

4.4: Latimer and Frost Diagrams

In addition to Pourbaix diagrams, there are two other kinds of redox stability diagrams known as Latimer and Frost diagrams. Each of these diagrams contains similar information, but one representation may be more useful in a given situation than the others.

Latimer and Frost diagrams help predict stability relative to higher and lower oxidation states, usually at one fixed pH. Pourbaix diagrams help understand pH-dependent equilibria, which are often coupled to solubility equilibria and corrosion (which will be talked about more later).



Manganese nodules on the sea floor contain Mn in oxidation states 2+, 3+, and 4+.

Latimer diagrams:

Latimer diagrams are the oldest and most compact way to represent electrochemical equilibria for substances that have multiple oxidation states. Electrochemical potential values are written for successive redox reactions (from highest to lowest oxidation state), typically under standard conditions in either strong acid ($[H^+] = 1\text{ M}$, pH 0) or strong base ($[OH^-] = 1\text{ M}$, pH 14). The oxidation states of successive substances in a Latimer diagram can differ by one or more electrons. Oxidation states for the element undergoing redox are typically determined by difference; we assign the oxygen atoms an oxidation state of -2 and the hydrogen atoms an oxidation state of +1.

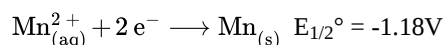
Example:

Mn in Acid

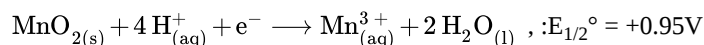


The Latimer diagram for Mn illustrates its standard reduction potentials (in 1 M acid) in oxidation states from +7 to 0.

The Latimer diagram compresses into shorthand notation all the standard potentials for redox reactions of the element Mn. For example, the entry that connects Mn^{2+} and Mn gives the potential for the half-cell reaction:



and the entry connecting Mn^{4+} and Mn^{3+} represents the reaction:



We can also calculate values for **multi-electron reactions** by first adding $\Delta G^\circ (= -nFE^\circ)$ values and then dividing by the total number of electrons

For example, for the 5-electron reduction of MnO_4^- to Mn^{2+} , we write

$$E^\circ = \frac{1(0.564) + 1(0.274) + 1(4.27) + 1(0.95) + 1(1.51)}{5} = +1.51\text{V} \quad (4.4.1)$$

and for the three-electron reduction of $\text{MnO}_4^-(\text{aq})$ to $\text{MnO}_2(\text{s})$,

$$E^\circ = \frac{1(0.564) + 1(0.274) + 1(4.27)}{3} = +1.70\text{V} \quad (4.4.2)$$

Remember to divide by the number of electrons involved in the oxidation number change (5 and 3 for the above equations).

Thermodynamically stable and unstable oxidation states

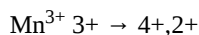
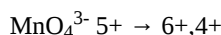
An unstable species on a Latimer diagram will have a lower standard potential to the left than to the right.

Example:

$\text{MnO}_4^{3-} \rightarrow \text{MnO}_2 + \text{MnO}_4^{2-}$ the MnO_4^{3-} species is unstable

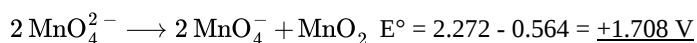
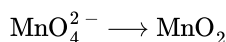
$$E^\circ = +4.27 - 0.274 = 3.997\text{V} \text{ (spontaneous disproportionation)}$$

Which Mn species are unstable with respect to disproportionation?



So stable species are: MnO_4^- , MnO_4^{2-} , MnO_2 , Mn^{2+} , and Mn^0 .

But MnO_4^{2-} is also unstable - why?



Moral: All possible disproportionation reactions must be considered in order to determine stability (this is often more convenient with a Frost diagram).

Note

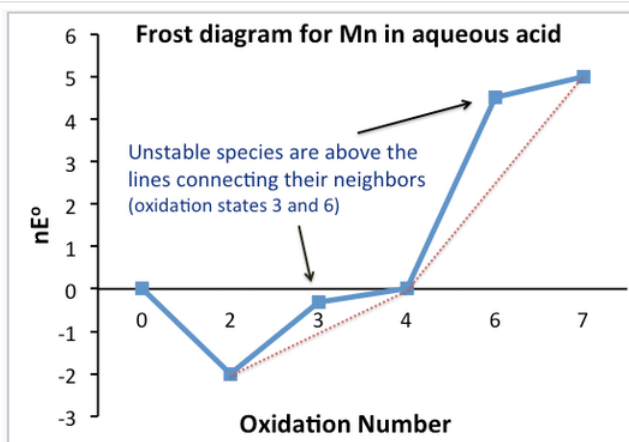
Thermodynamically unstable ions can be quite stable kinetically. For example, most N-containing molecules (NO_2 , NO , N_2H_4) are unstable relative to the elements (O_2 , N_2 , H_2), but they are still quite stable kinetically.

Frost diagrams:

In a Frost diagram, we plot $\Delta G^\circ/F (= nE^\circ)$ vs. oxidation number. The zero oxidation state is assigned a nE° value of zero.^[2]

Stable and **unstable oxidation states** can be easily identified in the plot. Unstable compounds are higher on the plot than the line connecting their neighbors. Note that this is simply a graphical representation of what we did with the Latimer diagram to determine which oxidation states were stable and unstable.

The **standard potential** for any electrochemical reaction is given by the **slope** of the line connecting the two species on a Frost diagram. For example, the line connecting Mn^{3+} and MnO_2 on the Frost diagram has a slope of +0.95, the standard potential of MnO_2 reduction to Mn^{3+} . This is the number that is written above the arrow in the Latimer diagram for Mn. Multielectron potentials can be calculated easily by connecting the dots in a Frost diagram.



A Frost diagram:

Contains the same information as in a Latimer diagram, but graphically shows stability and oxidizing power.

The lowest species on the diagram are the most stable (Mn^{2+} , MnO_2)

The highest species on diagram are the strongest oxidizers (MnO_4^-)

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