

CHAPTER III

THEORETICAL CONSIDERATION

Electrolytic Reduction and Oxidation

Oxidation and reduction, in the special sense of the terms, are equivalent to the removal and addition of electrons, respectively; when a current from an external source of E.M.F. is applied to a pair of electrodes in an electrolytic cell, so as to make them anode and cathode respectively, the former can act as a means for the continuous removal of electrons while the latter serves as a corresponding source of supply. It is apparent, therefore, that there is a possibility of oxidation being brought about electrolytically at an anode, where as reduction can occur at a cathode. The same conclusion may be reached in a less general manner when it is realized that there is always a tendency for oxygen to be formed at an anode and of hydrogen to be produced at a cathode, thus favoring oxidation and reduction, respectively. The materials which are reduced may be considered cathodic depolarizers; those which are oxidized are anodic depolarizers. Oxidation reactions may involve substances other than oxygen, such as chlorine. Anodes are selected with a high oxygen or hydrogen overvoltage, and cathodes are selected with a high hydrogen overvoltage. Substances which are easy to reduce may be acted on at the interface of cathodes with low hydrogen overvoltage; difficultly reducible materials may require much higher overvoltage reached as the result of either the cathode or the current density.

FACTORS INFLUENCING ELECTROLYTIC REDUCTION PROCESSES

I. Electrode Potential The potential being regarded as a measure of the potential energy of the hydrogen liberated at the electrode. For a given electrode, therefore, different cathodic potential will correspond to different energies of the discharged atoms; a high negative, i. e., high cathodic potential implies that the hydrogen liberated has a large energy content.

It has been shown by Habert, whom his work referred to GLASSTONE and HICKLING (1935) that the potential of the cathode is probably the most important factor in determining the reaction occurring during electrolytic reduction of a given substance. By using the same electrode, the same electrolyte and the same temperature it is often possible to obtain different products if suitable adjustment of the electrode potential is made. The reduction efficiency with a given cathode should depend on the cathode potential, being greater the higher its value.

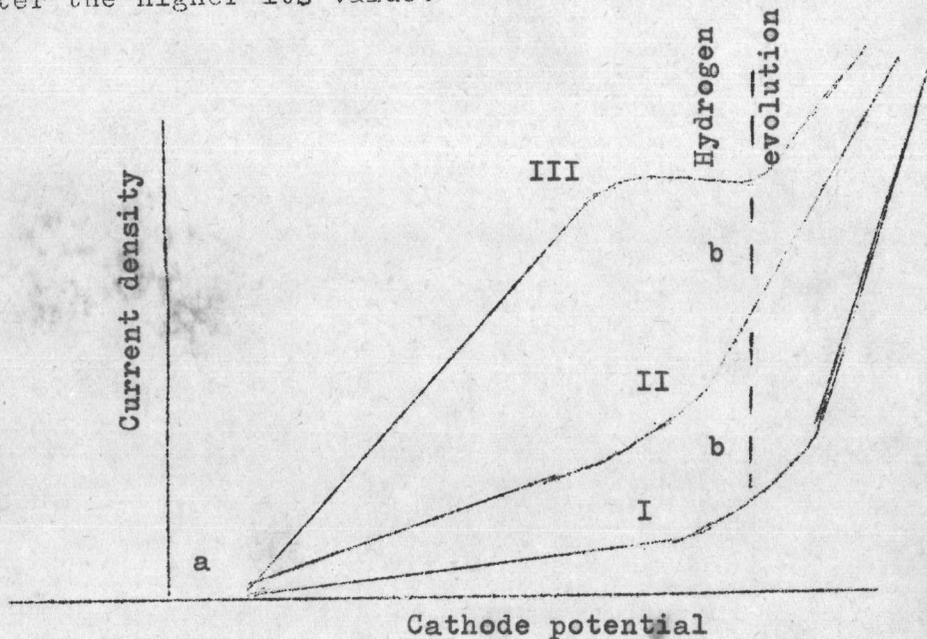


Fig. 1 Influence of Depolarisers on the Current Density - potential Curve

In the absence of a depolarizer the variation of cathode potential with current density will be represented by curve similar to curve I in Fig 1., the small current flowing between a and may be due to the presence of a small amount of reducible material in the solution or to diffusion of hydrogen away from the cathode. Visible hydrogen evolution commences in the vicinity of b, which give the so-called bubble overvoltage potential, beyond this the gas is evolved freely with but little further polarization. If a depolarizer is present, however, another process, i.e., reduction of the depolarizer will occur in preference to hydrogen evolution; if this reaction is relatively slow, the cathode potential will rise from a to b', as shown by curve II. Between a and b' the reduction efficiency is 100 percent, but at the potential b', which is close to that of b, appreciable hydrogen evolution will commence and the current efficiency will fall. For a rapid reduction process the cathode potential rises slowly, curve III, until the limiting current density is attained; there is then a rapid increase of potential and hydrogen liberation occurs.

II Nature of electrode material When a substance is difficult to reduce electrolytically, e.g., carbonyl compounds and pyridine derivatives, success can often be achieved by the use of a zinc, lead or mercury cathode. These metals all have high hydrogen overvoltages, and it is to this fact that the reducing efficiency is attributed. If the electrodes contain impurities of low overvoltages, or if the electrolyte contains traces of salts of metals with low overvoltages which can be deposited on the cathode, the electrolytic reduction may be entirely inhibited. Similarly, in the reduction of nitro-compounds the use of a zinc, lead, tin or mercury

cathode generally results in a good yield of amine; at low overvoltage cathodes; e.g., nickel, platinum or carbon, intermediate products, such as phenylhydroxylamine and benzidine, are obtained.

Since high overvoltage cathodes permit the attainment of a higher (cathodic) Potential before hydrogen evolution commences, there is clearly the possibility of a greater degree of reduction, but the actual reason for the increased efficiency is not clear. When the view was widely accepted that overvoltage was due to the slowness of the combination of hydrogen atoms, the reducing properties of high overvoltage cathodes were attributed to the appreciable concentration of atomic hydrogen. Since this theory is now believed to apply only to metals of low overvoltage, the interpretation of electrolytic reduction must be revised. One possibility is that since high overvoltage metals form weak M-H bonds where M represents the electrode material, the atoms are more readily detached and can consequently react more rapidly with the depolarizer than would be the case if strong M-H bonds were formed. Another possibility is that since the protons have to pass over a high energy barrier before they can reach the electrode in the case of a high overvoltage metal, they will have a higher potential energy, and consequently be more reactive, than if the barrier were a low one, as it is for low overvoltage cathodes. It is also possible that the reduction process may involve the transfer of a proton to the depolarizer adsorbed on the cathode; this represents an alternative to the transfer of the proton to the electrode resulting in hydrogen evolution. If the

later reaction takes place at an appreciable rate at low potentials the former may not be able to occur; on the other hand, if the overvoltage for hydrogen liberation is high, the cathode potential may rise sufficiently for transfer of the proton to the depolarizer to be possible before hydrogen evolution sets in,

III Concentration of Depolarizer As a general rule, the concentration of depolarizer does not affect the nature of the reduction product although it may affect the current efficiency for reduction. By increasing the concentration of the depolarizer or by agitating the electrolyte the rate of the cathodic reaction is increased and it is possible to increase the current density without the danger of hydrogen evolution. Any factor which facilitates access of the depolarizer to the cathode increases the slope of the current density-cathode potential curve in Fig 1.

IV Temperature Increase of temperature has three main effects;

1. It lowers overvoltage, 004673
2. It increases the rate of reaction between the depolarizer and hydrogen,
3. It increases the rate of diffusion of the depolarizer to the cathode.

The actual influence on the electrolytic reduction is a balance of the effects of these three factors. If the reduction process does not require too high an overvoltage, an increase of temperature would be expected to improve the reduction efficiency

because of the second and third factors; if, on the other hand, the process necessitates a high cathodic potential, an increase of temperature because it lowers the overvoltage, will be accompanied by a decreased efficiency. If an intermediate stage of reduction, at a lower cathode potential, is possible, it will generally be favored as the temperature is raised.

V Catalysts It is true that the overvoltage is a general indication of the reducing efficiency of an electrode material, but there are a number of instances in which a low overvoltage cathode is as effective or even more effective than others of high overvoltage. The addition of certain substances to the electrolyte often produces an increased reduction efficiency; such catalysts are of two main types. The first consists of salts of high overvoltage metals, e.g., zinc, tin or mercury; during the course of the electrolysis the metals are deposited on the cathode, thus raising its overvoltage. The second type are ions capable of existing in two stages of oxidation, e.g., titanium, vanadium, chromium, iron and cerium; these substances are sometimes called hydrogen carriers, and they act in the following manner. The higher valence stage of the carrier is reduced at the cathode to the lower stage, the latter, being a powerful reducing agent, reacts with the substance present in the solution and while doing so is re-oxidized to its original state. The resulting ions are once more reduced.

### FACTORS INFLUENCING ELECTROLYTIC OXIDATION PROCESSES

The factor affecting reduction processes have been already discussed, and many of these have an analogous influence in anodic oxidation

I Electrode Potential If electrolytic oxidation is brought about by active oxygen at the anode it would be expected that the higher the potential the more effective the oxidation, since a high potential corresponds to a high reactivity of the anodic oxygen.

#### II Nature of electrode material

Since there is, in general, a tendency for an anode to go into solution under the influence of a current, the choice of electrode is limited to those materials which can be made passive in the particular electrolytes used. It is difficult to lay down definite rules concerning the efficiency of an electrode for anodic oxidation. If the oxidation is brought about by oxygen in an active form or by an oxide of the electrode material, the highest efficiencies are obtained with lead dioxide and platinized platinum anodes.

III Depolarizer and Temperature The influence of these factors on electrolytic oxidation are similar to their effect in reduction processes.

IV Catalysts Electrolytic oxidation processes are frequently aided, and sometimes the nature of the products is changed, by the addition of catalysts or oxygen carriers; these are generally inorganic ions capable of undergoing reversible oxidation and reduction and their actions is exactly analogous to that of hydrogen carriers. Substances which have been suggested as carriers include compounds of chromium,

cerium, manganese, vanadium, The action of different oxygen carriers is, of course, not always the same.

### Electrolytic oxidation & reduction of organic compound

The only organic substances whose aqueous solutions are electric conductors are the alkali salts of organic acids. Other organic compounds are poor conductors, so that for their electrolysis it is necessary to add an electrolyte. In some cases it is the electrolyte that is decomposed by the electric current and the nascent electrode products combine with the organic compound which is suspended or dissolved in the electrolyte.

Practically all the reactions taking place during electrolysis of organic compounds occur at the anode, for with the exception of the relatively small number of organic bases, the actions of organic electrolytes do not usually take part in any reaction at cathode. At the anode the oxidizing action resembles, to some extent, that of any powerful chemical agent containing oxygen, although it is frequently more vigorous and with easily disrupted organic compounds often leads to the formation of carbon dioxide and water as the main products. There is, however, a marked tendency for ultimate complete oxidation to be preceded by the formation of hydroxylated derivatives, this type of oxidation is brought about by comparatively few chemical oxidizing agents e.g., hydrogen peroxide

### The mechanism of anodic oxidation of organic compounds

It is generally accepted that electrolytic reduction is due to the action of active, probably atomic, hydrogen although in some instances it has been suggested that a metal hydride is the effective agent; with anodic processes, however, the position is more complicated

and there is no general agreement as to the mechanism of the oxidation and the nature of the active oxidant. The earliest idea was that oxygen itself was the oxidising agent in question, but the inability of gaseous oxygen to imitate anodic reactions led almost at once to qualification of this simple hypothesis. The conception of oxygen activated in some way, by physical adsorption on the electrode or functioning through intermediate formation of peroxides with the electrode material, somewhat naturally arose, but whilst both these processes may occur and the nature of the anode material is often a dominating factor in electrolytic oxidations, the vagueness of the conceptions hinders their experimental application.

In recent years Fichter (Ref.5) has maintained the view that atomic oxygen is the effective oxidising agent, its activity determined by the potential at which it is liberated. Working on this idea he and his collaborators have sought to imitate anodic processes by the use of fluorine which has a very high potential as oxidising agent, and their efforts have met with considerable success. Before leaving this subject it must be emphasized that, in the present state of our knowledge it is impossible to determine by inspection the nature of the effective agent in a particular reaction.

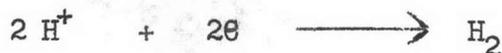
#### Electrolytic Oxidation & Reduction of Wastewater

All the wastewaters contains inorganic and organic chemical compound from the water supply, many complex materials derived from feces, urine and process wastes. At the cathode reduction reactions result primarily in the decomposition of water to produce nascent hydrogen and deposition of cations that appear lower on the standard reduction

series and the furthered away from the electrode potential will react first. At the anode, the anion will combine chemically with the anode material forming insoluble precipitants and oxidation occurs by four major means;

1. oxidation of chloride to chlorine or hypochlorite,
2. formation of highly oxidative materials such as ozone and peroxides,
3. direct oxidation by the anode surface,
4. electrolysis of water to give nascent oxygen.

Cathode Reaction



Anode Reaction

