J. Membrane Biol. 12, 349—360 (1973)

Precipitation Membranes

I. The "Conditioned" State

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Received 29 September 1972

Summary. Membranes which are generated from two ions of opposite charges by diffusion-controlled precipitation and which can act as selective ion barriers, are called "Precipitation Membranes." The "conditioned state" of the membrane is responsible for the barrier effect. A prerequisite for the existence of this state is that certain minimum concentrations of the two ions, from which the precipitate is formed, be present in the adjoining solutions.

The ion barrier is an electrical barrier formed by a positive and a negative equipotential plane within the membrane which are caused by adsorbed surplus ions on two precipitate layers.

Conditioning experiments are carried out with $BaSO_4$-cellophane membranes, the system studied particularly in this and the preceding papers. By studying the time evolution of the membrane potential, one gains insight into the process of "conditioning." A rather sudden rise of the curve indicates the spontaneous creation of the ion barrier. Obviously, this event is a cooperative phenomenon of a statistical character. The counter diffusion of the two reagents involved plays an essential role.

We shall, in this and subsequent papers, use the term "Precipitation Membranes"[1] in the following sense: They are membranes, generated from two ions of opposite sign by diffusion-controlled precipitation which can act as ion selective barriers when they are in the "conditioned state." The term "conditioned state" implies that they exhibit the characteristic properties as described for the $BaSO_4$-cellophane membrane [1–6]; i.e., impermeability to the ions from which the precipitate is formed (in the example Ba^{++} and SO_4^{--}), the characteristic membrane potentials and their capacity to act as electrical rectifiers.

There are situations under which the membrane loses these properties and becomes "deconditioned." Restoration of the initial situation brings

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[1] This term (in German "Fällungsmembranen"), I think, will express somewhat better the character of these membranes than the formerly used expression "precipitate membranes" ("Niederschlagsmembranen").

about "reconditioning" of the membrane. The nature of the conditioning is to be studied in this paper.

The conditioned state of the membrane depends upon the presence of the generating ions in the adjoining solutions, e.g., of Ba ions on one side of the membrane and of SO_4 ions on the other in the case of the $BaSO_4$ membrane [3, pp. 388–389]. This is, however, not just a question of the saturation of the solutions with $BaSO_4$. The conditioning of $BaSO_4$ membranes is lost, if they are brought between pure suspensions of freshly precipitated $BaSO_4$.

According to the theory on the functioning of the $BaSO_4$ membrane proposed by the author [5, p. 389], the precipitate in the conditioned membrane carries absorbed Ba^{++} ions on one side and adsorbed SO_4^{--} ions on the other. Thereby a double layer of positive and negative charges is formed. In other precipitation membranes, of course, other ions take the place of Ba^{++} and SO_4^{--}.

For effective conditioning a certain minimum density of adsorbed ions is required. The density of the adsorption depends on the concentrations of the ions in the adjoining solutions, according to their specific "adsorption isotherm." Diminishing their concentrations will cause desorption and, eventually, deconditioning[2].

There is a basic difference between a conditioned precipitation membrane and the well-known ion-exchange membranes. In the latter, the ionic charges are those of dissociating groups bound to the membrane matrix by main valencies. They are distributed homogeneously in the membrane phase. On the other hand, the charges in the precipitation membrane are those of ions adsorbed at the surface of the precipitate particles from which they can easily and reversibly be desorbed. Besides, they are localized in very thin, continuous layers parallel to the membrane surface[3]. These layers form a barrier which is selectively permeable to different kinds of ions. With deconditioning the barrier becomes ineffective.

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[2] A closer investigation into this "adsorption theory" of the conditioning is in progress.

[3] There are various experimental evidences to show that the $BaSO_4$ membrane is inhomogeneous across its width (that is to say in the direction of the diffusion). Counter diffusion of $Ba(OH)_2$ and H_2SO_4 along thin plates (3 to 4 cm long) of agar gels (enclosed in a correspondingly narrow vessel of thin glass) lead to the formation of easily visible zones or bands of the precipitate which are somewhat comparable to the Liesegang phenomenon (unpublished experiments carried out in Prof. A. Katchalsky's laboratory in the Weizmann Institute, in collaboration with J. Block). Analogous observations with the same reagent in cellophane strips have also been made (E. P. Honig and J. H. Th. Hengst in Philips' Research Laboratories, Eindhoven).

Finally, more precise experiments along these lines, by means of "diffusion channels" devised by the author, were carried out [7]. These go to show very clearly that the barrier effect is localized at definite planes within the precipitate bands [7, p. 1239].

Principles Involved in the Formation of the Barrier

It follows from what has been said above that a necessary condition for the existence of the barrier in the $BaSO_4$ membrane is that the concentrations of Ba^{++} and of SO_4^{--}, respectively, must be above a certain minimum level. In the first place, the solutions on both sides have to be saturated with $BaSO_4$. Among the values of $\{Ba^{++}\}$ and $\{SO_4^{--}\}$ consistent with this requirement, there is a unique pair of values, $\{Ba^{++}\}^0$ and $\{SO_4^{--}\}^0$, for which no surplus of either of the two kinds of ions is adsorbed on the surface of an immersed $BaSO_4$ particle. Thus it remains uncharged. This case is called the "zero point of charge." Obviously, it is unsuitable for the conditioning. This illustrates the point that saturation with $BaSO_4$ alone is not sufficient. To get surplus Ba^{++} and SO_4^{--} ions, on the respective sides onto the surface of $BaSO_4$ particles, one must have $\{Ba^{++}\} > \{Ba^{++}\}^0$ and $\{SO_4^{--}\} > \{SO_4^{--}\}^0$. Under equilibrium conditions, however, both these inequalities can be fulfilled only in two separated phases.

As long as there is no barrier, the carrier membrane forms a continuous diffusion space: $\{Ba^{++}\}$ as well as $\{SO_4^{--}\}$ differ from point to point across the membrane; diffusion and precipitation go on.

Once the barrier is formed, it divides the carrier membrane into two subspaces. Diffusion of $Ba(OH)_2$ and of H_2SO_4 between the two subspaces is then no longer possible and precipitations cease. Within each subspace, the concentrations tend to become uniform but vary from one subspace to the other. Thus, the concentration profiles become discontinuous at the interfaces. Then the requirement for the conditioning, as postulated above, can be fulfilled.

One then faces the following dilemma: The barrier can exist only if it is in direct contact with sufficiently high concentrations of Ba^{++} on one side and SO_4^{--} on the other. On the other hand, the required discontinuous concentration profiles can only be built up and remain stable when the barrier is present. The solution of this dilemma is that both the barrier and the discontinuous concentration profiles come simultaneously into existence. The barrier is not built up gradually, through equilibrium states.

We assume that for the conditioning of our $BaSO_4$ membranes the following conditions have to be met at the same time:

(1) A zone of supersaturations with gradients of $\{Ba^{++}\}$ and $\{SO_4^{--}\}$ in opposite directions is built up by counter diffusion. Supersaturations thereby increase until eventually nucleations and precipitations set in.

(2) Nucleations and precipitations have to take place at such a time and in such a manner that a dense layer of small crystallites, with only very small

interstices between them, is formed rapidly[4]. This layer has to extend within the carrier membrane without a break over its whole area.

(3) When precipitation occurs eventually, sufficient concentrations of Ba^{++} and SO_4^{--} must be left over (on the respective sides) so that conditioning occurs at the same time as well.

These observations suggest that the conditioning might be caused by a cooperative phenomenon. If these conditions adjust themselves simultaneously, conditioning occurs; the barrier and the concentration profiles belonging to it are generated at the same time.

To realize the requirements stated above, we need the following: (a) the medium must allow the necessary supersaturations; (b) the precipitate must remain where it is formed; (c) points (1) and (3) presuppose the existence of counter diffusion.

It is evident that in the present context counter diffusion and diffusion-controlled precipitation are very important. They provide the only mechanisms which render possible the kind of concentration profiles and precipitations postulated above. Hitherto, precipitation membranes with the properties mentioned in the beginning have exclusively been formed in this way. This is the reason why we found it justified to include diffusion-controlled precipitation in their definition.

To study the minimum concentrations necessary for the conditioned state, we carried out two kinds of experiments, again using $BaSO_4$ membranes. At first, in "conditioning experiments," we follow the development of conditioning starting from fresh cellophane sheets and using successively diminishing concentrations of $Ba(OH)_2$ and H_2SO_4. Thereafter, "deconditioning experiments" are described in which at a membrane, conditioned before, the concentrations of the two reagents are successively diminished until deconditioning occurs.

Experiments on the Conditioning of $BaSO_4$ Membranes

In our earlier investigations 0.05 N or 0.1 N solutions of the reagents were used to make $BaSO_4$ membranes from fresh samples of cellophane. We now apply smaller concentrations and also different samples of cellophane and follow the development of the membrane potentials. The experiments are performed in double-cell apparatus of the kind sketched in Fig. 1.

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[4] Even two such layers have to be formed at the same time, as we shall see later.

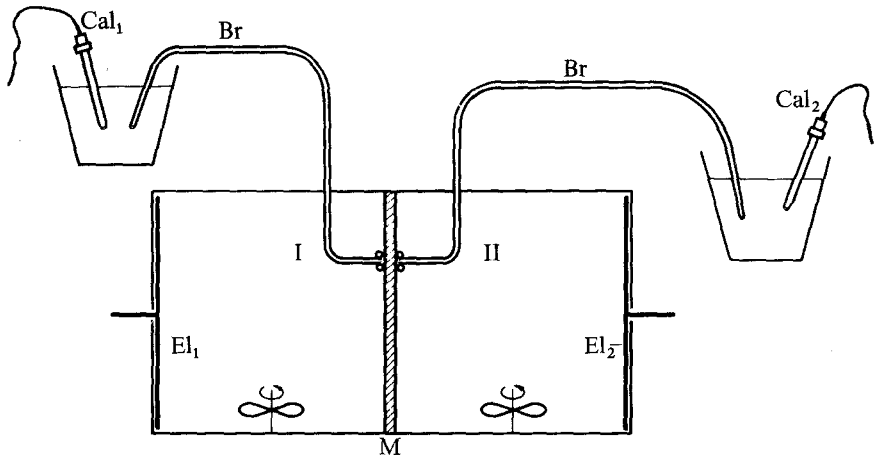

Fig. 1. Two-compartment apparatus used in the measurements of potentials and current densities. M is the membrane; Br: the contact bridges filled with KCl-agar; Cal$_1$ and Cal$_2$: two saturated calomel electrodes; El$_1$ and El$_2$: two big electrodes (Pt or Ti) for connection with an external voltage supply (in current-voltage studies)

Table 1. Samples of cellophanes used to observe the development of membrane potentials

Sample	Thickness[a]	Origin	Specifications
A	0.1	Kalle A. G., Wiesbaden	ϕ 140 mm } commercial
B	0.08	Kalle A. G., Wiesbaden	ϕ 140 mm } quality
C	0.08	Serva, Heidelberg	Dialysis tubing
D	0.025	Kalle A. G., Wiesbaden	"Pt 300/1"
O	0.08	Kalle A. G., Wiesbaden	Used in the beginning (about same quality as B)

[a] In the original, dry state.

Different Cellophane Samples. The development of the membrane potentials with 0.01 N solutions was observed in the samples of cellophane shown in Table 1.

The membrane potential versus time curves ($\Delta \psi_0$, t-curves) of materials A and B were similar to those of O in Fig. 2.

Since, in these orienting experiments, we did not bother to obtain the accurate end-values of the potential, the solutions were not renewed here.

The curves for individual membranes from the same material vary somewhat; bigger differences appear between membranes from different cellophanes. With the thin material D the increase in membrane potential is

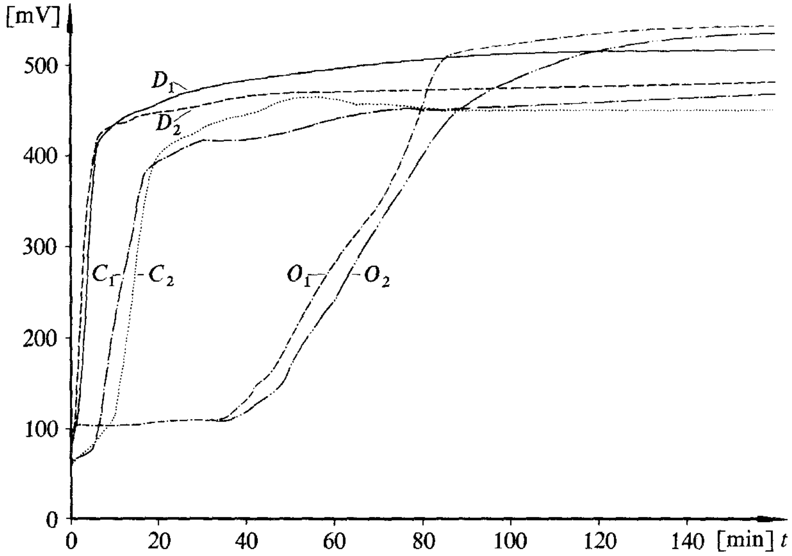

Fig. 2. Development of the membrane potential $\Delta\psi$ with time in different sorts of cellophane

especially quick. In the curves for C the increase is steeper than in those for B and O of the same thickness. The thickness is apparently not the only property of cellophane which influences the rate of the conditioning.

Diminishing of the Concentrations. Experiments with concentrations from 0.002 N to 0.0005 N, equal on both sides of the membrane, and one sort of cellophane "O" are given in Fig. 3.

In the experiments down to the concentration 0.001 N, a steep rise in the $\Delta\psi_0$, t-curves appeared; the more dilute the solutions were, the later the steep rise occurred. With 0.005 N solutions, the course of the conditioning was rather irregular and lingering. Four parallel experiments with 0.001 N solutions at cellophane "D" are reported in Table 2, also showing appreciable variations in the course of conditioning which finally was reached by all four membranes.

The lower the concentrations of the reagents, the more time it takes until the membranes are conditioned and the longer permeation and consumption of the reagents can take place, diminishing their concentrations. With concentrations below 0.001 N the solutions had to be renewed frequently.

If at the start of the experiment the concentrations would have the hypothetical limiting value, they would immediately fall below it and conditioning would not occur. Continuous renewel of the liquids in an experiment with continuous flowing through should bring an improvement in this respect.

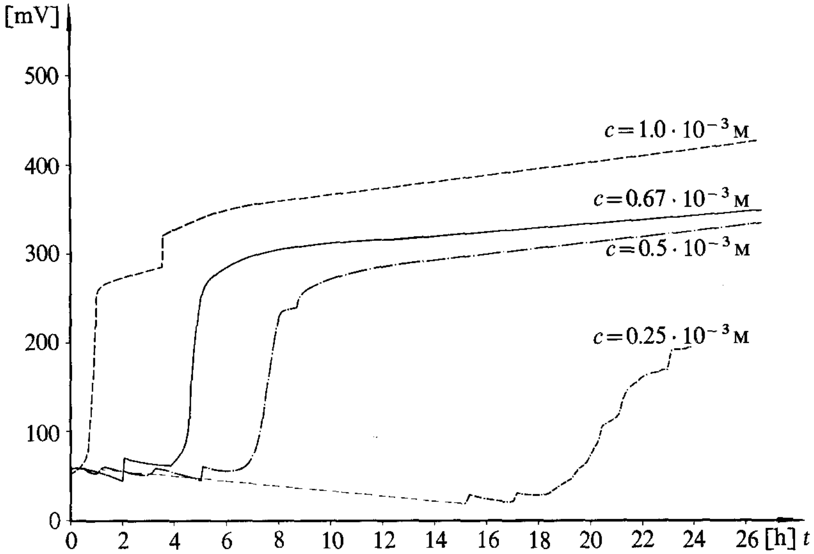

Fig. 3. Development of the membrane potential with different concentrations of $Ba(OH)_2$ and H_2SO_4 in the same cellophane sort "O". c: concentrations of both reagents; the time t is in hours. During these experiments the concentrations of the reagents decrease. To restore their original strength, the solutions were renewed repeatedly. A break in the curve each time shows when this occurred

Table 2. Four parallel experiments with 0.001 N solutions at cellophane sample D[a]

Membrane potential	I	II	III	IV	Unit
$\Delta\psi_0$, 1 hr after start of experiment	60	72	74	64	mV
100 mV or more were reached after:	3	6	7	24	hr
280 mV or more were reached after:	5	24	26	26	hr
$\Delta\psi_0$ after 50 hr	360	365	328	355	mV

[a] The solutions were renewed five times during the first 27 hr.

We do not know, however, how far the theoretical limit could be approximated in this way. Possibly permeation and precipitation then would continue until the membrane would be clogged mechanically. However, this is not of interest here.

Solutions of 0.00033 N still produced elevations of $\Delta\psi_0$ to about 200 mV; Solutions of 0.00025 N did not within 48 hr. So it may be said that under the circumstances of these experiments the minimum concentrations needed to produce a conditioned $BaSO_4$ membrane are approximately 1.5×10^{-4} M.

Discussion

The membrane potential versus time curves reflect a sequence of events leading to the formation of a conditioned membrane. The curves clearly show different sections, corresponding to different stages in the development.

In the initial *stage a* the curves run, on the whole, almost horizontally, with fluctuations of $\Delta\psi_0$ on a limited scale, mostly between 60 and 100 mV, positive on the Ba side. At the start of an experiment, the two reagents enter the cellophane and begin to diffuse towards each other. The reagents meet within the cellophane in a matter of seconds[5]. During the short period of pure diffusion, diffusion potentials must develop. All our measurements, however, were done when the reagents had already met. When they meet, H^+ and OH^- at once react to form water. Ba^{++} and SO_4^{--} accumulate until the point is reached where nucleation and precipitations come into play. These processes will perpetually alter the diffusion pattern and cause limited fluctuations in the diffusion potentials.

The potentials in *stage a* may be compared with earlier, direct measurements of liquid junction potentials (L.J.P.'s) carried out by the author in another context [1, p. 1067], in analogous systems such as $NaOH \| H_2SO_4$ and $Ba(OH)_2 \| HCl$, in addition to $Ba(OH)_2 \| H_2SO_4$, at 18 °C with 0.1 N solutions. In the junctions without precipitation, these L.J.P.'s were approximately 60 mV. In the system $Ba(OH)_2 \| H_2SO_4$, where $BaSO_4$ is precipitated at the junction, the value found was 115 mV. The potentials in *stage a* fluctuate just between these two values.

It is to be noted that the potentials in *stage a* appear to be remarkably insensitive to changes in the concentration, especially below the normality 0.01 N. It can be shown that this behavior, at least for equal concentrations of $Ba(OH)_2$ and H_2SO_4, is in accord with theory, applying some idealizations.

We apply the known equation of Henderson for diffusion potentials between solutions of two different electrolytes. We further assume that the solutions exhibit ideal behavior, that H_2SO_4 dissociates completely and that the mobilities of all ions are constant and differ from those in water all by the same factor. It then follows that $\Delta\psi_0$ is independent of the concentrations. In this part of the curve, $\Delta\psi_0$ thus in various respects behaves as diffusion potentials do. Conditioning has not yet occurred.

The system, meanwhile, is changing towards a state in which the conditioning becomes more and more probable until finally a combination of

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[5] According to estimation from Fick's second law using a model of diffusion into a plane sheet.

conditions as enumerated on pp. 351 – 352 is realized. At this point a precipitation occurs spontaneously and forms a barrier. A spontaneous steep rise of $\Delta \psi_0$ to appreciably higher values indicates a basic change in the permeability of the membrane to ions; it marks the end of *stage a* and the beginning of *stage b*. In the above experiments the duration of *a* varies approximately from 1 min to 2 days.

Let us consider Taylor's equation for membrane potentials:

$$\Delta \psi = -RT \frac{1}{F} \sum \frac{t_i}{z_i} \Delta \mu_i, \qquad \text{for the case } I = 0.$$

In the beginning of the experiments and in *stage a* the transference numbers t_i are not very different from those in water; the equation then gives the liquid junction potentials.

After complete conditioning, when perfect semipermeability is established the t's have the following values:

$$\text{on the Ba side (I): } t_{BA^{++}} = 0; \; t_{OH^-} = 1;$$

$$\text{on the } SO_4 \text{ side (II): } t_{SO_4^{--}} = 0; \; t_{H^+} = 1.$$

(H^+ and OH^- enter the membrane from the respective sides and react to form water.) The equation then gives:

$$\Delta \psi = -RT \frac{1}{F} (1 \Delta \mu_{H^+} - 1 \Delta \mu_{OH^-}) = 58 \text{ mV} (\text{pH}^{\text{I}} - \text{pH}^{\text{II}}).$$

This limiting value of $\Delta \psi$ is reached, in quite successful experiments, at the end. But when the conditioning occurs, the semipermeability is not at once ideal; there are still leaks and faults which have to be corrected. This is what takes place in *stage b*, while $\Delta \psi$ goes through the intermediate potential values. The rate at which this takes place determines the steepness of the curve there.

The shape of the curve depends also on the sort of cellophane used because the diffusion processes involved in the conditioning depend, in part, also on the properties of the carrier membrane.

The question arises, what will be the rate-determining step of the process and can we get information about its kinetics from the shape of the curve? It might be the nucleations and precipitations or the adsorption of the ions charging the barrier. Moreover, the steepness of the curve suggests that still other things may play a role: the highly discontinuous concentration and potential gradients suddenly formed at the barrier will presumably cause local flows of electricity and solution through the leaks. Such streaming motions can bring new building material to the spot and thereby greatly accelerate the closure of the leaks. (If they are too strong, they may also disturb the closing of the leaks and eventually bring about a breakdown of the barrier; *see* pp. 359 – 360.) All this makes it very difficult to analyze the kinetics of the process. Obviously, we are dealing with a cooperative phenomenon of a statistical character.

Stage c. The leaks are mended, strong streaming motions cease; the remaining imperfections are now corrected by slower processes. The curve now rises slowly to approach asymptotically a constant end value.

The "aging" of the membrane, a further phase, *stage d,* does not appear in the data presented in this paper. During longer periods of time, slow changes take place within the membrane by which it becomes, to a certain degree, less pervious. The precipitate layers presumably become more dense and, perhaps, the conditioning more perfect.

If the formation of $BaSO_4$ membranes takes place under different circumstances, as was the case with the experiments in the diffusion cells mentioned (*see* footnote 3), which allow to follow visually the forming of the precipitates, the course of events is in principle the same as for cellophane, but quantitatively different. The experiments in the diffusion channels are particularly instructive insofar as they demonstrate in a clear and nice fashion that the conditioning of the membrane is a cooperative phenomenon of a statistical character.

With an agar gel of 1.5% as carrier membrane and a total diffusion path of 4 cm, the generation of a barrier is obviously rendered more difficult than with swollen cellophane of 0.05 or 0.2 mm thickness. The membrane potentials remain below the theoretical value (by about 10 to 20%), the conditioning is remarkably less perfect than in cellophane. In the diffusion channel, the chance for the requirements stated on pp. 351 – 352 to adjust themselves simultaneously appears to be appreciably smaller, and the time it takes to get conditioning is much longer. This time also varies considerably, as shown in Fig. 4. Here, too, the curve rises very steeply in *stage b.*

An observation which stresses the importance of supersaturation in the process of conditioning is the following. If the agar gel contained a suspension of a finely divided $BaSO_4$ precipitate, the conditioning was very much retarded: the crystals of $BaSO_4$ present in the agar are crystallization points and render more difficult the development of $BaSO_4$ supersaturation.

In the diffusion channel experiments, the first precipitations are observed at the place where the two reagents, $Ba(OH)_2$ and H_2SO_4, first meet, according to their diffusion velocities. Relatively big crystals, but no barrier, form there. Diffusions go on and, after a time, further precipitation occurs in a restricted zone, more to the right or more to the left, forming a band of

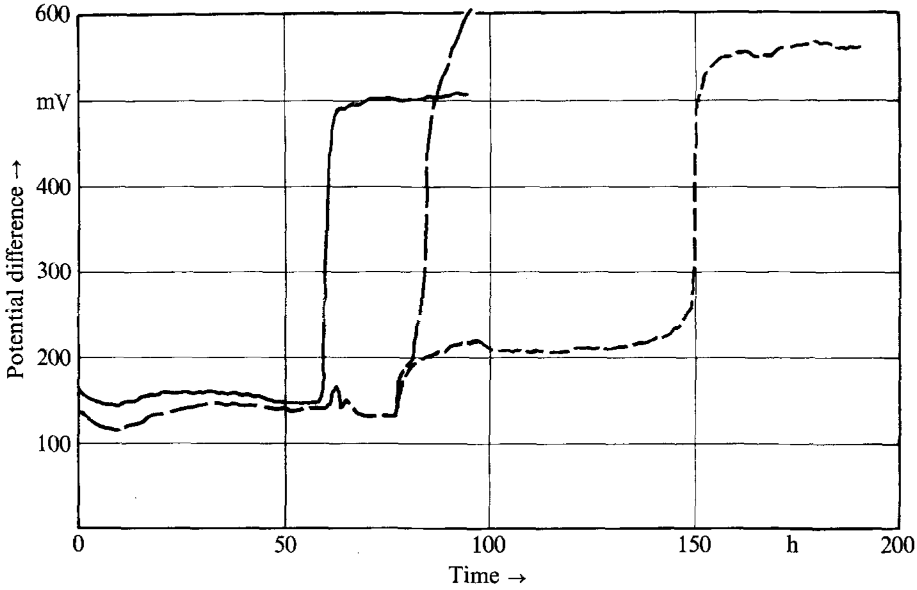

Fig. 4. Development of the membrane potential with time (in hours) in agar gel. Three parallel experiments with 0.05 N solutions of $Ba(OH)_2$ and H_2SO_4 in "diffusion channels" filled with 1.5% agar gel. Total diffusion path: 40 mm

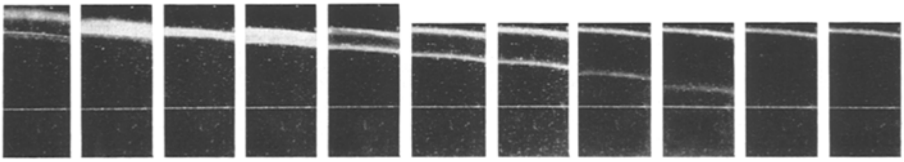

Fig. 5. Photographs taken in 5-min intervals during the development of a $BaSO_4$ membrane in 1.5% agar gel in a "diffusion channel" from 0.1 N $Ba(OH)_2$ (top) and 0.6 N H_2SO_4 (bottom), showing progressive displacement of a precipitation band. (The thin white line right of the center was a calibration mark.) One precipitation band, to the left, was already formed in the first photo. It remained in its place. A second slight band appears in the third photo which, in the following shots, becomes more dense and shifts more and more to the left, at last even passing through the first band. This displacement comes about by progressive redissolving and reprecipitation of $BaSO_4$

precipitate, more or less dense. If this precipitate is very dense, it may contain a barrier. If this is the case, diffusions and precipitations stop and the potential rises; if not, the diffusion goes on. If the precipitation band consisted of very small crystallites, it may be partly or even completely redissolved. Diffusions continue and, after a time, a new precipitation band appears at another place. The system makes another attempt to form a barrier. This process may be repeated a number of times, until finally an effective barrier has come about. It occurs that the beginning of a barrier is indicated by a rise in the potential, but is broken off again, presumably by the local streaming motions referred to earlier. The formation of the barrier is not a continuous process but it is governed by probabilistic laws (*see* Fig. 5).

With regard to the limiting concentrations for the existence of the conditioned state, it appeared that "deconditioning experiments" give more information than the conditioning experiments of the kind described here. In the next paper we will therefore pass over to the deconditioning experiments.

The author wishes to express his gratitude to the Max-Planck-Gesellschaft and to Prof. R. Schlögl for giving him the possibility to perform this investigation. He is especially grateful to Prof. Schlögl for many useful discussions on the subject.

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