

# Studies on Redox Equilibrium and Electrode Potentials

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## Abstract

Metal corrosion is very important factor for redox reaction during cell reactions. So that it has been studied in this research work. When metals react, they give away electrons and form positive ions. This particular topic describes how a metal form hydrated ions in solution. It can be considered the case of Magnesium and Copper in water. It can be compared the following two reactions how these two changes take place:



It is known that magnesium is more reactive than copper. The first reaction happens much more readily than the second one. Now it will be tried to express this with some numbers.

**Keywords:** Battery, Cell, Electrode, Magnesium Electrode, Copper Electrode, EMF

## I. Introduction

Let us consider a bar of magnesium in a beaker of water. There will be some tendency for the magnesium atoms to oxidized and leave electrons and go into solution as magnesium ions. The electrons will be left behind on the magnesium bar[1-24].

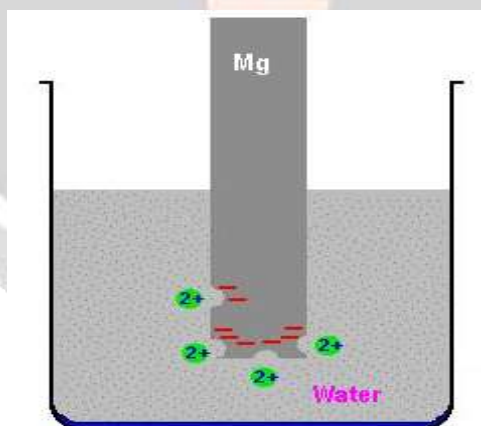


Fig.1: Magnesium in a beaker of water (a).

In a very short time, electrons will be a build-up on the magnesium bar and it will be surrounded in the solution by a layer of positive ions[25-45]. These will tend to stay close because they are attracted to the negative charge of electrons on the piece of metal.

Some of them will be attracted enough that they will reclaim their electrons and stick back on to the piece of metal.

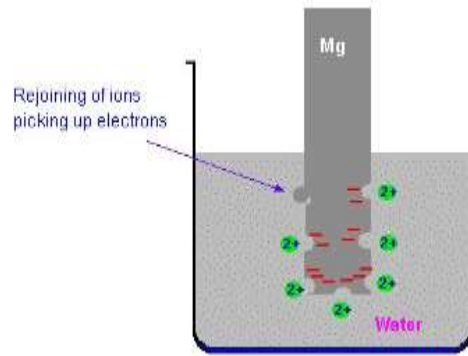


Fig.2: Magnesium in a beaker of water (b).

A dynamic equilibrium will be established when the rate at which ions are leaving the surface is exactly equal to the rate at which they are joining it again. At that point there will be a constant negative charge on the magnesium, and a constant number of magnesium ions present in the solution around it[46-69]. If we simplify the above diagram we can redraw it as shown in fig. 3.

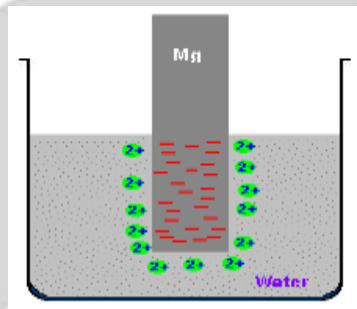


Fig. 3: Magnesium in a beaker of water (c)

This is just a snapshot of a dynamic equilibrium. Ions are continually leaving and rejoining the surface[70-80].

## II. Methodology

### II A. Copper from an Equilibrium Point of View

To understand the copper from equilibrium point of view we can examine the difference if we use a piece of copper bar instead of a piece of magnesium bar.

We know Copper is less reactive and so forms its ions less readily. Any ions which do break away are more likely to reclaim their electrons and stick back on to the metal again. It still will be reached an equilibrium position, but there will be less charge on the metal, and fewer ions in solution[81-86].

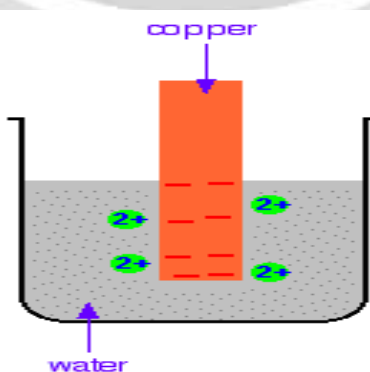


Fig. 4: Copper in a beaker of water.

If we draw these two equilibriums we get a diagram like as in fig.5

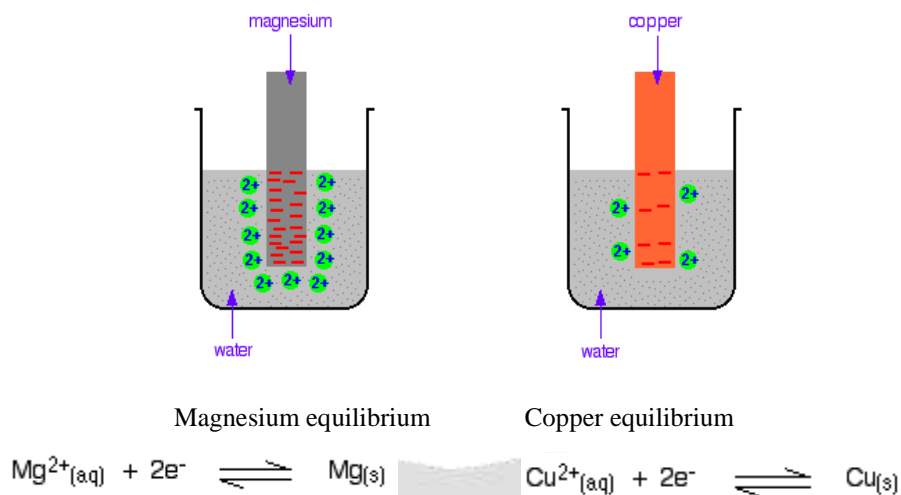


Fig.5: Equilibrium of Magnesium and copper.

The potential difference could be recorded as a voltage - the bigger the difference between the positiveness and the negativeness, the bigger the voltage. Unfortunately, that voltage is impossible to measure. Because it would be easy to connect a voltmeter to the piece of metal, but it is not possible to make a connection to the solution. We can try by putting a probe into the solution near the metal. But it will not work[100-102]. Because any probe we will put in will have the similar sort of equilibrium happening around it.

**IIB. Standard Electrode**

An electrode by definition is a point where current enters and leaves the electrolyte. Electrodes are vital components of electrochemical cells. They transport produced electrons from one half-cell to another, which produce an electrical charge. This charge is based off a standard electrode system. Standard Electrode System is recognized at a charge of 0 volts and serves as a medium for any cell potential calculation. The best we could measure would be some sort of combination of the effects at the probe as reference and the piece of metal we are testing. That means that we don't need to be able to measure the absolute voltage between the metal and the solution. It is enough to compare the voltage with a standardized system called a reference electrode. In this case the system used is called a standard hydrogen electrode[87-90].

**IIC. Anode and Cathode**

When the current leaves the electrodes it is known as the cathode and when the current enters it is known as the anode.

**IID. Standard Hydrogen Electrode**

Standard Hydrogen Electrode (SHE) is a redox electrode which forms the basis of Thermodynamics scale of oxidation reduction potential. Its absolute electrode potential is estimated to be 4.44±0.02 V at 25<sup>0</sup>C but to form a basis for comparison with all other electrode potential (E<sup>0</sup>) is declared to be zero at all temperature<sup>19</sup>. Potential of any other electrodes are compared with that of the standard hydrogen electrode at the same temperature[91-99]. Hydrogen electrode is based on the redox half cell: 2H<sup>+</sup>(aq) + 2e<sup>-</sup> → H<sub>2</sub>(g)

**III. Construction of a Standard Hydrogen Electrode**

The construction of a standard hydrogen electrode is shown in fig. 6.

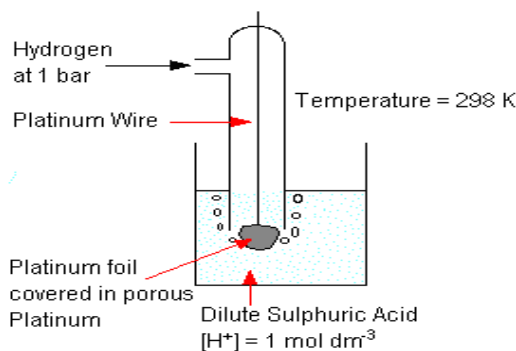


Fig. 6: Standard Hydrogen Electrode.

It consists of a platinum wire which consists of a platinum foil covered in porous platinum. The system is placed in a tube through which Hydrogen gas is passed. This redox reaction occurs at platinum electrode. The electrode is dipped in an acidic solution and pure hydrogen gas is bubbled through it. The concentration of both the reduced form and oxidised form is maintained at unity. That implies that the pressure of hydrogen gas is 1 bar and the activity of hydrogen ions in the solution is unity. The activity of hydrogen ions is their effective concentration, which is equal to the formal concentration times the activity coefficient. This unit-less activity coefficients is close to 1.00 for very dilute water solutions, but is usually lower for more concentrated solutions. As the hydrogen gas flows over the porous platinum, equilibrium is set up between hydrogen molecules and hydrogen ions in solution[103]. The reaction is catalyzed by the platinum,  $2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g})$

This is the equilibrium that we have to compare with all the others.

### III. The Standard Conditions for Standard Hydrogen Electrode

The standard conditions of Hydrogen Electrode are as below:

1. The hydrogen pressure is 1 bar (100 kPa).
2. The temperature is 298 K (25°C).
3. The concentration of the hydrogen ions in solution is  $1 \text{ mol dm}^{-3}$ .

### II G. Measurement of Magnesium Potential

Using the standard hydrogen electrode we can measure the potential of all other electrodes. Here is an example for measuring the potential of Magnesium electrode. In this case the standard hydrogen electrode is attached to the magnesium electrode - for example, a piece of magnesium in a solution containing magnesium ions. The whole of this set-up shown in the figure is called a cell. It is a simple system which generates a voltage. Each of the two beakers and their contents are described as half cells.

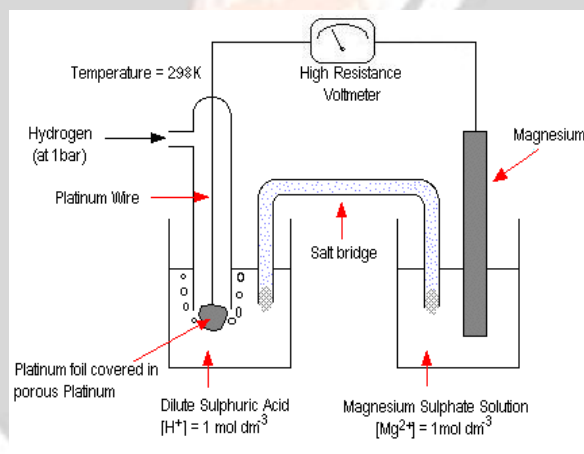
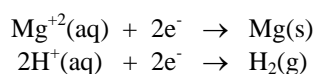


Fig. 7: Measurement of the Potential of Magnesium Electrode.

Here the salt bridge is used to complete the electrical circuit. It is just a glass tube filled with an electrolyte like Sodium Chloride or Potassium Chloride or potassium nitrate solution etc. The electrolyte in the salt bridge is chosen so that it doesn't react with the contents of either beaker. The ends are "stoppered" by bits of cotton wool. This stops too much mixing of the contents of the salt bridge with the contents of the two beakers.

At this stage the two equilibria are set up on the two electrodes- one around the magnesium electrode and other in the porous platinum electrode.



Since Magnesium has a much greater tendency to form its ions than hydrogen does, there will be a much greater build-up of electrons on the piece of magnesium than on the platinum. This is shown in fig. 8

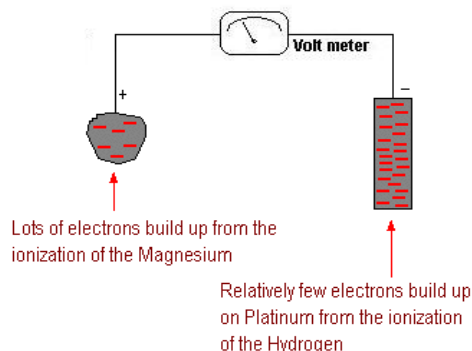
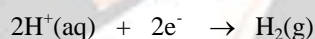
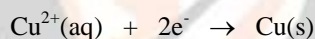


Fig. 8: Magnesium has greater tendency to form its ions than hydrogen.

If we measure the voltage between the two electrodes by attaching a voltmeter between the two electrodes we will find the voltage 2.37 volts and the voltmeter would show the magnesium as the negative electrode and the hydrogen electrode as being positive. It can be noted here that, the platinum in the hydrogen electrode and is not positive in real terms - there is a slight excess of electrons built up on it. But voltmeters don't deal in absolute terms - they simply measure the difference. Since the magnesium has the greater amount of negativeness - the voltmeter records it as negative[104]. Therefore the platinum of the hydrogen electrode is relatively more positive. The voltmeter records it as positive. Throughout the whole of this redox potential work, you have to think in relative terms. For example, +0.5 is relatively more negative than +1.7; or, another example, -0.6 is relatively more positive than -0.85.

### III. Measurement of Copper Potentials

We can measure the Cu potential easily by replacing the magnesium half cell by copper half cell with a solution containing  $\text{Cu}^{2+}$  ions with a concentration of  $1 \text{ mol dm}^{-3}$ . We can choose  $\text{CuSO}_4$  solution[24]. Copper forms its ions less readily than hydrogen does;



In this case there will be less build-up of electrons on the copper than that on the platinum of the hydrogen electrode.

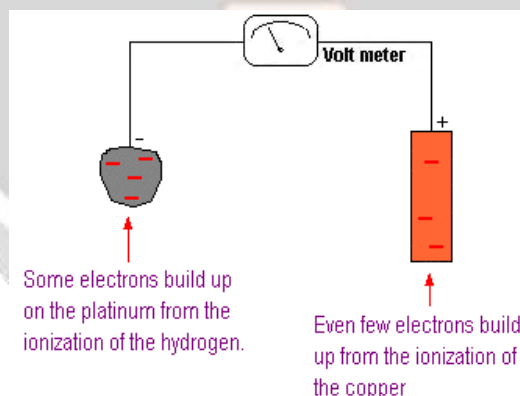


Fig. 9: Measurement the Cu Potential.

There will be less difference between the electrical charges on the two electrodes and so the voltage measured will be less. This time it will be only 0.34 volts.

That this time the copper will be the more positive electrode and the platinum of the hydrogen electrode will be the negative electrode. The voltmeter will show the hydrogen electrode as the negative one and the copper electrode as positive. Similarly, we can measure the Zn potential and it will show -0.76 volts.

### II.I Standard Electrode Potential

The values that we have just we have examined for the two cells are actually the standard electrode potentials of the  $\text{Mg}^{2+} / \text{Mg}$  and  $\text{Cu}^{2+} / \text{Cu}$  systems. The emf measured by coupling a metal / metal ion electrode to a hydrogen electrode under standard conditions is known as the standard electrode potential of that metal / metal ion combination[67]. It is written as by the symbol  $E^0$ . By convention, the hydrogen electrode is always written as the left-hand electrode of the cell.

Therefore the sign of the voltage quoted always gives us the sign of the metal electrode. A list of Standard Electrode Potential for some materials is given in table-1.

**Table-1: Standard Electrode Potential**

| Reduction Half-reaction                              | Standard Potential |
|--|--------------------|
| $F_2(g) + 2e^- \rightarrow 2F^-(aq)$                 | +2.87              |
|  | +2.01              |
| $S_2O_8^{2-}(aq) + 2e^- \rightarrow 2SO_4^{2-}(aq)$  | +1.23              |
| $O_2(g) + 4H^+(aq) + 4e^- \rightarrow$<br>$2H_2O(l)$ | +1.09<br>+0.80     |
| $Br_2(l) + 2e^- \rightarrow 2Br^-(aq)$               | +0.77              |
| $Ag^+(aq) + e^- \rightarrow Ag(s)$                   | +0.54              |
| $Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$          | +0.34              |
| $I_2(l) + 2e^- \rightarrow 2I^-(aq)$                 | +0.15              |
| $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$               | +0.14              |
| $Sn^{4+}(aq) + 2e^- \rightarrow Sn^{2+}(aq)$         | 0.00               |
| $S(s) + 2H^+(aq) + 2e^- \rightarrow H_2S(g)$         | -0.14              |
| $2H^+(aq) + 2e^- \rightarrow H_2(g)$                 | -0.26              |
| $Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$               | -0.44              |
| $V^{3+}(aq) + e^- \rightarrow V^{2+}(aq)$            | -0.74              |
| $Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$               | -0.76              |
| $Cr^{3+}(aq) + 3e^- \rightarrow Cr(s)$               | -1.18              |
| $Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$               | -2.71              |
| $Mn^{2+}(aq) + 2e^- \rightarrow Mn(s)$               | -3.00              |
| $Na^+(aq) + e^- \rightarrow Na(s)$                   |                    |
| $Li^+(aq) + e^- \rightarrow Li(s)$                   |                    |

### III. Conclusion

The standard electrode potential of a metal / metal ion combination is the emf measured when that metal / metal ion electrode is coupled to a hydrogen electrode under standard conditions. What we are doing is comparing the position of the metal / metal ion equilibrium with the equilibrium involving hydrogen. Here are a few typical standard electrode potentials:

Metal / Metal ion combination       $E^\circ$  (volts)

$Mg^{2+} / Mg$                                   -2.37

$Zn^{2+} / Zn$                                   -0.76

$Cu^{2+} / Cu$                                   +0.34

$Ag^+ / Ag$     +0.80

Please note that each of these is comparing the position of the metal / metal ion equilibrium with the equilibrium involving hydrogen. If you compare these with the  $E^\circ$  values, we can see that the metal in the upper position has the most negative  $E^\circ$  values. That is because they form ions more readily leaving more electrons behind on the metal, making it more negative. Those which do not shed electrons as readily have lower position in the list. Their  $E^\circ$  values get progressively more positive [24].

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