

Correcting Frost Diagram Misconceptions Using Interactive Frost Diagrams

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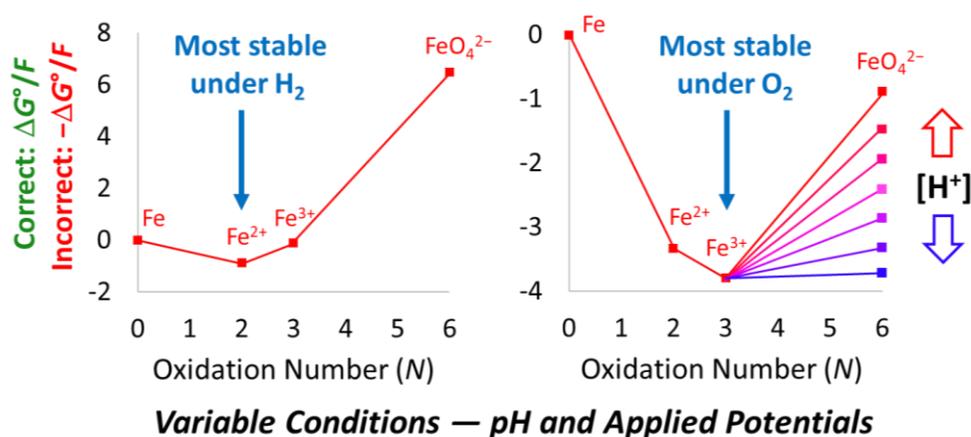
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ABSTRACT

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 nE° or $-nE^\circ$, 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

Interactive Frost Diagrams



Variable Conditions — pH and Applied Potentials

KEYWORDS

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

Frost diagrams¹ 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., $\text{Fe}^{2+}_{\text{aq}}$) 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 $\Delta G^\circ/F$ (or $\Delta G/F$ if $\text{pH} \neq 0$ or 14), the slopes connecting each point correspond to the reduction potentials E° (or E for $\text{pH} \neq 0$ or 14) connecting these oxidation states owing to the relationship $\Delta G^\circ = -nFE^\circ$. In this regard, Frost diagrams visually depict the electrode

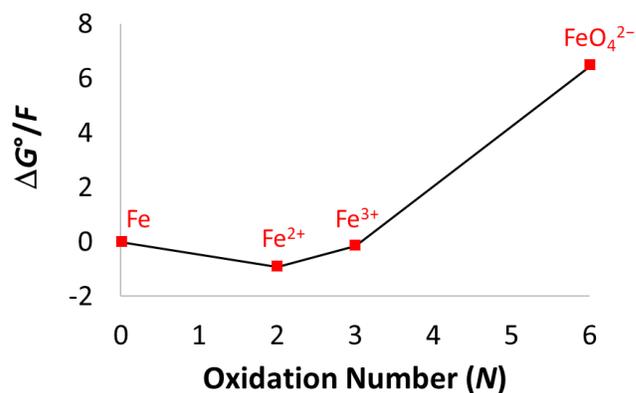


Figure 1. Frost diagrams for iron in $\text{pH} = 0$ solution.

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.

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 $-nE^\circ$ to correspond to $\Delta G^\circ/F$ ($F = \text{Faraday's constant}$). 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 $-\Delta G^\circ/F$,^{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

50 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.

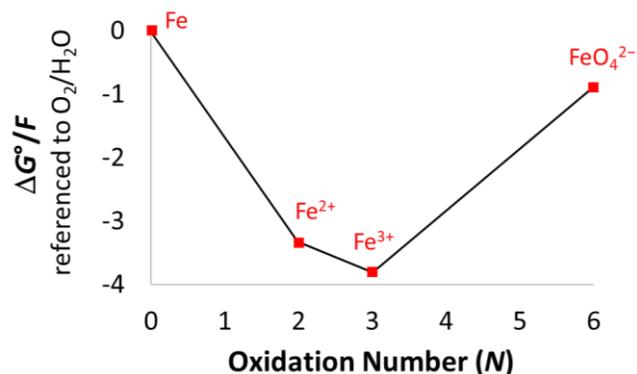


Figure 2. Frost diagram for iron at pH = 0 with reduction potentials referenced to O_2/H_2O couple.

60 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.

CORRECTING MISCONCEPTIONS

Y-Axis Free Energy Label.

70 In the 1951 paper introducing Frost diagrams¹, 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 $\Delta G^\circ/F$ is the standard free energy change in eV (note: $\Delta G/F$ and E apply when pH \neq 0 or 14).

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

Thus, it would seem that the y-axis of Frost diagrams should be labeled $-nE^\circ$ to correspond to $\Delta G^\circ/F$,

80 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

$E^\circ_{\text{ox}} = -E^\circ_{\text{red}}$). This can create confusion since

85 the IUPAC defines E° to refer specifically to

standard reduction potentials (i.e., $E^\circ = E^\circ_{\text{red}}$).

A common alternative convention

labels the y-axis of Frost diagrams as nE° ,⁴⁻

14,19 in which n equals the oxidation state

90 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

95 state. For oxidation states > 0 , the use of E°

$= E^\circ_{\text{red}}$ 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 $E^\circ_{\text{red}} =$

100 $-E^\circ_{\text{ox}}$. 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 nE° . 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.

A Common valid y-axis Labels:

(1) $\Delta G^\circ/F = -nE^\circ$ where n = number of electrons

E° = standard reduction potential for

$[N = 0] \rightarrow [N < 0]$

or

standard oxidation potential for

$[N = 0] \rightarrow [N > 0]$

Better: $\Delta G^\circ/F = -nE^\circ_{\text{rxn}}$ where " E°_{rxn} " replaces " E° " for potentials

(2) $\Delta G^\circ/F = nE^\circ$ where n = oxidation state

E° = standard reduction potential for

$[N = 0] \rightarrow [N < 0]$ and $[N > 0] \rightarrow [N = 0]$

Better: $\Delta G^\circ/F = NE^\circ$ where " N " replaces " n " for oxidation state

B

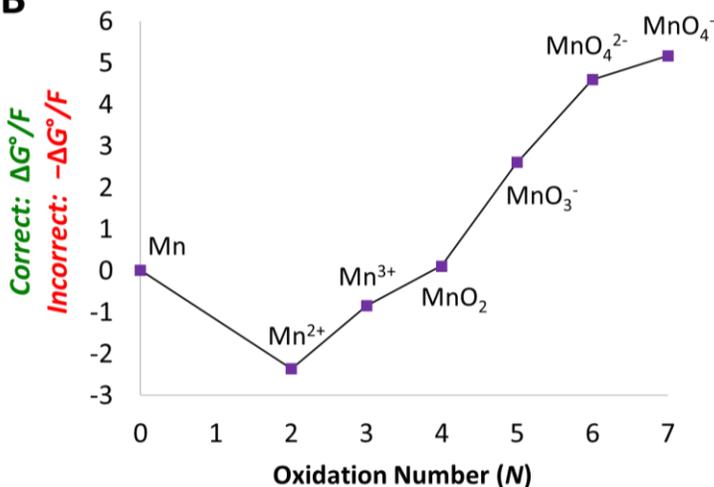


Figure 3. (A) Common conventions for labeling the y-axis of Frost diagrams and suggested clarifications. (B) Frost diagram for manganese with the correct energy label for the y-axis (green) and a common incorrect (red) y-axis label.

105 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 $-nE^\circ_{\text{rxn}}$ 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.

120 Many textbooks describe the lowest point on a Frost diagram as the most stable oxidation state of the element in water at $\text{pH} = 0$ (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 $E^\circ = 0$ 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

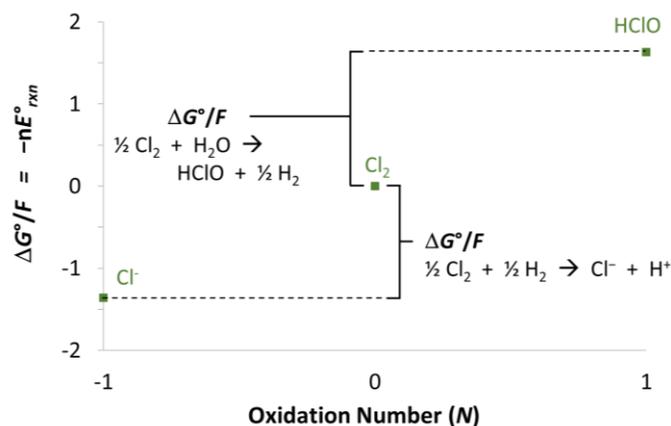


Figure 4. Partial Frost diagram for chlorine illustrating the full redox reactions connecting the oxidation states.

130 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,

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 publications²¹ from researchers in the field of electrochemistry, suggesting that textbooks are introducing a persistent misunderstanding. Labeling the y-axis $-nE^\circ_{\text{rxn}}$ 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°_{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.

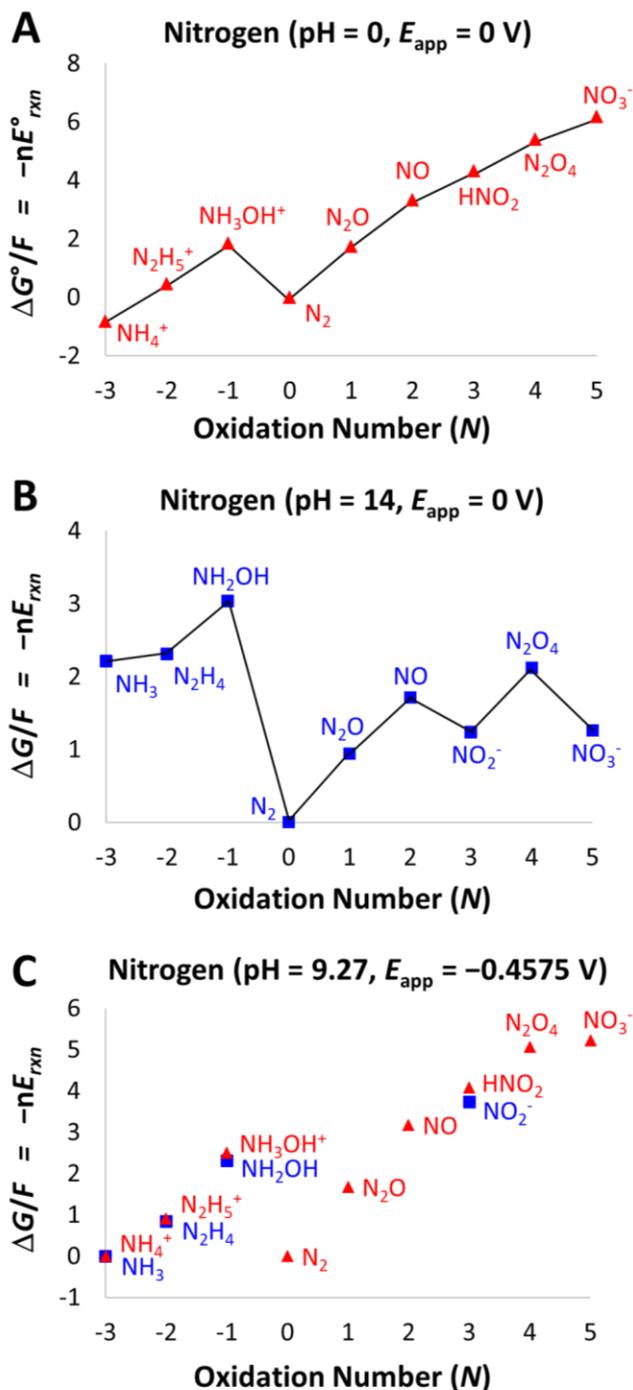


Figure 5. (A) Frost diagram for nitrogen at pH = 0. (B) Frost diagram for nitrogen modified to represent pH = 14 conditions. (C) A customized Frost diagram for nitrogen representing conditions (pH = 9.27, $E_{app} = -0.4575$ V vs. SHE) in which NH_4^+ , NH_3 , and N_2 are equal in energy.

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 $-nE_{\text{rxn}}$ 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	Species	Ox. # (N)	Erxn (1 step)	Erxn (from N = 0)	-nErxn
NO3(1-)/N2O4	1	2	0.798	NO3 (1-)	5	-0.162	-1.046	5.230
N2O4/HNO2	1	1	1.07	N2O4	4	-0.981	-1.267	5.068
HNO2/NO	1	1	0.996	HNO2	3	-0.907	-1.363	4.088
NO/N2O	1	1	1.59	NO	2	-1.501	-1.591	3.181
N2O/N2	1	1	1.77	N2O	1	-1.681	-1.681	1.681
N2/NH3OH(1+)	1	2	-1.87	N2	0	0	0	0
NH3OH(1+)/N2H5(1+)	1	0.5	1.41	NH3OH (1+)	-1	-2.506	-2.506	2.506
N2H5(1+)/NH4(1+)	1	1.5	1.275	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	Species	Ox. # (N)	Erxn (1 step)	Erxn (from N = 0)	-nErxn
NO2(1-)/NO	1	2	-0.46	NO2 (1-)	3	-0.556	-1.246	3.737
NO/N2O	1	1	0.764	NO	2	-1.501	-1.591	3.181
N2O/N2	1	1	0.944	N2O	1	-1.681	-1.681	1.681
N2/NH2OH	1	1	-3.04	N2	0	0	0	0
NH2OH/N2H4	1	1	0.73	NH2OH	-1	-2.303	-2.303	2.303
N2H4/NH3	1	1	0.1	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 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

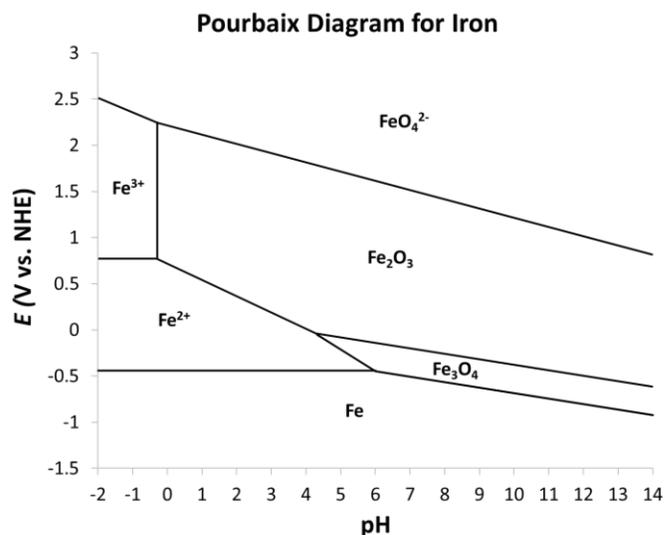


Figure 6. Pourbaix diagram for iron.²²⁻²⁴

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.

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

- 225 **Supporting Information**
Supporting Information available:

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

Interactive Frost Diagrams (XLS)

230 AUTHOR INFORMATION

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- 275 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 $[\text{Fe}(\text{OH})_6]^{3+}$, which exists
280 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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