

STUDIES ON THE DIFFUSION EFFECT UPON IONIC DISTRIBUTION

II. EXPERIMENTS ON IONIC ACCUMULATION

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The present report furnishes experimental confirmation of the first paper of this series (1), which gave a theory for the ionic distribution in the steady state of a system of a type that may well occur in biology (*cf.* Fig. 1).

Review of the Theory

The system considered and the theoretical results are recapitulated as follows:

Across a permeable boundary m there was supposed to be present a constant difference in concentration of either the cation D^+ or the anion A^- . The maintenance of this condition, accomplished, for example, by a continuous addition of the substance DA to the rather small volume (i), causes DA to act as a "diffusion agent" which steadily diffuses across m into the part (o). In (o) a fixed, constant composition was maintained by keeping the volume large.

It was predicted that the continuous steady diffusion of DA was bound to influence the distribution of other electrolytes present, denoted by $M'B'$; $M''B''$ etc., which were not participating in any active diffusion as was DA . These ions were called "passive ions." If, for example, the initial composition was the one graphically shown in Fig. 2 *a*, the ultimate effect of the steady diffusion of DA would consist in an accumulation of M^+ ions and an impoverishment of B^- ions on the inside, as pictured in Fig. 2 *b*. It was supposed that the D^+ ions had a higher mobility than the A^- ions.

* The experiments were carried out when the author held a Rockefeller Foundation Fellowship.

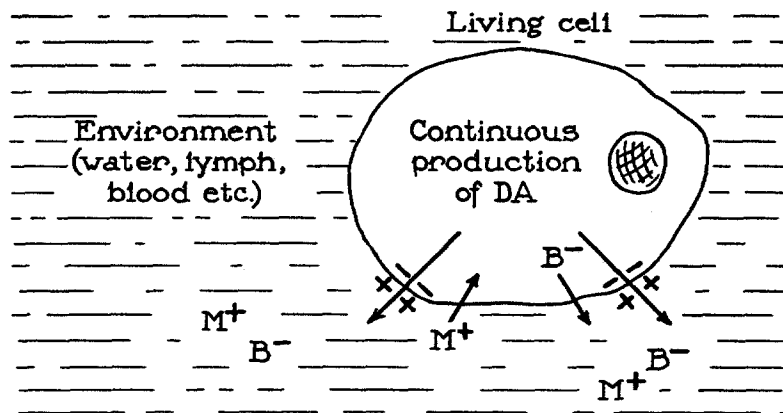
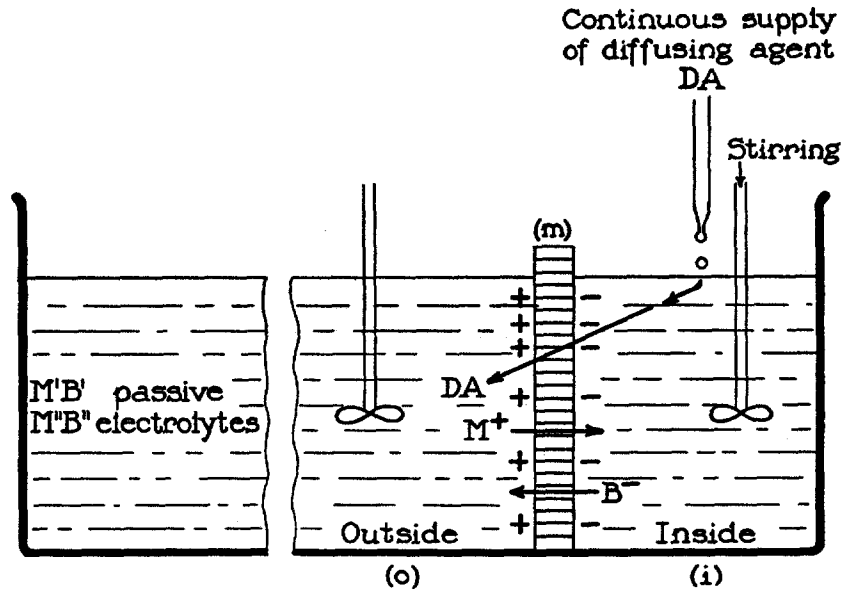


FIG. 1. Scheme of the system considered. The upper part shows the principle of the experimental arrangement. The lower part demonstrates schematically a biological analogy to this system.

The theory leads to the following alternative expressions for the distribution of the passive ions:

(a) In terms of the final electrical (diffusion) potential π , for univalent ions,

$$\log \frac{M_i^+}{M_o^+} = \log \frac{B_o^-}{B_i^-} = \frac{F}{RT} \cdot \pi \quad (1)$$

where M_i^+ , B_i^- , and M_o^+ , B_o^- , denote concentration inside and outside respectively, F is the Faraday, R is the gas constant, and T the absolute temperature. When π is expressed in millivolts, F/RT is equal to 1/58 (at 18°C.).

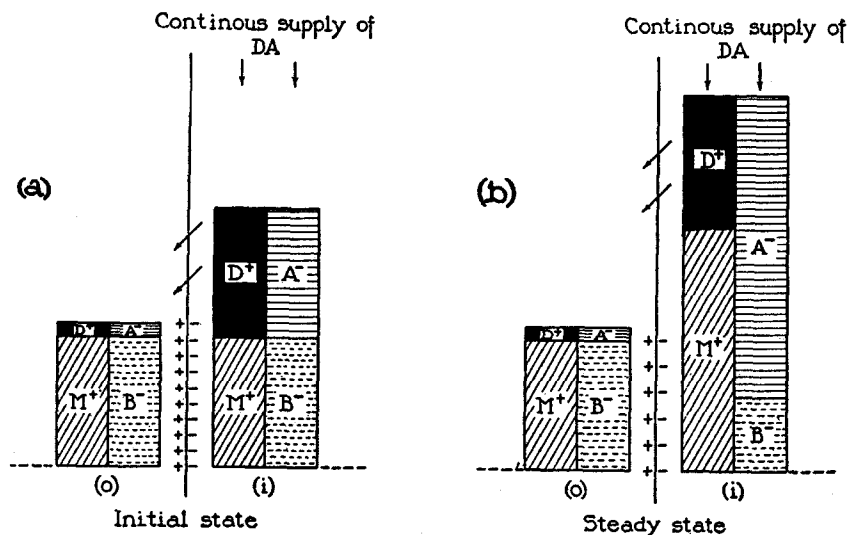


FIG. 2. The effect of a steady diffusion of DA upon the ionic distribution when $u_D > v_A$. DA is by some means (by addition or production) steadily supplied inside (i). The concentrations of the electrolytes outside (o) are kept constant. An electrical potential arises across the boundary (membrane). This causes an inward migration of M^+ and an outward migration of B^- . Finally the concentration gradients have become sufficiently large to balance the electrical gradient and the system approaches a steady state. Thus the M ions became accumulated and the B ions diminished in amount inside.

The scale used in this figure corresponds very closely with the conditions of Experiment 1 (see Table I).

(b) In terms of known concentrations the distribution can be explicitly calculated from the following transcendental equation

$$\log \xi = \log \frac{M_i^+}{M_o^+} = \log \frac{B_o^-}{B_i^-} = \frac{u_D - v_A}{u_D + v_A} \log \frac{D_i^+ + \Sigma M_i^+}{D_o^+ + \Sigma M_o^+} \quad (2)$$

Here u_D and v_A denote the mobility of the D^+ and A^- ions in the diffusion layer. It should be noticed that $(D^+ + \Sigma M^+)$ is equal to the *total* concentration of the electrolytes.

Furthermore, the fact was brought forward, as is evident from Equations 1 and 2 here, that the relationship

$$\frac{M_i'^+}{M_o'^+} = \frac{M_i''^+}{M_o''^+} = \dots = \frac{B_o'^-}{B_i'^-} = \frac{B_o''^-}{B_i''^-} = \dots = \xi \quad (3)$$

must be valid. Equation 3 is immediately recognized as being characteristic also for the Gibbs-Donnan equilibrium, which obviously constitutes a special case of the more general system described by Equation 2, obtained when u_D or v_A approaches zero.

It should be emphasized that neither Equation 1 nor Equation 3 alone permits any explicit calculation of the ionic distribution. The factors which determine the distribution picture are: (a) The mobility relation u_D/v_A , (b) the concentration ratio $D_i^+/ \Sigma M_o^+$, and, (c) the concentration ratio D_i^+/D_o^+ .

The further from unity u_D/v_A is and the higher $D_i^+/ \Sigma M_o^+$ or D_i^+/D_o^+ is, the higher accumulation (or impoverishment) will be attained by the passive ions. This statement follows from Equation 2. In a less abstract way, it can also be expressed with the aid of Equation 1 by saying that the greater diffusion potential present across the boundary, the more marked accumulation effects (or the reverse) are obtained.

Finally it should be emphasized that this diffusion effect upon ionic distribution is *not* any kind of cataphoresis effect, because no current is flowing. Although interpretations in terms of a (diffusion) potential are rather convenient, it might be more correct to employ a concept of ionic exchange.

Earlier Experiments

The phenomenon of accumulation and impoverishment of certain ions in a system where a steady diffusion takes place is related to a great many experimental observations.

These are described in the literature as "*Diffusion gegen das Konzentration-gefälle*" by Behn (2) in 1897; "*Diffusion retrograde*" by Thovert (3) in 1902; "Counterdiffusion" by Osborne and Jackson (4) in 1914; and Walpole (5) in 1915, etc. These workers simply placed two solutions on top of one another, one containing the diffusion agent, both having another electrolyte in common. After an arbitrary time two or more parts of the diffusion column were analyzed. In general a redistribution of all ions could be observed. Apparently there was no possibility of obtaining any steady state with these conditions. The effects shown ought correctly to be classified as "temporary diffusion effects" (see (1) p. 155) and were in most cases rather small. In the best cases the differences of passive ion concentration amounted to from 15 to 20 per cent. Some experiments with condi-

tions corresponding to the theory outlined above and of the same type as will be reported here, were carried out some years ago by Straub (6). He observed an accumulation of cations and a simultaneous impoverishment of anions in a clay cylinder, inside of which acid was supplied. Straub failed, however, to offer any satisfactory discussion of what he called the "*Harmonie-Einstellung*" of the ions, nor did his data seem to be suitable for any treatment in regard to the theory now accessible.

This subject is also related to the numerous cases of "accelerated or retarded diffusion" of electrolytes reported, for instance by McBain and Dawson (7) (*cf.* also reference (8)). This is quite natural, because the theoretical considerations here advanced are founded on the basis of Nernst's (9) classical kinetical theory for electrolyte diffusion.

Summarizing the previously published works, it may be said, that there were no experiments available for use as a test for the theory proposed for a steady state.

EXPERIMENTAL PROCEDURE

In principle the set up was that sketched in Fig. 1: a small "inside volume," 10–30 cc., was separated from a large "outside" volume (0.5–1.5 liters) by a porous convection-proof membrane, *m*. Both solutions were kept homogeneous up to the membrane by stirring. In (*i*) the diffusing agent was continuously supplied either in the form of a slow stream of a concentrated solution (HClO_4), or by addition of the agent in a solid form so as to maintain a saturated solution (KIO_3).

Apparatus.—The apparatus used has been described in another paper (10). The supply of the concentrated diffusing agent in Experiment 1, HClO_4 , was regulated by varying the level of a Mariotte's vessel, which, through a flexible tube ending in a long capillary jet, was in communication with the inside solution. Only one membrane was employed, consisting of four superimposed layers of cellophane 600 (Du Pont Company), in wet condition of a total thickness of 0.28 mm. With one or two layers the results showed great divergences from the theoretically expected. This circumstance is to be ascribed to the influence of "unstirred layers" adhering to the membrane surfaces. These extra diffusion layers are not convection-proof. By means of a special method their thickness is estimated to be approximately 0.03 mm. The cellophane may have a slight influence upon the mobilities of the ions here investigated, which, however, will be accounted for when comparing the results with the theory.

Choice of Electrolytes.—This was dictated partly by a desire to produce pronounced distribution differences, partly by attention to available analytical methods. Therefore, the first experiment to be reported was carried out with an acid as a diffusing agent and with NH_4Cl as source of the passive ions ($u_{\text{H}}/v_{\text{ClO}_4}$ being large (*cf.* p. 110), H_4N and Cl are easily determined). In the second experiment a neutral salt, K-iodate, was used as a diffusing agent, because the iodate ions have a rather low mobility compared with K ($u_{\text{K}} = 65$, $v_{\text{IO}_3} = 33$). Hydrochloric acid furnished the passive ions.

Analyses.—The analyses were performed with micro methods. The samples taken had a volume ranging from 0.05 to 1 cc. depending upon the circumstances. H was determined by titration with 0.01 N NaOH using methyl red as indicator. Cl was determined electrometrically after the acidity titration, employing 0.005 N AgNO₃ and sulfuric acid. NH₄ was analyzed iodometrically with 0.05 NaBrO

TABLE I

Development of Ionic Accumulation and Impoverishment in a System Subjected to a Steady Diffusion

Experiment 1

Initial state
 (10 cc.) 0.1 N HClO₄ | 0.1 N H₄NCl (1500 cc.)
 0.1 N H₄NCl |
 Inside (*i*) | Outside (*o*)
 (Membrane)

H₂ maintained constant by continuous addition of 5 N HClO₄.

Time	Inside (<i>i</i>)				Outside (<i>o</i>)				$\frac{(\text{H}_4\text{N})_i}{(\text{H}_4\text{N})_o}$	$\frac{(\text{Cl})_o}{(\text{Cl})_i}$
	H	H ₄ N	Cl	ClO ₄ *	H	H ₄ N	Cl	ClO ₄ *		
<i>hrs.</i>	<i>mm./l</i>	<i>mm./l</i>	<i>mm./l</i>	<i>mm./l</i>	<i>mm./l</i>	<i>mm./l</i>	<i>mm./l</i>	<i>mm./l</i>		
0	90.9	99.1*	99.1	90.9	0	99.9*	99.9	0	1.00	1.01
0.5	84.1	111	89.0	106	—	—	—	—	1.11*	1.12
2	96.5	159	62.1	193	2.95	99.9	100.9	2.0	1.59	1.62
4	99.6	188	51.6	236	4.31	99.1	101.8	(1.6)	1.90	1.97
6	99.6	207	48.6	258	5.85	102	102	5.9	2.03	2.10
7	96.5	212	48.6	260	—	—	—	—	2.08*	2.10*
8	111	215	47.9	278	8.00	102	101.4	8.6	2.11	2.12
9	105	214	48.6	271	8.40	101	101.5	7.9	2.13	2.09
9 ²⁰	Potential (<i>i</i>)-(o): Calomel electrodes + 21.0 mv.; Ag/AgCl - 0.8 mv.†									
20	121	214	49.1	286	17.7	101	100	18.7	2.13	2.04
20 ³⁰	Potential (<i>i</i>)-(o): Calomel electrodes + 20.2 mv.; Ag/AgCl - 1.2 mv.†									

* Calculated figures.

† Sign outside.

and 0.01 N Na₂S₂O₃ according to (13). IO₃ was titrated as I₂ with thiosulfate after addition of KI and acid. Other concentrations were calculated by difference. All pipettes, burettes, and solutions were calibrated against standard solutions. No analytical error is likely to exceed ± 2 per cent.

Potential Measurements.—The potential measurements were performed by means of calomel electrodes, as described elsewhere (11). Supplementary meas-

urements were made with Ag/AgCl electrodes prepared according to Brown (14). The electrodes were connected either to a push pull vacuum tube voltmeter, or to a Leeds-Northrup Type K potentiometer. The potential figures are regarded as accurate to ± 0.5 mv.

TABLE II
Development of Ionic Accumulation and Impoverishment in a System Subjected to a Steady Diffusion

Experiment 2

Initial state
(10 cc.) $ca. 0.4$ N KIO_3 | 0.01 N HCl (500 cc.)
saturated plus
crystals
Inside (*i*) | Outside (*o*)
(Membrane)

Time	Inside (<i>i</i>)				Outside (<i>o</i>)*				$\frac{(H)_i}{(H)_o}$	$\frac{(Cl)_o}{(Cl)_i}$
	H	K \dagger	Cl	IO_3	H	K \dagger	Cl	IO_3		
<i>hrs.</i>	<i>mm./l</i>	<i>mm./l</i>	<i>mm./l</i>	<i>mm./l</i>	<i>mm./l</i>	<i>mm./l</i>	<i>mm./l</i>	<i>mm./l</i>		
0	0	—	—	—	10.0	—	—	—	—	—
0.1	1.7	371	0.9	372	10.0	0.4	10.0	0.4	0.17	11.1
0.5	10.3	—	—	336	10.0	1.6	10.5	1.1	1.03	—
1	21.0	327	2.9	345	9.8	1.7	9.7	1.8	2.14	3.34
2	37.4	333	4.0	366	—	—	—	2.7	(3.82)	—
3	47.5	328	4.6	376	9.2	4.5	9.9	3.8	5.16	2.15
4	56.0	311	5.0	362	10.2	1.2	9.8	1.6	5.50	1.60
5	62.1	318	5.1	375	10.1	2.5	9.5	2.5	6.16	1.86
6	63.0	315	5.3	383	9.8	4.0	10.1	3.8	6.44	1.90
7	63.0	303	5.2	366	10.9	1.9	10.2	2.6	5.78	1.96
9	61.0	271	5.6	326	10.2	3.3	10.3	3.3	5.98	1.84
10	57.1	248	5.6	300 \ddagger	—	—	—	—	—	—
9 30	Potential (<i>i</i>)-(o): Calomel electrodes + 25.5 mv. §									

* The solution was renewed after 3 and 6 hrs., thereby restoring the initial composition.

\dagger Calculated values.

\ddagger The decrease in KIO_3 concentration after 6 hrs. was probably due to a fall of the room temperature, hence decrease of solubility.

§ Sign outside.

The pH and Cl activity measurements were made by means of a glass electrode (type MacInnes and Dole) (18), and a Ag/AgCl electrode (Brown (14)) respectively, using a saturated calomel electrode as reference. A Compton electrometer served as zero instrument.

RESULTS AND DISCUSSION

In Tables I and II two typical experiments are recorded (Experiments 1 and 2).

Experiment 1.—This was designed to fulfill, as completely as possible, the main assumptions on which the theory was based: (a) Uni-univalent electrolytes being present only, all known as strong and free from complicating phenomena; (b) no migration of water across the convection-proof boundary. Perchloric acid served as diffusing agent and the passive ions were H_4N and Cl. The $HClO_4$ concentration in the small inside chamber was maintained at about 1/10 molarity by means of an external supply. The experiment was started with equal concentration of H_4N and Cl ions inside and outside. During the following time, however, one could observe that the H_4N ions moved inwards and, simultaneously, Cl ions moved outwards. Finally a steady state was approached inside, resulting in a 2.13 fold accumulation of H_4N and a Cl impoverishment of almost the same magnitude. Fig. 2 corresponds very closely with the conditions of this experiment. No appreciable water migration could be detected.

The experimental results will now be compared with a theory: The theoretical distribution ratio

$$\xi = \frac{(\text{Passive cation concentration})_i}{(\text{Passive cation concentration})_o} = \frac{(\text{passive anion concentration})_o}{(\text{passive anion concentration})_i}$$

can be calculated from either of Equations 1 or 2.

According to Equation 1, at 20°C. and with the diffusion potential expressed in millivolts,

$$\pi = 58.1 \log \xi \quad (3)$$

In the experiment the membrane potential π , was + 20.2 mv., hence, the distribution ratio is

$$\xi = 2.23, \text{ calculated from observed } \pi \\ (\text{Observed value for } H_4N \text{ is } 2.13, \text{ for Cl is } 2.04 \text{ after } 20 \text{ hours.})$$

According to Equation 2 combined with the relation $\xi = \frac{(H_4N)_i}{(H_4N)_o}$

$$\log \xi = \frac{\mu_H - \nu_{ClO_4}}{\mu_H + \nu_{ClO_4}} \log \frac{(H)_i + \xi \cdot (H_4N)_o}{(H)_o + (H_4N)_o} \quad (4)$$

potential has, the negative sign being inside, an accumulation of passive cations and impoverishment of anions is to be expected, and was also found. As to the quantitative relations this experiment, at first, seems to show some discrepancies between theory and observations.

TABLE III

*Hydrogen Ion Activity Measurements of Inside and Outside Solutions after 9 Hours**Experiment 2*

(P.D. measured with glass electrode/calomel electrode, "slope" 57.5 mv.)

Solution	Total H concentration	Millivolts	pH	a_{H}
	<i>mm./l</i>			<i>mm./l</i>
Inside.....	61.0	-18.6	1.61	38.9
Outside.....	10.2	+5.1	2.02	9.55
0.01 N HCl (control).....	10.0	+5.6	2.03	9.34
(i)-(o).....	50.8	-23.7	-0.41	$\frac{(a_{\text{H}})_i}{(a_{\text{H}})_o} = 2.57$

TABLE IV

*Chloride Ion Activity Measurements of Inside and Outside Solutions after 9 Hours**Experiment 2*

(P.D. measured with Ag/AgCl electrode/calomel electrode, "slope" 57.7 mv.)

Solution	Total Cl concentration	Millivolts	pCl	a_{Cl}
	<i>mm./l</i>			<i>mm./l</i>
Inside.....	5.6	-118.8	2.37	4.20
Outside.....	10.3	-96.5	1.98	10.2
0.01 N HCl (control).....	10.0	-98.9	2.03	9.34
(i)-(o).....	-4.7	-22.3	0.39	$\frac{(a_{\text{Cl}})_o}{(a_{\text{Cl}})_i} = 2.43$

However, when due attention is paid to certain interfering circumstances, the results also appear to agree quantitatively in a satisfactory manner with the theory. For this purpose the following discussion is given.

First, in Table II it will be noticed that the final distribution ratio

H_i/H_o is as high as 5.98; the ratio Cl_o/Cl_i , however, is much lower, 1.84. The H figures were determined by titration, accordingly all hydrogen ions, both free and bound, were included. It is well known that IO_3 ions can form $H(IO_3)_2$, bi-iodate, in *acid* solution, thus binding hydrogen ions. Unfortunately, pH measurements were not performed during the actual run, but afterwards "artificial" inside and outside solutions were made up to correspond with the analytical figures recorded in Table II at 9 hours.³ In these solutions pH and a_{Cl} were determined by means of the glass electrode and AgCl electrode respectively. The results are summarized in Tables III and IV. It can be seen that the H ion activity inside is considerably lower than the total H concentration, as pointed out, probably due to formation of bi-iodate ions. From these measurements the ionic distribution ratios, expressed in activity figures, will be found as

$$\begin{array}{l} \text{Observed } \xi = 2.57 (5.98), \text{ corrected for H activity} \\ \text{ " } \xi = 2.43 (1.84), \text{ " " Cl " } \end{array}$$

The values within brackets are the ones obtained from total concentration figures.

Hence, the relation $H_i/H_o = Cl_o/Cl_i$ seems to be obeyed, as demanded by the theory. The theoretical ξ values are calculated, as in Experiment 1, either from the observed diffusion potential (Equation 1), or from the transcendental formula (Equation 2). For the first alternative is obtained

$$\xi = 2.75, \text{ calculated from the diffusion potential}$$

Calculations on the basis of Equation 2 can be performed in several different ways. First, there are two choices of the relation u/v or of q , referring to free water or to cellophane. Secondly, when dealing with a rather concentrated salt solution (saturated KIO_3), some kind of correction for activity changes may be demanded. Based on concentration figures given for 9 hours in Table II it is found that

³ These "artificial" solutions were made: *inside*, 5.6 cc. 0.1 N HCl, 55.4 cc. 0.1 N HIO_3 , 5.79 gm. KIO_3 ; *outside*, 10.2 cc. 0.1 N HCl, 0.1 cc. 0.1 N KCl, 3.2 cc. 0.1 N KIO_3 ; in all cases H_2O was added to make 100 cc. of solution. The reagents were Kahlbaum brands; the solutions were freshly made and standardized.

$$\begin{aligned}\xi &= 2.86, \text{ calculated from Equation 2 when } q = 0.327 (\text{H}_2\text{O})^4 \\ \xi &= 5.14, \text{ " " " " when } q = 0.509 (\text{cellophane})\end{aligned}$$

Corrections for Activity Changes.—When attempting activity corrections, it was assumed that the mean activity coefficient, γ , for the K-iodate inside was the same as for 0.3N KCl being 0.67. γ_{HCl} outside was taken as 0.93, a figure valid for 0.01 N HCl (according to MacInnes and Noyes). Any further corrections do not have any appreciable effect upon the results and must also be rather ambiguous. Therefore they are omitted. The ξ values obtained from activity figures were

$$\begin{aligned}\xi &= 2.55, \text{ calculated from Equation 2 and corrected for activity when } q = 0.327 (\text{H}_2\text{O}) \\ \xi &= 4.25, \text{ " " " " " " " " when } q = 0.509 (\text{cellophane})\end{aligned}$$

TABLE V
Comparison between Observed and Theoretical Distribution Ratios (ξ) of Passive Ions in Steady State

$$\xi = \frac{(\text{Passive cation})_{\text{inside}}}{(\text{Passive cation})_{\text{outside}}} = \frac{(\text{passive anion})_{\text{outside}}}{(\text{passive anion})_{\text{inside}}}$$

Experiment	Diffusing agent	Passive ion	Observed from		Calculated from Equation 2 (4)				Calculated from diffusion potential
			Concentration	Activity	Free water		Cellophane		
					Concentration	Activity	Concentration	Activity	
1	HClO ₄	H ₄ N	2.13	1.91	1.89	1.54	2.30	1.70	2.23
		Cl	2.04	(1.87)					
2	KIO ₃	H	5.98	2.57	2.86	2.55	5.14	4.25	2.75
		Cl	1.84	2.43					

SUMMARY OF RESULTS AND CONCLUSIONS

In Table V the experimental and theoretical results are put together. The figures seem to justify the following conclusions:

1. The agreement between observed and calculated ξ values is, on the whole, quite satisfactory in both the experiments, if proper attention is paid to activity conditions. ξ as calculated from the transcendental

⁴ Calculated value from $u_{\text{K}}/v_{\text{IO}_3}$ determined from diffusion potential across cellophane of 0.1 – 0.01 N KIO₃ according to (11). This value was found to be 3.08 (in free water 65/33 = 1.98).

Equations 2 or 4, using the ionic mobilities for free water, yields the best agreement.

2. If the mobility relations as determined for cellophane are used in the theoretical calculations, much higher ξ values than those actually observed would be expected in the KIO_3 experiment. In the HClO_4 experiment it is hard to point out any significant difference as to the outcome of different choice of mobility relations. Hence, it appears that it would be better to assume a validity of free water ionic mobilities, in spite of the fact that the diffusion effects occurred across cellophane. Such a conclusion also follows from the views expressed by the author, that the cellophane mobility figures as determined are only *apparent* values. The reason is to be sought in interference from the membrane itself (Teorell (12)).

3. The theoretically expected ξ values when calculated from the *measured* diffusion potential are of the same magnitudes as the observed figures corrected for activity. The latter are only 14 and 9 per cent lower than the former, in Experiments 1 and 2 respectively; these differences may very likely arise from small, unavoidable liquid junction potentials at the calomel electrodes. This fact seems to offer an ample confirmation of one consequence of the theory, namely, that the distribution of the passive ions is completely determined by the *observed* diffusion or membrane potential according to the simple Equation 1, or

$$\log \xi = \frac{\pi}{0.1983 T} \quad (1)$$

(π = millivolts; T = absolute temperature.)

In regard to the thermodynamical interpretation of this equation we may refer to the first paper in this series (1), paragraphs IVb and c.

4. The agreement between experiment and theory according to Equation 1 is of a profound and essential significance. This shows that the water migration does not have any appreciable influence upon the expected ionic distribution, although amounting to about 40 per cent as volume increase inside in Experiment 2. Furthermore, the high ξ values as calculated from cellophane mobilities in Experiment 2 can be ruled out as being improbable, because such figures would correspond to a value of the diffusion potential much higher than that

actually observed. This point offers additional evidence for the views expressed under paragraph 2 above.

5. Still, there are some other points which can be advanced giving beautiful confirmation of the proposed theory. In the theoretical paper (1), in paragraph IVc it was remarked:

“... As the diffusion potential π is equal to the expression for the electrode potential for any passive ion, a concentration chain consisting of reversible electrodes for such an ion species placed in the solutions (*o*) and (*i*) should give no current, ...”

In Experiment 1 the actual “concentration chain potential” with AgCl electrodes, reversible in regard to the passive chloride ions, was measured from -0.8 to -1.2 mv. The theoretical value should be ± 0 mv., accordingly the result is not far outside the experimental limit of error. At the same time π was about $+21$ mv. (cf. Table I).

In Experiment 2 the same thing can be shown somewhat more indirectly. Here reversible electrodes for both the passive ion species were available, the glass electrode for the H ions, and the AgCl electrode for the Cl ions. The “electrode potentials” for these two ion species are simply found as differences between the potential values recorded in Tables III and IV, as measured against the same reference (calomel) electrode. These values are (cf. also the tables),

Electrode potentials	{	[(mv.) _i - (mv.) _o] _{glass/Hg₂Cl₂}	-23.7 mv.
		[(mv.) _i - (mv.) _o] _{AgCl/Hg₂Cl₂}	-22.3 mv.
		Diffusion potential observed, π ,	+25.5 mv.

It is noticed that the figure for the diffusion potential is almost equal to the figures for the practically identical electrode potentials. As it carries opposite sign, the resulting concentration chain potentials, being the sum of both (diffusion potential + electrode potential), also in this case, will not be far from zero.

SUMMARY

The aim of this paper is to present confirmation of the theory of the diffusion effect. By diffusion effect is understood a redistribution of the ions in a system where a continuous diffusion of one electrolyte is going on, which results in a steady state showing accumulation and impoverishment of certain ions.

Some typical experiments are recorded and discussed. The results are found in satisfactory agreement with the theory: this can be demonstrated in several ways.

The importance of considering activity changes is pointed out. Water migration and the diffusion membrane probably have no appreciable influence upon the diffusion effect under the conditions of these experiments.

The diffusion effect may have biological analogies.

BIBLIOGRAPHY

1. Teorell, T., *Proc. Nat. Acad. Sc.*, 1935, **21**, 152.
2. Behn, U., *Wied. Ann.*, 1897, **62**, 54.
3. Thovet, J., *Compt. rend. Acad. sc.*, 1902, **134**, 826.
4. Osborne, W. A., and Jackson, L. C., *Biochem. J.*, London, 1914, **8**, 246.
5. Walpole, G. S., *Biochem. J.*, London, 1915, **9**, 132.
6. Straub, J., *Kolloid-Z.*, 1933, **62**, 13; 1933, **64**, 72.
7. McBain, J. W., and Dawson, C. R., *J. Am. Chem. Soc.*, 1934, **56**, 52.
8. *Tr. Faraday Soc.*, 1935, **31**, several papers on diffusion.
9. Nernst, W., *Z. phys. Chem.*, 1888, **2**, 617; 1889, **4**, 154. Cf. also Planck, M., *Wied. Ann.*, 1890, **40**, 561.
10. Teorell, T., *J. Biol. Chem.*, 1936, **113**, 735.
11. Teorell, T., *J. Gen. Physiol.*, 1935-36, **19**, 917.
12. Teorell, T., *Proc. Soc. Exp. Biol. and Med.*, 1935, **33**, 382.
13. Teorell, T., *Acta med. Scand.*, 1928, **68**, 305.
14. Brown, A. S., *J. Am. Chem. Soc.*, 1934, **56**, 646.
15. Landolt, H., and Börnstein, R., *Physikalisch-chemische Tabellen*, Berlin, Julius Springer, 5th edition (Roth, W. A., and Scheel, K.), 1923, **1**, 170.
16. Falkenhagen, H., *Die Elektrolyte*, Leipsic, S. Hirzel, 1932.
17. MacInnes, D. A., and Noyes, A. A., *J. Am. Chem. Soc.*, 1920, **42**, 239.
18. MacInnes, D. A., and Dole, M., *Ind. and Eng. Chem., Analytical Edition*, 1929, **1**, 57.