CHEY0016 Lecture 15

Corrosion Science and the application of the Butler-Volmer equation to measure the rate of corrosion

Corrosion is one of the most important examples of surface chemistry. Corrosion is thought to cost around 3.5 % of the G.D.P. of industrialised societies and is thought to cost the US Air-Force more than $1 bn per year. Corrosion is an interesting phenomenon, because it is an example of surface chemistry, with electrochemical mechanisms. Indeed, without understanding electrochemistry and especially electrode kinetics it is not really possible to understand corrosion.

Basic concepts

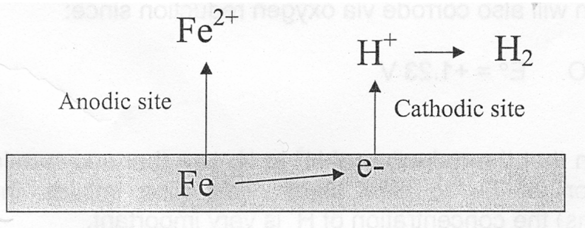
Corrosion involves (using a rather specific definition) the oxidation of a metal at a surface. Since an oxidation process must necessarily be supplied with electrons, in most corrosion situations a second reduction process takes place in the vicinity of the oxidation site.

For example:

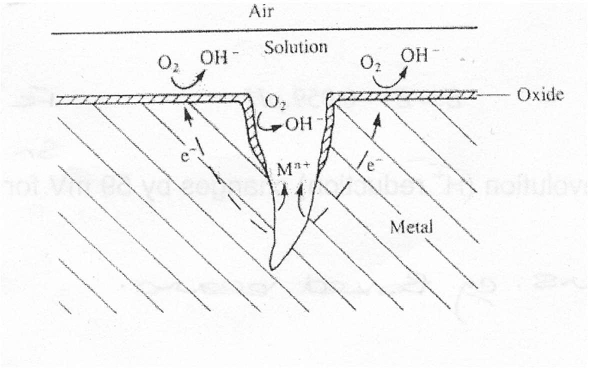
$Fe \rightarrow Fe^{2+} + 2e^-$	Metal oxidation	Anodic process
$2H^+ + 2e^- \rightarrow H_2$	Hydrogen evolution	Cathodic processes
$O_2 + 4e^- \rightarrow 2H_2O$	Oxygen reduction	

It is important to remember that both anodic and cathodic (oxidative and reductive) processes must be present for corrosion to take place. This fact though allows for control of corrosion, by suppression of one or both of the processes.

An overly simplistic picture might look like this:



An example is crevice corrosion, where the separate anodic and cathodic sites are clearly identified and result in morphological change of the surface.



Naturally, corrosion processes, like everything else are controlled both by thermodynamics and kinetics. Both are important, since thermodynamics tells us the fundamental feasibility of the reaction, kinetics the rate.

A brief revision of 1st year thermodynamics:

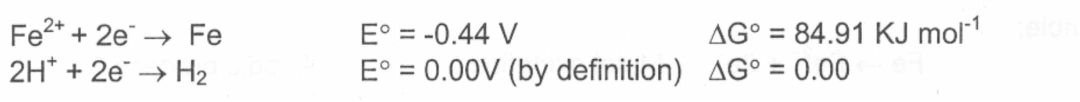
The standard free energy, ΔG^o tells us the thermodynamic feasibility of a reaction. Since the standard electrode potential of a reaction, $E°$ and $\Delta G°$ are intimately linked; one can use the standard electrode potentials of a reaction to calculate the thermodynamic feasibility of a reaction.

$$\Delta G^o = -nFE^o$$

For the example of iron corroding in deoxygenated acid solution:

$$Fe + 2H^+ \rightarrow Fe^{2+} + H_2$$

Standard reduction potentials (from Atkins)



$Fe^{2+} + 2e^- \rightarrow Fe$	$E° = -0.44$ V	$\Delta G° = 84.91$ KJ mol^{-1}
$2H^+ + 2e^- \rightarrow H_2$	$E° = 0.00$V (by definition)	$\Delta G° = 0.00$

So, we have a Galvanic cell and can write the above in terms of an overall cell reaction. The convention is to place the oxidising system on the Left Hand Side (LHS) and the system being reduced on the RHS:

$Fe \mid Fe^{2+} \parallel 2H^+ \mid H_2$

The cell potential is the RHS – LHS or more formally: E° (cell) = E° (RHS) - E° (LHS).

So for Fe corroding in 1M acid can write:

$E° = 0.00 - -0.44$
$E° = +0.44$ V.

So, this reaction is thermodynamically feasible since:

$\Delta G = -nFE°$

To correct for different concentrations of acid, use the Nernst equation.

Moreover, it can be seen that the reduction of oxygen to water also forms a convenient half reaction with iron oxidation:

$O_2 + 4e^- + 4H^+ \rightarrow 2H_2O$

The effect of pH

It can already' be seen that the reduction of H+ to H2 is a thermodynamically feasible way to allow the oxidation of Fe to take place. This also implies that (especially in deoxygenated solutions) the concentration of H+ is very important.

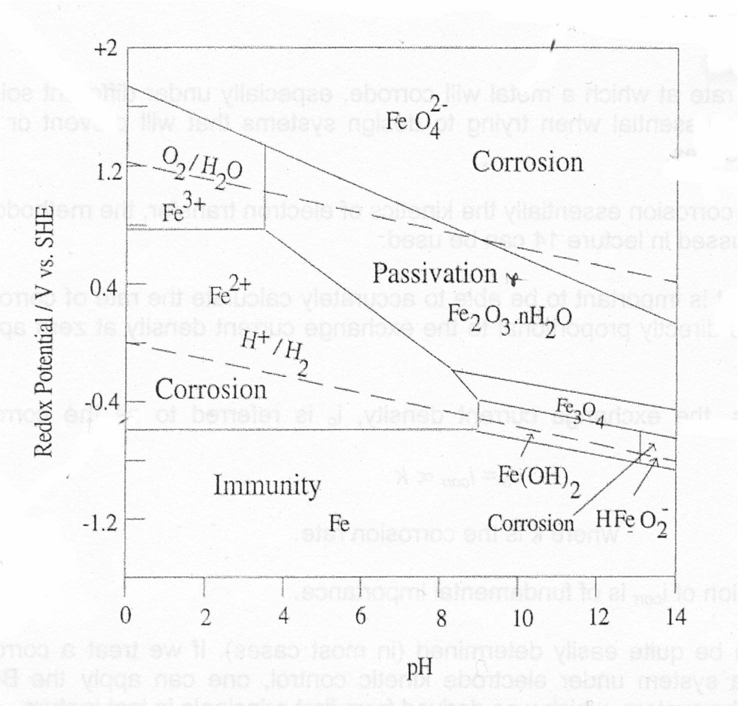
Since pH = -log [H+], then:

using the Nernst equation one can write:

$$E = E^{o} + \frac{2.3RT}{nF}\log a_{H+} \qquad = \qquad E = E^{\circ} - 0.059.pH$$

So, E for the hydrogen evolution (H+ reduction) changes by 59 mV for every change in pH unit.

The Effect of pH and applied potential on corrosion – The Pourbaix Diagram



The Pourbaix diagram is commonly used by corrosion engineers to determine the pH and potential where a metal will either be stable to corrosion, will corrode or form a passivating layer. Note, this is a very simplified diagram, with

Looking at the above diagram, it can be seen that at applied potentials more negative than -0.6 V vs. SHE (Standard Hydrogen Electrode), Fe will not corrode (at all but very high pH's). At potentials more positive than -0.6 V Fe will corrode, but to different products depending on pH, however at pH's> 4, Fe will form a blocking passive layer of Fe_20_3.

This diagram is important, since it shows that by controlling the applied potential on a piece of metal, and or the pH of the immersing solution one can control the corrosion rate. This leads to two methods of protecting metal from corrosion known as *Cathodic protection* and *Anodic protection.*

Cathodic Protection

This involves applying a negative potential to the metal to be protected, so taking the metal into the immunity region on the Pourbaix diagram. This can be done via an external electrical circuit, or by attaching a sacrificial anode to the metal, which corrodes more readily, donating its electrons to the host metal hence reducing its potential. This method is commonly used on pipelines.

Zinc galvanisation is a good example of cathodic protection, where the Zn layer as well as forming a protective coating forms a sacrificial anode which cathodically protects the underlying metal.

Anodic Protection

This involves applying a positive potential to a piece of metal, to form a passivating layer. This is risky, since if the potential and pH are not finely controlled, the corrosion rate can actually increase (see Pourbaix diagram).

Kinetics of Corrosion

A knowledge of the rate at which a metal will corrode, especially under different solution conditions and pH is essential when trying to design systems that will prevent or slow down corrosion processes.

Since the kinetics of corrosion essentially the kinetics of electron transfer, the equations used to understand electrode kinetics can be used (refer to Dr. Marken's lectures). Most importantly, the Butler-Volmer equation since this relates current (rate of interfacial reaction) with both applied voltage and the E^o for a specific system.

The corrosion form of the Butler-Volmer equation:

$$i = i_o \left[\exp - \frac{\alpha n F (E - E_{corr})}{RT} - \exp \frac{(1-\alpha) n F (E - E_{corr})}{RT} \right]$$

In corrosion studies, it is important to be able to accurately calculate the rate of corrosion. The corrosion rate is directly proportional to the exchange current density at zero applied potentials.

In corrosion studies, the exchange current density, i_o is referred to as the corrosion current:

$$i_o = i_{corr} \propto k$$

where k is the corrosion rate.

Hence, a determination of i_{corr} is of fundamental importance.

Fortunately, i_{corr} can be quite easily determined (in most cases). If we treat a corroding piece of metal as an electrochemical system under electrode kinetic control, one can apply the Butler- Volmer equation to the system, which was derived from first principals in last lecture.

This equation can be simplified as shown below to:

$$i = i_o\left[\exp - \frac{\alpha nF(E - E_{corr})}{RT} - \exp\frac{(1-\alpha)nF(E - E_{corr})}{RT}\right]$$

$$\log|i| = \log i_{corr} - \frac{\alpha nF(E - E_{corr})}{2.3RT}$$ **At Cathodic potentials**

$$\log|i| = \log i_{corr} + \frac{(1-\alpha)nF(E - E_{corr})}{2.3RT}$$ **At Anodic potentials**

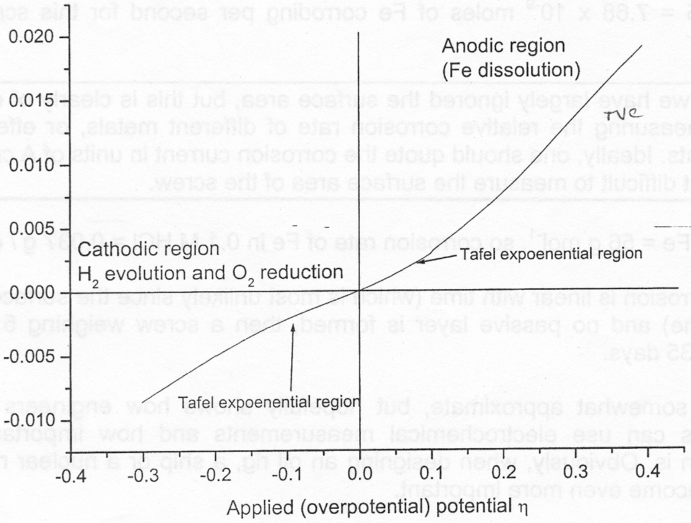
A corroding system has both anodic and cathodic processes taking place, with the electrons being liberated by the oxidation process being used up in the reduction process. Hence, one would expect the value of icorr in both the anodic and cathodic reactions to be identical.

Experimental determination of i_{corr}

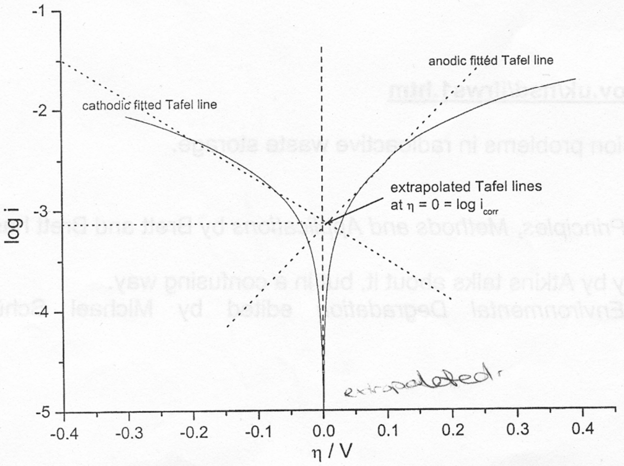
Experimentally, the easiest way to determine i_{corr} is to connect the corroding system to a potentiostat via a 3 electrode cell. The corroding sample forms the working electrode. The system is polarised, that is both anodic and cathodic over-potentials (η) applied to the sample by sweeping the applied potential and the current measured. This is essentially a linear sweep voltammetry experiment, but potential sweep should be slow to prevent mass transfer effects.

Clearly then for both anodic and cathodic half reactions, by plotting log i vs. η will yield a straight line, with intercept at η = 0 giving log i_{corr}. Moreover, both straight lines will intercept at η = O. In fact, one has to extrapolate the linear part of the B-V equation to the η= 0 case, since at very low applied potentials the exponential relationship between η and i breaks down.

In the following example, a steel nail was placed in 0.1 M HCl and the corrosion rate determined by sweeping a potential each side of the open circuit potential (-0.495 V vs. Ag/AgCl) at 5 mV s^{-1}.



This is real data! The anodic and cathodic Tafel regions can clearly be seen. The following graph shows how Tafel analysis can be used to determine corrosion rate:



So, by extrapolation of the η vs. log Iii plot, the corrosion current could be determined:

log i_{corr} = -3.13
i_{corr} = 7.41 x 10^{-4} A.

Now, 1 A = 1 coulomb s^{-1}.

And 1 F = 96485 C, moreover, F = N_Ae (N_A = Avagadro constant), e = charge on electron. That is, 1 F is 1 mole of charge.

So, a current of 7.41 x 10^{-4} A =

7.41 x 10-4 / 96485 = 7.68 x 10-9 moles of Fe corroding per second for this screw of surface area *x*.

Note, for simplicity, we have largely ignored the surface area, but this is clearly of crucial importance when measuring the relative corrosion rate of different metals, or effects of different environments. Ideally, one should quote the corrosion current in units of A cm-2. In this case, it was a bit difficult to measure the surface area of the screw.

Molecular weight of Fe = 56 g mol-1, so corrosion rate of Fe in 0.1 M HCl = 0.037 g / day.

So, if this rate of corrosion is linear with time (which is most unlikely since the surface area will change with time) and no passive layer is formed, then a screw weighing 5 g will entirely corrode in 135 days.

This calculation is somewhat approximate, but hopefully shows how engineers when designing structures can use electrochemical measurements and how important the problem of corrosion is. Obviously, when designing an oil rig, a ship or a nuclear reactor such calculations become even more important.

The study of corrosion is a good example of how the analytical methods described in this lecture course can be combined to build up a complete picture of a process. For example, corrosion in the stainless steel tanks used to hold radioactive waste at Sellafield, Cumbria is a big problem. Research at Sellafield into this problem combines electrochemical methods as show here with surface infra-red, AFM, STM, XPS and other methods.

Check out: http://www.hse.gov.uk/nsd/ilrws1.htm

for more on corrosion problems in radioactive waste storage.

Further reading
Electrochemistry, Principles, Methods and Applications by Brett and Brett has a chapter on corrosion.
Physical Chemistry by Atkins talks about it, but in a confusing way.
Corrosion and Environmental Degradation edited by Michael Schotze is very comprehensive.