The Pourbaix diagram or the potential−pH thermodynamic equilibrium representation. It is named after Marcel Pourbaix (1938) and is mainly used in corrosion. However, it is a powerful tool for predicting the reaction of a system when certain parameters are changed (pH or potential). It is a diagram which indicates all the compounds obtained, for an element, according to its state of oxidation and the pH of the solution. A Pourbaix diagram is made up of several sections separated by lines.

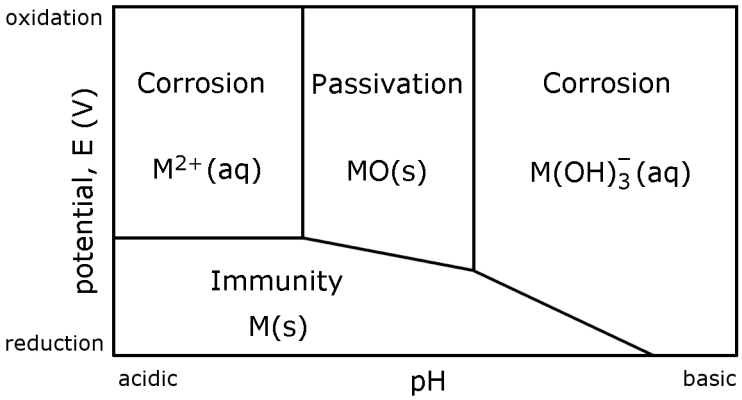

Figure 1. The Pourbaix representation of the metal M

The abscissa (X−axis) is the pH and the ordinate (Y−axis) is the potential. Therefore, the left part of the diagram corresponds to an acidic condition (right part is basic) and the top area of the diagram is the region associated to oxidized species while the lower part, indicate the reduced compounds.

The purpose of the lines

A line is a boundary between two phases that exist at equilibrium.

- A vertical line separates two compounds that are in acid−base equilibrium with each other. They are not affected by the potential (no electron exchanged).
- A horizontal line separates two compounds in an oxidation−reduction equilibrium. These reactions are not affected by the pH.
- A slope indicate that both H^+ (or OH^-) and the potential are responsible for the equilibrium position between two compounds. The slope follows the Nernst law.

The meaning of the regions

There are several regions in a Pourbaix diagram.

Immunity: Range of pH and potential where the bare metal is stable (non reactive). Often, it is at the bottom of the diagram where the potential is low. Some metals do not have an immunity region.

Corrosion: Regions where the compound is soluble and favor the dissolution of the material.

Passivation: Chemical state in which the material has reacted but forms a stable and insoluble compound, (i.e. oxide, hydroxide) which prevents corrosion. It could be a protective layer on the metal with high electrical resistance like Al_2O_3 or conductive like $Pt(OH)_2$.

The stability of the solvent

Since the pH of the solution can be changed, the solvent used in a Pourbaix diagram is water. However, water also have its own thermodynamic stability.

In oxidation, creation of oxygen gas: $2H_2O(\ell) \longrightarrow 4H^+(aq) + O_2(g) + 2e^-$

In reduction, creation of hydrogen gas: $H_2O(\ell) + 2e^- \longrightarrow H_2(g) + OH^-(aq)$

At high concentrations of either H^+ or OH^-, these ions are also involved in the thermodynamic stability of the electrolyte solution as shown in figure 2.

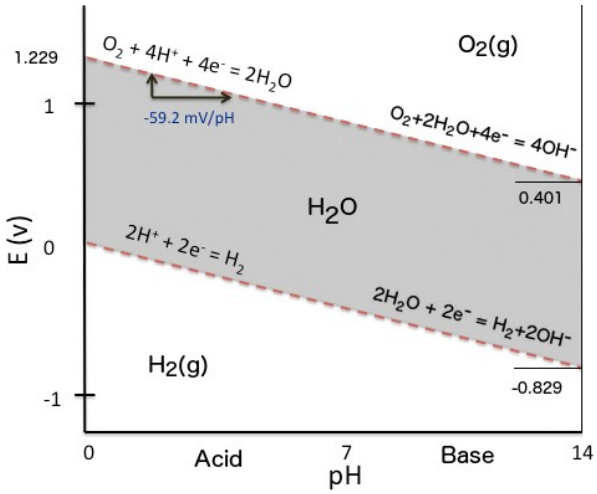

Figure 2. Pourbaix diagram of water (from https://commons.wikimedia.org/wiki/File:H2OPourbaix.png)

The gray zone in the diagram is the stability range of the water+electrolyte solution.

The two diagonal lines represent the thermodynamic stability of water. The slopes were calculated from the Nernst equation, here $\Delta E/\Delta pH = -59$ mV/pH.

Practical stability of the water solvent

A Pourbaix diagram is built from the thermodynamic stability and equilibrium of the compounds. However, in actual conditions, an overpotential (η) or a potential higher than the one calculated from thermodynamic values is needed for an electrochemical process to start. The overpotential changes according to the nature of the material of the electrode.

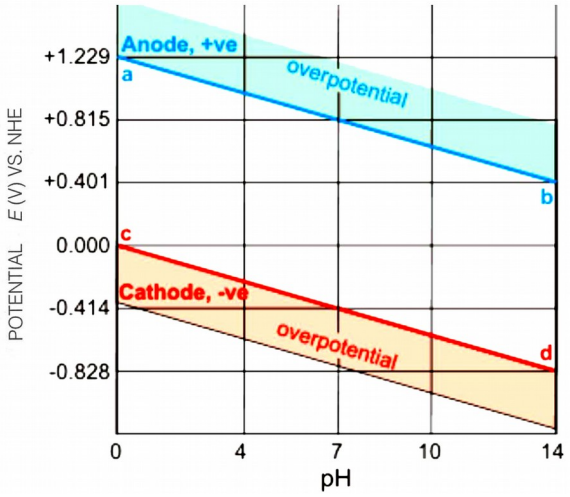

Figure 3. Overpotential (η) for the oxidation or reduction reaction of water.

Because of the overpotential, it is possible to run a process in water at a potential above the one of the stability of the water. For instance, consider the reduction of the Zn^{2+} ion in water under standard conditions:

$$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s) \quad E° = -0.76 \text{ V vs. NHE}$$

According to the Pourbaix diagram for zinc, the reduction of Zn^{2+} in an aqueous acidic solution is impossible to perform since the $H^+(aq)$ ion, present in large amount, will be reduced before the zinc ion. However, the reduction of the zinc ion is still possible at pH close to 7 where the water overpotential is important. In this case, under certain conditions, such a process becomes possible.

Combination of reactants

A Pourbaix diagram can represent the thermodynamic equilibrium of a system made up of several components. The lead sulfur diagram is a convenient way to analyze the lead acid cell developed by Planté in 1859, which was the first rechargeable cell.

Charged cell: $Pb(s) \mid H_2SO_4(aq) \mid PbO_2(s)$ FEM° = 1.33 V

Discharged cell: $PbSO_4(s) \mid H_2SO_4(aq) \mid PbSO_4(s)$ FEM° = 0.00 V

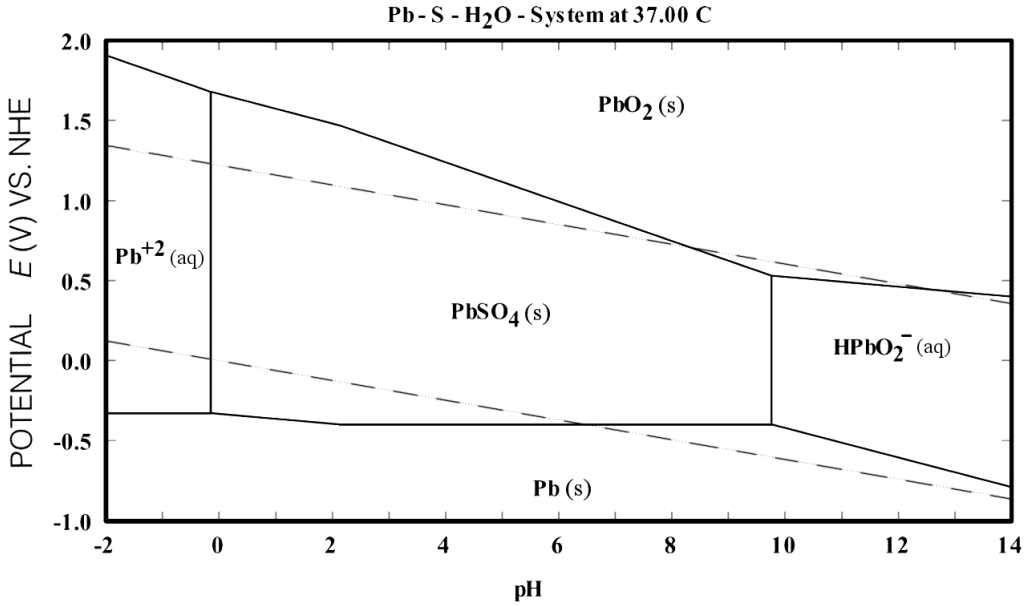

Figure 4. Pourbaix diagram for the lead−sulfur system.

The electrodes of the cell do not corrode because they are passivated with $PbO_2(s)$ and $PbSO_4(s)$. Hence, no separator (i.e. salt bridge) is required between the electrodes since the reagents / products are both insoluble.

The cell is rechargeable even if the potential required for this process exceeds the thermodynamic stability of the water (oxidation and reduction). The water overpotential needed to initiate the water electrolysis process is so important on a lead sulfate electrode that the oxidation and reduction of $PbSO_4$ will proceed first (before water electrolysis) when the cell is recharged.

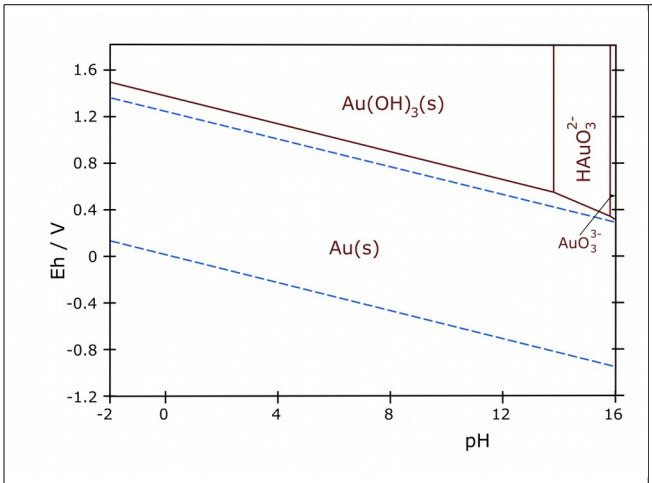

Figure 5. Gold

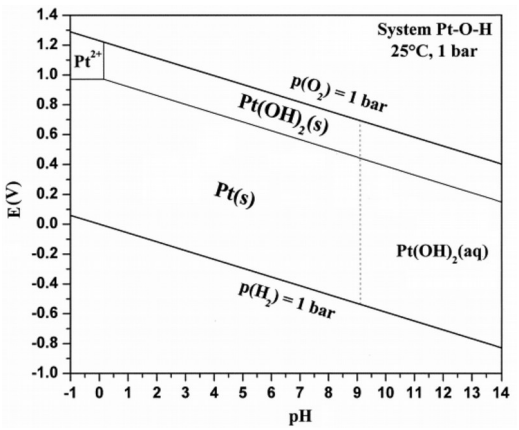

Figure 6. Platinum

The gold and platinum metals are the best materials to use as electrodes in electroanalytical chemistry. Despite the fact that platinum forms oxides at high potential, those are stable, non−soluble and electrically conductive.

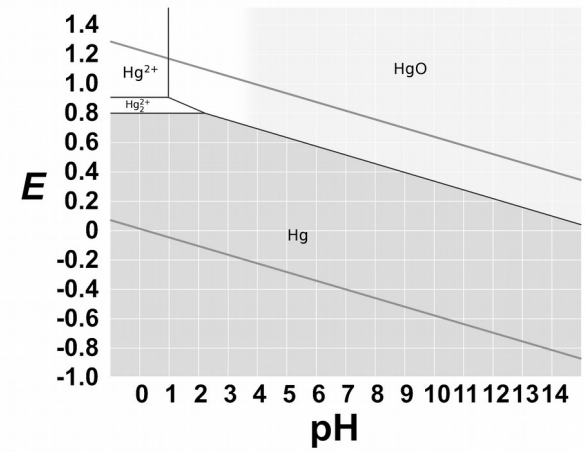

Figure 7. Mercury

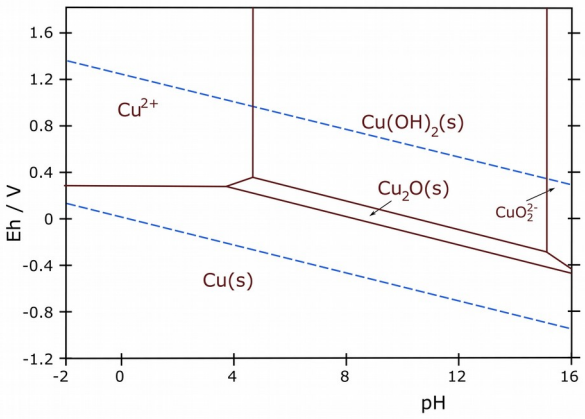

Figure 8. Copper

In reduction, the mercury electrode is an excellent material for metal analysis. Copper is also an interesting choice in reduction, however, it forms alloys with several metals (Zn, Ni, Fe, Al, Sn, etc.).

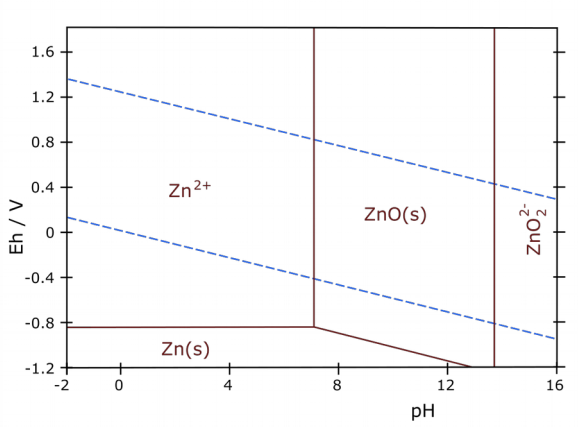

Figure 9. Zinc

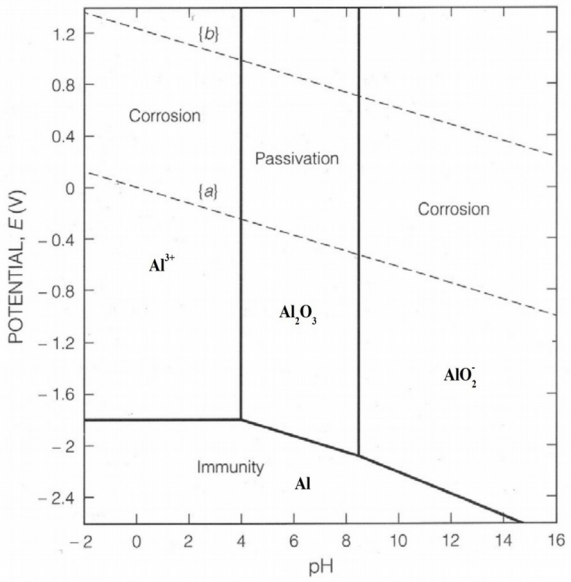

Figure 10. Aluminum

Zinc and aluminum are both amphoteric compounds. They can react with strong acids or strong bases to produce water soluble compounds, regardless of the potential.

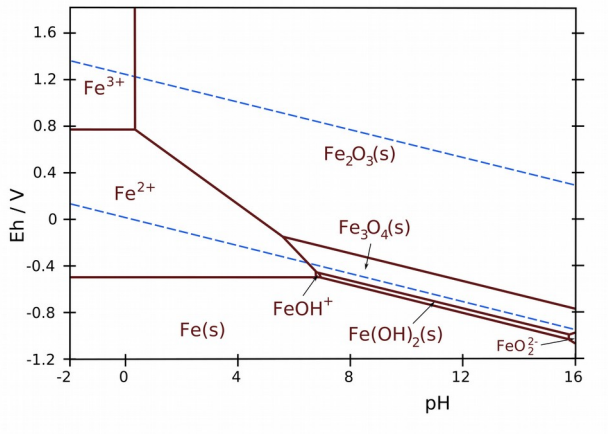

Figure 11. Iron

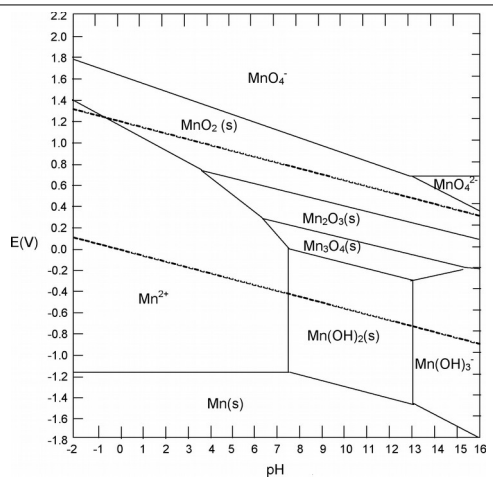

Figure 12. Manganese

There is no immunity for iron in water regardless of the pH of the solution.

Manganese can have several oxidation states. In this case, it gives a complex Pourbaix diagram.

Problems

To answer the following problems, please refer to the corresponding Pourbaix diagram (figures 4 to 12).

1. You want to plate (reduce) copper or Cu(s) on an electrode from a $CuSO_4$(aq) solution.
   a. What should be the pH of the solution?
   b. What is the maximum potential required vs. NHE to initiate the copper reduction when pH = 3.0?

2. Is it possible to reduce manganese ion in water to obtain manganese metal?

3. Potassium permanganate, $KMnO_4$(aq) is a powerful oxidizing agent. It exists in aqueous solution, but it is thermodynamically unstable and slowly decomposes in water. What is the product of this decomposition at pH = 7.0?

4. Aluminum is soluble in a 1.0 M acidic solution.
   a. If NaOH is added to this solution, at what pH will the aluminum ion start to precipitate?
   b. Write the chemical reaction for this precipitation (Hint: use H_2O and the Pourbaix diagram).

5. Can a copper electrode be used to:
   a. reduce water and produce hydrogen gas?
   b. oxidize water and produce oxygen gas?

6. A copper metal electrode is stable in acidic solution at E = 0 V. What will happen if the pH of the solution increases while keeping the potential constant? (write the reaction)

7. You want to study the oxidation of manganese (II) ion ($E° = 1.22$ V vs, NHE) at pH = 2.0. You have three electrodes: platinum, gold and mercury. Which one would be the best electrode to use?

8. Is it possible to either reduce or oxidize gold in water?

9. At any pH, what is the potential range (ΔE) corresponding to the thermodynamic stability of water?

Answers

1. a. $pH \leq 4.0$ b. $E \approx 0.3$ V
2. No. The manganese immunity (solid metal) is around 1 V below the reduction of water making H_2(g).
3. MnO_2(s).
4. a. $4.0 \leq pH$ b. $2Al^{3+}(aq) + 3H_2O(\ell) \longrightarrow Al_2O_3(s) + 6H^+(aq)$
5. a. Yes, at any pH. b. No. The copper is either ionic in acid or oxidized in basic solution.
6. $2Cu(s) + H_2O(\ell) \longrightarrow Cu_2O(s) + 2H^+(aq) + 2e^-$
7. Gold: best choice since it is still a metal under these conditions.
8. This is not thermodynamically possible as long as there is no other "redox" reagent in the solution.
9. The difference of potential between the two slope for the water is $\Delta E \approx 1.2$ V at any pH.

More information: https://www.gscsg.com/mini-corrosion-course-thermodynamics.html