determine the reduction potentials connecting nearest neighbor oxidation states. It is also possible (and less work) to reach the free energy values directly using the half reactions starting from CO_2. For this latter approach, determine the free energies relative to CO_2 and then convert these to the values relative to C.

See the additional excel sheet for an example answer. Since all the reduction potentials are provided from the +4 state, the Frost diagram table was constructed somewhat differently than the examples provided for N, Cl, Fe, and Mn. The column labeled "E_{rxn} (from N = 4)" was filled in with formulas for the pH and E_{app} dependent reduction potential for reducing CO_2 to each of the other species. Then the column "$-nE_{rxn}$ (from N = 4)" was filled in to provide the energy of each oxidation state relative to CO_2. The final column "$-nE_{rxn}$" converts the values relative to the N = 4 state to the values relative to the N = 0 state. The relative energies at pH = 0 and $E_{app} = 0$ are:

CO_2 (+0.84 eV); $CO_2^{\bullet-}$ (+2.740 eV); CO (+1.06 eV); CH_3OH (+0.66 eV); CH_4 (−0.52 eV)

c. Electrochemists studying how to convert CO_2 to the industrially useful gas CO typically want to employ the minimum reducing potential necessary in order to maximize electrical efficiency. Explain why $CO_2^{\bullet-}$ must be avoided as an intermediate in order to achieve such efficiency.

When the applied potential is set equal to the thermodynamic potential of the CO_2/CO reduction half reaction, then CO_2 and CO are equal in free energy at +1.28 eV relative to the N = 0 state (assuming pH 0), while $CO_2^{\bullet-}$ is at a much higher energy of +3.07 eV. Passing through such an unfavorable intermediate would be prohibitively slow at the thermodynamic potential for CO_2/CO reduction, while applying a stronger driving force (−1.90 V) to achieve rapid reduction of CO_2 to $CO_2^{\bullet-}$ would waste a considerable amount of energy to reach CO.

d. Presently, CO is produced industrially in a process known as steam reforming, following the equation:

$$CH_4 + H_2O \rightarrow CO + 3\,H_2$$

Use the interactive Frost diagram to determine whether this reaction is thermodynamically possible under standard conditions. What about at a pH of 7? (note: in practice this reaction is performed at very high temperatures and pressures, but this detail can be ignored for the question at hand)

The reaction is thermodynamically unfavorable under standard conditions since CO (+1.06 eV relative to carbon) is thermodynamically uphill from CH_4 (−0.52 eV relative to carbon) by 1.58 eV when the applied potential is equal to the H^+/H_2 redox couple, which is equivalent to the reduction of $H_2O \rightarrow H_2$ present in the equation provided above. The reaction becomes favorable at pH = 7 since CO (+0.234 eV relative to carbon) is lower in energy than CH_4 (+1.132 eV relative to carbon) by 0.898 eV.

Other files

InteractiveFrostDiagrams_N_Cl_Fe_Mn.xlsx (42.15 KiB)	view on ChemRxiv • download file
InteractiveFrostDiagram_Carbon.xlsx (15.14 KiB)	view on ChemRxiv • download file