$$\mathrm{Fe}^{3+} + \mathrm{e}^{-} \rightarrow \mathrm{Fe}^{2+}$$

Corrosion Potential Ecorr:

When two half cell reactions occur simultaneously on a metal surface, both of them will change the potential to an intermediate value called the corrosion potential. At the corrosion potential all the rates (current densities) are equal:  $i_c = i_a = i_{corr}$ . This is schematically shown in the figure.



**FIGURE 3.7** Polarization of anodic and cathodic half-cell reactions for zinc in acid solution to give a mixed potential, *E*<sub>corr</sub>, and a corrosion rate (current density), *i*<sub>corr</sub>. (*From M. G. Fontana*, Corrosion Engineering, *3rd ed., McGraw-Hill, New York, p.* 457, 1986. Reprinted by permission, *McGraw-Hill Book Company.*)

Effect of Exchange Current Density:

The exchange current density often outweighs the thermodynamic driving force in determining the rate of reaction. This is shown for the example of Fe and Zn. The half cell potential for the anodic oxidation of Fe is about -0.44V, while for Zn it is about -0.76V. Therefore Zn should corrode before Fe. Figure 3.8. shows the polarization diagrams for Zn (dashed lines) and Fe (solid lines). One can see that the current density at the corrosion potential for Fe is larger than the current density for Zn at the respective potential. Therefore Zn corrodes slower than Fe, although it has the more negative  $E_{corr}$ . Both  $i_{corr}$  and  $E_{corr}$  are used in corrosion protection of iron with a Zn coating, as the Zn starts to corrode first ( $E_{corr}$ ), and the corrosion is much slower than that of Fe ( $i_{corr}$ ).



**FIGURE 3.8** Comparison of electrochemical parameters for iron and zinc in acid solution, demonstrating the importance of  $i_o$  on determination of corrosion rates. Dashed lines represent lines from Figure 3.7 superimposed for comparison.

Effect of added oxidzer:

The driving force of corrosion is increased by the addition of a stronger oxidizer. In other words, when a redox system with a much more noble half cell potential is added to the system, the corrosion will increase. For example we consider the addition of  $Fe^{3+}/Fe^{2+}$  to an acid solution. Figure 3.9 shows the determination of the resulting mixed potential  $E_{corr}$  for the corroding metal M. The horizontal lines mark the half cell potentials for the three reactions that occur in the system. The dashed lines represent the total reduction rate and the total oxidation rate. Again  $E_{corr}$  is found where the total reduction rate equals the total oxidation rate. In figure 3.10 the determination of the anodic oxidation rate ( $i_{corr}$ ) is shown for the same system as in figure 3.9. As the oxidation of M is the only oxidation reaction,  $i_{corr}$  equals the sum of the two cathodic reduction reactions  $i(Fe^{3+} \rightarrow Fe^{2+})$  and  $i(H^+ \rightarrow H_2)$ .

Figure 3.9 shows that the added oxidizer only has an effect, when its exchange current density  $i_0$  is large. With a low  $i_0$  as shown in figure 3.11 there is no increase in the oxidation due to the added oxidizer, as the total rate of reduction is only due to  $i(H^+ \rightarrow H_2)$  in this case.



**FIGURE 3.9** Determination of the mixed potential  $E_{corr}$  for a corroding metal M exposed to acid solution with a second oxidizer,  $Fe^{3+}/Fe^{2+}$ , present. (From M. G. Fontana, Corrosion Engineering, 3rd ed., McGraw-Hill, New York, p. 466, 1986. Reprinted by permission, McGraw-Hill Book Company.)



**FIGURE 3.10** Rates of reduction  $(i_{Fe^{3+}} \rightarrow Fe^{2+})$  and  $i_{H^+} \rightarrow H_2$  and oxidation  $(i_{corr})$  from Figure 3.8 (*From M. G. Fontana*, Corrosion Engineering, *3rd ed., McGraw-Hill, New York, p. 467, 1986. Reprinted by permission, McGraw-Hill Book Company.*)



**FIGURE 3.11** No effect on corrosion when oxidizer of low *i*<sub>o</sub> is added to an acid solution. (*From M. G. Fontana,* Corrosion Engineering, 3rd ed., McGraw-Hill, New York, p. 467, 1986. Reprinted by permission, McGraw-Hill Book Company.)