A COURSE IN INDUSTRIAL CHEMISTRY

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(Part Two)

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Preface

Although it has been evolved from the basic principles underlying the main limbs of chemistry, such as physical organic-inorganic—, and biochemistry, industrial chemistry forms a separate branch by itself. In a technological age, where most industrial processes involve the use of chemical principles, the importance of industrial chemistry cannot be over-emphasised. Therefore, it is heartening to note that Industrial Chemistry has become a part of the syllabus at the undergraduate level in some universities.

There is as yet no suitable book for the undergraduate level describing the industries operating under the conditions obtaining in developing countries. This has prompted us to write this book. It is obvious that it is not possible for any single person to give satisfactory treatment to the wide-ranging industries based on different principles. We hope our readers will appreciate our combined effort.

As it is not possible to cover a complete course on Industrial Chemistry in one semester, the book is written in parts so that it is convenient for the undergraduate student to study each part within a period of about forty lectures.

We have covered various aspects of each industry, such as raw materials, physico-chemical principles underlying the manufacturing process, industrial operations, economics of the industry, and the pollution problem. We have tried to make the discussion as simple and easy as possible. Illustrations, diagrams and exercises will, we hope, make the book more useful.

If this book helps the student to discover his inclination towards a career in a particular industry and stimulates his desire for more knowledge about it, we shall feel amply rewarded.

Any suggestions for the improvement of the book in its next edition are most welcome.

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—D. L. Roy

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ELECTROCHEMICAL PROCESSES

D. L. ROY

1.1 GENERAL INTRODUCTION

The essential difference between an electrochemical reaction and a chemical reaction is that, in the former, the electrons taking part in the oxidation / reduction reactions travel distances greater than interatomic distances. Dissolution of zinc oxide, for example, in sulphuric acid to generate zinc sulphate is a chemical reaction, whereas dissolution of technical grade zinc metal in the same acid is electrochemical. The overall reaction of zinc dissolution consists of two partial reactions, that is,

$$Zn \rightarrow Zn^{2+} + 2e^- \quad .. \quad \text{(oxidation)} \quad .. \quad (1.1)$$

$$2H^+ + 2e^- \rightarrow H_2 \quad .. \quad \text{(reduction)} \quad .. \quad (1.2)$$

The reaction will come to a halt if one of the two reactions above is prevented. It is possible to suppress the hydrogen evolution reaction, and hence the dissolutions, considerably by using super purity stress-free zinc metal. Fig. 1.1, which illustrates the electrochemical dissolution of zinc, brings out the salient features of an electrochemical reaction. It involves :

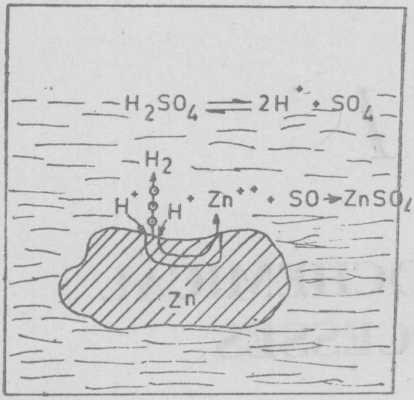

Fig. 1.1 : Electrochemical Nature of Dissolution of Zinc in Sulphuric Acid

(a) Net electrochemical oxidation (loss of electrons)

(b) Net electrochemical reduction (gain of electrons)

(c) Movement of electrons outside the electrolyte and those of ions within the electrolyte.

At steady state, the rate of electrons generated due to oxidation should equal the rate of their consumption by reduction. The overall rate is the slower of the two. It is conventional to denote the sites of oxidation reactions as anode (+ ve) and those of reduction reactions as cathode (– ve). In the above example, the anodic and cathodic sites have been inherently short-circuited whereas most of the electrochemical processes take place or are carried out in such a manner that the anodic reactions take place at a considerable distance from cathodic reactions.

On the basis of free energy of total reaction, the various electrochemical processes can be identified with one of the following groups (Fig. 1.2).

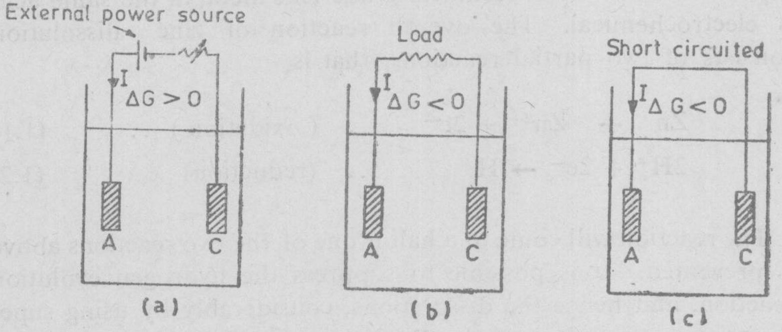

Fig. 1.2 : Thermodynamic Classification of Electrochemical Processes (a)— Energy Consumer (b)— Energy Producer (c)— Electrochemical Corrosion (Dissolution of Zinc for Example)

(i) $\Delta G < O$ e.g. Dry cells, charged lead acid battery etc. "ENERGY PRODUCERS"

(ii) $\Delta G > O$ e.g. Electroplating, refining, chlor-alkali cells etc. "ENERGY CONSUMERS"

(iii) $\Delta G < O$ (the anodes and cathodes inherently short-circuited)

e.g. Corrosion of zinc in sulphuric acid, etc. "ENERGY WASTERS"

We will primarily be concerned with non-spontaneous processes in which external energy has to be fed for the process to take place. In an electrochemical system the required external energy is usually supplied by means of applying a potential difference (voltage) between the anode and cathode. The energy supplied is usually computed by the following equation :

$$\text{Energy input} = \text{Voltage} \times \text{current} \times \text{time} = VIt\ (KWH) \quad (1.3)$$

Whether the energy put in has been fully utilised in producing the desired amount of anodic and cathodic reactions can only be answered if the Thermodynamics and Kinetics of the anodic, cathodic processes are understood. Before we deal with them it is worth noting that the total energy input is spent for (a) Net anodic reaction, (b) Net cathodic reaction, (c) Ionic transport across the electrolyte and electronic conduction through the external circuit. Thus, it becomes convenient to study the anodic and cathodic reactions and ionic transport mechanisms individually and in isolation, although with the tacit understanding that all the three processes are necessary for any electrochemical reaction to take place.

The various processes can be classified according to the nature of electrolyte used. They are (a) aqueous, (b) organic, (c) fused salt and (d) solid. Whereas solid electrolytes are of insignificant commercial interest, processes using aqueous electrolytes are the greatest in number. Fused salt and organic electrolytes certainly are of, although restricted commercial interest. The basic principles of electrochemical Thermodynamics and Kinetics will be discussed later assuming aqueous electrolyte. Nevertheless these principles invariably apply to nonaqueous electrolytes too.

The various cathodic and anodic processes in an energy consuming aqueous electrochemical system are, for example :

- (i) Metal deposition and dissolution represented by $M^{n+} + ne^- \rightleftharpoons M$
- (ii) Gas evolution such as hydrogen (cathodic) and oxygen, chlorine (anodic)
- (iii) Redox reactions such as $Fe^{+++} + e \rightleftharpoons Fe^{++}$
- (iv) Formation of oxidized compounds such as MnO_2, chlorates, hydroxides etc.

Each of these reactions can be written as an equilibrium reaction involving a reduced state (Red), oxidized state (ox) and electrons, i. e...

$$(\text{Red}) + \text{electrons} \rightleftharpoons (\text{ox}) \qquad .. \ (1.4)$$

In a particular electrochemical process the species taking part in the oxidation reaction at the anode may or may not take part in the reduction reaction at the cathode. Besides, more than one species may take part (which may or may not be desirable) in either or both cathodic and anodic reactions. Thus in the electrorefining of metals the desirable anodic reaction is metal dissolution ($M \rightarrow M^n + ne^-$), the cathodic reaction being ($M^{n+} + ne^- \rightarrow M$). Although all efforts are made to restrict the anodic and cathodic reactions to the above, the side reactions such as the cathodic reduction of H^+ ion to liberate hydrogen and the anodic evolution of oxygen may also be present,leading to decreased current efficiency.

Consider the surface of a metal M contained in a vacuum. Each of the atoms in the metal surface is in fact an ion occupying its own energy well and stabilized in its position by the electron ' gas' in the metal. If sufficient energy is available (about 6 ev), it will be possible to pull an ion out of its energy well in the surface, so forming a highly unstable gaseous metal ion M^{n+}. However, if the metal is immersed in a polar solvent such as water instead of in a vacuum, there exists an alternative deep energy well having the same sort of chemical free energy as that of a metal ion bound to the metal surface. This second energy well corresponds to the state in which the metal ion is surrounded by a cage of (usually) four or six water molecules called the primary solvation sheath. The primary solvation sheath may consist of other entities besides water molecules ; it may, for example, contain complexing ions or molecules such as hydroxyl or ammonia. Now because water molecules are relatively small and mobile and can approach very close to the metal surface, the two energy wells shown in Fig. 1.3

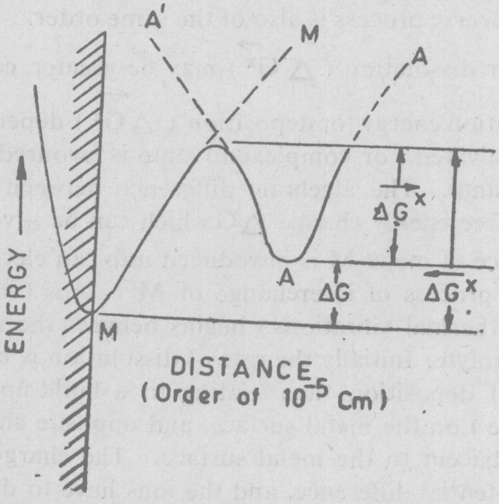

Fig. 1.3 (I) : Energy-Distance Diagram of M^{n+} IONS in Metallic (M-M') and Equated (A-A') State

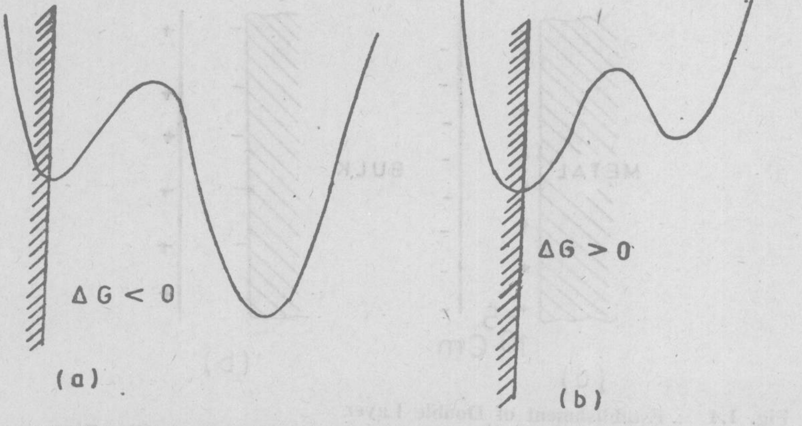

Fig. 1.3 (II) : Equated State is more Stable (Zn, Fe etc.)
Metallic State is more Stable (Cu, Au, Ag etc.)

are very close together in space, so that there is no need for an ion to acquire an energy of 6 ev (in the case of vacuum) before it can go into solution. It needs only a thermal energy of about 0.5 ev after which it falls down an energy slope into the well provided for it by the waiting water molecules. The activation energy requirement for the reverse process is also of the same order. The activation energy for dissolution ($\Delta \overrightarrow{G^x}$) may be greater, equal or less than the activation energy for deposition ($\Delta \overleftarrow{G^x}$) depending upon whether the solvated (or complexed) state is favoured relative to the metallic state. The algebraic difference between the two is the chemical free energy change ΔG which can be +ve or −ve.

When a piece of metal M is introduced into an electrolyte containing M^{n+}, process of interchange of M^{n+} ions (initiated and sustained by thermal vibrations) begins between the metal phase and the electrolyte. Initially the rate of dissolution is not the same as the rate of deposition, thus leading to a build-up of charges (+ve or −ve) on the metal surface, and opposite charges in the electrolyte adjacent to the metal surface. The charge separation leads to a potential difference, and the ions have to do additional or less work to cross over from one phase to the other. Thus, at equilibrium, the rate of dissolution equals the rate of deposition. Metals which have a greater tendency to remain in the metallic state develop +ve charges and +ve potential with respect to the electrolyte (*Fig.* 1.4). On the other hand metals which have a

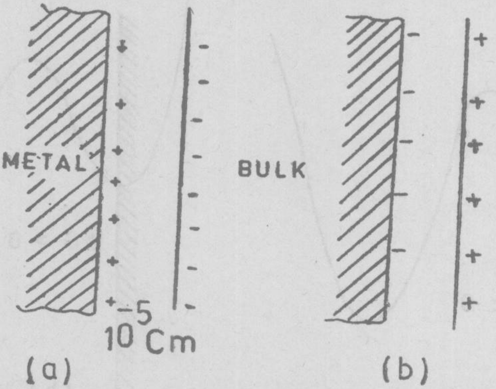

Fig. 1.4 : **Establishment of Double Layer**
(a) —Metals like Cu **(b) —Metals like Zinc**

greater tendency to remain in the aquated state develop –ve charges and –ve potential with respect to the electrolyte. It is impossible to measure this potential directly but, if the metal/solution system is coupled back-to-back with a secondary arbitrarily chosen electrode system, it is possible to obtain a relative potential difference. The arbitrary reference electrode which is almost invariably used is the "standard" hydrogen electrode (S. H. E.), although a number of more convenient standards (Table 1) are also used. The hydrogen electrode consists of a suitably inert metal such as platinum, dipping into a standard acid solution (1.2 N HCl) at 25°C, through which is passed purified hydrogen at 1 atm. The electrode potential for such a system is arbitrarily taken as zero, the equilibrium reaction being

$$2H^{+}aq + 2e^{-} \rightleftharpoons H_2(g) \qquad .. \quad (1.5)$$

TABEL 1.1

REFERENCE ELECTRODES

Name	Half cell system	Potential at 18°C w. r. t. N. H. E.	Use
Saturated calomel electrode (S.C.E.)	Hg/HgCl Sat KCl	+ 0.240	General
Normal Calomel electrode	Hg/HgCl N KCl	+ 0.286	,,
Normal mercurous oxide electrode	Hg/HgO N NaOH	+ 0.117	Alkaline electrolyte
Normal mercurous sulphate electrode	Hg/Hg_2SO_4 NH_2SO_4	+ 0.685	Acid electrolyte

The development of electrode potentials is not restricted to reactions such as $M^{n+} + ne^{-} \rightleftharpoons M$. Any electrochemical reaction associated with electron transfer has an electrode potential. Table 1.2 gives the electrode potentials of some important reactions on the basis of which the important series known as the electrochemical series has been developed.

TABLE 1.2

STANDARD EQUILIBRIUM POTENTIALS FOR SOME ELECTRODE REACTIONS AT 25°C

Reaction	Potential w. r. t. N. H. E. E_o° in Volts
$K^+ + e \rightleftharpoons K$	−2.924
$Na^+ + e \rightleftharpoons Na$	−2.712
$Mg^{++} + 2e \rightleftharpoons Mg$	−2.400
$Al^{+++} + 3e \rightleftharpoons Al$	−1.700
$Mn^{++} + 2e \rightleftharpoons Mn$	−1.120
$Zn^{++} + 2e \rightleftharpoons Zn$	−0.758
$Fe^{++} + 2e \rightleftharpoons Fe$	−0.44
$Cd^{++} + 2e \rightleftharpoons Cd$	−0.39
$Co^{++} + 2e \rightleftharpoons Co$	−0.29
$Ni^{++} + 2e \rightleftharpoons Ni$	−0.22
$Sn^{++} + 2e \rightleftharpoons Sn$	−0.13
$Pb^{++} + 2e \rightleftharpoons Pb$	−0.12
$2H^+ + 2e \rightleftharpoons H_2$	0.00
$Sb^{+++} + 3e \rightleftharpoons Sb$	0.10
$Cu^{++} + 2e \rightleftharpoons Cu$	0.34
$Ag^+ + e \rightleftharpoons Ag$	0.79
$Hg^{++} + 2e \rightleftharpoons Hg$	0.86
$Cl_2^+ + 2e \rightleftharpoons 2Cl^-$	1.35
$Au^+ + e \rightleftharpoons Au$	1.5

In the previous discussion we considered only reactions between ions and a neutral element, i.e. $M^{n+} + ne^- \rightleftarrows M$. This need not always be the case. Besides the above, there can be any one of the following types of equilibrium reactions under a given set of conditions.

$$M^{m+} + (m - n)e^- \rightleftarrows M^{n+} \quad .. \tag{1.6}$$

$$M(OH)_n + nH^+ + ne^- \rightleftarrows M + nH_2O \quad .. \tag{1.7}$$

and so on. In fact it is possible to write out equations involving the metal (as metal, ions of different valencies, oxides and hydroxides), hydrogen ions, hydroxyl ions, hydrogen, oxygen and electrons. For each of these reactions it is possible to compute equilibrium electrode potentials, provided the free energy of formation of each of these reactions are known. Potentials may or may not be a function of "pH" depending upon whether H^+ or OH^- entet into the reaction. On the other hand some equilibrium reactions may be written without involving any electrons, and these are potential independent (chemical) reactions. A typical example is the precipitation of metal hydroxides from solution by the adjustment of pH. Some reactions may involve both hydrogen ions and electrons. Precipitation of ferric hydroxide from a ferrous sulphate solution is a typical example. The potential—pH relationships differ from metal to metal and also on complexing ions if present. For a simple $M - H_2O$ system it is possible to plot potential (Y – axis) pH (X – axis) relationships to give what are known

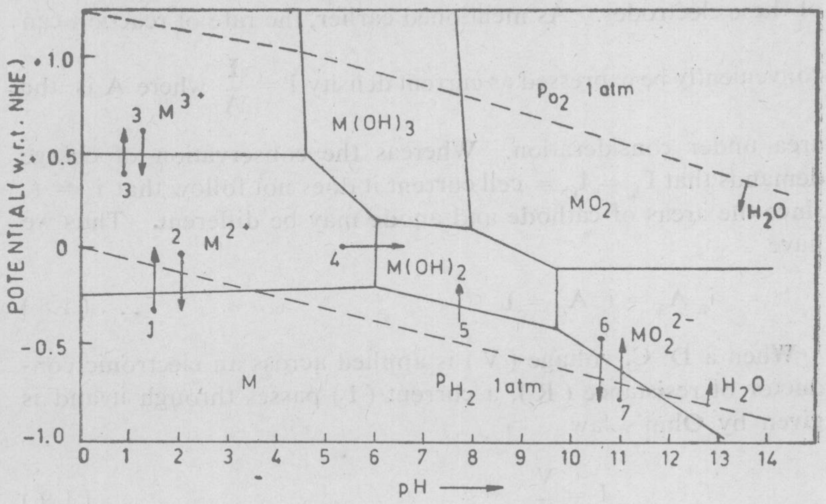

Fig. 1.5 : Hypothetical* potential pH diagram of $M-H_2O$ equilibrium system 1. Anodic dissolution in acid baths; 2. Cathodic deposition in acid baths; 3. Redox reaction such as Fe^{2+} Fe^{3+}; 4. Precipitation reaction; 5. Passivation (possibly); 6. Cathodic Deposition in alkaline baths; 7. Anodic dissolution in alkaline baths;.

* In actual cases these diagrams get modified (Various zones broadened or narrowed) due to complexants etc. Kinetically the above shown reactions need not necessarily be favourable

as Pourbaix diagrams. Superimposed on these diagrams we have two lines (dotted) corresponding to hydrogen and oxygen evolution reactions as a function of pH. The diagram as a whole tells you the general stability of the metal, its oxide, etc. under varying potential, pH conditions. Figure 1.5 gives a hypothetical $E_h - pH$ diagram and of a $M - H_2O$ system.

So far we have considered equilibrium cases in which there is no net reaction. Industrial processes would consist of some net reduction of certain species at the cathode, and net oxidation of some other species at the anode. This is achieved by applying a certain predetermined voltage across the electrodes, resulting in a certain current I through the circuit. The choice of the voltage (or current) would depend on the maximum permissible current densities at the anode and cathode, and the relative dipping areas of these electrodes. As mentioned earlier, the rate of reaction can conveniently be expressed as current density $i = \frac{I}{A}$ where A is the area under consideration. Whereas the conservation of charge demands that $I_A = I_C$ = cell current it does not follow that $i_a = i_c$ since the areas of cathode and anode may be different. Thus we have

$$i_a A_a = i_c A_c = I \qquad .. \quad (1.8)$$

When a D. C. voltage (V) is applied across an electronic conductor of resistance (R), a current (I) passes through it and is given by Ohm's law

$$I = \frac{V}{R} \qquad .. \quad (1.9)$$

On the other hand this law is not obeyed in the case of an electrolytic conductor. Till a voltage V_d is reached, the current would be zero, and at voltage V_d, the current would start passing but still would not obey Ohm's law of linear relationship. The current-voltage relationship for the cases mentioned above is shown in Fig. 1.6. The behaviour observed is due to polarization effects at the anode and cathode. The minimum decomposition voltage is given by the algebraic difference between the equilibrium poten-