



Ready for Redox?

Let's start by looking at a solution used to "pickle" (rough-clean) steel, which initially contains ferric sulfate $\text{Fe}(+3)$ and sulfuric acid. With time, iron, which dissolves from rust or from the metal, may enter the solution as ferrous sulfate $\text{Fe}(+2)$, and may be partially air-oxidized to $\text{Fe}(+3)$. To prevent pitting of the metal, experience has shown that the ratio of $\text{Fe}(+3)$ to $\text{Fe}(+2)$ must remain high. This ratio can be monitored with a redox electrode, making what is also called an **ORP (Oxidation Reduction Potential)** measurement. What happens when we make this measurement?

The difference between $\text{Fe}(+2)$ and $\text{Fe}(+3)$ is only one electron in the outermost shell. It is entirely possible that there is an interchange taking place between $\text{Fe}(+2)$ and $\text{Fe}(+3)$ ions in solution so that, while the total number in either state remains the same, any individual ion may occasionally switch from one state to the other by an electron transferring from one ion to another. We have no direct way of detecting this.

How the Electrode Works

Suppose that we now introduce an inert metal (one that does not react with the solution or with air, like platinum or gold) into this solution. Some $\text{Fe}(+2)$ ions will collide with the metal and on leaving, leave an electron behind on the metal surface, becoming $\text{Fe}(+3)$. Similarly, some $\text{Fe}(+3)$ ions will collide with the metal and take an electron from the surface, becoming $\text{Fe}(+2)$.

Whether the metal surface comes to

equilibrium with more or less electrons than it started with will depend on the ratio of $\text{Fe}(+3)$ to $\text{Fe}(+2)$. For example, if we add more $\text{Fe}(+3)$ to the solution, more electrons are likely to be removed, and we would observe that the metal becomes more positive.

In the bulk of the solution, the interchange of electrons (if it occurs) cannot change the ratio of $\text{Fe}(+3)/\text{Fe}(+2)$ because $\text{Fe}(+3)$ becomes $\text{Fe}(+2)$ and vice versa. Is this also true at the metal surface? Suppose we start with a solution that is all $\text{Fe}(+3)$, will it all go to $\text{Fe}(+2)$ at the surface? The answer, as you may suspect, is no.

The reason is that as the first $\text{Fe}(+3)$ ions acquire electrons from the metal, the surface becomes more positive. The next $\text{Fe}(+3)$ ions to arrive find that it is harder to pull the negative electrons out of a positive surface, so the rate of that reaction slows down as it proceeds ⁽¹⁾.

Meanwhile some $\text{Fe}(+2)$ is formed. Those ions find it relatively easy to donate the negative electrons to a positive surface. It is clear that any ratio of $\text{Fe}(+3)/\text{Fe}(+2)$ will come to an equilibrium and that the charge on the surface of the metal will be related in some fashion to that equilibrium ratio. We have formed our redox potential, and not significantly changed the solution.

ORP Measurements

We can expect that the more oxidizing the solution (for example, the more $\text{Fe}(+3)$), the more positive the potential. In fact, the relationship between the ratio and the potential turns out to be our old



friend, the Nernst Equation, which says that the potential is proportional to the log of the ratio for $\text{Fe}^{(+3)}/\text{Fe}^{(+2)}$.

To use this exchange of electrons as an analytical tool, there are only two deceptively simple requirements. First, the reaction of Fe ions with the platinum surface must be the predominant reaction in the solution. The exchange has to be the only reaction creating a potential on the metal surface. This means that there is some lower limit of concentration where, even if both $\text{Fe}^{(+2)}$ and $\text{Fe}^{(+3)}$ are present, other trace reactions might also be exchanging significant numbers of electrons.

Secondly, the exchange must occur at a high enough rate to fix the potential. Meters draw a tiny amount of current when measuring a potential, and this means they withdraw or add some electrons. The exchange must be able to quickly restore the equilibrium potential at the surface. This rapid exchange is what electrochemists mean when they say "the reaction must be reversible". Unfortunately for analytical chemistry, there are only a limited number of electrochemically reversible reactions.

Other Redox Pairs

The most famous (for us) is the reaction of I⁻ exchanging electrons with I₂. This reaction is very fast, and occurs at a high rate. A particular concentration of iodide and iodine, in contact with a platinum wire, is the basis of the Ross® reference element in the Ross® electrode. Other usable pairs with a high exchange rate are silver/silver ion, mercurous/mercuric, cerous/ceric, manganous/manganous

dioxide, chromic/ dichromate. (Notice that the first two are the basis of the other kinds of reference electrodes - silver chloride and calomel.)

⁽¹⁾ If we separate the Fe^{+3} and Fe^{+2} solutions (except for a salt bridge), put electrodes in each compartment and close the external circuit, then the electrons removed by Fe at one electrode are contributed by Fe at the other, and the electrons flow through the wire until the Fe^{+3} and Fe^{+2} concentrations are the same in both compartments. This is a battery.