

# “ELECTROLYTE DIODE” ANALYSIS OF ISOTHERMAL TRANSPORT PROCESSES IN THE INTERFACES OF AQUEOUS SOLUTIONS OF ACIDS AND BASES. I

By

Z. NOSZTICZIUS and A. SCHUBERT

Department of Physical Chemistry, Technical University, Budapest

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## The basic idea of the “electrolyte diode”

A theoretically and perhaps also practically interesting example of transport processes in electrolyte solutions will be presented. Let us submerge two indifferent electrodes in a system of two vessels (*A* and *B*) connected by a capillary tube containing different electrolytes. The electric current flowing through the capillary tube is to be measured and calculated as a function of the voltage drop in the special case where vessels *A* and *B* contain dilute aqueous solutions of a strong univalent acid, and a strong univalent base, respectively. The voltage-to-current (in short:  $\Delta U-I$ ) characteristics of this system will show a diode character, that is, the current intensity will depend on the direction of the voltage. This can be explained qualitatively as follows:

*a)* A positive electrode in the basic solution and a negative one in the acidic solution produce an electric field that drives the cation of the base and the anion of the acid inwards the capillary tube, where a salt is formed (“forward direction”).

*b)* In the reverse case the  $H^+$  and the  $OH^-$  ions flow into the capillary tube and there they recombine, whereas the other ions leave the capillary. Hence in the capillary tube a region poor in ions, i.e. an insulating layer is formed, its great resistance causing intensive voltage drop (“backward direction”).

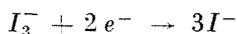
We named this acid-base electrolyte system “electrolyte diode”.

## Rectifier systems containing electrolytes

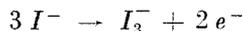
Some electrolyte systems of diode character are known from the literature, but the principles of their function are different. Let us survey them in short:

1. “Solion” — an electrochemical diode [1—3]. An electrode of larger

and another one of smaller surface are submerged in a solution of  $I_2/KI$ . The cathode and the anode will be affected by reactions



and



respectively. If the quantity of  $I_3^-$  ions is small as compared to that of the  $I^-$  ions, the electric current crossing the cell is the diffusional limiting current of the  $I_3^-$  ions, which is in turn proportional to the surface of the cathode. The current is more intensive if the cathode is the electrode of the larger surface ("forward direction") than in the reverse case.

2. "Ice diode" [4]. Crystals of ice doped with acids or bases ( $LiOH$ ,  $NH_3$ ) form systems, exhibiting proton-excess or proton-lack conduction, the counterions ( $F^-$  and  $Li^+$  or  $NH_4^+$ ) being almost motionless. These systems can be combined to a perfect analogon of the  $p-n$  semiconductor diodes where the proton assumes the role of electron.

3. Systems of diode character can be constructed using ion-exchange membranes [5—7]. The basic concept is to realize the analogon of the  $p-n$  semiconductor diode with a kind of acidic-basic interface, where the counterions are of very low — practically negligible — mobility. Separating e.g. the aqueous solutions of polyvinyl toluene sulfonic acid and polyvinyl trimethyl benzil ammonium hydroxid by some kind of membrane, in "forward direction" the  $H^+$  and  $OH^-$  ions are recombining, whereas in "backward direction" there is much less current since here the current is conducted by big counterions in the membrane. The same principle is underlaying the function of the contacting membranes exchanging anions and cations (here the counterions are really of zero mobility).

It can be concluded that "Solion" is the analogon by principle of the vacuum diode and has nothing in common with the "electrolyte diode". The "electrolyte diode", just as the "ice diode" and the "ion-exchange diode", is somehow related to the semiconductor diode. Notice, however, that while the  $p-n$  diode is based on the immobility of the soiling atoms, the "ice-diode" and the "ion-exchange diode" on that of the counterions, the "electrolyte diode" is based exactly on their mobility. Thus, it is an essentially different one.

### The fundamentals of the theory of transport processes

Transport processes in electrolyte solutions are dealt with in several theoretical and experimental studies. Relevant surveys including some experimental technical details are contained e.g. in [8] and [9]. The modern phenomenological theory is based on the non-equilibrium thermodynamics [10

through 12], and especially in the last two decades the transport processes in electrolyte solutions have often been discussed involving irreversible thermodynamics [13 through 20]. Based on these works, the theoretical relations essential for our present work can be summarized as follows: Let us consider an electrolyte solution of  $K + 1$  components, denoting by subscript 0 the neutral solvent and by subscripts 1, 2, . . .  $K$  the number  $K$  of ionic components. If  $R$  chemical reactions can take place, then the entropy production  $\sigma$  per unit volume and time is expressed as:

$$\sigma = \sum_{j=1}^R J_j A_j + \bar{J}_q \bar{X}_q + \sum_{k=0}^K \bar{J}_k \bar{X}_k, \quad (1)$$

omitting viscous phenomena [11]. Here  $A_j$  is the chemical affinity of the  $j$ -th reaction, that is the scalar thermodynamical force conjugated to the scalar chemical reaction rates  $J_j$ ,  $\bar{X}_q$  is the vectorial thermodynamical force conjugated to the heat flux vector  $\bar{J}_q$ , causing heat transfer effects:

$$\bar{X}_q = \bar{V} \left( \frac{1}{T} \right). \quad (2)$$

The diffusional forces

$$\bar{X}_k = \frac{\bar{F}_k}{T} - \bar{V} \left( \frac{\mu_k}{T} \right) \quad (3)$$

conjugated to the diffusional flux vectors  $\bar{J}_k$  include external forces  $\bar{F}_k$  affecting one mole of the  $k$ -th component. Here  $\mu_k$  is the chemical potential of the  $k$ -th component. Thus the entropy production can be considered as the sum of three source terms: the entropy source of  $R$  chemical reactions:

$$\sigma_c \equiv \sum_{j=1}^R J_j A_j, \quad (4)$$

the entropy production due to heat transfer:

$$\sigma_q \equiv \bar{J}_q \bar{X}_q \quad (5)$$

and to diffusion:

$$\sigma_d \equiv \sum_{k=0}^K \bar{J}_k \bar{X}_k. \quad (6)$$

Thus:

$$\sigma = \sigma_c + \sigma_q + \sigma_d. \quad (7)$$

The diffusional flux  $\bar{J}_k$  is defined by

$$\bar{J}_k = c_k (\bar{V}_k - \bar{V}), \quad (8)$$

where  $\vec{V}_k$  is the mean velocity of the  $k$ -th component in an arbitrary frame of reference, whereas  $\vec{V}$  is the velocity of the mass center in the same frame of reference.  $c_k$  is the mole number in unit volume of the  $k$ -th component i.e. the molar concentration:

$$c_k = \frac{\rho_k}{M_k}, \quad (9)$$

where  $M_k$  is the molar weight of the  $k$ -th component and  $\rho_k$  is its mass per volume. The local density  $\rho$  is

$$\rho = \sum_{k=0}^K \rho_k \quad (10)$$

and the velocity of the mass center  $\vec{V}$  is

$$\vec{V} = \frac{\sum_{k=0}^K \rho_k \vec{V}_k}{\rho}. \quad (11)$$

The fluxes  $\vec{J}_k$  are seen not to be independent:

$$\sum_{k=0}^K M_k \vec{J}_k = \sum_{k=0}^K \rho_k (\vec{V}_k - \vec{V}) = 0 \quad (12)$$

and using expression (12) as a local constraint any component — e.g. flux  $\vec{J}_0$  of the solvent — can be eliminated from the expression  $\sigma_d$ .

Thus, the diffusional entropy production, expressed by independent fluxes and forces:

$$\sigma_d = \sum_{k=1}^K \vec{J}_k \vec{X}'_k, \quad (13)$$

where

$$\vec{X}'_k = \vec{X}_k - \frac{M_k}{M_0} \vec{X}_0 \quad (14)$$

or, in particular:

$$\vec{X}'_k = \frac{\vec{F}_k - \frac{M_k}{M_0} \vec{F}_0}{T} - \vec{V} \left( \frac{\mu_k - \frac{M_k}{M_0} \mu_0}{T} \right). \quad (15)$$

Onsager's linear laws can be written for an isotropic system as:

$$J_j = \sum_{r=1}^R L_{jr} A_r, \quad (16)$$

$$\vec{J}_q = L_{qq} \vec{X}_q + \sum_{k=1}^K L_{qk} \vec{X}'_k, \quad (17)$$

$$\vec{J}_i = L_{iq}\vec{X}_q + \sum_{k=1}^K L_{ik}\vec{X}'_k, \quad (18)$$

since isotropic systems undergo Curie's principle: thermodynamical forces and fluxes of different tensorial orders do not interfere.

The general theory above is involved to illustrate the kind of neglections to be used in the followings.

1. The system is supposed to be isothermal.

2. All external forces  $\vec{F}_k$  but electrostatic forces will be ignored; also the always acting but negligible gravitational term is disregarded:

$$\vec{F}_k = z_k F \vec{E}, \quad (19)$$

where  $z_k$  is the valency of the  $k$ -th ionic component,  $F$  is the Faraday number,  $\vec{E}$  is the electric field strength.

$$\vec{F}_0 = 0 \quad (20)$$

as  $z_0 = 0$ .

3. Only dilute electrolyte solutions are considered, that is, the quantity of the solvent is greater by orders than that of the ionic components. Thereby two practically important neglections can be made:

3.1. The velocity of the mass center is approximately equal to the velocity of the solvent:

$$\vec{V} = \vec{V}_0, \quad (21)$$

while if the solvent is not streaming mechanically, then taking the vessel containing the electrolyte as frame of reference:

$$\vec{V}_0 = 0. \quad (22)$$

3.2. In case of isothermy, the second term of (15) becomes:

$$-\frac{1}{T} \left( \vec{v}\mu_k - \frac{M_k}{M_0} \vec{v}\mu_0 \right) \quad (23)$$

with assumption 3. In view of the usual expression for the chemical potential, it is evident that  $\vec{v}\mu_0 \ll \vec{v}\mu_k$ . Taking water as solvent, for most ions  $\frac{M_k}{M_0} < 10$ .

Thus, the neglection of the second term of (23) seems to be justified.

With the three neglections above, (18) and (15) simplify to:

$$\vec{J}_i = \sum_{k=1}^K L_i \vec{X}'_k \quad (24)$$

and

$$\vec{X}'_k = \frac{1}{T} [z_k F \vec{E} - \nabla \mu_k]. \quad (25)$$

4. Omit the cross effects:

$$\begin{aligned} L_{ik} &= 0 & \text{if } i \neq k, \\ L_{kk} &\neq 0. \end{aligned} \quad (26)$$

5. Approximate the usual expression of the chemical potential

$$\mu_k = \mu_k^* + RT \ln y_k c_k \quad (27)$$

by

$$\bar{V} \mu_k = \frac{RT}{c_k} V c_k \quad (28)$$

neglecting the expression  $\bar{V} \ln y_k$  with respect to  $\bar{V} \ln c_k$ .

6. Introduce notation

$$L_{kk} \frac{RT}{c_k} \equiv D_k. \quad (29)$$

As a first approximation  $D_k$  (diffusion coefficient of the  $k$ -th ionic component) can be considered as independent of the concentration.

Using all these approximations (24) and (25) yield the well-known equation [22]:

$$\bar{J}_k = D_k \frac{z_k F}{RT} \bar{E} c_k - D_k \bar{V} c_k. \quad (30)$$

(30) will be the starting point of our further investigations. It is to be stressed again that the importance of deducing (30) lies in making clear the applied neglects. Under different experimental conditions it is always expedient to verify the above neglects (isothermal, convection-free processes etc.).

### Stationary voltage-current characteristics of the electrolyte diode for great forward and backward voltages

Let us consider a capillary tube of length  $d$ , ends being submerged in compartments filled with aqueous solutions of  $KOH$  in the concentration  $c_0$  moles/l, and of  $HCl$  in the same concentration. The  $U-I$  characteristics can be deduced by starting from the local equations based on (30)

$$\begin{aligned} J_K &= -D_K \frac{\partial c_K}{\partial x} - \frac{D_K F}{RT} c_K \frac{\partial U}{\partial x}, \\ J_H &= -D_H \frac{\partial c_H}{\partial x} - \frac{D_H F}{RT} c_H \frac{\partial U}{\partial x}, \end{aligned} \quad (31)$$

$$J_{Cl} = -D_{Cl} \frac{\partial c_{Cl}}{\partial x} + \frac{D_{Cl}F}{RT} c_{Cl} \frac{\partial U}{\partial x},$$

$$J_{OH} = -D_{OH} \frac{\partial c_{OH}}{\partial x} + \frac{D_{OH}F}{RT} c_{OH} \frac{\partial U}{\partial x}.$$

For capillary tubes it is sufficient to consider only the component  $x$  of the vector equation (30). Within electrolyte solutions, electroneutrality can be supposed [21, 22]:

$$c_K + c_H = c_{Cl} + c_{OH}. \quad (32)$$

The equation of continuity

$$\frac{\partial c_k}{\partial t} + \text{div } \bar{J}_k = \sigma_k \quad (33)$$

can be made "one-dimensional":

$$\frac{\partial c_k}{\partial t} + \frac{\partial J_k}{\partial x} = \sigma_k. \quad (34)$$

In stationary state

$$\frac{\partial c_k}{\partial t} = 0. \quad (35)$$

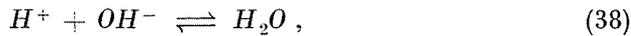
The ions  $K^+$  and  $Cl^-$  have no source

$$\sigma_K = \sigma_{Cl} = 0 \quad (36)$$

hence

$$\frac{dJ_K}{dx} = \frac{dJ_{Cl}}{dx} = 0 \quad (37)$$

i.e.  $J_K$  and  $J_{Cl}$  are place-independent constants. According to the reaction



$$\sigma_H = \sigma_{OH}, \quad (39)$$

thus

$$\frac{dJ_H}{dx} = \frac{dJ_{OH}}{dx}. \quad (40)$$

Furthermore the equilibrium concentration of  $H^+$  and  $OH^-$  can be supposed at every point:

$$c_H \cdot c_{OH} = K_w \quad (41)$$

where  $K_w = 10^{-14} \left( \frac{\text{mole}}{l} \right)^2$  at 25°C. The equilibrium is set in very quickly; the rate constant of the recombination reaction (38) is  $k = 1.3 \cdot 10^{11} l \cdot \text{moles}^{-1} \text{s}^{-1}$  at 25°C [6].

### Characteristics of forward direction

Let us assume co-ordinate system according to Fig. 1. A stationary state can come about only for unchanged concentrations at the ends of the capillary tube. Experimentally this is possible by choosing the volume of the compartments much greater than that of the capillary tube, and continuously stirring. It is difficult to solve the inhomogeneous partial differential equation system

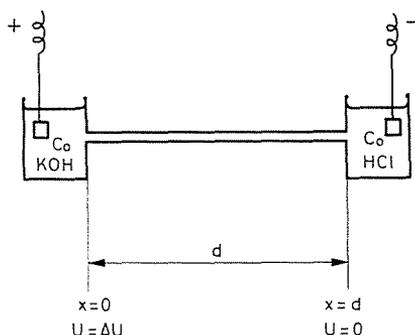


Fig. 1

of first order (31) through (41) for a general case. But if the voltage of forward direction is higher, respective approximations

$$|J_H| \ll |J_k|, \quad |J_{OH}| \ll |J_{Cl}| \quad (42)$$

are permitted since the electric field strength favors the fluxes of  $K^+$  and  $Cl^-$ , and hinders the fluxes of  $H^+$  and  $OH^-$ .

1.1. Using (31) the following sum can be formed:

$$\frac{J_k}{D_k} + \frac{J_H}{D_H} + \frac{J_{Cl}}{D_{Cl}} + \frac{J_{OH}}{D_{OH}} = -\frac{dc_k}{dx} - \frac{dc_H}{dx} - \frac{dc_{Cl}}{dx} - \frac{dc_{OH}}{dx}. \quad (43)$$

Considering (32) and (42):

$$\frac{J_K}{D_K} + \frac{J_{Cl}}{D_{Cl}} = -2 \frac{d(c_K + c_H)}{dx}. \quad (44)$$

Based on (37), however:

$$\frac{d(c_K + c_H)}{dx} = \text{const} = \frac{\Delta(c_K + c_H)}{\Delta x} \quad (45)$$

If  $x = d$ , then  $\Delta(c_K + c_H) \approx c_{HCl} - c_{KOH}$ , since

$$\begin{aligned} \text{for } x = 0 \quad c_K + c_H &= c_{KOH} + \frac{K_w}{c_{KOH}} \approx c_{KOH} \\ \text{for } x = d \quad c_K + c_H &= c_{HCl} \end{aligned}$$

In our case  $c_{HCl} = c_{KOH} = c_0$ , thus

$$\frac{\Delta(c_K + c_H)}{\Delta x} = \frac{d(c_K + c_H)}{dx} = 0; \quad \frac{J_K}{D_K} + \frac{J_{Cl}}{D_{Cl}} = 0 \quad (46)$$

furthermore

$$c_K + c_H = c_0 \quad (47)$$

i.e. the sum of the concentrations of  $K^+$  and  $H^+$  is a place-independent constant  $c_0$ .

1.2. Now, based on (31), let the following sum be formed

$$\frac{J_K}{D_K} + \frac{J_H}{D_H} - \frac{J_{Cl}}{D_{Cl}} - \frac{J_{OH}}{D_{OH}} = -\frac{2F}{RT}(c_K + c_H) \frac{dU}{dx}; \quad (48)$$

with the aid of (42) and (47)

$$\frac{J_K}{D_K} - \frac{J_{Cl}}{D_{Cl}} = -\frac{2F}{RT} c_0 \frac{dU}{dx} \quad (49)$$

This differential equation can be integrated taking into account the boundary conditions

$$\frac{J_K}{D_K} - \frac{J_{Cl}}{D_{Cl}} = \frac{2F}{RT} c_0 \frac{\Delta U}{d} \quad (50)$$

1.3. The electric current density

$$i = F(J_K + J_H - J_{Cl} - J_{OH}) \quad (51)$$

with (42) simplifies into the form:

$$i = F(J_K - J_{Cl}) \quad (52)$$

Finally, based on (46) and (52), the equation of the characteristics in the forward direction is:

$$i = \frac{F^2}{RT} \frac{(D_K + D_{Cl}) c_0}{d} \Delta U \quad (53)$$

i.e. the capillary tube behaves as if it would be filled with *KCl* solution of  $c_0$  concentration.

### Characteristics of backward direction

In case of great backward voltage, by analogy to (42) it can be supposed that

$$|J_H| \gg |J_K| \quad \text{and} \quad |J_{OH}| \gg |J_{Cl}|. \quad (54)$$

The system of equations (31) through (41), using (54), can be solved exactly. Now, a simplified deduction will be presented which is an excellent practical approximation. Let us consider Fig. 2.

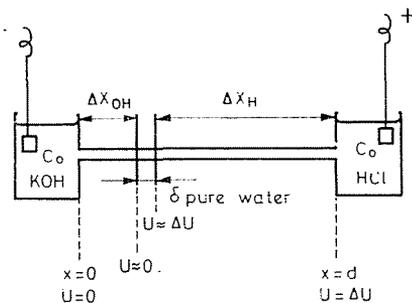


Fig. 2

For great backward voltages the capillary tube can be divided to three sections, an alkalic one of length  $\Delta X_{OH}$  an acidic one of length  $\Delta X_H$  and a pure aqueous one of length  $\delta$  between them. Recombination (38) occurs only on the interfaces, elsewhere  $\sigma_H = \sigma_{OH} = 0$ . Hence, within each of the sections,  $J_{OH}$  and  $J_H$  are place-independent constants.

2.1. In the alkalic section

$$\frac{J_{OH}}{D_{OH}} + \frac{J_K}{D_K} = -\frac{dc_{OH}}{dx} - \frac{dc_K}{dx}. \quad (55)$$

Supposing  $c_{Cl} \approx 0$  the electroneutrality can be expressed as

$$c_{OH} = c_K + c_H = c_K + \frac{K_w}{c_{OH}} \quad (56)$$

$$c_{OH} \approx c_K.$$

With the aid of (54) and (56), Eq. (55) simplifies to

$$\frac{J_{OH}}{D_{OH}} = -2 \frac{dc_{OH}}{dx} = \text{const} = -2 \frac{\Delta c_{OH}}{\Delta x} \quad (57)$$

$J_{OH}$  being a place-independent constant in the alkalic section. The electric current density in the alkalic section (taking (54) and (56) into account):

$$i = F(-J_{OH}), \quad (58)$$

thus (57) becomes

$$\frac{2FD_{OH}}{i} = \frac{\Delta c_{OH}}{\Delta x}. \quad (59)$$

In our case  $\Delta c_{OH} = -c_0$  and  $\Delta x = \Delta x_{OH}$

$$\frac{i}{2FD_{OH}} = -\frac{c_0}{\Delta x_{OH}} \quad (60)$$

2.2. For the acidic section, by analogy to the former deduction:

$$\frac{i}{2FD_H} = -\frac{c_0}{\Delta x_H}. \quad (61)$$

2.3. From (60) and (61)  $\Delta x_H$  and  $\Delta x_{OH}$  can be expressed. The two lengths add to  $d - \delta$ :

$$\Delta x_H + \Delta x_{OH} = -\frac{2F}{i}(D_{OH} + D_H)c_0 = d - \delta \quad (62)$$

or

$$-i = \frac{2F}{d - \delta}(D_H + D_{OH})c_0. \quad (63)$$

2.4. In the pure aqueous section the  $OH^-$  and  $H^+$  ions conduct electricity. Since in this section their concentration gradient is zero, therefore

$$J_H = -D_H c_H \frac{dU}{dx} \frac{F}{RT} \quad (64)$$

$$J_{OH} = D_{OH} c_{OH} \frac{dU}{dx} \frac{F}{RT} \quad (65)$$

$$c_H = c_{OH} = \sqrt{K_w} \quad (66)$$

$$i = F(J_H - J_{OH}). \quad (67)$$

From (64) through (67)

$$-i = \frac{F^2}{RT} \sqrt{K_w} \frac{dU}{dx} (D_H + D_{OH}). \quad (68)$$

i.e.  $\frac{dU}{dx}$  is constant within the pure aqueous section:  $\frac{dU}{dx} = \frac{\Delta U_\delta}{\delta}$ , where  $\Delta U_\delta$  is the voltage drop in the pure aqueous section. Since most of the voltage drop belongs here, as a first approximation:

$$\Delta U_\delta = \Delta U \quad (69)$$

thus, the electric current density:

$$-i = \frac{F}{RT} \sqrt{K_w} \frac{\Delta U}{\delta} (D_H + D_{OH}). \quad (70)$$

Finally, comparing (63) with (70)  $\delta$  can be eliminated to obtain the characteristics of backward direction:

$$-i = \frac{F}{d} (D_H + D_{OH}) \left[ 2c_0 + \frac{F}{RT} \sqrt{K_w} \Delta U \right]. \quad (71)$$

The negative sign of the current density refers to a current opposite in direction to the positive  $x$  axis.

### Summary

The rectifying properties of an electrolyte system consisting of a strong acidic and a strong basic compartment separated by a membrane are discussed. The  $U-I$  plot of such an "electrolyte diode" is deduced. A survey of other types of rectifying systems containing electrolytes is given.

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Dr. Zoltán NOSZTICZIUS }  
András SCHUBERT } 1502 Budapest P. O. B. 91. Hungary