

ELECTROCHEMISTRY BASIS



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The performance of a fuel cell is mainly determined by the kinetics of the reactions occurring at the electrode, and by the transport processes through the solution and in the electrode. It is to be emphasized that the ideal or maximum efficiency of an electrochemical energy converter depends upon electrochemical thermodynamics, whereas the real efficiency depends on electrode kinetics. The fact that the real efficiencies are less than the ideal efficiencies instils interest in understanding the fundamental theory governing this direct electrochemical conversion of chemical energy to electricity. Further, in fuel cell applications, the power per unit weight as well as the efficiency are important factors to be considered. Since power is the rate of producing energy, the kinetics of the electricity producing interfacial charge transfer reactions, that is, electrode kinetics, becomes important.

2.1 Thermodynamic Aspects of Electrochemical Energy Conversion

Three possible routes for the conversion of the chemical energy of fuels into electrical energy are given in Fig. 2.1

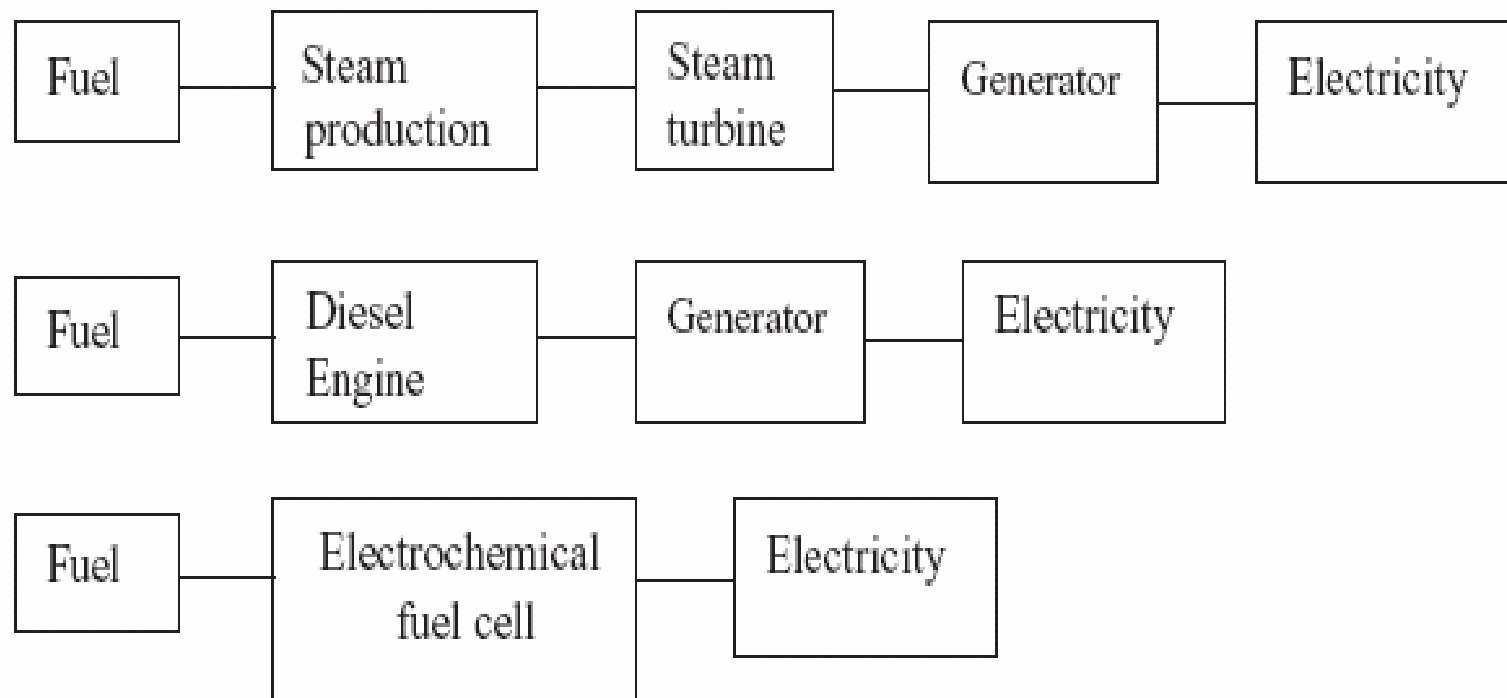


Figure 2.1 Possible routes in the conversion of chemical energy of fuels into electrical energy

Table 2.1 Thermodynamic data for some fuel cell reactions at temperature 298 K

Reaction	ΔG° , kcal mole ⁻¹	ΔH° , kcal mole ⁻¹	n	Δn	E_r° , volts	$\partial E_r^\circ / \partial T$, mV/°C	$\partial E_r / \partial \log P$, mV	s_1
1. $\text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O}$	-56.69	-68.32	2	-1.5	1.229	-0.84	45	0.830
2. $\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$	-195.50	-212.80	8	-1	1.060	-0.31	15	0.919
3. $\text{C}_2\text{H}_6 + \frac{3}{2}\text{O}_2 \rightarrow 2\text{CO}_2 + 3\text{H}_2\text{O}$	-350.73	-372.82	14	-2.5	1.087	-0.23	10.7	0.941
4. $\text{C}_3\text{H}_8 + 5\text{O}_2 \rightarrow 3\text{CO}_2 + 4\text{H}_2\text{O}$	-503.93	-530.61	20	-3	1.093	-0.19	9	0.950
5. $\text{C}_4\text{H}_{10} + \frac{13}{2}\text{O}_2 \rightarrow 4\text{CO}_2 + 5\text{H}_2\text{O}$	-656.74	-687.99	26	-3.5	1.095	-0.17	8	0.955
6. $\text{C}_3\text{H}_{18} + 8\text{O}_2 \rightarrow 5\text{CO}_2 + 6\text{H}_2\text{O}$	-809.48	-845.17	32	-4	1.097	-0.16	7.5	0.958
7. $\text{C}_8\text{H}_{18}(\text{g}) + \frac{25}{2}\text{O}_2 \rightarrow 8\text{CO}_2 + 9\text{H}_2\text{O}$	-1268.43	-1317.46	50	-5.5	1.100	-0.14	6.6	0.963
$\text{C}_8\text{H}_{18}(\text{l}) + \frac{25}{2}\text{O}_2 \rightarrow 8\text{CO}_2 + 9\text{H}_2\text{O}$	-1265.87	-1307.54	50	-4.5	1.098	-0.12	5.4	0.968
8. $\text{C}_{10}\text{H}_{22}(\text{g}) + \frac{31}{2}\text{O}_2 \rightarrow 10\text{CO}_2 + 11\text{H}_2\text{O}$	-1574.42	-1632.35	62	-6.5	1.101	-0.13	6.3	0.965
9. $\text{CH}_3\text{OH}(\text{g}) + \frac{3}{2}\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$	-168.05	-182.61	6	-1.5	1.215	-0.35	15	0.920
$\text{CH}_3\text{OH}(\text{l}) + \frac{3}{2}\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$	-167.91	-173.67	6	-0.5	1.214	-0.13	5	0.967
10. $\text{NH}_3 + \frac{3}{2}\text{O}_2 \rightarrow \frac{1}{2}\text{N}_2 + \frac{3}{2}\text{H}_2\text{O}$	-85.04	-91.44	3	-1.25	1.225	-0.31	25	0.930
11. $\text{N}_2\text{H}_4 + \text{O}_2 \rightarrow \text{N}_2 + 2\text{H}_2\text{O}$	-143.83	-148.69	4	-1	1.560	-0.18	15	0.967
12. $\text{C} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}$	-32.81	-26.42	2	+0.5	0.711	+0.46	-15	1.24
13. $\text{C} + \text{O}_2 \rightarrow \text{CO}_2$	-94.26	-94.05	4	0	1.022	0	0	1.002
14. $\text{CO} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2$	-61.45	-67.63	2	-0.5	1.333	-0.44	15	0.909
15. $\text{Li} + \frac{1}{2}\text{Cl}_2 \rightarrow \text{LiCl}(\text{g})$	-58	-53.00	1	0.5	2.515	-0.72	-30	1.094

Table 2.1 (continued)

Reactions	ΔG° , kcal mole ⁻¹	ΔH° , kcal mole ⁻¹	n	Δn	E_γ° , volts	$\partial E_\gamma^\circ / \partial T$, mV/°C	$\partial E_\gamma / \partial \log P$, mV	s_f
Temperature, 423 K								
1. $\text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O}$	-52.94	-58.142	2	-0.5	1.14799	-0.25	21	0.911
2. $\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$	-191.29	-191.42	8	0	1.03702	0	0	0.999
3. $\text{C}_2\text{H}_6 + \frac{3}{2}\text{O}_2 \rightarrow 2\text{CO}_2 + 3\text{H}_2\text{O}$	-346.99	-340.66	14	0.5	1.07491	+0.04	-3	1.019
4. $\text{C}_3\text{H}_8 + 5\text{O}_2 \rightarrow 3\text{CO}_2 + 4\text{H}_2\text{O}$	-499.54	-487.82	20	1	1.08324	+0.05	-4.2	1.024
5. $\text{C}_4\text{H}_{10} + \frac{13}{2}\text{O}_2 \rightarrow 4\text{CO}_2 + 5\text{H}_2\text{O}$	-651.94	-634.29	26	1.5	1.08747	+0.06	-4.9	1.028
6. $\text{C}_8\text{H}_{12} + 8\text{O}_2 \rightarrow 5\text{CO}_2 + 6\text{H}_2\text{O}$	-804.98	-781.19	32	1	1.09099	+0.07	-5.4	1.030
7. $\text{C}_6\text{H}_{18} + \frac{25}{2}\text{O}_2 \rightarrow 8\text{CO}_2 + 9\text{H}_2\text{O}$	-1263.72	-1221.70	50	3.5	1.09614	+0.08	-5.9	1.034
8. $\text{C}_{10}\text{H}_{32}(g) + \frac{31}{2}\text{O}_2 \rightarrow 10\text{CO}_2 + 11\text{H}_2\text{O}$	-1569.62	-1515.37	62	4.5	1.09796	+0.08	-6.2	1.036
9. $\text{NH}_3 + \frac{3}{2}\text{O}_2 \rightarrow \frac{1}{2}\text{N}_2 + \frac{3}{2}\text{H}_2\text{O}$	-47.28	-77.28	3	0.25	0.6835	-0.96	-7.1	0.612
10. $\text{C} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}$	-36.09	-26.31	2	0.5	0.782	0.47	-21	1.372
11. $\text{C} + \text{O}_2 \rightarrow \text{CO}_2$	-94.09	-94.08	4	0	1.02309	0	0	1.003
12. $\text{CO} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2$	-58.26	-67.77	2	-0.5	1.26335	-0.46	21	0.860
13. $\text{Li} + \frac{1}{2}\text{Cl}_2 \rightarrow \text{LiCl}(g)$	-81.38	-52.01	1	0.5	3.52942	+2.84	-42	1.565

Thermodynamic data presented are for the oxidation of one mole of fuel.

Conventional thermodynamic parameters like free energy, activity, equilibrium constant, temperature and pressure dependence and cell potentials and its coefficients with variables

For an electrochemical energy converter working ideally, it has been shown that the free energy change of the reaction may be converted totally into electrical energy. Thus, an electrochemical energy converter has an intrinsic maximum efficiency given by

$$\varepsilon_i = \Delta G / \Delta H = 1 - (T \Delta S / \Delta H) \quad (2.43)$$

It is perhaps not appropriate to regard this equation as indicative of an intrinsic maximum efficiency of less than 100 percent, since there is a possibility that in some reactions ΔG can exceed ΔH . Overpotential losses reduce the practical efficiencies of fuel cells to values less than the intrinsic

2.3.2 Voltage efficiency

The cell voltage E under load is less than the thermodynamic reversible potential E_r . Factors affecting this deviation of E from E_r are dealt with in the following section. The voltage efficiency is defined as:

$$\varepsilon_e = E/E_r \quad (2.44)$$

Voltage efficiencies observed in some fuel cells (for example, hydrogen–oxygen) are as high as 0.9 at low current densities and decrease only slowly with increasing current drawn from the cell, until a limiting value is attained.⁷

2.3.3 Faradaic efficiency

The Faradaic efficiency is defined as

$$\varepsilon_f = I/I_m \quad (2.45)$$

where I is the observed current from the fuel cell and I_m is the maximum theoretically expected current on the basis of the amount of reactants consumed, assuming that the overall reaction in the fuel cell proceeds to completion. Faradaic efficiency is analogous to current efficiency in conventional electrochemical cells. In most fuel cells, ε_f can be unity. ε_f may be less than 1 because of: (1) parallel electrochemical reactions yielding fewer electrons per mole of reactant consumed,⁸ (2) chemical reaction of reactants, catalyzed by electrodes⁹ and (3) direct chemical reaction of the two electrode reactants.¹⁰

2.3.4 Overall efficiency

The overall efficiency ε in electrochemical energy conversion is the product of the efficiencies considered

$$\varepsilon = \varepsilon_i \varepsilon_e \varepsilon_f \quad (2.46)$$

For an electrochemical reaction under the chosen conditions of temperature, pressure, and concentration of reactants and products, ε_i is a definite quantity, and the maximum possible value of ε is ε_i . The main target in electrochemical energy conversion is to make both, ε_e and ε_f tend to unity. It is not a difficult task to make ε_f tend to unity in many of the fuel cell reactions.

Fuel cell systems are often used as co-generation systems, and total efficiency often includes the thermal and electrical efficiency. It is necessary to make an energy analysis that also includes application of the second law of thermodynamics.

Fundamental types of overpotential

When electrons or metallic ions pass through the interface of a simple electrode, a thermodynamically defined reversible electrode potential E_{rev} is set up. The equilibrium involved is a dynamic one, and the rates at which charge carriers pass through the interface in either direction are equal. In other words, the exchange current density i_0 is same in both directions. If the anodic and cathodic partial current densities are respectively denoted by i_+ and i_- , then at equilibrium,

$$i_+ = |i_-| = i_0 \quad (2.47)$$

Overpotential may be observed when an additional external current is superimposed on the system by means of a suitable counter electrode, as occurs, for example, during electrolysis or during withdrawal of current from a galvanic cell. The electrode will then assume a potential E_i , which will differ from the equilibrium value to an extent governed by the current density. The differences between E_i and the equilibrium potential E_{rev} is known as the electrical overpotential, which is generally denoted by η , so that

$$\eta = E_i - E_{\text{rev}} \quad (2.48)$$

When no thermodynamic equilibrium potential is established for zero external current, the difference of the potential at $i = 0$ and $i \neq 0$ is termed polarization:

$$\eta = E_i - E_{(0)} \quad (2.49)$$

In some cases $E_{(0)} = E_{\text{rev}}$, that is, polarization and overpotential are equal to each other. $E_{(0)} \neq E_{\text{rev}}$ is realized whenever the electrode potential is a so-called mixed potential.

Overpotential and polarization are determined with the aid of a suitable reference electrode (for example, a calomel electrode), connected to the electrode under test to form a galvanic cell. The voltage of such a cell is then measured in the presence and in the absence of a polarizing current. Two values are obtained, whose difference is the overpotential or the polarization, respectively.

The overpotential, which is generally positive when the experimental electrode works as anode ($i > 0$) and negative when $i < 0$, will in general assume a stationary value after an initial period of adjustment. A plot of these stationary values of η as a function of i is termed the 'overpotential–current curve'.

The initial slope of the overpotential–current curve,

$$R_p = \left(\frac{d\eta}{di} \right)_{i \rightarrow 0} \quad (2.50)$$

is known as polarization resistance. Since the charge e is equal to it , the polarization capacitance per unit area is defined by

$$\frac{de}{d\eta} = \frac{idt}{d\eta} \equiv C_t \quad (2.51)$$

The initial capacitance when time $t = 0$ is identical to the capacitance of the electrochemical double layer. The e – η curve must therefore possess a finite initial slope, corresponding to the

The overpotential can be ascribed to three principal causes.

1. During the passage of a current, the activities (or concentrations) of the reactants near the electrode surface undergo a change, resulting in a corresponding alteration in the equilibrium electrode potential.
2. An additional overpotential may be required to enable the charge carriers to cross the interface (transition reaction).
3. The incorporation of atoms into the lattice of the electrode (or the reverse process) may be hindered. The resulting overpotential is termed as crystallization overpotential η_y .

The observed total overpotential, η , may thus be resolved into three additive components: the concentration overpotential η_c , the transition overpotential η , and the crystallization overpotential η_y . The concentration overpotential can be further subdivided into diffusion overpotential η_d and reaction overpotential η_r .

The *diffusion overpotential*, η_d , is caused by depletion or enrichment of the reactants at the surface of the electrode. When AgNO_3 solution is electrolyzed using silver electrodes, the silver is dissolved from the anode and gets deposited at the cathode, and the total concentration of Ag ions remains unchanged throughout. An increase in the concentration of silver ions will however be observed at the anode, while a corresponding decrease occurs at the cathode. Even when the electrolyte is vigorously stirred, concentration gradients of this type within a layer adhering to the electrodes may only be overcome by diffusion.

To understand the cause of the *reaction overpotential*, η_r , it should be realized that the potential determining transition reaction may be preceded or followed by chemical reactions whose rates are lower than its own. The equilibrium concentrations required to produce E_{rev} will not be established in time. The slow step may therefore be regarded as inhibiting (for establishment of E_{rev}).

Crystallization overpotential, η_y , is treated as a special type of overpotential, and is observed when the inhibiting step consists of the addition of metallic ions to a crystal lattice, or their separation from it.

The *resistance overpotential*, η_Ω , corresponds to an ohmic potential drop at the electrode and can be due to the presence of surface films.

The *total overpotential* is given by the algebraic sum of the various components, since several of them usually operate simultaneously.

$$\eta = \eta_t + \eta_y + \eta_d + \eta_r + \eta_\Omega \quad (2.53)$$

The resistance polarization, η_Ω , and the transition overpotential (η_t) are characteristic of irreversible reactions and are therefore collectively termed 'irreversible overpotential'. On the other hand, since deviations from the equilibrium potential due to changes in the concentrations of the reactants are largely reversible, the diffusion overpotential (η_d) and the reaction overpotential (η_r) are collectively known as 'reversible polarization'.

2.4.2 Activation overvoltage

Activation overvoltage is voltage loss caused by the charge transport/transfer of any material or process that has a limited speed. That is, activation over potential results from the slowness of one or more of the intermediate steps in either one or both of the electrode reactions. The open circuit voltage, E_a , is generally less than the thermodynamically reversible potential, E_r , for the specified conditions of temperature, pressure, activities of reactants and products, because of interference caused by adventitious reactions of impurities. When the net current drawn from the cell is small, cell potentials may tend to be controlled by these impurity reactions. However, due to their low concentrations, impurity effects are small at higher currents generated from the cell. Further, it is found that at low current densities there is a very sharp decrease of E with i . This type of behaviour is characteristic of highly irreversible processes and is caused by activation over potential. These limitations can generally be overcome by employing an 'activation catalyst' and by increasing the temperature.

2.4.3 Concentration overvoltage

It is the voltage difference caused by diffusion processes due to pressure gradients, and changes in the utilization rates of gases or liquids. The delay caused in reaching steady-state conditions, or the absence of equilibrium conditions as a result of the current flow using up or producing materials, are sources of concentration differences. Other factors could be the porosity of materials that influence the gas or liquid flow, or the permeability of membrane changing the ionic flow.

2.4.4 Reaction overvoltage

A voltage difference arises when a preceding or simultaneous (related) chemical reaction produces another compound which changes the operating conditions. For instance, water produced in a hydrogen–oxygen cell dilutes the electrolyte, which then causes an electrolyte concentration change at the electrode interface.

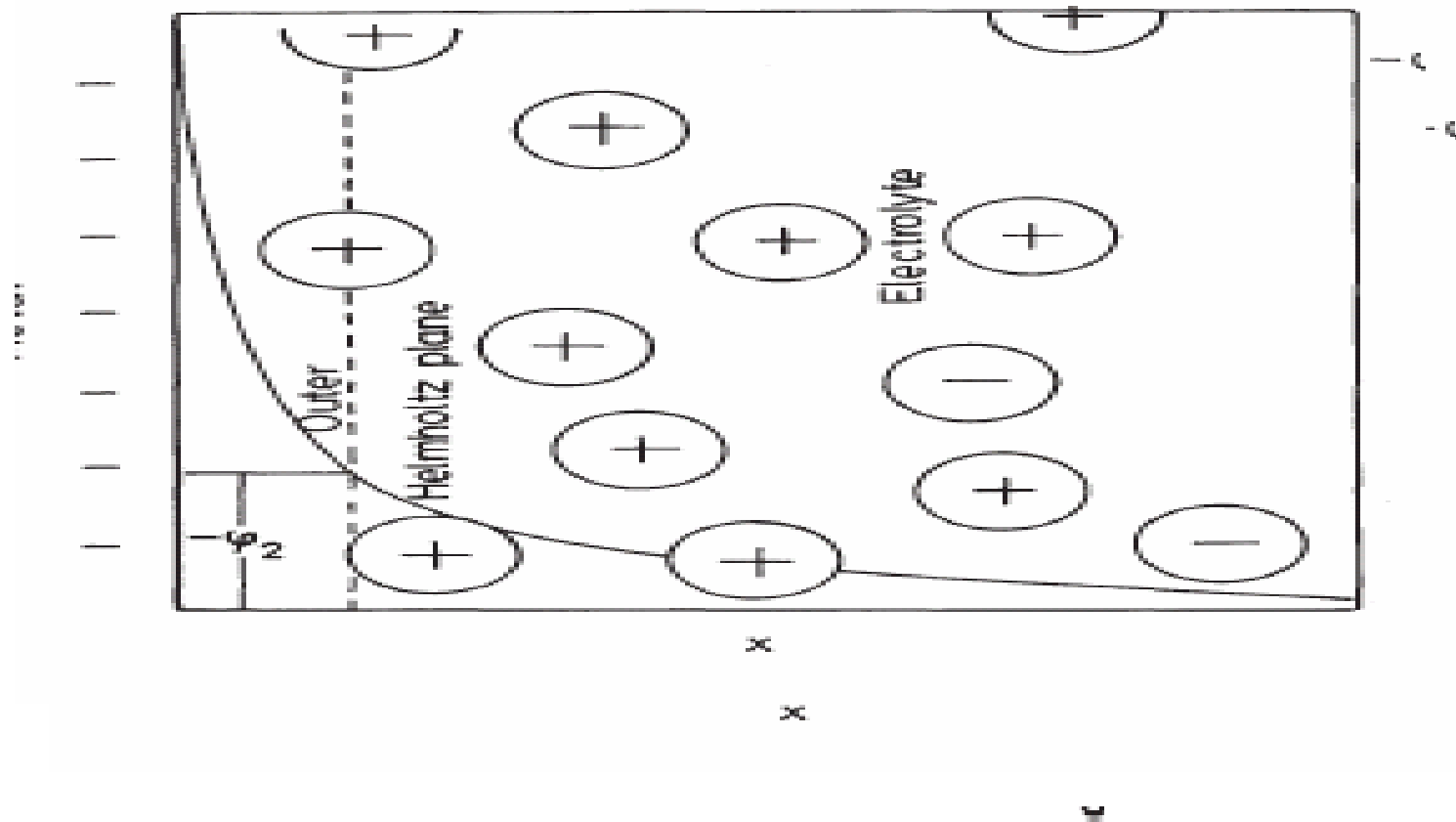


Figure 2.2 Double layer structure at metal–electrolyte interface and dependence of innerpotential, ϕ , on the distance x in the electrical double layer

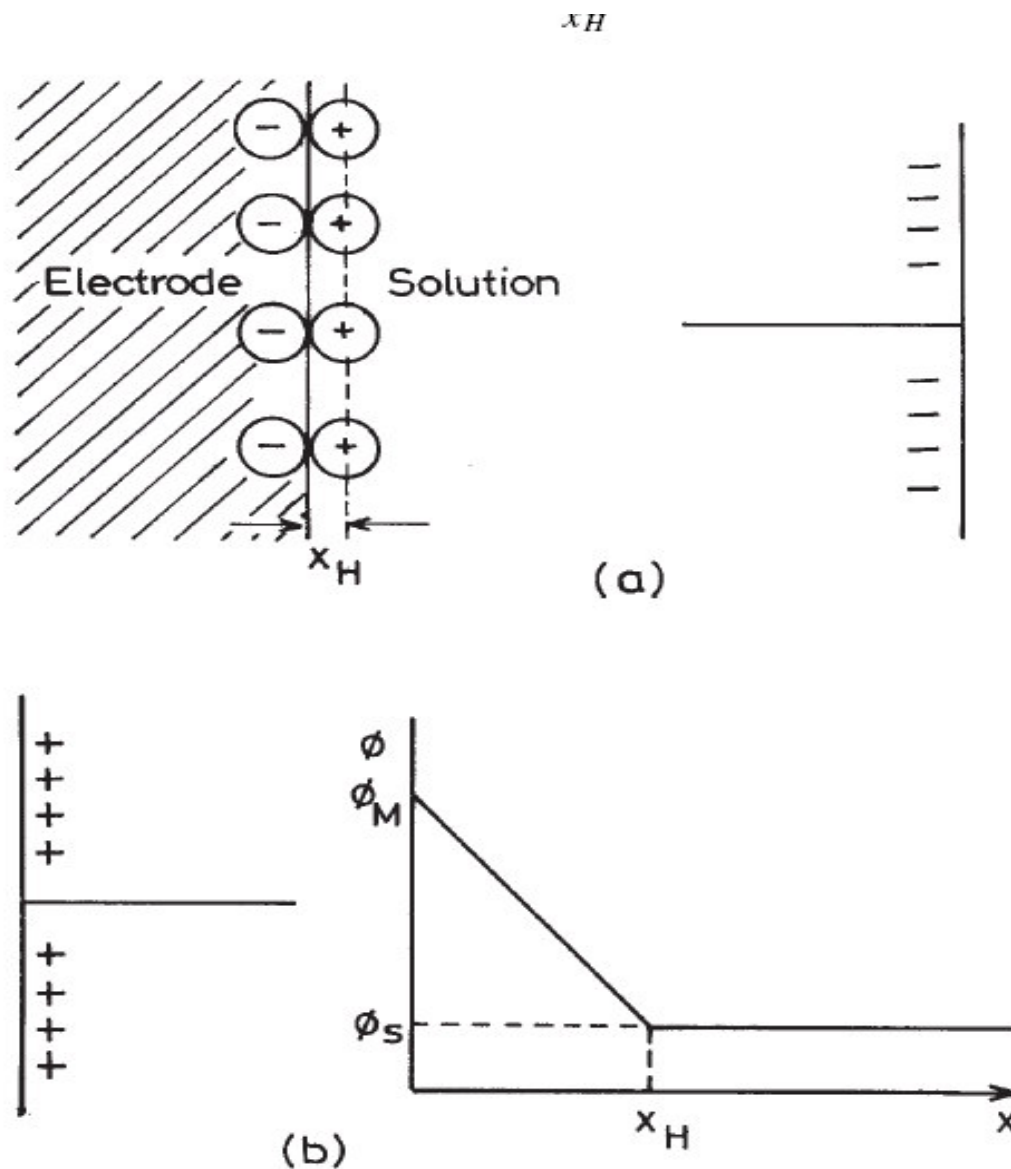


Figure 2.4 (a) Pictorial representation of Helmholtz model of double layer with arrangement of point charges to give rise to a situation similar to parallel plate capacitor
 (b) The variation of electrostatic potential ϕ as a function of distance x from the electrode

This model has two serious shortcomings:

1. The interactions with ions in the subsequent layers to the first layer is neglected.
2. The dependence of electrolytic concentration on the accumulation of charges in the double layer has not been taken into account.

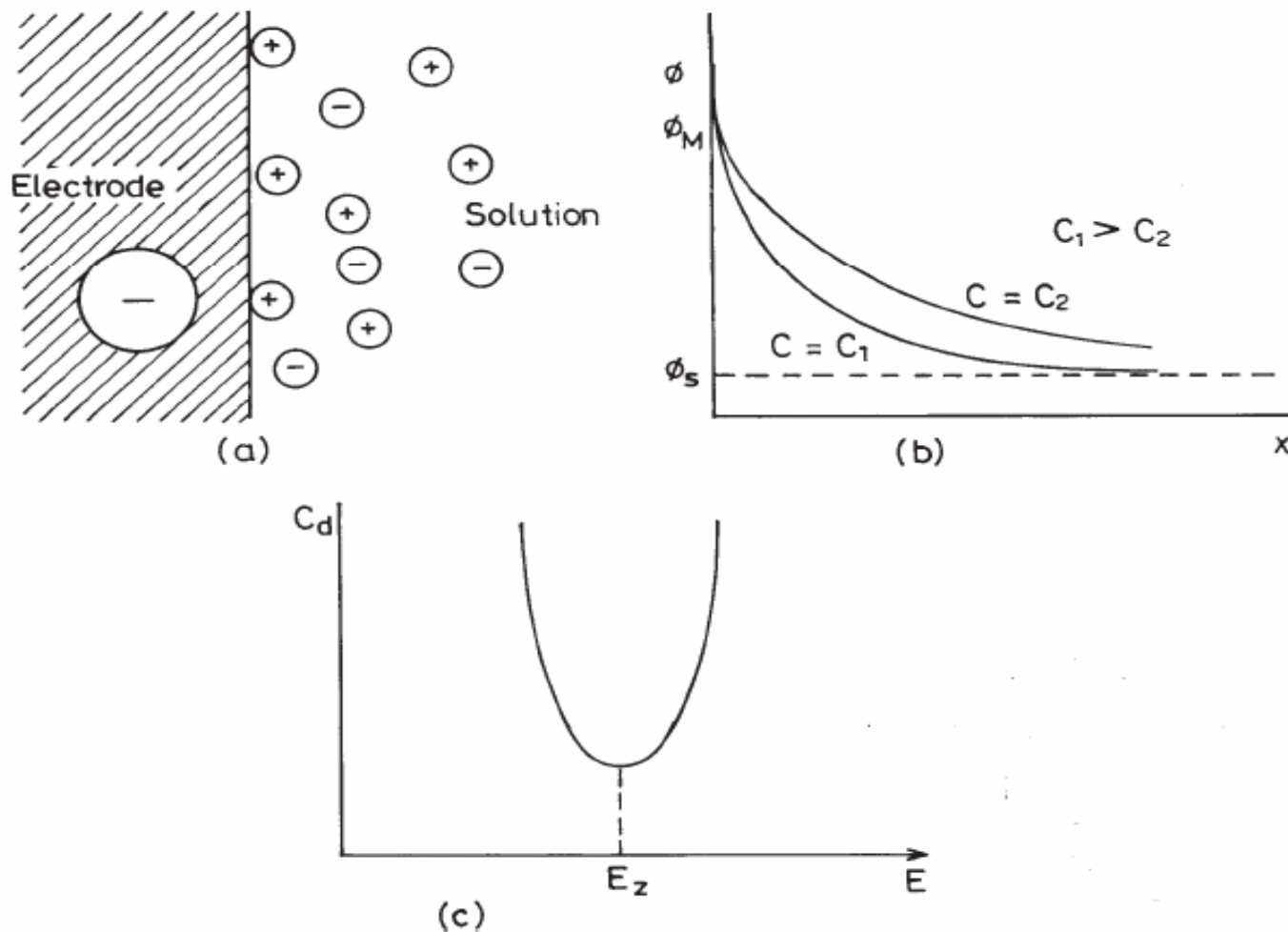


Figure 2.5 (a) Pictorial representation of ions in the diffuse double layer according to Gouy–Chapman model
 (b) The variation of electrostatic potential ϕ as a function of distance x from the electrode. The variation of potential as a function of concentration of the ion is also shown in this figure
 (c) Variation of C_d with potential, showing the minimum at the point of zero charge E_z

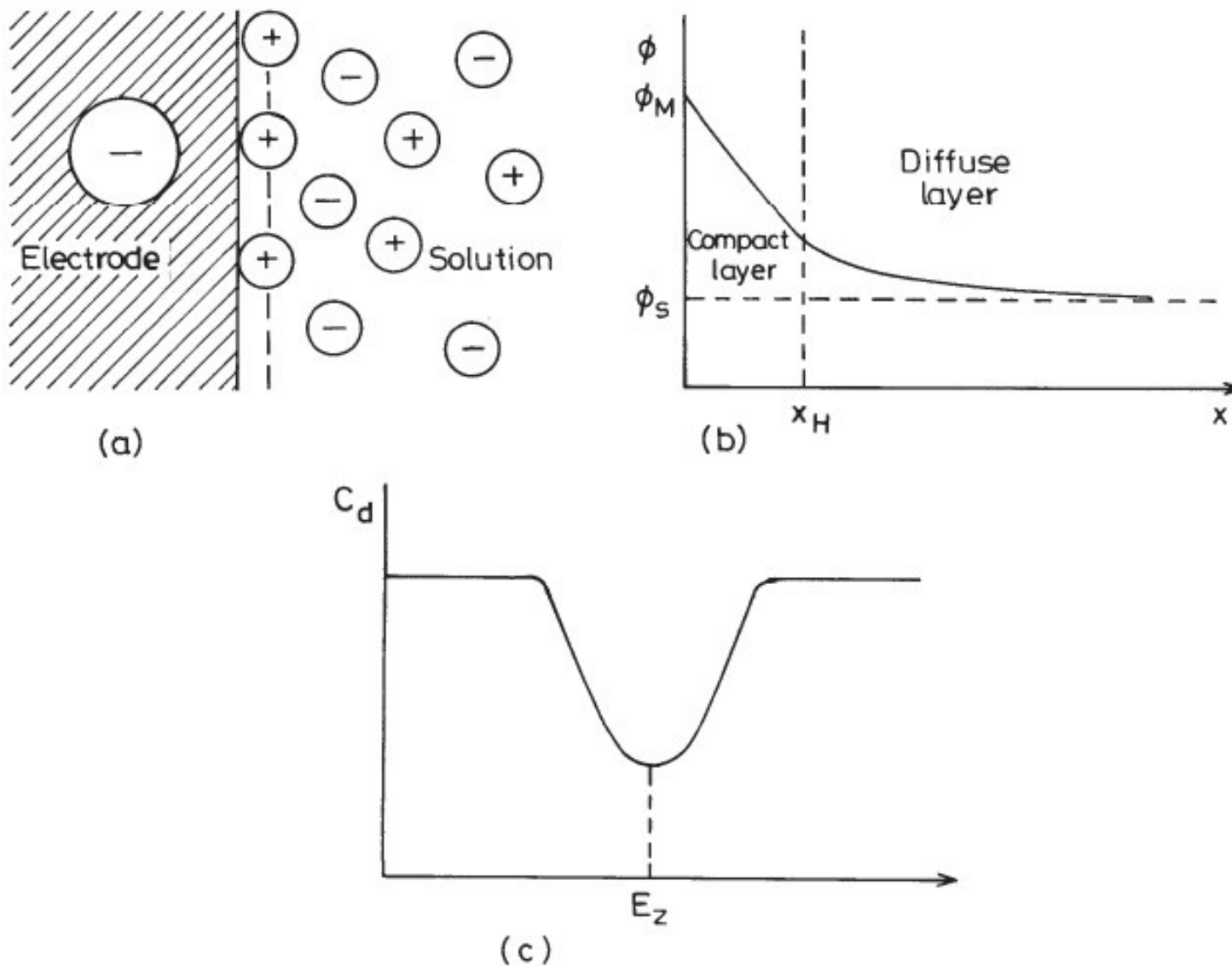


Figure 2.6 Pictorial representation of Stern model of double layer (a) compact layer (similar to Helmholtz double layer model) close to the electrode and a diffuse layer extending in the solution side (Guoy–Chapmann model); (b) and (c) the variation of potential ϕ and C_d with distance and potential respectively

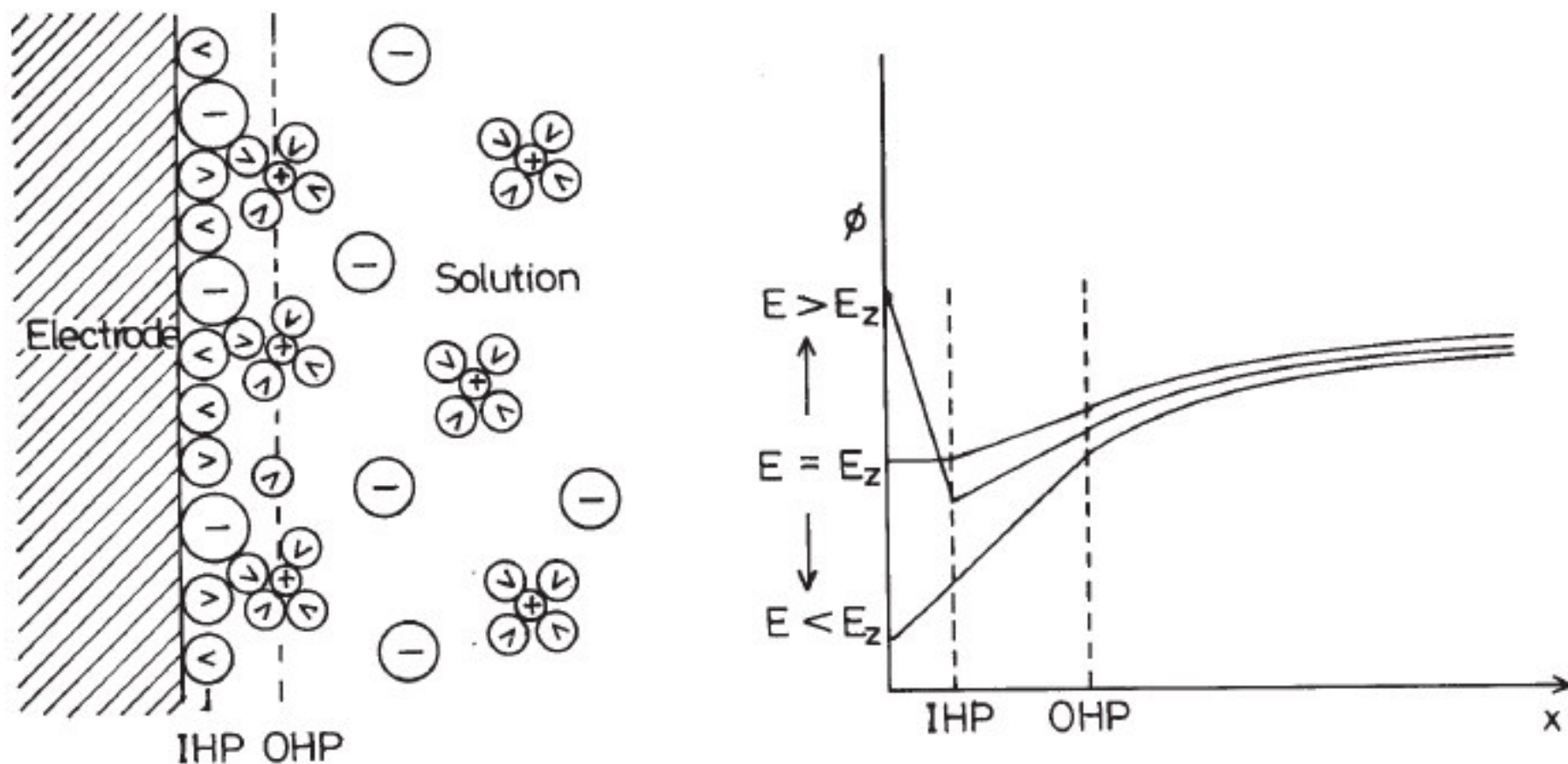


Figure 2.7 The double layer model of Bockris et al: (a) arrangement of ions and solvent molecules (\curvearrowright represents a water molecule, and (b) the variation of electrostatic potential ϕ as a function of distance x from the electrode

Summarizing remarks on models for the double layer

The first model for the structure of the double layer is analogous to a parallel plate condenser with a plane of charges on the metal and a second plane of opposite charges in the solution. According to this model, the capacity of the double layer should be independent of the potential across the metal–solution interface, which contradicts the experimentally observed behaviour.

The next model considered that the charges in the solution side are not located in one plane but diffuse into the bulk of the solution. This model yields a parabolic dependence of capacity on charge. Though this model is satisfactory for very dilute solutions (concentration $< 10^{-3} \text{ mol l}^{-1}$), the predicted values of the capacity are far too high in concentrated solutions.

A combination of the compact and diffuse layer models proved to be satisfactory. However, (1) in very dilute solutions, it became in practice identical with Helmholtz model (2) in the region of constant capacity, the dependence of the capacity on the radius of the ion present in the solution is not seen, though the model shows this, and (3) it cannot also explain the increase in the capacity which occurs in the anodic region.

The three layer model—the metal surface, an inner Helmholtz layer that is the locus of centers of specifically adsorbed ions, and an outer Helmholtz plane that is the locus of centers of the first layer of hydrated ions—has several satisfactory features. However, it does not provide a satisfactory explanation for the constant capacity observed in the negative branch or the hump on the anodic side.

In all these models, the role of water was ignored, even though it is the predominant species in solution. The current accepted model is that the electrode is covered with a layer of completely oriented water molecules. Specific adsorption of ions occurs in certain regions of potential by a replacement of some of the water molecules by the partially desolvated ions. The second layer of water molecules is not oriented, because these water molecules are under the influence of both the electric field and thermal fluctuations. They are like the secondary hydration sheath around an ion. Some of these water molecules can belong to the hydration sheaths of a layer of ions that are present in the outer Helmholtz plane. The dielectric constant of the first layer of oriented water molecules can be taken to be 6 to 7 and that of the second—partly oriented water layer—can be about 30 to 40. Considering the double layer as two capacitors in series, one with a low value of $\epsilon = 6$ and the other a high value of $\epsilon \sim 40$, the region of constant capacity with potential may be understood.

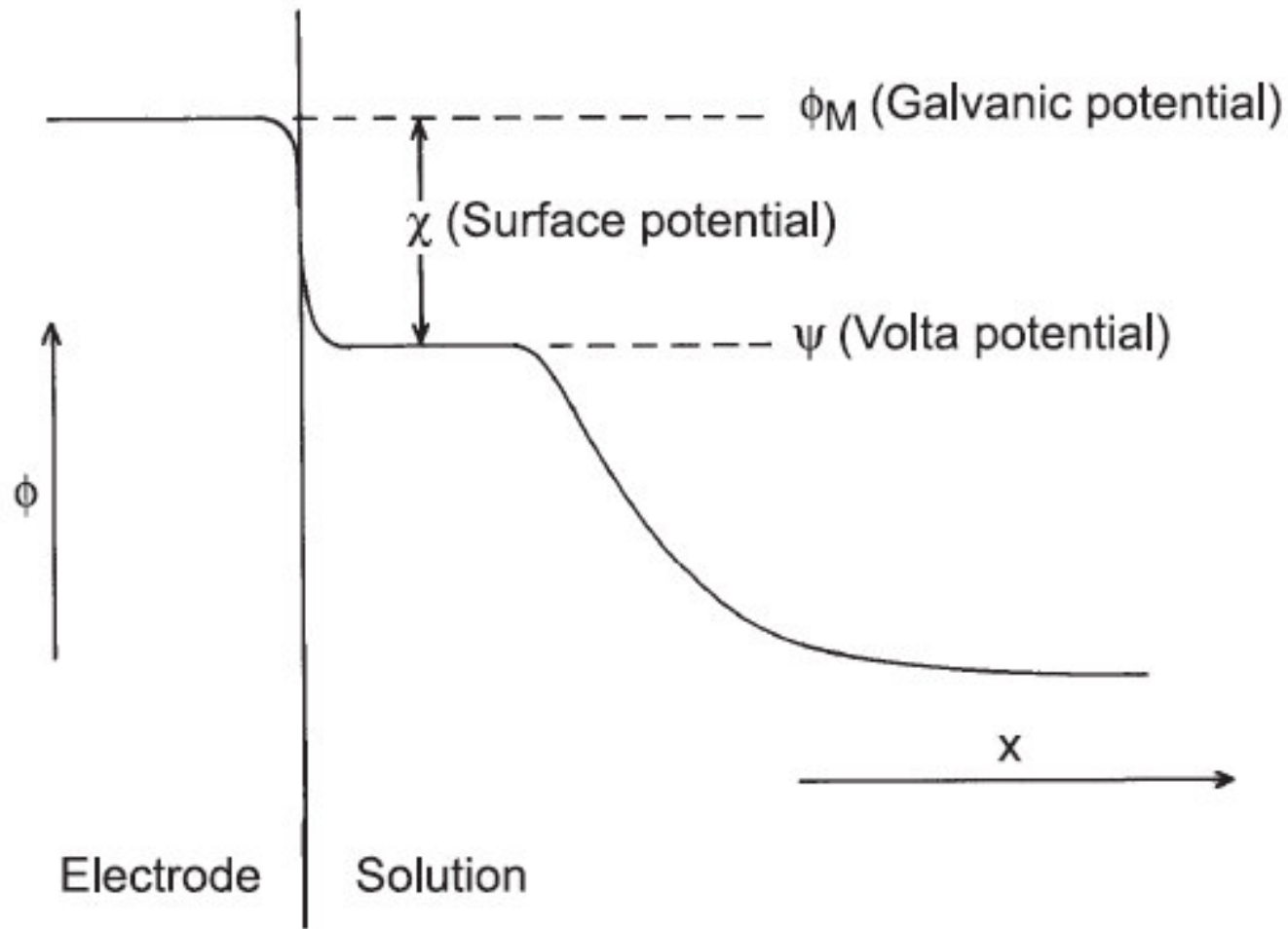


Figure 2.9 Potential variation as a function of distance from a metal electrode that is separated from electrolyte solution without charge modification (not to scale). ψ is the potential caused by the charge distributions when the electrode and solution are in contact

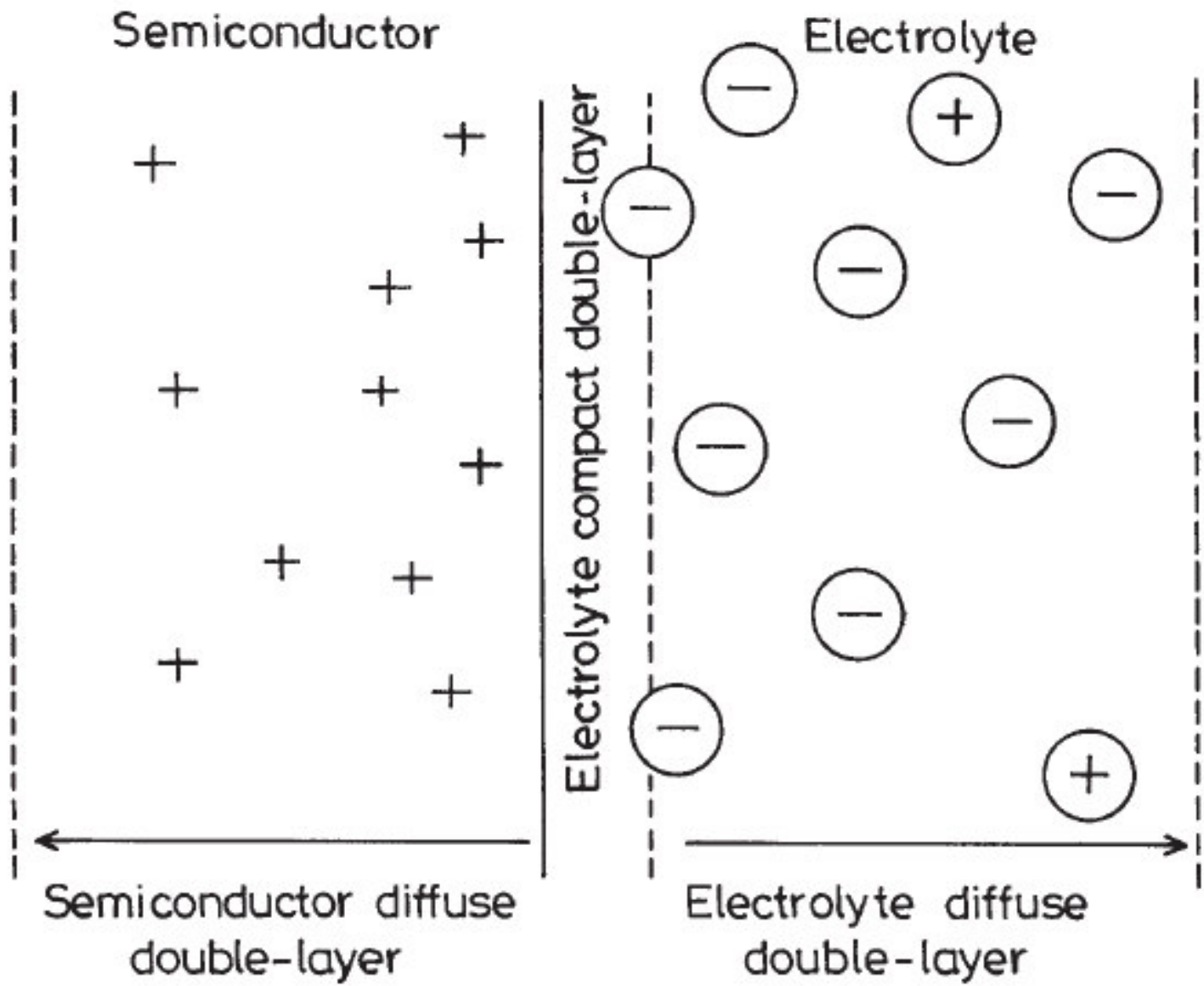


Figure 2.12 Double layer structure at a semi-conductor-electrolyte interface

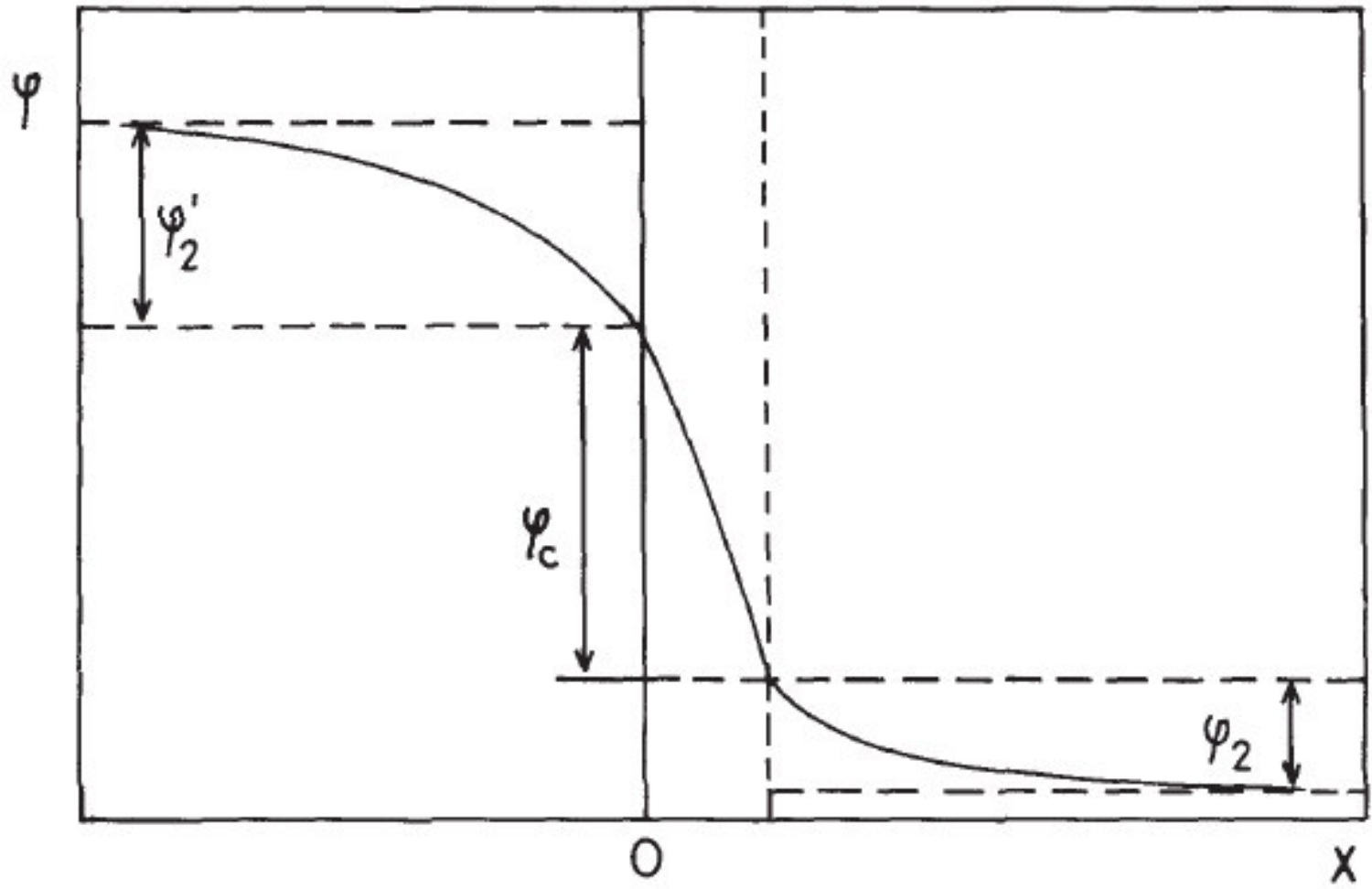


Figure 2.13 Dependence of the inner potential ϕ on the distance from the surface of the semiconductor x

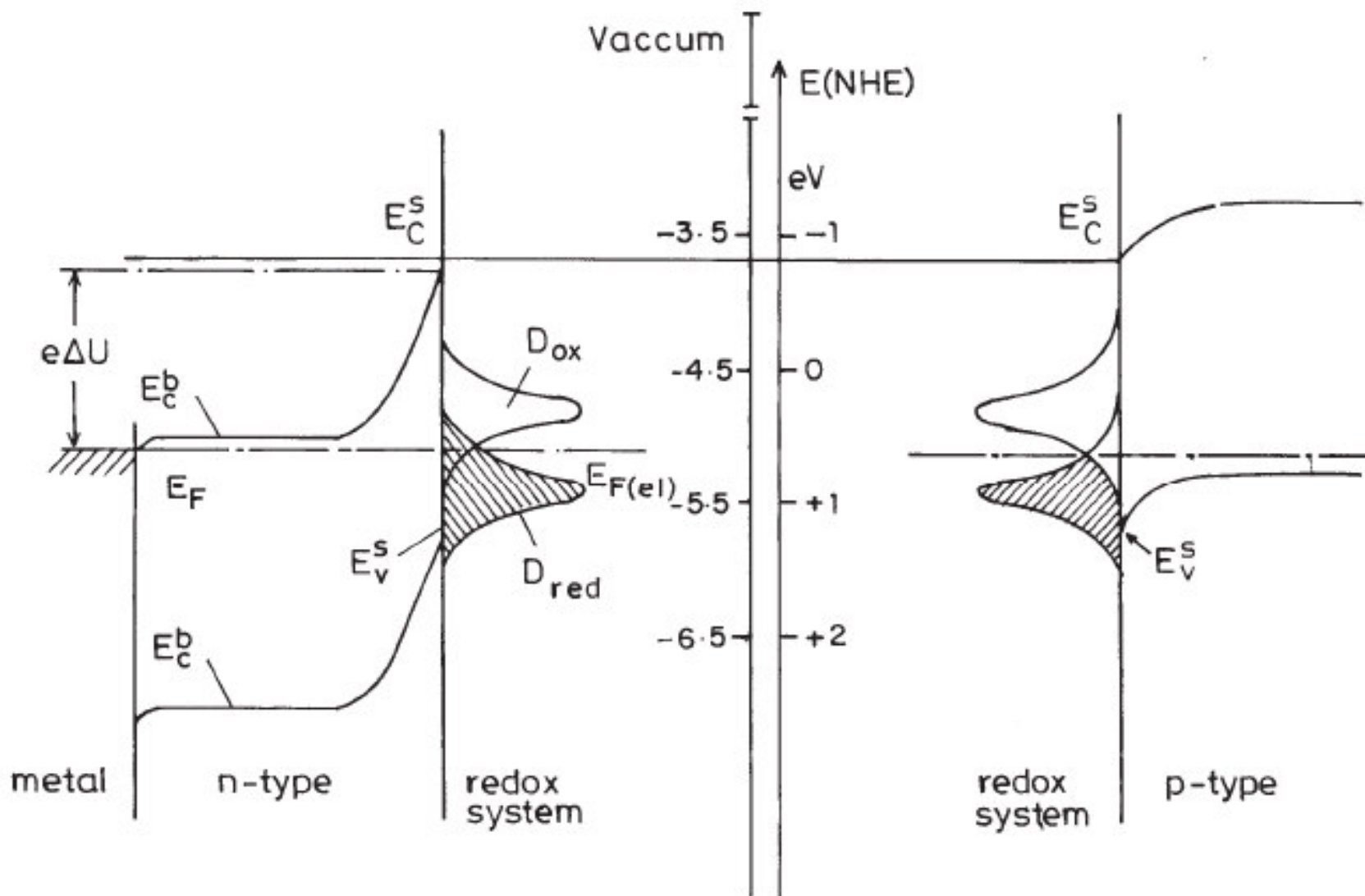


Figure 2.14 Energy states of semiconductor electrodes and redox systems [Reproduced from Ref. 29]

1. At a certain potential, the Fermi energy lies at the same energy as the solution redox potential. There is no net transfer of charge, and hence there is no band bending. This potential is therefore referred to as the *flatband potential*, E_{fb} .
2. Depletion region arises at potentials positive of the flat band potential for an *n*-type semiconductor and at potentials negative of the flatband potential for a *p*-type semiconductor.
3. At potentials negative of the flatband potential for an *n*-type semiconductor, there is now an excess of the majority charge carrier (electrons) in this space-charge region, which is referred to as an *accumulation region*. An accumulation region arises in a *p*-type semiconductor at potentials more positive than the flatband potential.

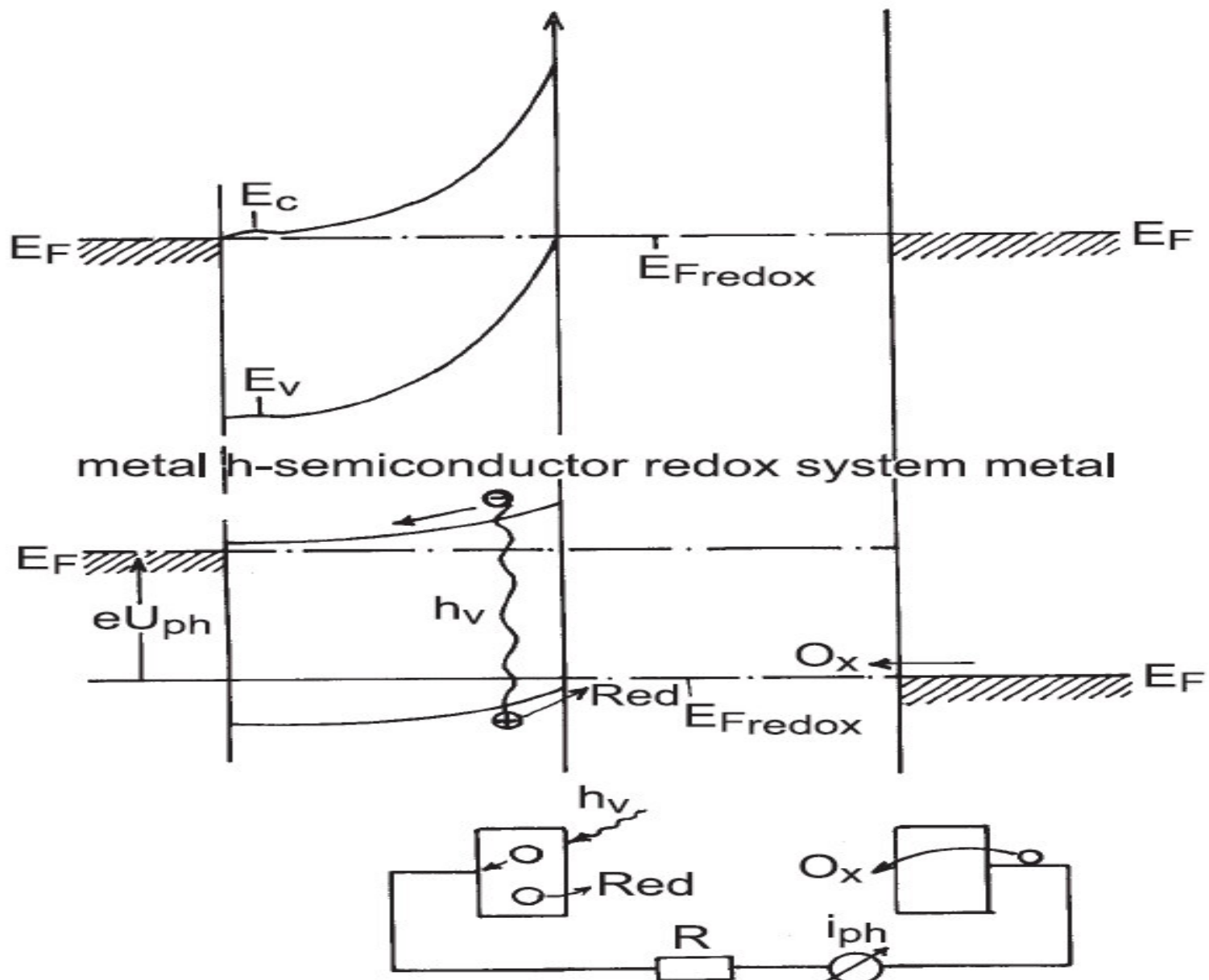


Figure 2.15 Energy scheme of a regenerative solar cell, with *ideal behavior* of an n-type semicon-

- For a certain value of applied potential, there is equality between the number of electrons removed from and supplied to the electrode. In this situation there will be no space-charge region and the potential is called the flat-band potential E_{fb} ;
- Electrons accumulate in the space-charge layer by injection, giving rise to an accumulation layer;
- Electrons are removed from the space-charge layer, creating a depletion layer;
- The force necessary to extract electrons from the electrode is so great that they are extracted not only from the conduction band but also from the valence band (equivalent to hole injection). An inversion layer is formed, because the n -type semiconductor is converted into a p -type semiconductor at the surface. Adsorbates can facilitate this process.

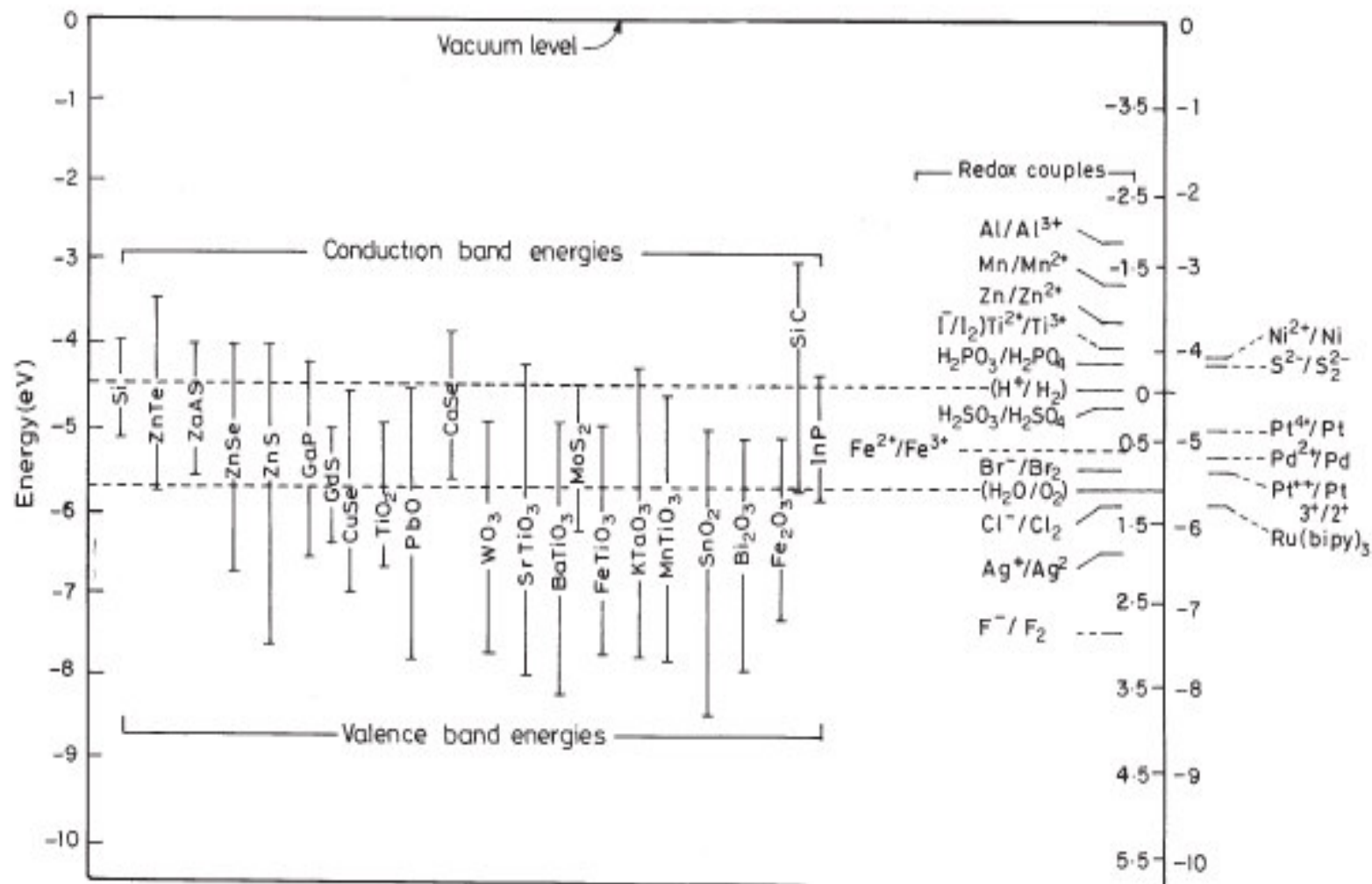


Figure 2.16 Relative energy levels of some common semiconductor electrode materials and redox systems [Reproduced from Ref. 35]

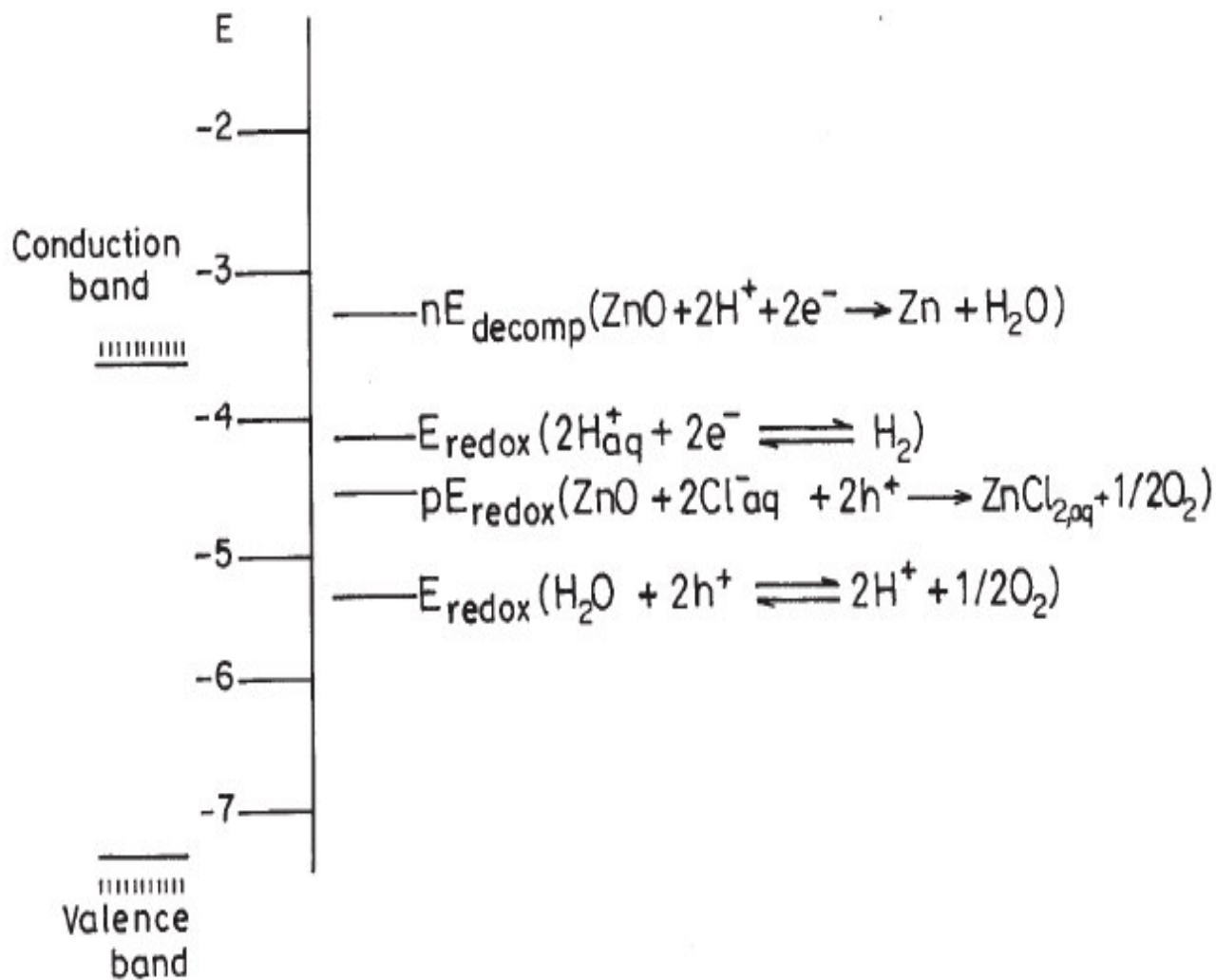


Figure 2.17 Relative positions of the redox potentials of the substrate and semiconductor dissolution for ZnO at $pH = 0$ [Reproduced from Ref. 35]

1. *Electrophoresis*: Charged solid particles (colloidal particles) moving through the liquid under the influence of an electric field. It is called *sedimentation potential* when it is due to gravitational force.
2. *Electroosmosis*: Liquids moving past charged solid surfaces (or possibly through membranes) under the influence of an electric field. It is called *streaming potential* when it is due to an applied pressure difference. These effects are normally studied in fine capillaries in order to maximize the ratio of the solid surface area to the liquid volume.

The four manifestations of the electrokinetic effect are summarized in Table 2.2

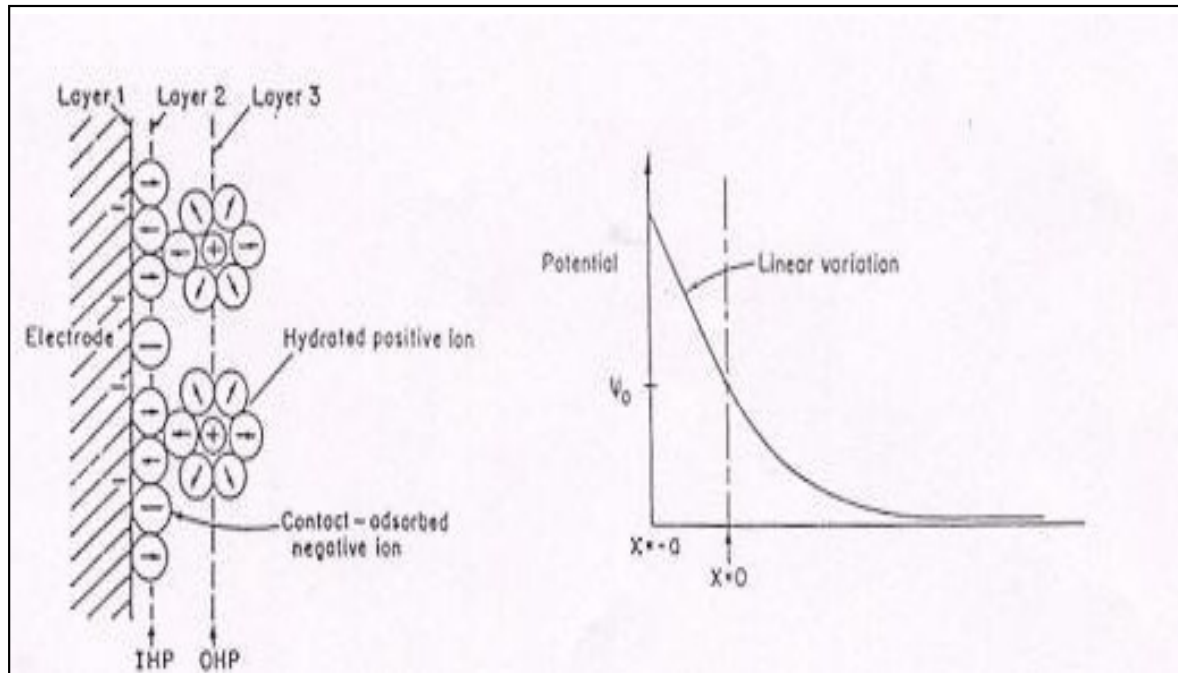
Table 2.2 Electrokinetic phenomena

Mobile phase / Stationary phase	Phenomenon (Force applied)	Property measured
Solid / Liquid	Electrophoresis (Electric field)	Electrophoretic mobility via mass transport measurement, microscope or Doppler effect
Solid / Liquid	Sedimentation potential (Force of gravity)	Potential difference
Liquid / Solid	Electroosmosis (Electric field)	Rate of liquid movement, pressure
Liquid / Solid	Streaming potential (Pressure)	Potential difference

The size of the particles that is calculated from these experiments corresponds to particle dimensions plus the double layer thickness. The shear plane is defined such that inside it the adsorbed species are rigidly held, and outside it there is free movement. The shear plane can therefore be associated roughly with the outer Helmholtz plane. The value of the electrostatic potential at the shear plane with respect to the value in bulk solution is called the electrokinetic or zeta potential, ξ .⁴⁰



Metal/Electrolyte Interface

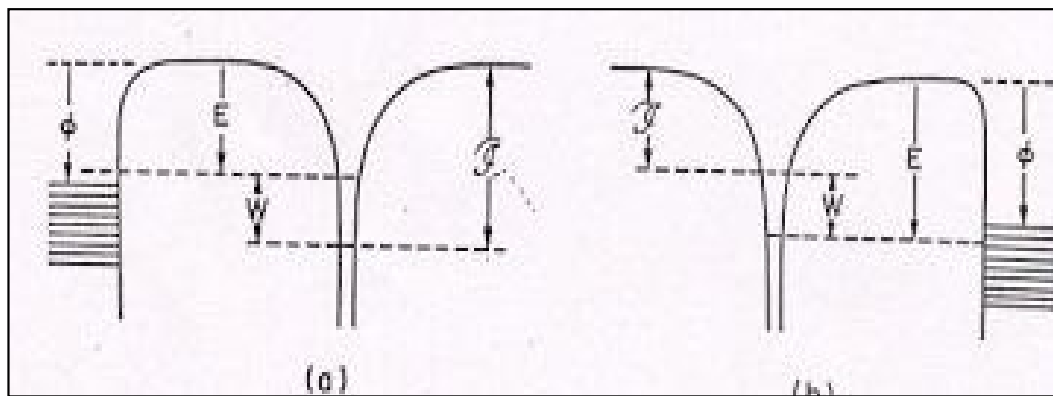


$$1/C_{dl} = 1/C_H + 1/C_{GC}$$

- ▶ The density of states is $10^{22} \text{ cm}^{-3}\text{V}^{-1}$
- ▶ The space charge of the metal is all squeezed onto the surface.
- ▶ Field gradient is absent in the bulk of metal.



Electron transfer at Metal electrode/electrolyte interface

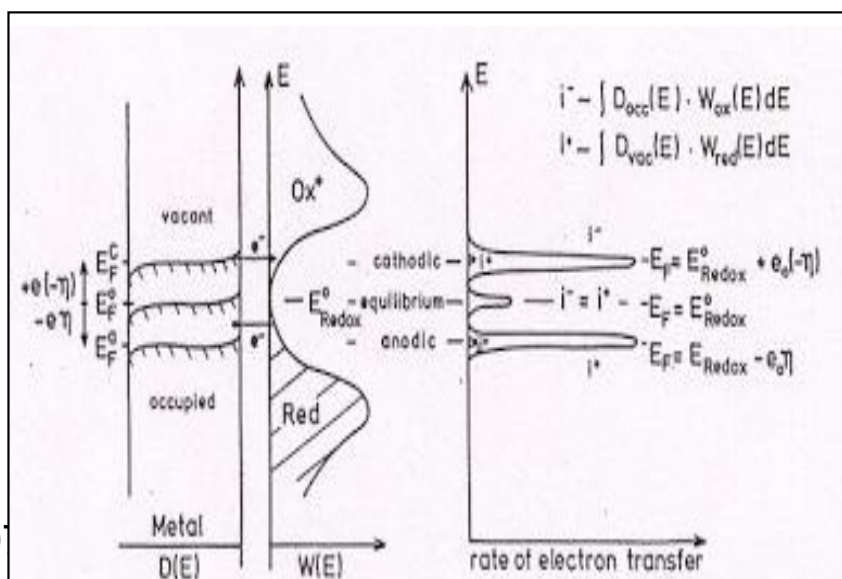


▶ Gurney's model : Electron passes from

Oxidation → Filled donor state of redox species to the Fermi level of the metal

Reduction → Fermi level of the metal to the empty acceptor states of an oxidant

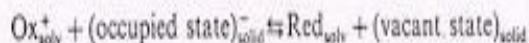
▶ Electron transfer rate at Metal/electrolyte interface



▶ The electron transfer occurs in an energy range close to the Fermi level

▶ not too far from equilibrium condition – does not go to high overvoltages

☞ Rate equation at Metal electrodes



Metal electrodes:

$$j^- = e_0 \cdot N_{\text{ox}} \cdot \sigma_{\text{ox}} \cdot \sigma_{\text{el}} \cdot \nu_n \cdot \kappa_{\text{el}} \times \int_{-\infty}^{\infty} W_{\text{ox}}(E) \cdot D_{\text{occ}}(E) dE$$

$$j^+ = e_0 \cdot N_{\text{red}} \cdot \sigma_{\text{red}} \cdot \sigma_{\text{el}} \cdot \nu_n \cdot \kappa_{\text{el}} \times \int_{-\infty}^{\infty} W_{\text{red}}(E) \cdot D_{\text{vac}}(E) dE$$

e_0 = electric charge of the electron

$N_{\text{ox}}, N_{\text{red}}$ = number of reactants cm^{-3}

$\sigma_{\text{ox}}, \sigma_{\text{red}}, \sigma_{\text{el}}$ = reaction cross sections of the reaction partners at the interface

ν_n = averaged frequency of the nuclear modes in the activated complex of Ox^+ or Red

$$\kappa_{\text{el}} = \frac{2 \left[1 - \exp\left(-\frac{\nu_{\text{el}}}{2\nu_n}\right) \right]}{2 - \exp\left(-\frac{\nu_{\text{el}}}{2\nu_n}\right)}$$

adiabaticity coefficient
($\nu_{\text{el}} \gg \nu_n$ adiabatic process)

$D_{\text{occ}}(E), D_{\text{vac}}(E)$ = density of occupied and vacant electronic states in the solid

$$\nu_{\text{el}} = \frac{2|H_{if}|^2}{h} \left(\frac{\pi}{2\lambda kT} \right)^{1/2}$$

frequency factor for
electronic transitions

$|H_{if}|$ = coupling energy between initial and final state

λ = reorganization energy

$$W_{\text{ox}}(E) = \exp\left(-\frac{(E_{\text{ox}}^0 - E)^2}{4\lambda kT}\right)$$

probability distribution
of energy states in the
oxidized species

$$W_{\text{red}}(E) = \exp\left(-\frac{(E_{\text{red}}^0 - E)^2}{4\lambda kT}\right)$$

probability distribution
of energy states in the
reduced species

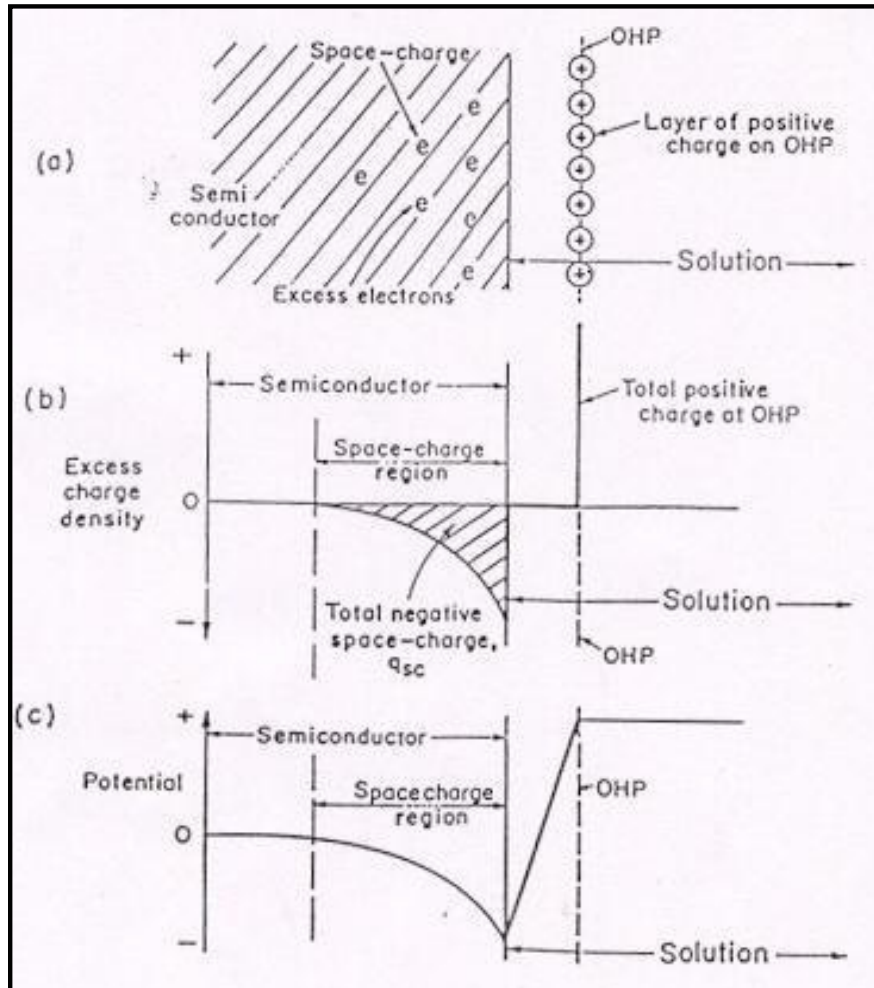
► The integrals represents the currents for metal electrodes

→ probability distribution of energy states in the Ox^+ or Red species.

→ density of occupied or vacant electronic states in the solid



Semiconductor/Electrolyte Interface



$$1/C_{dl} = 1/C_{SC} + 1/C_H + 1/C_{GC}$$

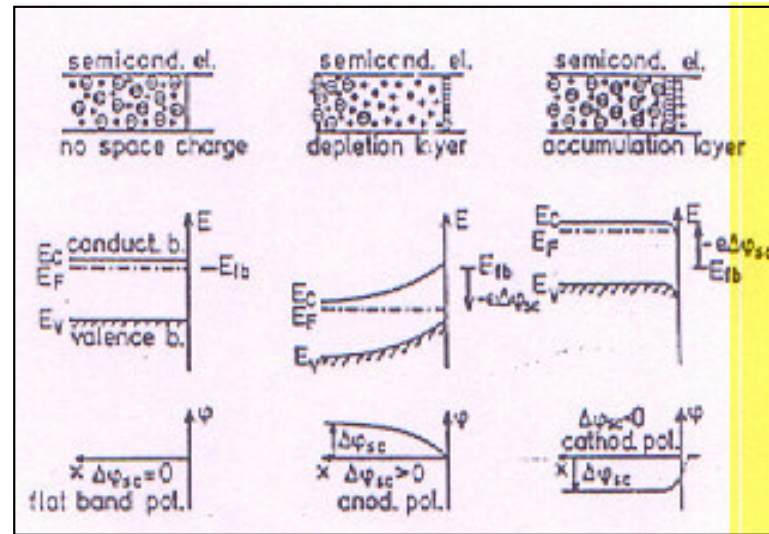
► The potential due to atmosphere of holes and electrons is given by

$$\chi = (\delta\pi\eta^0 e_0^2 / \epsilon kT)^{1/2}$$

χ^{-1} → Thickness of the Garrett-Brattain space charge inside a semiconductor.

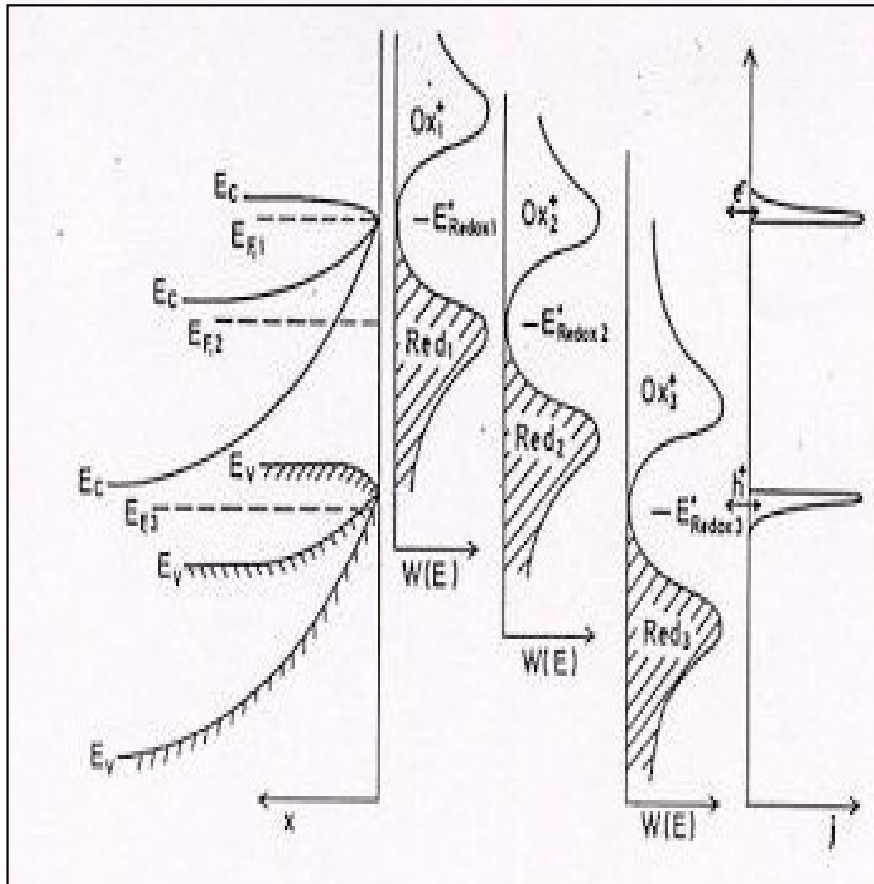


Effect of potential on the Energy levels of the Semiconductor



- ▶ are
- ▶ The energy bands near the surface of the Semiconductor are disturbed by the existence of the field.
- ▶ of
- ▶ The bending of the bands up or down depends on the sign of the ionic charge populating the OHP.
- ▶ Field penetration exists inside the Semiconductor.
- ▶ Field gradient depends on
 - (i) Density of states
 - (ii) Surface states
 - (iii) Adsorption capacity

☞ Electron transfer at Semiconductor electrode/electrolyte interface



Redox system 1 → E°_{redox} close to CB edge
Accumulation layer
High rate of e^- exchange can be expected

Redox system 2 → **Depletion layer**

Ox^+ reduced conduction

Electron transition to species nor from species reach the band energy.

Redox system 3 → **The barrier height for electron is even higher**

(close to E_g energy)

**E°_{redox} close to VB edge
 e^- exchange is possible
 VB edge.**

with

Reference: H. Gerischer, Electrochimica Acta, 35 (1990) 1677.



Electron transfer at the Semiconductor/electrolyte interface:

Current via the conduction band

$$j_c = k_c^+ \cdot N_c \cdot N_{\text{red}} - k_c^- \cdot n_s \cdot N_{\text{ox}}$$

$$n_s = n_o \cdot \exp(e_o \Delta \phi_{\text{SC}} / kT)$$

where n_s is surface concentration of electrons

Current via the valence band

$$j_v = k_v^+ \cdot p_s \cdot N_{\text{ox}} - k_v^- \cdot N_v \cdot N_{\text{ox}}$$

$$p_s = p_o \cdot \exp(e_o \Delta \phi_{\text{SC}} / kT)$$

where p_s is surface concentration of holes

▶ **Equilibrium between the Semiconductor electrode and a redox system/depolarizer in solution can result in a situation where the Fermi level is located in the band gap of the semiconductor.**

▶ **Considerable electron transfer can occur only if the redox potential of the redox system is located close to the band edges of a semiconductor.**

▶ **The rate of electron transfer across the semiconductor/depolarizer depends only the surface concentration of the charge carriers (density of states).**

H. Gerischer, Electrochimica Acta, 35 (1990) 1677

S. Trasatti and J. Ulstrup, Electrochimica Acta, 45 (1999) 2339



Fermi level and Density of states

- ▶ **The position of the Fermi level determines the chemisorption of the surface and controls the equilibrium species created by the adsorbed**
properties population of the various species.
- ▶ **By suitable doping of oxides with small amounts of foreign atoms the Fermi level which reflects the availability of carrier (density of states) at the surface.**
 - **accelerated by the rise of F.L – availability of electrons – n-class or acceptor reaction**
 - **accelerated by lowering of F.L – availability of holes – p-class or donor reactions.**
- ▶ **States without intervention of foreign atoms – broken bonds on the surface.**



Selection criteria for Multicomponent system

1. Field gradient

Insulators (10^5 V/cm)

Semiconductors

Metals (10^7 - 10^8 V/cm)

2. Adsorption capacity depends on the nature of active site

depolarizer

3. Potential range of application

4. Identifying the possible candidates



above

Perovskites, Pyrochlores and Spinel - satisfies the condition to some extent