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Electrochemistry and Redox Reactions in Chemistry Education

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Summary. Electrochemistry is defined as the study of the interchange of chemical and electrical energy that occurs through oxidation-reduction (redox) reactions, in which electrons are transferred from a reducing agent to an oxidizing agent. Electrochemistry is the most important interfaces between chemistry and everyday life (batteries in car, radio, mobile phone, *etc.* are depending on electrochemical reactions) in spite of this there is not very favorite part of chemistry among the students. In this paper some spectacular and interesting experiments are presented, that are suitable for primary and secondary schools students and they can be made by most students in any laboratory or most classrooms.

Introduction

Electrochemistry is not very favorite part of chemistry among the students in spite of this there are the most important interfaces between chemistry and everyday life (batteries in car, radio, mobile phone, *etc.* are depending on electrochemical reactions). Students at different levels have common misconceptions in electrochemistry. Similarly, concepts are often poorly presented to students, who then typically just memorize the concepts without gaining a meaningful understanding [1].

In this work some experiments have been introduced which presented spontaneous and nonspontaneous redox reactions taking place especially in electrochemical cells (voltaic and electrolytic cell) and their use in practice.

An electrochemical cell is a system consisting of two electrodes that dip into an electrolyte (two half-cells) that are electrically connected and in which a chemical reaction either uses or generates electric current. A voltaic cell is an electrochemical cell in which a spontaneous reaction generates an electric current. An electrolytic cell is an electrochemical cell in which is an electric current used to drive a nonspontaneous reaction (called electrolysis). A half-cell is the portion of an electrochemical cell in which half-reaction takes place. Whether a cell operates as a voltaic or an electrolytic the electrode at which reduction occurs is called cathode, and the electrode at which oxidation occurs is called the anode.

Spontaneous redox reactions

When Zn metal is added to an aqueous solution of $CuSO_4$, Cu^{2+} ions are converted to Cu, the copper is reduced and appears as a black coating on the zinc and Zn atoms enter the solution as Zn^{2+} ions. In time the blue colour of the $CuSO_4$ solution disappears:

$$Zn(s) + Cu^{2+}(aq) \leftrightarrows Zn^{2+}(aq) + Cu(s)$$

When a piece of Cu wire is placed in an aqueous $AgNO_3$ solution, Cu atoms enter the solution as Cu^{2+} ions and Ag^+ ions are converted to Ag. The solution obtains the characteristic blue colour due the hydrated Cu^{2+} ions:

$$Cu(s) + 2\,Ag^+(aq) \leftrightarrows Cu^{2+}(aq) + 2\,Ag(s)$$

To determine the direction of spontaneity of a reaction we need to know only standard electrode potential (also known as standard reduction potential) $E°$. The more positive the value, the greater the driving force for the reduction half-reaction:

$E°(Zn^{2+}/Zn) = -0.76$ V $\quad$ $E°(Cu^{2+}/Cu) = 0.34$ V $\quad$ $E°(Ag^+/Ag) = 0.80$ V

Because of standard electrode potential of copper electrode is greater than that of the zinc electrode; copper ion is more easily reduced than zinc ion, but not more than silver ion. The same spontaneous reaction will take place in the cells zinc-copper (consisting of zinc metal-zinc ion and copper metal-copper ion half-cells) and copper-silver (consisting of copper metal-copper ion and silver metal-silver ion half-cells) which are written:

$Zn(s)|Zn^{2+}(aq)||Cu^{2+}(aq)|Cu(s)$ $\quad$ $Cu(s)|Cu^{2+}(aq)||Ag^+(aq)|Ag(s)$

and cell EMF is calculated as follows

$$E°(\text{cell}) = E°(\text{cathode}) - E°(\text{anode})$$

For zinc-copper cell is $E°(\text{cell}) = 0.34\text{ V} - (-0.76\text{ V}) = 1.1$ V, and for copper-silver cell is $E°(\text{cell}) = 0.80\text{ V} - 0.34\text{ V} = 0.46$ V.

Electrolysis

In contrast to spontaneous redox reactions, which result in the conversion of chemical energy into electrical energy, electrolysis is process in which electrical energy is used to cause a non-spontaneous chemical reaction to occur.

The chemical reaction between hydrogen and oxygen producing water is spontaneous and can take place in a hydrogen-oxygen fuel cell too. The water decomposition to oxygen and hydrogen is non-spontaneous reaction and take place in electrolytic cell.

Water does not conduct an electric current in its pure form. An electrolyte (ionic substance, *e.g.* Na_2SO_4) must be dissolved into the water for electrolysis to occur. Sodium sulfate will dissociate in water to its ions

$$Na_2SO_4 \leftrightarrows 2\,Na^+ + SO_4^{2-}$$

Two half-reactions can take place at the cathode:

$$2\,H_2O(l) + 2\,e^- \leftrightarrows H_2(g) + 2\,OH^-(aq) \qquad E° = -0.83\text{ V}$$
$$Na^+(aq) + e^- \leftrightarrows Na(s) \qquad E° = -2.71\text{ V}$$

Two half-reactions can also occur at the anode:

$$S_2O_8^{2-}(aq) + 2\,e^- \leftrightarrows 2\,SO_4^{2-} \qquad E^0 = +2.01\text{ V}$$
$$O_2(g) + 4\,H^+ + 4\,e^- \leftrightarrows 2\,H_2O \qquad E^0 = +1.23\text{ V}$$

Because of standard electrode potentials described above it is easier to reduce H_2O than Na^+ ions at the cathode and it is easier to oxidize H_2O than SO_4^{2-} at the anode [2]. The electrode half-reactions during the electrolysis of water are as follows:

- anode (+) $\quad 6\,H_2O(l) \leftrightarrows 4\,H_3O^+(aq) + O_2(g) + 4\,e^-$
- cathode (–) $\quad 4\,H_2O(l) + 4\,e^- \leftrightarrows 4\,OH^-(aq) + 2\,H_2(g)$
- overall $\quad 2\,H_2O(l) \leftrightarrows O_2(g) + 2\,H_2(g)$

During the electrolysis of water the region around the anode becomes acidic, the region around the cathode basic.

Procedure: Two syringes containing a dilute aqueous solution of sodium sulfate with Bromthymol Blue indicator are immersed into a sodium sulfate solution which is placed in Petri dish. Each of them has a platinum electrode connected to a power supply. When electricity passes through the system, oxidation occurs at the anode (oxygen gas is produced) and reduction at the cathode (hydrogen gas and hydroxide ions are produced and the solution turns blue).

Protection iron from corrosion

Corrosion can be defined as the degradation of a material due to a reaction with its environment. Most metals corrosion is electrochemical in nature. Corrosion involves oxidation of the metal. This spontaneous process has great economic impact (enormous damage to buildings, bridges, ships and cars).

Cathodic protection is a process in which the metal that is to be protected from corrosion becomes the cathode in the electrochemical (voltaic or electrolytic) cell.

Procedure: Three test-tubes contain a solution of 0.1 mol dm^{-3} HCl, 3% H_2O_2, and 0.1 mol dm^{-3} KSCN in ratio 1:1:1. The first test-tube contains an iron wire. The solution in the test-tube turns a reddish-brown colour, and the intensity of the colour increases over time. The reddish-brown colouration is due to the formation of $[Fe(SCN)]^{2+}$ to $[Fe(SCN)_6]^{3-}$ complexes. This indicates that the iron metal is being oxidized to the Fe^{3+} ion.

The second test-tube contains an iron wire wrapped around a piece of zinc metal (zinc-iron cell). The colour of the solution in the test-tube is unchanged and the reddish-brown colour does not appear because of iron becomes the cathode in the zinc-iron voltaic cell. Zinc is than oxidized in preference to iron.

- anode (–) $Zn(s) \leftrightarrows Zn^{2+}(aq) + 2\,e^-$
- cathode (+) $Fe^{2+}(aq) + 2\,e^- \leftrightarrows Fe(s)$

When the connection between the iron and the zinc metal is severed, the solution begins to turn reddish-brown.

In the third test-tube are immersed in the solution an iron wire and a zinc metal. The metals are connected to a power supply. When electricity passes through the system, oxidation occurs at zinc (anode) and reduction at iron (cathode). The hydrogen is formed at the iron's cathode. The electrodes half-reactions are as follows:

- anode (+) $Zn(s) \leftrightarrows Zn^{2+}(aq) + 2\,e^-$
- cathode (–) $2\,H^+(aq) + 2\,e^- \leftrightarrows H_2(g)$

Conclusion

In this contribution we focus on explaining some problems associated with understanding the basic knowledge from electrochemistry. The experiments described here are well-known and simple. They can be realized in any laboratory or most classrooms during the general chemistry lessons. The microelectrochemistry experiments [4], computer animations [5] and small-scale and low-cost galvanic cells [6] were published recently.

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