☐ CURRENT-POTENTIAL RELATION AT A SEMI-CONDUCTOR / ELECTROLYTE INTERFACE

From the point of view of kinetics, the main difference between the metal and semi-conductor cases is the location of the potential difference (P.D.), which affects the rate of electron transfer. In the metal-solution case, any potential difference inside the metal is neglected. This is because there is a huge excess of electrons in the metal and the kind of current densities used in electrochemistry

are far too low to disturb the large electron concentration. As the overpotential changes from that at equilibrium ($\eta = 0$) to that at a certain finite net reaction rate, $\eta = \eta$, the quantity that varies is the potential difference in the Helmholtz layer.

On the other hand, in a semi-conductor, the electron concentration may be some 10^6 to 10^8 times less than in a metal. Thus, at a semi-conductor/solution interface, the excess charge on the semi-conductor is spread out inside the semi-conductor because the interfacial activity is enough to significantly use up or add to the sparsely available electrons. In the absence of the special traps called **surface states**, there is a negligible excess charge at the semi-conductor surface (conversely, in the metal, the excess charge is exactly on the surface of the metal). Thus, for a p-type semi-conductor-solution interface, the two situations for the potential-distance plot inside the semi-conductor corresponding to $\eta = 0$ and $\eta = \eta$ are as shown in fig (6).

To deduce a current-potential relation at a semi-conductor/solution interface, one can make an approximate argument. The basic approximation is that there are no "surface states," which in practice means a surface state concentration of $< 10^{10}$ cm^{-2}. If no surface states for electrons exist, the charge is spread back into the semi-conductor and the charge actually at the surface will be small compared with the surface concentration of electrons at metal/solution interfaces. It follows that the electrical double layer on the solution side will have no adherent Helmholtz layer and the charge on the solution will be spread out (but will be equal in magnitude though opposite in sign to the charge on the semi-conductor).

It is easy to see how the concentration of electrons at the surface will depend on the overpotential. As shown above, in dealing with the rate of electron transfer at an n-p junction, the form of the expression [outside the reversible region, i.e., for $\eta > (RT/F)$] is given by

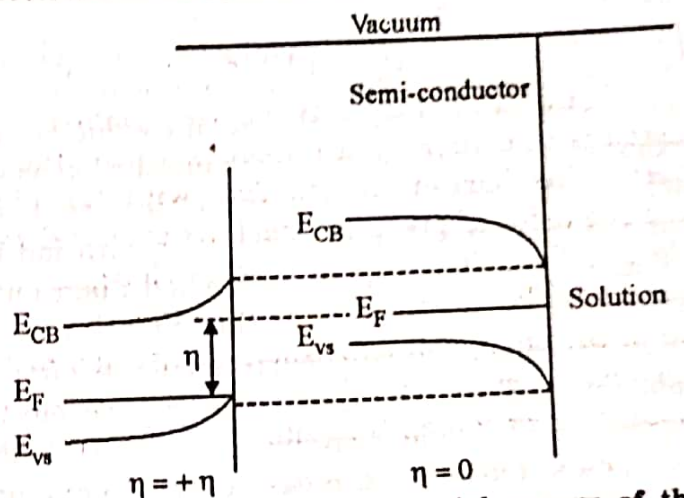$$i = i_0 e^{-\eta F/RT} \qquad \text{... (17)}$$

Fig. 6. Changes in the potential energy of the electrons in a p-type semi-conductor at the semi-conductor/solution interface, when there are no surface states at the semi-conductor electrode surface.

for an electron-transfer reaction from an n-type semiconductor to an acceptor. There is no β. Thus, the concentration of electrons at the surface can be expressed in a Nernst-type equation :

$$\eta = \frac{RT}{F} \ln \frac{c_{e,\,equil}}{c_e \cdot \eta} \qquad \text{... (18)}$$

i.e.,

$$c_e \cdot \eta = c_{e,\,equil}\, e^{-\eta F/RT} \qquad \text{... (19)}$$

The reaction rate between these interfacial electrons from the n-type semi-conductor and receptor in solution (say, on an Fe^{3+} ion) will be given by an expression for the electrochemical rate of reaction by

$$i = Fk c_{e,\,\eta}\, c_{Fc^{3+}} \qquad \text{... (20)}$$

From equation (19),

$$i = Fk c_{e,\,equil}\, c_{Fe^{3+}}\, e^{-\eta F/RT} \qquad \text{... (21)}$$

Thus,

$$\eta = \frac{RT}{F} \ln \frac{i_0}{i} \qquad \text{... (22)}$$

An important distinction between metals and semi-conductor electrodes is apparent. Thus, if one puts equation (22) in the form of a Tafel equation,

$$\eta = a - \frac{RT}{F} \ln i \qquad \qquad ...(23)$$

the corresponding form of the equation for metals is [from equation (23)]

$$\eta = a - \frac{RT}{\beta F} \ln i \qquad \qquad ...(24)$$

(with $\beta \approx 1/2$).

Thus, in a region in which the current density at a driven semi-conductor/solution interface is low enough such that the electrons in the semi-conductor are in equilibrium between surface and bulk (*i.e.*, not rate-determined by charge carrier transport— diffusion— inside the semi-conductor), the gradient of the overpotential with respect to log i will be half that for a metal.

However, all this (*i.e.*, the dependence of i on η before exhaustion of charge carriers occurs) is less stressed in the practical use of semi-conductors in electrochemistry because diffusion-limited currents caused by electron or hole exhaustion inside the semi-conductor (rather than exhaustion of transporting ions in solution as with metals) are usually orders of magnitude less than the limiting current densities due to difficulties with ion transport in solution. For this reason, published diagrams of current potential dependence at the semi-conductor/solution interface show limiting currents more often than Tafel behaviour. Thus, in fig. (7), the *p*-type electrode shows exponential behaviour on the anodic side (plenty of holes to receive electrons from redox ions undergoing oxidation), but only a low limiting current when electrons are required. The converse is true for the electron-rich *n*-type.
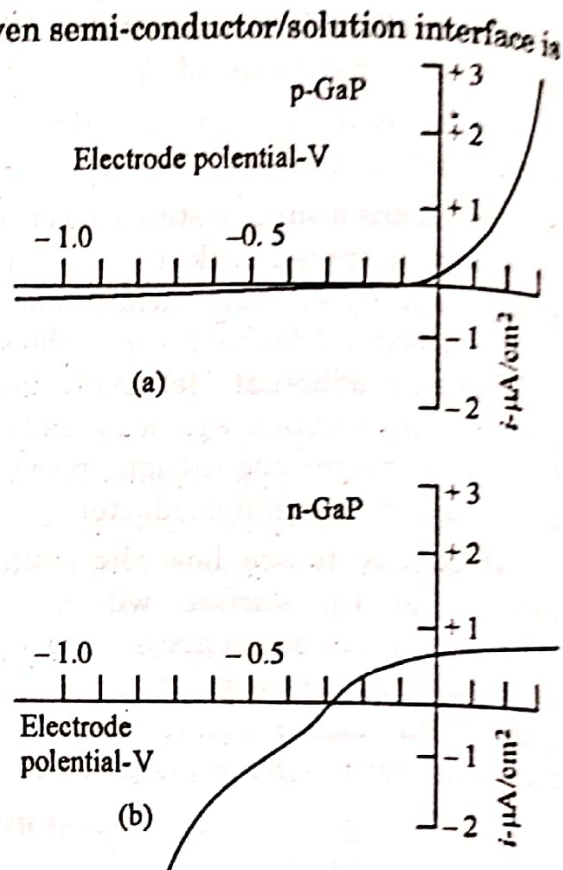

Fig. 7. Current-potential dependence at *n*-and *p*-type GaP in 0.1 N H_2SO_4.

☐ LIMITING CURRENT IN SEMI-CONDUCTOR ELECTRODES

As already stated, when metal electrodes are used in electrochemical reactions and one speaks of a limiting diffusion current, one is referring to ionic charge carriers is solution, which cannot diffuse up to the electrode at a sufficient rate to donate or pick up the number of charges demanded by the electrode potential. Although the same phenomenon is possible with semi-conductor electrodes, a limiting current usually arises because of a limiting transport rate of charge carriers in the electrode. Thus, in an *n*-type semi-conductor with no surface states, electrons must be transported to the semi-conductor/solution interface. They do this partly under a diffusion gradient that impels them to the surface, but their direction is also affected by the electirc field near the electrode surface [Fig. (8)]

Similar statements can be made about holes. They, too, have to be transported to the interface to be available for the receipt of electrons there. All these matters come under the influence of the *Nernst-Planck equation*, where it is shown that a charged particle can move under two influences. One is the concentration gradient, so here one is back with Fick's law. On the other hand, as the particles are changed, they will be influenced by the electric field, the gradient of the

potential-distance relation inside the semi-conductor. Electrons that feel a concentration gradient near the interface, encouraging them to move from the interior of the semiconductor to the surface, get "seized" by the electric field, the gradient of the potential-distance relation inside the semi-conductor. Electrons that feel a concentration gradient near the interface, encouraging them to move from the interior of the semi-conductor to the surface, get "seized" by the electric field inside the semi-conductor and are accelerated further to the interface.

Holes, too, are subject to analogous events. They carry a positive charge and diffuse and act under potential gradients just as electrons do, except that they react in an opposite way to electric field because they have an opposite charge.
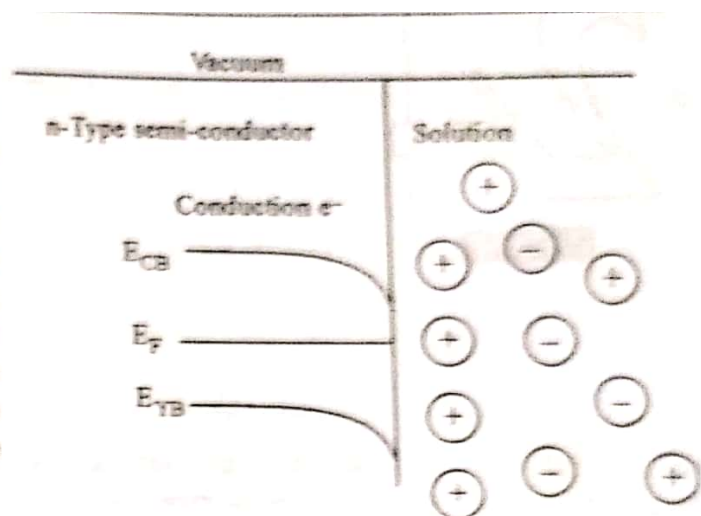

Fig. 8. An n-type semiconductor acts as a cathode in thermal reaction under dark conditions.