

6 Simplified Procedure for Constructing Pourbaix Diagrams*

E. D. VERINK, JR.

Distinguished Service Professor Emeritus
Department of Materials Science and Engineering
University of Florida
Gainesville, Florida

A. INTRODUCTION

For the behavior of metals in aqueous solutions, one of the most important contributions to the corrosion literature has been the work of Pourbaix [1,2] and his associates in the development of thermodynamic equilibrium diagrams (E vs. pH), called Pourbaix diagrams. A vast amount of data may be presented simply and concisely in Pourbaix diagrams. When the advantages and limitations of such diagrams are understood, valuable inferences may be made regarding corrosion phenomena. The selection of conditions for cathodic and anodic protection is simplified. Candidates for consideration as inhibitor species may be selected with greater efficiency. Critical corrosion experiments may be designed with equal efficiency.

Corrosion processes involve both chemical and electrochemical phenomena. In 1923, Evans [3] observed that, if two samples of iron connected by a galvanometer are immersed in two solutions of potassium chloride, separated by a porous membrane, and if a stream of air is bubbled through one of these solutions, an electric current circulates between the aerated sample, which becomes the cathode, and the nonaerated sample, which becomes the anode and corrodes. On the other hand, if a sample of iron and a sample of another metal (copper, zinc, or magnesium) are connected as above, a passage of electric current is also observed. Under these circumstances, iron becomes the anode and corrodes when connected to copper, whereas zinc or magnesium become the anode and corrode providing protection to iron. Thus, it is necessary to consider not only chemical thermodynamics, but also electrochemical thermodynamics when considering corrosion reactions.

Chemical equilibria are defined as those that do not involve oxidation–reduction processes, but do involve the law of mass action and the law of solubility product (involving partial pressures or fugacities and concentrations or activities). By contrast, electrochemical reactions are defined as those in which free electric charges, or electrons, participate.

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B. THERMODYNAMIC BACKGROUND

The procedure for calculating Pourbaix diagrams is straightforward and is amenable to computer calculation. On the other hand, certain assumptions are made that must be borne in mind when applying the information available from Pourbaix diagrams in “real” situations. First is the assumption of equilibrium. Since Pourbaix diagrams are equilibrium diagrams, they give no information on the kinetics of the reactions considered. Kinetic information may be obtained experimentally by methods described elsewhere [4]. It also is assumed that the reaction products are known and that the free energy information of each solid and ionic species is known for the conditions of temperature and pressure of interest. The pH of the solution is assumed to be known and constant in the bulk as well as at the metal or reaction-products surface. Temperature and pressure are considered to be constant and are usually assumed to be 298 K (25°C) and 1 atm, respectively. Pourbaix diagrams may be calculated for other temperatures if thermodynamic data are available or may be estimated [5]. Generally, the features of Pourbaix diagrams are not significantly altered by increased pressures since thermodynamic properties are relatively insensitive to pressure (as compared with temperature).

The simple graphical methods described herein greatly facilitate the practical consideration of the various equilibrium reactions involved. For chemical reactions, it is convenient to make use of the Van't Hoff equation, which involves the equilibrium constant:

$$\Delta G^\circ = -RT \ln K = -2.303 \times 1.987 \times 298 \log K$$

For electrochemical reactions, the procedures involve manipulation of the Nernst equation, which can be written

$$\phi = \phi^\circ + \frac{0.0591}{n} \log \frac{(a_P)^p (a_{H^+})^h}{(a_R)^r (a_{H_2O})^w} \quad (1)$$

where

ϕ = reduction potential

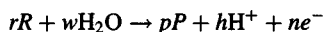
$$\phi^\circ = \frac{\Delta G^\circ}{n\mathcal{F}}$$

ΔG° = standard free energy change

\mathcal{F} = Faraday's constant

n = Number of free electrons

for the general reaction,



Note that electrochemical reactions are written as oxidation reactions; that is, electrons on the right.

Taking

$$a_{H_2O} = 1$$

and

$$\text{pH} = -\log a_{\text{H}^+}$$

then,

$$\phi = \frac{\Delta G^\circ}{n\mathcal{F}} + \frac{0.0591}{n} \log \frac{(a_P)^p}{(a_R)^r} + \frac{[-0.0591h]}{n} \text{pH} \quad (2)$$

The standard free energy change, ΔG° , for the reaction can be obtained readily from tabulated thermodynamic data. Therefore, the first term to the right of the equality sign in Eq. (2) is a constant. The second term also becomes a constant when values of a_P and a_R are chosen in the normal manner. In constructing Pourbaix diagrams, the concentration of the ionic species at the boundary between a solid substance and a dissolved substance is usually taken as a very low value, such as $10^{-6} M$. The sum of the first two terms in Eq. (2) gives a constant equal to the value of the potential, ϕ , at $\text{pH} = 0$. The resulting expression is the equation of a straight line of slope equal to the coefficient of the pH term, $-0.0591 h/n$, and intercept equal to ϕ at $\text{pH} = 0$.

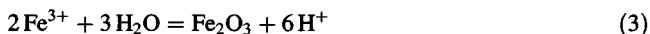
Pourbaix diagrams are constructed from the three, and only three, types of straight line relationships, which result from the analysis of the possible chemical and electrochemical equilibria in the system under consideration. Depending on the reactants and products of the assumed reactions, these straight lines will be either horizontal, vertical, or sloping.

1. A reaction involving a solid substance, a dissolved substance, and hydrogen ion in water without free electrons gives a vertical straight line; that is, independent of potential (when $n=0$, the slope of the line equals ∞).
2. A reaction involving a solid substance and a dissolved substance in water, plus free electrons but without hydrogen ion gives a horizontal straight line; that is, independent of pH (when $h=0$, the slope = 0).
3. A reaction involving a solid substance, a dissolved substance, free electrons, and hydrogen ion will give a straight line with a slope equal to $-0.0591h/n$.

After plotting the straight lines on potential versus pH coordinates, the domain of the thermodynamic stability for each individual species is determined by requiring that all equations involving that species be satisfied simultaneously.

Example 1

One solid substance, one dissolved substance plus hydrogen ion in water without free electrons.



Assuming the activities of H_2O and Fe_2O_3 to be unity, the equilibrium constant may be expressed

$$K = \frac{(a_{\text{H}^+})^6}{(a_{\text{Fe}^{3+}})^2} \quad (4)$$

$$\begin{aligned} \log K &= 6 \log(a_{\text{H}^+}) - 2 \log(a_{\text{Fe}^{3+}}) \\ &= -6 \text{pH} - 2 \log(a_{\text{Fe}^{3+}}) \end{aligned} \quad (5)$$

Referring to tabulated thermodynamic data and substituting in the Van't Hoff equation, $\log K$ may be calculated

$$\Delta G^\circ = -RT \ln K = -2.303 \times 1.987 \times 298 \log K$$

$$\log K = \frac{-\Delta G^\circ}{2.303 \times 1.987 \times 298} \quad (6)$$

$$= \frac{-(-1970)}{1373} \quad (7)$$

$$= 1.43$$

Substituting in Eq. (5) and rearranging, we obtain a generalized Pourbaix equation,

$$\log(a_{\text{Fe}^{3+}}) = -0.72 - 3\text{pH} \quad (8)$$

In the case where

$$(a_{\text{Fe}^{3+}}) = 10^{-6}$$

then $\text{pH} = 1.76$.

This gives a vertical line on the Pourbaix diagram.

Example 2

One solid substance, one dissolved substance, and electrons, but without H^+ as a reactant or product.



$$K = a_{\text{Fe}^{2+}} \quad (10)$$

$$\log K = \log(a_{\text{Fe}^{2+}}) \quad (11)$$

Using tabulated thermodynamic data, substitution in Eq. (2) gives

$$\phi = \frac{-20,300}{2 \times 23,060} + \frac{0.0591}{2} \log(a_{\text{Fe}^{2+}}) \quad (12)$$

$$\phi = -0.440 + 0.0295 \log(a_{\text{Fe}^{2+}})$$

which is a generalized Pourbaix equation.

In the case where

$$a_{\text{Fe}^{2+}} = 10^{-6}$$

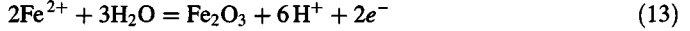
then

$$\phi = -0.617 \text{ V}$$

This gives a horizontal line on the Pourbaix diagram.

Example 3

One solid substance, one dissolved substance in water, plus free electrons, and hydrogen ion.



The equilibrium constant for this reaction may be expressed as

$$K = \frac{(a_{\text{H}^+})^6}{(a_{\text{Fe}^{2+}})^2} \quad (14)$$

and

$$\begin{aligned} \log K &= 6 \log(a_{\text{H}^+}) - 2 \log(a_{\text{Fe}^{2+}}) \\ &= -6 \text{pH} - 2 \log(a_{\text{Fe}^{2+}}) \end{aligned} \quad (15)$$

Substitution into Eq. (2) gives

$$\begin{aligned} \phi &= \frac{33,570}{2 \times 23,060} + \frac{0.0591}{2} - 6 \text{pH} - 2 \log(a_{\text{Fe}^{2+}}) \\ \phi &= 0.728 - 0.1773 \text{pH} - 0.0591 \log(a_{\text{Fe}^{2+}}) \end{aligned} \quad (16)$$

a generalized Pourbaix equation.

In the case where

$$a_{\text{Fe}^{2+}} = 10^{-6}$$

then

$$\phi = 1.0826 - 0.1773 \text{pH}$$

This gives a sloping line on the Pourbaix diagram.

C. CONSTRUCTION OF DIAGRAMS

Table 1 lists the data for the iron–water diagram together with the various reactions and equilibrium formulas [1]. Figure 1 shows a resulting Pourbaix diagram considering that the only solid species are iron, Fe_3O_4 , and Fe_2O_3 . Naturally, a number of other assumptions could have been made. However, this serves to illustrate the construction of a diagram. Lines ④ and ⑥ designate the limits of thermodynamic stability of water at 298 K and 1-atm pressure. Above line ⑥, water is unstable with regard to the evolution of oxygen, and below line ④, water is unstable with respect to the evolution of hydrogen. The other dashed lines on the diagram comprise an “ionic species diagram.” For ionic species (dashed lines), the coexistence lines represent the condition wherein the thermodynamic activity of the species on each side of that line is the same. For example, on line 6', the activities of Fe^{2+} and $\text{Fe}(\text{OH})_2^+$ are equal. The triple point involving lines 1', 6', and 7' is an invariant point at which the activities of Fe^{2+} , $\text{Fe}(\text{OH})_2^+$, and HFeO_2^- are the same.

TABLE 1. Information, Reactions, and Equilibrium Formulas for the Iron–Water System at 298°K (25°C) and 1 atm^a

A. Substances Considered and Substances not Considered					
	Oxidation Number (Z)	Considered	Not Considered	μ° (cal)	Name, Color Crystalline System
Solid substances	0	Fe		0	α -Iron, light gray, face centered cubic (fcc)
	+2	FeO hydr		– 58 (880)	Ferrous hydroxide Fe (OH) ₂ , white, rhomb
	+2		FeO anh.		Ferrous oxide, black, cubic
	+2.67	Fe ₃ O ₄ anh		– 242 (400)	Magnetite, black, cubic
	+2.67		Fe ₃ O ₄ × H ₂ O		Hydrated magnetite, green-black
	+3	Fe ₂ O ₃ anh		(a) – 177 (100)	Haematite, red brown, rhomb or cubic
	+3	Fe ₂ O ₃ hydr		(b) – 161 (930)	Ferric hydroxide Fe (OH) ₃ , red brown, fcc
Dissolved Substances	+2	Fe ²⁺		– 20 (300)	Ferrous ion, green
	+2	HFeO ₂ [–]		– 90 (627)	Dihypoferrite ion, green
	+2		FeO ₂ ^{2–}		Hypoferrite ion
	+3	Fe ³⁺		– 2 (530)	Ferric ion, colorless
	+3	FeOH ²⁺		– 55 (910)	Ferric ion, colorless
	+3	Fe (OH) ₂ ⁺		– 106 (200)	Ferric ion, colorless
	+3		FeO ₂ [–]		Ferrite ion
	+4		FeO ₂ ²⁺		Ferryl ion
	+4		FeO ₃ ^{2–}		Perferrite ion
	+5		FeO ₂ ⁺		Perferryl ion
	+6	FeO ₄ ^{2–}		– 111 (685)	Ferrate ion, violet

^a Excerpted from [1].

TABLE 1. (Continued)

B. Reactions and Equilibrium Formulas Two Dissolved Substances <i>Relative Stability of the Dissolved Substances</i>		
	Z = +2	
1.		$\text{Fe}^{2+} + 2 \text{H}_2\text{O} = \text{HFeO}_2^- + 3 \text{H}^+$
		$\log \frac{(\text{HFeO}_2^-)}{(\text{Fe}^{2+})} = -31.58 + 3\text{pH}$
	Z = +3	
2.		$\text{Fe}^{3+} + \text{H}_2\text{O} = \text{FeOH}^{2+} + \text{H}^+$
		$\log \frac{(\text{FeOH}^{2+})}{(\text{Fe}^{3+})} = -2.43 + \text{pH}$
3.		$\text{FeOH}^{2+} + \text{H}_2\text{O} = \text{Fe(OH)}_2^+ + \text{H}^+$
		$\log \frac{[\text{Fe(OH)}_2^+]}{(\text{FeOH}^{2+})} = -4.69 + \text{pH}$
	+2 → +3	
4.		$\text{Fe}^{2+} = \text{Fe}^{3+} + e^-$
		$E_0 = 0.771 + 0.0591 \log \frac{(\text{Fe}^{3+})}{(\text{Fe}^{2+})}$
5.		$\text{Fe}^{2+} + \text{H}_2\text{O} = \text{FeOH}^{2+} + \text{H}^+ + e^-$
		$E_0 = 0.914 - 0.0591\text{pH} + 0.0591 \log \frac{(\text{FeOH}^{2+})}{(\text{Fe}^{2+})}$
6.		$\text{Fe}^{2+} + 2\text{H}_2\text{O} = \text{Fe(OH)}_2^+ + 2\text{H}^+ + e^-$
		$E_0 = 1.191 - 0.1182 \text{pH} + 0.0591 \log \frac{[\text{Fe(OH)}_2^+]}{(\text{Fe}^{2+})}$
7.		$\text{HFeO}_2^- + \text{H}^+ = \text{Fe(OH)}_2^+ + e^-$
	+2 → +6	
		$E_0 = -0.675 + 0.0591 \text{pH} + 0.0591 \log \frac{[\text{Fe(OH)}_2^+]}{(\text{HFeO}_2^-)}$
8.		$\text{HFeO}_2^- + 2\text{H}_2\text{O} = \text{FeO}_4^{2-} + 5 \text{H}^+ + 4e^-$
	+3 → +6	
		$E_0 = 1.001 - 0.00738 \text{pH} + 0.0148 \log \frac{(\text{FeO}_4^{2-})}{(\text{HFeO}_2^-)}$
9.		$\text{Fe}^{3+} + 4 \text{H}_2\text{O} = \text{FeO}_4^{2-} + 8 \text{H}^+ + 3e^-$
		$E_0 = 1.700 - 0.1580 \text{pH} + 0.0197 \log \frac{(\text{FeO}_4^{2-})}{(\text{Fe}^{3+})}$
10.		$\text{FeOH}^{2+} + 3 \text{H}_2\text{O} = \text{FeO}_4^{2-} + 7 \text{H}^+ + 3e^-$
		$E_0 = 1.652 - 0.1379 \text{pH} + 0.0197 \log \frac{(\text{FeO}_4^{2-})}{(\text{FeOH}^{2+})}$
11.		$\text{Fe(OH)}_2^+ + 2\text{H}_2\text{O} = \text{FeO}_4^{2-} + 6 \text{H}^+ + 3e^-$
		$E_0 = 1.559 - 0.1182 \text{pH} + 0.0197 \log \frac{(\text{FeO}_4^{2-})}{[\text{Fe(OH)}_2^+]}$
<i>Limits of the Domains of Relative Predominance of the Dissolved Substances</i>		
1'.		$\text{Fe}^{2+}/\text{HFeO}_2^-$
		$\text{pH} = 10.53$
2'.		$\text{Fe}^{3+}/\text{FeOH}^{2+}$
		$\text{pH} = 2.43$
3'.		$\text{FeOH}^{2+}/\text{Fe(OH)}_2^+$
		$\text{pH} = 4.69$
4'.		$\text{Fe}^{2+}/\text{Fe}^{3+}$
		$E_0 = 0.771$
5'.		$\text{Fe}^{2+}/\text{FeOH}^{2+}$
		$E_0 = 0.914 - 0.0591 \text{pH}$

TABLE 1. (Continued)

6'.		$\text{Fe}^{2+}/\text{Fe}(\text{OH})_2^+$	$E_0 = 1.191 - 0.1182 \text{ pH}$
7'.		$\text{HFeO}_2^-/\text{Fe}(\text{OH})_2^+$	$E_0 = -0.675 + 0.0591 \text{ pH}$
8'.		$\text{HFeO}_2^-/\text{FeO}_4^{2-}$	$E_0 = 1.001 - 0.0738 \text{ pH}$
9'.		$\text{Fe}^{3+}/\text{FeO}_4^{2-}$	$E_0 = 1.700 - 0.1580 \text{ pH}$
10'.		$\text{FeOH}^{2+}/\text{FeO}_4^{2-}$	$E_0 = 1.652 - 0.1379 \text{ pH}$
11'.		$\text{Fe}(\text{OH})_2^+/\text{FeO}_4^{2-}$	$E_0 = 1.599 - 0.1182 \text{ pH}$
Two Solid Substances			
<i>Limits of the Domains of Relative Stability of Iron and Its Oxides and Hydroxides</i>			
12.	0 → +2	$\text{Fe} + \text{H}_2\text{O} = \text{FeO} + 2\text{H}^+ + 2e^-$	$E_0 = -0.047 - 0.0591 \text{ pH}$
13.	0 → +2.67	$3\text{Fe} + 4\text{H}_2\text{O} = \text{Fe}_3\text{O}_4 + 8\text{H}^+ + 8e^-$	$E_0 = -0.085 - 0.0591 \text{ pH}$
14.	0 → +3	$2\text{Fe} + 3\text{H}_2\text{O} = \text{Fe}_2\text{O}_3 + 6\text{H}^+ + 6e^-$	(a) $E_0 = -0.051 - 0.0591 \text{ pH}$ (b) $= -0.059 - 0.0591 \text{ pH}$
15.	+2 → 2.67	$3\text{FeO} + \text{H}_2\text{O} = \text{Fe}_3\text{O}_4 + 2\text{H}^+ + 2e^-$	$E_0 = -0.197 - 0.0591 \text{ pH}$
16.	+2 → +3	$2\text{FeO} + \text{H}_2\text{O} = \text{Fe}_2\text{O}_3 + 2\text{H}^+ + 2e^-$	(a) $E_0 = -0.057 - 0.0591 \text{ pH}$ (b) $= 0.271 - 0.0591 \text{ pH}$
17.	+2.67 → +3	$2\text{Fe}_3\text{O}_4 + \text{H}_2\text{O} = 3\text{Fe}_2\text{O}_3 + 2\text{H}^+ + 2e^-$	(a) $E_0 = 0.221 - 0.0591 \text{ pH}$ (b) $= 1.208 - 0.0591 \text{ pH}$
One Solid Substance and One Dissolved Substance			
<i>Solubility of Iron and Its Oxides and Hydroxides</i>			
18.	Z = +2	$\text{Fe}^{2+} + \text{H}_2\text{O} = \text{FeO} + 2\text{H}^+$	$\log(\text{Fe}^{2+}) = 13.29 - 2 \text{ pH}$
19.		$\text{FeO} + \text{H}_2\text{O} = \text{HFeO}_2^- + \text{H}^+$	$\log(\text{HFeO}_2^-) = -18.30 + \text{pH}$
20.	Z = +3	$2\text{Fe}^{3+} + 3\text{H}_2\text{O} = \text{Fe}_2\text{O}_3 + 6\text{H}^+$	(a) $\log(\text{Fe}^{3+}) = -0.72 - 3 \text{ pH}$ (b) $= 4.84 - 3 \text{ pH}$

TABLE 1. (Continued)

21.		$2 \text{FeOH}^{2+} + \text{H}_2\text{O} = \text{Fe}_2\text{O}_3 + 4 \text{H}^+$	(a) $\log (\text{FeOH}^{2+}) = -3.15 - 2 \text{pH}$ (b) $= 2.41 - 2 \text{pH}$
22.		$2 \text{Fe}(\text{OH})_2^+ = \text{Fe}_2\text{O}_3 + \text{H}_2\text{O} + 2 \text{H}^+$	(a) $\log [\text{Fe}(\text{OH})_2^+] = -7.84 - \text{pH}$ (b) $= -2.28 - \text{pH}$
23.	$0 \rightarrow +2$	$\text{Fe} = \text{Fe}^{2+} + 2e^-$	$E_0 = -0.440 + 0.0295 \log (\text{Fe}^{2+})$
24.		$\text{Fe} + 2 \text{H}_2\text{O} = \text{HFeO}_2^- + 3 \text{H}^+ + 2e^-$	$E_0 = 0.493 - 0.0886 \text{pH} + 0.0295 \log (\text{HFeO}_2^-)$
25.	$0 \rightarrow +3$	$\text{Fe} = \text{Fe}^{3+} + 3e^-$	$E_0 = -0.037 + 0.0197 \log (\text{Fe}^{3+})$
26.	$+2 \rightarrow +2.67$	$3 \text{Fe}^{2+} + 4 \text{H}_2\text{O} = \text{Fe}_3\text{O}_4 + 8 \text{H}^+ + 2e^-$	$E_0 = 0.980 - 0.2364 \text{pH} - 0.0886 \log (\text{Fe}^{2+})$
27.		$3 \text{HFeO}_2^- + \text{H}^+ = \text{Fe}_3\text{O}_4 + 2 \text{H}_2\text{O} + 2e^-$	$E_0 = -1.819 + 0.0295 \text{pH} - 0.0886 \log (\text{HFeO}_2^-)$
28.	$+2 \rightarrow +3$	$2 \text{Fe}^{2+} + 3 \text{H}_2\text{O} = \text{Fe}_2\text{O}_3 + 6 \text{H}^+ + 2e^-$	(a) $E_0 = 0.728 - 0.1773 \text{pH} - 0.0591 \log (\text{Fe}^{2+})$ (b) $= 1.057 - 0.1773 \text{pH} - 0.0591 \log (\text{Fe}^{2+})$
29.		$2 \text{HFeO}_2^- = \text{Fe}_2\text{O}_3 + \text{H}_2\text{O} + 2e^-$	(a) $E_0 = -1.139 - 0.0591 \log (\text{HFeO}_2^-)$ (b) $= -0.810 - 0.0591 \log (\text{HFeO}_2^-)$

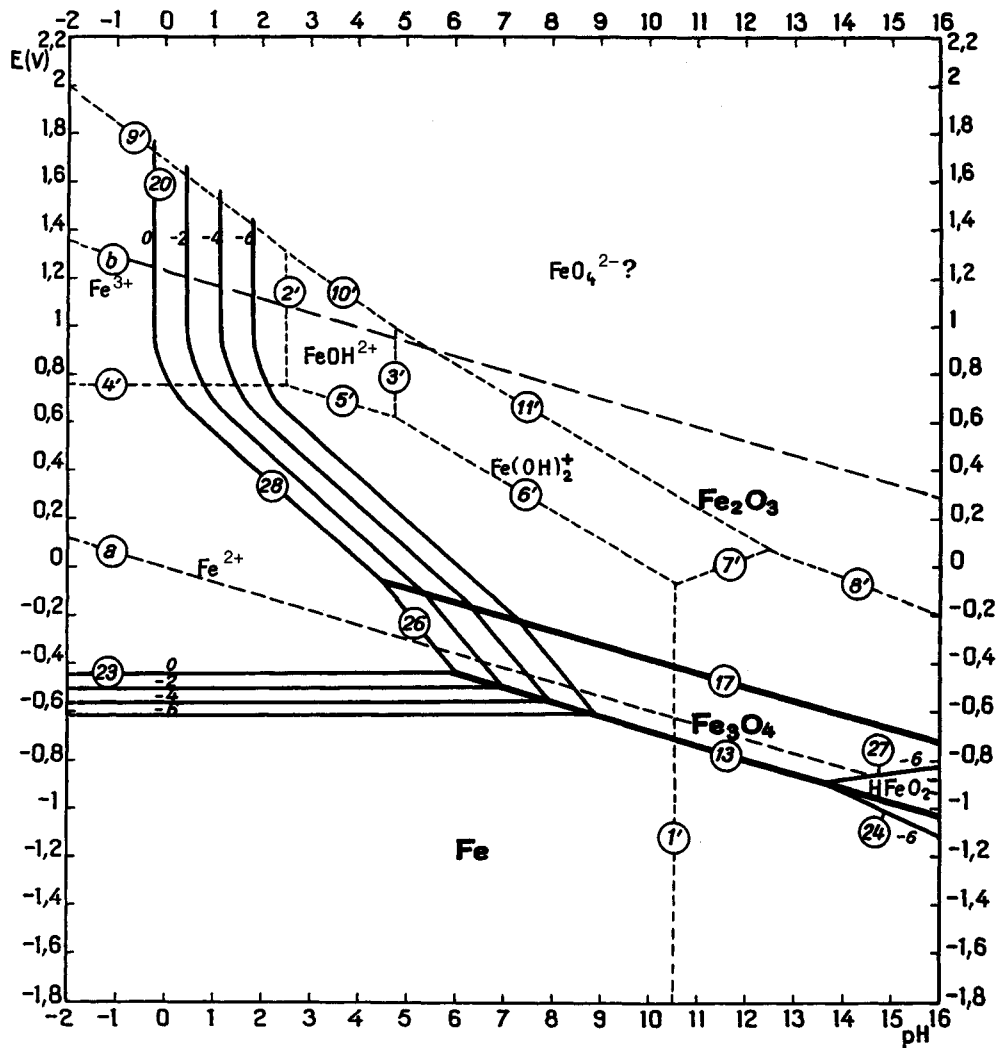


FIGURE 1. Potential–pH equilibrium diagram for the system iron–water at 25°C (considering as solid substances only Fe, Fe₃O₄, and Fe₂O₃) [1]. Reproduced with permission from [1]. Copyright © Marcel Pourbaix.

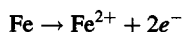
A line on the diagram represents a univariant system, whereas a family of lines, each of which is related to a value of a parameter, represents a divariant or trivariant system depending on whether the parameter contains one component (concentration) or two components (a term containing two concentrations). Heavy solid lines are used to separate solid species, whereas lighter weight solid lines are used to delineate the boundaries between a solid species and an ionic species.

Example Problem

It is suggested that the reader construct the Pourbaix diagram for the Fe–H₂O system (considering the solid species Fe, Fe₃O₄, and Fe₂O₃) at 298 K and 1-atm pressure. Plot the diagram on graph paper using pH ranging from –2 to +16 and the electrode potential from –1.8 to +2.2 V_{SHE}. The equations for each coexistence already have been calculated and are listed in Table 1. It will be

necessary to define what ionic activity will be considered to represent "significant corrosion." The establishment of what is considered to be "corrosion" evolves into a determination as to the amount of metal dissolution, which is permissible "for all practical purposes." It often has been found convenient to consider the solubility of 10^{-6} gram atoms of soluble ion per liter as representing "no corrosion for all practical purposes." On Figure 1, this assumption is represented by the lines marked -6 (the logarithm of the activity).

The domain of the metal is found at the bottom of the diagram. For simplicity, it is suggested that the equilibrium involving the metal and its least highly oxidized ionic form is an easy equilibrium to start with. In this case, we are considering Eq. (23¹) in Table 1 involving iron and ferrous ion. Inasmuch as no hydrogen ion is involved, it is apparent that this equilibrium coexistence involves a family of horizontal lines on potential versus pH coordinates the position of which depends on the assumed value of thermodynamic activity chosen for the ferrous ion. If you choose 10^{-6} for the ionic activity, you will obtain only one line. The question arises as to whether the domain of iron is above or below the line. Referring to the electrochemical equation,



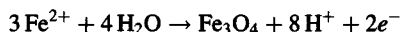
a "thought experiment" is helpful in answering this question. If electrons were added, the reaction would be driven in the direction of iron; thus, the addition of electrons (and hence, more negative potentials) favors iron rather than Fe^{2+} . Therefore, Fe is below the line and Fe^{2+} above the line.

The next question is "How far along the pH axis does the horizontal Fe/Fe^{2+} equilibrium coexistence extend?" To the left, the boundary is usually chosen arbitrarily by selecting the range of pH of interest. The limit for this line in the direction of higher pH depends on the activities of the ionic species and the restrictions imposed by other equilibria e.g., line 13 in Fig. 1, which is the coexistence between iron and Fe_3O_4 .



This is a logical choice for next consideration, since Fe_3O_4 is the solid species that involves oxide with the lowest level of oxidation of iron. Reaction (13) in Table 1 involves both electrons and hydrogen ion and will be a sloping line on the diagram. Another thought experiment will reveal on which side of line 13 iron is stable and on which side Fe_3O_4 is stable. Since this is a sloping line, there are two ways in which this decision can be made. Adding electrons will favor Fe; hence, Fe will be on the more negative side of the line (i.e., below the line). Addition of hydrogen ion (lower pH) also stabilizes the species iron. Thus, iron should be to the left (or below) the line and Fe_3O_4 to the right (or above). Simultaneous solution of the equations for lines 23 and 13 will reveal the point of intersection, and consequently, the termination of dominance of the Fe/Fe^{2+} coexistence.

A similar calculation for Reaction (26) in Table 1 between Fe^{2+} and Fe_3O_4 yields another line with a slope different from Reaction (13).



Adding either H^{+} or electrons to the right side pushes the reaction to the left to restore equilibrium. This favors the species on the left (Fe^{2+}). By using the same procedures, it is observed that lines 23, 26, and 13 in Figure 1 intersect at an invariant point for a given activity of ferrous ion.

Line 20, the equilibrium between Fe^{3+} and Fe_2O_3 , represents a reaction in which there is no electron transfer. Thus, by inspection of the equation, this coexistence will appear as a vertical line on the Pourbaix diagram. The decision of which species is on which side of the line can easily be made by assessing the effect of adding hydrogen ions and observing that this addition favors Fe^{3+} . Thus, Fe^{3+} is on the low-pH side of the line.

TABLE 2. Corrosion, *Y*, and Noncorrosion, *N*, of Iron at 298 K^{a,b}

Experiment	Sample No.	Solution	pH	$E_H(V)$	State of Metal ^c	Gas	
a.	1	H ₂ O distilled	8.1	-0.486	Y		
	2	NaCl	1 g/L	6.9	-0.445	Y	
	3	H ₂ SO ₄	1 g/L	2.3	-0.351	Y	H ₂
	4	NaHSO ₄	1 g/L	6.4	-0.372	Y	
	5	NaOH	1 g/L	11.2	+0.026	N	
	6	K ₂ CrO ₄	1 g/L	8.5	+0.235	N	
	7	K ₂ CrO ₄ + NaCl	1 g/L	8.6	-0.200	Y/N	
	8	KMnO ₄	0.2 g/L	6.7	-0.460	Y	
	9	KMnO ₄	1 g/L	7.1	+0.900	N	
	10	H ₂ O ₂	0.3 g/L	5.7	-0.200	Y	
	11	H ₂ O ₂	3.0 g/L	3.4	+0.720	N	O ₂
	12	Brussels city water		7.0	-0.450	Y	
b	13	NaOH	40 g/L degassed	13.7	-0.810	Y	H ₂
c	14	city water-iron-copper		7.5	-0.445	Y	
	15	city water-iron-zinc		7.5	-0.690	N	H ₂
	16	city water-iron-magnesium		7.5	-0.910	N	H ₂
	17	city water-iron-platinum		7.5	-0.444	Y	
	17'	city water-iron-platinum		8.7	-0.495	N	H ₂
c'	14'	city water-iron-copper		7.8	-0.385		Y
	15'	city water-iron-zinc		7.7	-0.690	N	H ₂
	16'	city water-iron-magnesium		8.7	-0.495	N	H ₂
	17'	city water-iron-platinum				Y	
	18	NaHCO ₃ 0.1 M Pole -		8.4	-0.860	N	H ₂
e	19	NaHCO ₃ 0.1 M Pole +		8.4	-0.350	Y	
	20	NaHCO ₃ 0.1 M Pole -		8.4	-0.885	N	H ₂
	21	NaHCO ₃ 0.1 M Pole -		8.4	+1.380	N	O ₂
	22	NaHCO ₃ 0.1 M Pole -		8.4	-0.500	Y	
	23	NaHCO ₃ 0.1 M Pole +		8.4	+1.550	N	O ₂
	24	NaHCO ₃ 0.1 M Pole -		8.4	-1.000	N	H ₂
	25	NaHCO ₃ 0.1 M Pole +		8.4	+1.550	N	O ₂

^a Experimental conditions used to test the predictions of the Pourbaix diagram for the iron-water system.

^b Excerpted from M. Pourbaix, "Lectures on Electrochemical Corrosion," Plenum, New York, 1973.

^c The abbreviations Y = corrosion; N = no corrosion.

It is suggested that the equilibrium coexistences be taken one at a time progressing from the elemental state through the various oxidized states, to establish the limits of each of the lines. It usually becomes complicated to draw all the lines and to remove those lines and portions of lines that are redundant or improper.

When the diagram is complete, it is possible to test the predictions of the Pourbaix diagram you have just drawn. Table 2 reports a number of experiments conducted by Pourbaix in which iron electrodes were immersed in various solutions. The pH and the electrode potential were measured in each case, and the specimens were allowed to stand in beakers containing each of the indicated chemical environments. Now plot on the diagram the data from the experiments numbered 1–25 in Table 2. For convenience, the sample numbers should be written beside each data point. This will make it possible to compare the experimental results of Pourbaix with the predictions based on the Pourbaix diagram. Remember, the term “immunity” is reserved for noncorrosion and represents the

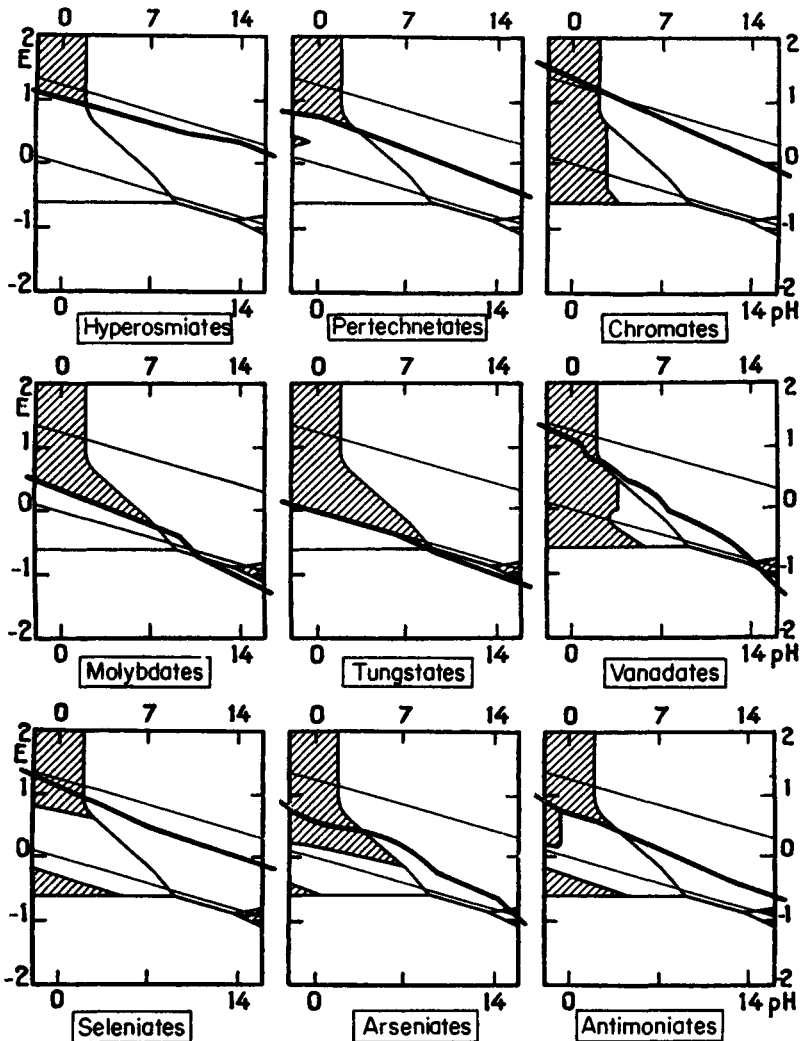


FIGURE 2. Oxidizing corrosion inhibitors. The hatched regions indicate theoretical corrosion domains in the presence of 0.01 M solutions of inhibitor. Reproduced with permission from [1]. Copyright © Marcel Pourbaix.

case in which corrosion cannot occur for thermodynamic reasons. The term "corrosion" is reserved for areas of the diagram where an ionic species is the stable species thermodynamically. "Passivation" describes the portion of the diagram where a solid reaction product is formed. Presumably, if the solid reaction product is protective, corrosion will stop. Thus, the term "passivation" might be said to apply to a region in the diagram where (thermodynamically) corrosion is possible, but it does not occur, because of the formation of a barrier coating. The diagram is not sufficient to decide whether a solid reaction product is also protective. This information can only be gained by performing an experiment. Comparison between the data points on your diagram with the information contained in Table 2 should reveal that in each case shown, the Pourbaix diagram would have predicted correctly whether or not corrosion would occur merely by knowing the electrode potential and the pH of the solution.

D. APPLICATIONS OF POURBAIX DIAGRAMS

It is possible to predict conditions under which corrosion, noncorrosion, and passivation are possible. It is also possible to make a number of other useful predictions. For example, the electrode potential for cathodic protection is represented by the equilibrium coexistence line between ferrous ion and iron in Figure 1. The domain of potential and pH in which anodic protection may be considered is represented by the passive region (either Fe_3O_4 or Fe_2O_3), but care should be exercised to avoid the domains where Fe^{2+} , Fe^{3+} , or HFeO_2^- are stable.

If the electrode potential falls in a corrosion regime (e.g., in the region where ferrous ion is stable) it is possible to stop corrosion either by adding an oxidant that would bring the electrode potential into the region of stability for Fe_2O_3 by raising the electrode potential, or by changing the pH in the alkaline direction so as to move horizontally into the passive region, or by cathodic protection that has the effect of lowering the potential into the immunity region. It should be emphasized that the predictions made by using the Pourbaix diagram should be tested prior to actual use, since the formation of a reaction-product film does not necessarily mean that this film is protective. In addition, cathodic protection may result in hydrogen evolution at the cathode, which could have an adverse effect on protective coatings or might under some circumstances induce hydrogen embrittlement of certain metals.

It is also possible to predict the types of ions that have promise as oxidizing corrosion inhibitors. Superposition of the chromium-water diagram over the iron-water diagram, for example, shows that the region of stability for Cr_2O_3 coincides with a portion of the iron diagram wherein ferrous ion is the stable species.

Consequently, in the absence of an inhibitor, corrosion of iron would be anticipated in this domain of potential and pH. The effect of adding chromates is to provide a means of forming a protective Cr_2O_3 film that inhibits corrosion. Figure 2 suggests the influence of various oxidizing inhibitors on the corrosion of iron [1]. These predictions should be tested before actual use.

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