VII. THE PENETRATION OF ELECTROLYTES INTO GELS.

I. THE PENETRATION OF SODIUM CHLORIDE INTO GELS OF AGAR-AGAR CONTAINING SILVER NITRATE.

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INTRODUCTION.

"THE manifestly colloidal nature of living protoplasm demonstrated *ad oculos* the significance of studies on colloids for Biology," says a distinguished continental plant physiologist [Czapek, 1911], and indeed the importance of investigations on sols and gels from the point of view of physiology needs no emphasis at the present time. An enquiry into the penetration of salts into gels may help towards the solution of problems of permeability in living and dead plant and animal tissues, and it is from this point of view that the experiments described in this and following papers were made.

A number of investigations on the penetration of electrolytes into gels have been made since the time of Graham. As well as the researches of Graham himself may be mentioned those of de Vries [1884], Coleman [1887, 1888], Chabry [1888], Voigtländer [1889], Durrant [1906], Bechhold and Ziegler [1906], Öholm [1913], Vanzetti [1914], and von Fürth and Bubanović [1918].

In the majority of the cases cited above the method employed to study the diffusion of substances into gels consisted in analysing different layers of the gel after penetration of salt had proceeded for a certain time. Working in this way Graham concluded that diffusion of crystalloids proceeds as rapidly in a gel as in water. Voigtländer investigated the diffusion of a number of chlorides in agar gels of different concentrations and came to the conclusion that the rate of diffusion was independent of the concentration of the gel. Öholm investigated the diffusion of potassium chloride from a solution of normal concentration into 2, 5 and 10 per cent. gelatin, the amount of potassium chloride being determined in four successive layers of the gelatin by titration with silver nitrate. Öholm found a progressive decrease in the rate of diffusion with increasing concentration of the gelatin and concludes that as a first approximation the presence of gelatinous substances affects the

diffusion of an electrolyte in the same way as a non-electrolyte in general, such as sugar or glycerol [cf. Öholm, 1912].

The method used by Coleman, Chabry, Durrant, Vanzetti and von Fürth and Bubanović is similar to that introduced by Lodge for comparing the mobilities of ions. The characteristic of this method is that the diffusion into the gel is followed by means of an indicator in the gel. Thus the penetration of an acid may be followed by means of litmus or other indicator; the diffusion of chlorides by means of silver nitrate. The chief researches by means of this method are those of von Fürth and Bubanović [1918], who have followed the penetration of a large number of salts, acids and alkalies into gels of 5 per cent. gelatin and principally 2 per cent. agar-agar. From their experimental results they draw a number of conclusions in regard to diffusion in gels and water and the various factors determining the rate of diffusion.

While von Fürth and Bubanović are quite right in emphasising the importance of these researches for physiology and physical chemistry, it would appear that they have not realised the complexity of the system with which they deal. As an example of this may be quoted their experiment 7, in which the diffusion of hydrochloric, sulphuric and oxalic acids, sodium chloride, and ammonium, potassium, magnesium and zinc sulphates was followed in gels of 2 per cent. agar containing silver nitrate and barium nitrate. From the rate at which the zone of precipitated silver chloride or barium sulphate moves onward conclusions are drawn as to the abnormal behaviour of sulphates compared with chlorides in regard to the diffusion of these substances in gelatin. Now this can only be the case if the silver and barium salts in the gel are without influence on the rate of diffusion of the salts through gelatin, as the concentration of the indicators in the gel is not mentioned and is evidently regarded as having no influence on the rate of diffusion. But from first principles it is not to be expected that this is the case, and the first step in obtaining data as to penetration into gels by the indicator method is obviously to determine how variation of the different factors in the case of one system influences the experimental results.

In this paper therefore the system consisting of an agar gel which is penetrated by sodium chloride is investigated, the various factors, concentration of sodium chloride in the external solution, concentration of gel and concentration of silver nitrate in the gel being varied and the effect of variation of these factors on the penetration of the chloride determined.

METHOD.

The gel was prepared by dissolving ordinary shred agar in distilled water so as to make a solution $\frac{2}{3}$ times as concentrated as required. A solution of silver nitrate four times as strong as that required in the gel was then added to the warm agar solution the proportions by volume of agar and silver nitrate solution being 3 to 1. The mixture after well stirring was poured into test-tubes to a constant height (generally 6 or 7 cm.) and after the gel had

cooled and set a definite height of the sodium chloride solution was added (this was generally 6 or 7 cm.). The tubes were kept in racks in a dark cupboard in which the temperature was measured by means of a self-recorder. The temperature never varied more than 2° or 3° throughout an experiment.

As the chloride penetrates the gel the silver is precipitated as chloride, the limit of which is sharply marked from the gel below containing no precipitated silver chloride. The distance between the upper surface of the gel and this sharp line of demarcation is called by Voigtländer and by von Fürth and Bubanović the "Diffusionsweg": it will be called here the "penetration," and the movement forward of the silver chloride the "march of diffusion." The penetration of course increases with time, though as we shall see, not at a constant rate. The line of demarcation represents of course a layer of a definite concentration of chloride, namely the saturation concentration of silver chloride in the gel. The saturation concentration of silver chloride in water at 20° is 0.00015 g. of salt in 100 g. of water. It is thus the movement forward of a concentration of sodium chloride of this order of magnitude that is followed by the indicator method.

EXPERIMENTAL RESULTS.

A. Influence of concentration of sodium chloride.

In a number of experiments with 2 per cent. agar gels containing some silver nitrate von Fürth and Bubanović have shown that the march of diffusion is more rapid the stronger the solution of salt external to the gel, provided the comparison is made with the same gel.

A large number of experiments have been made in the present research with gels of 0.5, 1, 2, 3 and 4 per cent. agar containing varying quantities of silver nitrate, and the observation of von Fürth and Bubanović as to the influence of concentration in affecting the march of diffusion has been confirmed.

From 30 series of experiments in which the concentration of sodium chloride was the only factor varied three examples will suffice to indicate the influence of concentration of the external salt. The results are shown in the following tables. One series of results is shown graphically in Fig. 1. The others are similar.

Table I. 0.5 per cent. agar gel containing 0.005N AgNO_3 . Each number is the mean of two determinations.

1.2N NaCl		N NaCl		0.5N NaCl		0.2N NaCl		0.1N NaCl		0.05N NaCl	
Time in hrs	Penet. in mm.	Time in hrs	Penet. in mm.	Time in hrs	Penet. in mm.	Time in hrs	Penet. in mm.	Time in hrs	Penet. in mm.	Time in hrs	Penet. in mm.
2.92	13.8	2.92	13.5	2.90	12.4	2.90	10.6	2.88	9.1	2.87	7.9
20.33	38	20.33	37.2	20.32	34.1	20.32	30	20.30	26.2	20.38	22
27.58	44.5	27.58	43.8	27.57	40	27.57	35	27.55	31	27.53	25.8
44.25	56	44.25	54.7	44.23	50.2	44.23	44.1	44.22	38.6	44.2	32.2
70.0	>70	70.0	>70	70.0	64.5	70.0	55.1	70.0	48.1	70.0	40.1

Table II. 2 per cent. agar containing 0.1N AgNO_3 .

5N NaCl		2N NaCl		N NaCl		0.5N NaCl		0.2N NaCl		0.1N NaCl	
Time in hrs	Penet. in mm.	Time in hrs	Penet. in mm.	Time in hrs	Penet. in mm.	Time in hrs	Penet. in mm.	Time in hrs	Penet. in mm.	Time in hrs	Penet. in mm.
2.68	10.5	2.55	7.9	2.42	6.3	2.32	4.8	2.18	2.4	2.10	1.0
4.97	14.5	4.83	11.2	4.70	9.1	4.60	7.4	4.47	4.1	4.40	1.0
23.78	39.2	23.65	25.8	23.5	21.3	23.4	17.1	23.3	10.2	23.2	5.0
29.40	45	29.27	29	29.1	24.5	29.0	19.4	29.9	12.1	29.8	5.5
48.42	58.5	48.28	37.5	48.1	31.5	48.0	25	48.9	15	48.8	7
		71.33	45.5	71.2	38.2	71.0	30.5	70.9	18	70.9	8
		95.4	53.5	95.3	44.5	95.2	35	95.1	25	95	8.2

Table III. 4 per cent. agar containing 0.05N AgNO_3 .

5N NaCl		2N NaCl		N NaCl		0.5N NaCl		0.2N NaCl		0.1N NaCl	
Time in hrs	Penet. in mm.	Time in hrs	Penet. in mm.	Time in hrs	Penet. in mm.	Time in hrs	Penet. in mm.	Time in hrs	Penet. in mm.	Time in hrs	Penet. in mm.
3.10	13.5	2.98	10	2.83	8.2	2.72	6.5	2.60	2	2.50	1.3
5.27	19.0	5.15	13.2	5.00	11.4	4.88	8.8	4.77	7	4.67	2.5
24.1	39	24.0	29.2	23.8	25	23.7	21	23.6	15.6	23.5	8.5
29.8	43	29.7	33	29.6	28.5	29.4	17.5	29.3	17.5	29.3	10
48.7	52.6	48.6	42.2	48.5	37	48.3	30	48.2	22.2	48.1	13
71.8	65	71.1	52	71.6	45	71.3	37	71.3	27	30.5	16.2
		95.6	64	95.5	53	95.4	42.5	95.2	30.5	95.2	18.4

Fig. 1. Penetration of sodium chloride into 0.5 per cent. agar gels containing 0.005N silver nitrate. The initial concentrations of sodium chloride are indicated.

From the data obtained experimentally by von Fürth and Bubanović these authors conclude that the influence of concentration on the march of diffusion can be expressed by the simple relation

$$d = mt^{\frac{1}{2}}c^n,$$

where

d is the distance penetrated,

t „ „ time,

c „ „ concentration,

and

m and n are constants.

In their experiments with sodium chloride they obtained $m = 41.96$ and $n = 0.12$, t being measured in days, d in millimetres and c in normalities.

Put into words this equation states that the march of diffusion is proportional to the square root of the time and to some fractional power of the concentration. The results recorded in Tables I to III show that the march of diffusion is approximately proportional to the square root of the time. This conclusion has also been reached in regard to penetration of acids, alkalies and salts into gels by Coleman [1888], Chabry [1888] and Voigtländer [1889]. How near this approximation is may be seen from the following tables, which show that the march of diffusion is generally approximately proportional to the square root of the time in the case of any particular gel and any particular concentration of penetrating salt. At the beginning of the diffusion the ratio $P/\sqrt{t}$ is constantly lower, and towards the bottom of a tube generally higher than the approximately constant value for the greater part of the experimental period. The greatest divergences appear when the concentration of the silver nitrate in the gel approaches that of the penetrating salt.

If now we return to von Fürth and Bubanović's equation $P = mt^{\frac{1}{2}}c^n$, where the distance penetrated is denoted by P and the initial concentration of the penetrating salt by c , we have

$$\frac{P}{\sqrt{t}} = mc^n,$$

or
$$\log \frac{P}{\sqrt{t}} = \log m + n \log c,$$

whence if $\log P/\sqrt{t}$ is plotted against $\log c$ a straight line should be obtained.

Table IV. 0.5 per cent. agar gel containing 0.005N AgNO₃. (For data see Table I.) P represents penetration in mm. and t the time in hours.

1.2N NaCl		N NaCl		0.5N NaCl		0.2N NaCl		0.1N NaCl		0.05N NaCl	
P	$\frac{P}{\sqrt{t}}$	P	$\frac{P}{\sqrt{t}}$	P	$\frac{P}{\sqrt{t}}$	P	$\frac{P}{\sqrt{t}}$	P	$\frac{P}{\sqrt{t}}$	P	$\frac{P}{\sqrt{t}}$
13.8	8.08	13.5	7.90	12.4	7.28	10.6	6.23	9.1	5.36	7.9	4.65
38	8.43	37.2	8.25	34.1	7.56	30	6.55	26.2	5.81	22	4.88
44.5	8.47	43.8	8.34	40	7.62	35	6.66	31	5.91	25.8	4.92
56	8.42	54.7	8.13	50.2	7.55	44.1	6.63	38.6	5.80	32.2	4.84
				64.5	7.71	55.1	6.59	48.1	5.75	40.1	4.79

Table V. 2 per cent. agar containing 0.1N AgNO₃.
(For data see Table II.)

5N NaCl		2N NaCl		N NaCl		0.5N NaCl		0.2N NaCl		0.1N NaCl	
<i>P</i>	$\frac{P}{\sqrt{t}}$	<i>P</i>	$\frac{P}{\sqrt{t}}$	<i>P</i>	$\frac{P}{\sqrt{t}}$	<i>P</i>	$\frac{P}{\sqrt{t}}$	<i>P</i>	$\frac{P}{\sqrt{t}}$	<i>P</i>	$\frac{P}{\sqrt{t}}$
10.5	6.41	7.9	4.94	6.3	4.05	4.8	3.15	2.4	1.63	1.0	0.690
14.5	6.51	11.2	5.09	9.1	4.20	7.4	3.45	4.1	1.94	5.0	0.825
39.2	8.04	25.8	5.31	21.3	4.39	17.1	3.54	10.2	2.06	5.5	1.008
45	8.30	29	5.36	24.5	4.54	19.4	3.68	12.1	2.21	7	1.002
58.5	7.65	37.5	5.40	31.5	4.54	25	3.61	15	2.14	8	0.950
		45.5	5.39	38.2	4.53	30.5	3.62	18	2.14	8.2	0.840
		53.5	5.48	44.5	4.51	35	3.59	25	2.56		

Table VI. 4 per cent. agar containing 0.05N AgNO₃.
(For data see Table III.)

5N NaCl		2N NaCl		N NaCl		0.5N NaCl		0.2N NaCl		0.1N NaCl	
<i>P</i>	$\frac{P}{\sqrt{t}}$	<i>P</i>	$\frac{P}{\sqrt{t}}$	<i>P</i>	$\frac{P}{\sqrt{t}}$	<i>P</i>	$\frac{P}{\sqrt{t}}$	<i>P</i>	$\frac{P}{\sqrt{t}}$	<i>P</i>	$\frac{P}{\sqrt{t}}$
13.5	7.67	10	5.79	8.2	4.87	6.5	3.94	2	1.24	1.3	0.821
19.0	8.27	13.2	5.81	11.4	5.09	8.8	3.98	7	3.20	2.5	1.16
39	7.94	29.2	5.96	2.5	5.12	21	4.31	15.6	3.21	8.5	1.75
43	7.88	33	6.05	28.5	5.24	23.5	4.33	17.5	3.23	10	1.85
52.6	7.54	42.2	6.05	37	5.31	30	4.32	22.2	3.20	16.2	1.92
		64	6.54	53	5.42	42.5	4.35	30.5	3.13	18.4	1.89

In Table VII are given the average values of $P/\sqrt{t}$ and the corresponding values of c in normalities, and Fig. 2 shows the curves obtained when values of $\log P/\sqrt{t}$ are taken as ordinates and values of $\log c$ as abscissae. It will be observed that they are certainly not straight lines, and accordingly von Fürth and Bubanović's equation does not hold. A reference to von Fürth and Bubanović's results discloses that these workers only used a very restricted range of concentrations of the penetrating solutions namely from N to $N/4$. This corresponds in the curves in Fig. 2 to the portions between the vertical lines *A* and *B*. Even within this very restricted range the curves are only very approximate straight lines when the concentration of silver nitrate in a gel is low. The statement of von Fürth and Bubanović that their law is of wide applicability certainly cannot be accepted.

Table VII.

0.5 per cent. agar containing 0.005N AgNO ₃		2 per cent. agar containing 0.1N AgNO ₃		4 per cent. agar containing 0.05N AgNO ₃	
$\frac{P}{\sqrt{t}}$	<i>c</i>	$\frac{P}{\sqrt{t}}$	<i>c</i>	$\frac{P}{\sqrt{t}}$	<i>c</i>
8.35	1.5	7.38	5	7.83	5
8.15	1	5.28	2	6.05	2
7.54	0.5	4.39	1	5.20	1
6.55	0.2	3.52	0.5	4.23	0.5
5.73	0.1	2.10	0.2	2.92	0.2
4.82	0.05	0.886	0.1	1.61	0.1

The results of a large number of experiments are similar to those recorded above. They indicate that the law connecting the march of diffusion with the square root of the time can be extended with a certain degree of approximation and within certain limits to the case of penetration of an electrolyte into a gel containing a substance with which the penetrating substance reacts. Von Fürth and Bubanović's further extension of this law to include the concentration of the penetrating electrolyte is not of the wide applicability claimed for it, and only holds over very limited ranges of concentration and is then only a crude approximation.

Fig. 2. Curves showing the relation between $\log P/\sqrt{t}$ and $\log c$ in the case of three agar-agar gels. I: 0.5 per cent. agar containing 0.005N AgNO_3 ; II: 2 per cent. agar containing 0.1N AgNO_3 ; III: 4 per cent. agar containing 0.05N AgNO_3 . The vertical lines A and B indicate the limits of external concentrations employed in the experiments of von Fürth and Bubanović.

B. *Influence of concentration of silver nitrate in the gel.*

Although it is tacitly assumed by von Fürth and Bubanović that the concentration of silver nitrate in the gel is without influence on the march of diffusion, this is far from being the case. Tables VIII—X show some results representative of a great number which show clearly that increasing the concentration of silver nitrate in the gel reduces the rate at which the sodium chloride penetrates it. The results given in Tables VIII and X are also shown graphically in Fig. 3.

Table VIII. Penetration of sodium chloride of initially normal concentration into gels of 1 per cent. agar containing various concentrations of silver nitrate.

N AgNO ₃		0.5N AgNO ₃		0.2N AgNO ₃		0.1N AgNO ₃		0.05N AgNO ₃	
Time	Penet.	Time	Penet.	Time	Penet.	Time	Penet.	Time	Penet.
in hrs	in mm.	in hrs	in mm.	in hrs	in mm.	in hrs	in mm.	in hrs	in mm.
None		2.17	3	2.22	5	2.25	6	2.28	6.5
„		4.55	5.1	4.58	7.6	4.60	9.4	4.62	10
„		23.32	12.9	23.4	18.5	23.4	22	23.4	23.8
„		28.90	14	29.0	21	29.0	25	29.0	27
„		47.93	18.3	48.0	27	48.0	32	48.0	34.5
„		70.9	21.5	70.9	32.5	70.9	39.5	70.9	42
„		95.4	25	95.4	37	95.4	45.4	95.4	50

Similar results have been obtained with these concentrations of silver nitrate in the case of gels of 1, 2, 3 and 4 per cent. agar and of concentrations of sodium chloride ranging from 5N to 0.1N. But the same results are obtained when the range of silver nitrate concentrations is extended in the lower direction to the limiting concentration which is necessary for the silver chloride to be precipitated, as the following tables show.

Table IX. Penetration of 0.5N sodium chloride into gels of 0.5 per cent. agar containing various concentrations of silver nitrate.

0.05N AgNO ₃		0.025N AgNO ₃		0.005N AgNO ₃	
Time	Penet.	Time	Penet.	Time	Penet.
in hrs	in mm.	in hrs	in mm.	in hrs	in mm.
3.75	10.0	3.75	12	3.75	15
23.0	26.4	23.0	30	23.0	39
28.8	30.0	28.8	34	28.8	43.5
46.9	38.0	46.9	43	46.9	60
71.2	47.1	71.2	54		

Table X. Penetration of sodium chloride of initially normal concentration into 0.5 per cent. gels of agar containing various concentrations of silver nitrate.

0.005N AgNO ₃		0.001N AgNO ₃		0.0005N AgNO ₃		0.0001N AgNO ₃	
Time	Penet.	Time	Penet.	Time	Penet.	Time	Penet.
in hrs	in mm.	in hrs	in mm.	in hrs	in mm.	in hrs	in mm.
2.92	13.5	2.75	16.0	2.70	16.6	2.65	18.6
20.3	37.2	20.2	44.2	20.07	47.0	Precipitation of silver chloride not obvious after this time	
27.6	43.8	27.45	51.8	27.32	55		
44.25	54.7	44.1	66.0	44.1	75		
70	70	69.8	70				

These results show that in the lowest concentrations usable the concentration of silver nitrate in the gel influences the march of diffusion of sodium chloride through the gel. Thus von Fürth and Bubanović's comparison of the diffusion of chlorides and sulphates into gels containing unknown quantities of silver nitrate and barium nitrate as indicators is not legitimate.

Fig. 3. Penetration of sodium chloride of initially normal concentration into gels containing different concentrations of silver nitrate as indicated.

C. Influence of the concentration of the gel.

No conclusive evidence could be obtained by the indicator method of any influence of the concentration of the gel on the march of diffusion. The results shown in Table XI are representative of a large number of series of experiments.

In this particular series the march of diffusion was slightly more rapid in the 0.5 per cent. agar than in more concentrated gels. In other series on the contrary it was slightly less rapid in the 0.5 per cent. gel than in others, while in yet other cases the penetration was quicker in gels of intermediate concentration than in gels of either the weakest or strongest concentrations. The

conditions are perhaps complicated by the action between the gel itself and the silver nitrate. If for instance a 2 per cent. agar gel combines with more silver nitrate than a 1 per cent. gel containing the same amount of silver nitrate, the concentration of silver salt able to combine with the chlorion of the sodium chloride may be less, and as has already been shown in the previous section of this paper the concentration of silver nitrate influences the rate of penetration of the sodium chloride into the gel. Loeb [1918] has recently brought forward evidence of the combination of silver nitrate with gelatin, and the colour change which sometimes takes place when silver nitrate is added to agar gels suggests that chemical compounds or adsorption compounds are produced. The method of preparing the gel probably influences the action between the agar and silver nitrate.

Table XI. Penetration of sodium chloride of initial concentration $2N$ into agar gels of various concentrations containing $0.05N$ $AgNO_3$.

0.5 per cent. agar		1 per cent. agar		2 per cent. agar		3 per cent. agar		4 per cent. agar	
Time in hrs	Penet. in mm.	Time in hrs	Penet. in mm.	Time in hrs	Penet. in mm.	Time in hrs	Penet. in mm.	Time in hrs	Penet. in mm.
2.25	10	2.25	9.5	2.28	9.5	2.28	9.0	2.32	9.5
4.35	14	4.35	13.2	4.38	13.5	4.38	13	4.42	13
22.8	34.2	22.8	31	22.8	30.5	22.8	30.2	22.8	31.5
28.4	38.2	28.4	35	28.6	35	28.6	34	28.6	34
46.8	51	46.8	45	46.8	45	46.9	44	46.9	44.2

Under these circumstances the indicator method cannot be expected to yield very exact information as to the influence of the concentration of the gel on the rate of penetration of sodium chloride into the gel. This is a question which has already been the subject of a number of researches to which attention has been directed in the introduction to this paper. The divergent conclusions of Voigtländer working with chlorides diffusing in agar gels and Öholm on the diffusion of potassium chloride into gelatin are sufficient evidence of the unsettled state of this question.

D. The influence of the concentration of silver nitrate in the gel considered in relation to the effect of concentration of the penetrating salt on the march of diffusion.

In part A of the present section of this paper it has been shown that the rate of penetration of the gel by sodium chloride depends on the concentration of the penetrating salt, and in part B it is shown that it is also dependent on the concentration of silver nitrate. It is of importance to consider these two influences in conjunction, that is, how far the differences produced by varying the concentration of sodium chloride are affected by the concentration of silver nitrate in the gel.

In comparing the penetrating power of sodium chloride under different conditions it may be recalled that the penetration (P) is approximately proportional to the square root of the time (t) so that $P/\sqrt{t}$ is a constant for the

penetration of sodium chloride into any particular gel. It may be called the penetration factor. In the following tables are shown the values of $P/\sqrt{t}$ for a number of agar gels containing quantities of silver nitrate varying from N to $0.05N$, with external solutions of sodium chloride of initial concentrations varying from $5N$ to $0.1N$.

Table XII. Values of $P/\sqrt{t}$ for different concentrations of sodium chloride and silver nitrate.

1 per cent. agar.						
	2N NaCl	N NaCl	0.5N NaCl	0.2N NaCl	0.1N NaCl	
N AgNO ₃	—	—	—	-2.54	-3.75	
0.5 N "	4.802	2.64	1.44	-1.161	-2.64	
0.2 N "	5.16	4.00	2.68	1.44	0.235	
0.1 N "	5.58	4.65	3.56	2.56	1.37	
0.05N "	6.64	4.97	4.21	2.93	1.93	

2 per cent. agar.						
	5N NaCl	2N NaCl	N NaCl	0.5N NaCl	0.2N NaCl	0.1N NaCl
N AgNO ₃	3.825	—	—	—	-2.37	-4.06
0.5 N "	—	3.416	2.38	1.40	-1.327	-2.56
0.2 N "	—	4.50	3.59	2.65	1.35	0.00
0.1 N "	—	5.35	4.49	3.58	2.16	1.02
0.05N "	7.08	6.07	5.40	4.49	3.24	2.13

3 per cent. agar.						
	5N NaCl	2N NaCl	N NaCl	0.5N NaCl	0.2N NaCl	0.1N NaCl
N AgNO ₃	4.14	2.46	1.04	0	-2.44	-3.92
0.5 N "	5.16	3.71	2.47	1.51	-0.814	-2.59
0.2 N "	—	4.39	3.69	2.63	1.09	-1.00
0.1 N "	6.87	5.43	4.39	3.52	2.17	0.816
0.05N "	—	6.05	5.28	4.40	3.23	1.68

4 per cent. agar.						
	5N NaCl	2N NaCl	N NaCl	0.5N NaCl	0.2N NaCl	0.1N NaCl
N AgNO ₃	5.15	2.85	1.34	—	-2.09	-3.44
0.5 N "	6.91	3.70	2.54	1.565	-1.23	-2.64
0.2 N "	6.75	4.56	3.70	2.825	1.395	-0.982
0.1 N "	7.50	5.54	4.93	3.875	2.45	0.663
0.05N "	7.78	5.98	5.23	4.32	3.21	1.83

An inspection of the numbers in this table indicates that there is no suggestion of differences among them due to variation in the concentration of the gel, and differences in the corresponding numbers in the different tables are in strong probability best described as due to experimental error. The fairest way of considering them is to take the mean values of the corresponding numbers in the four sets of results. These mean values are shown in Table XIII.

In Table XIV are shown the values of the penetration factor obtained in two other series of experiments in which the concentration of silver nitrate

in the gel varied in one case between 0.05*N* and 0.005*N* and in the other between 0.005*N* and 0.0005*N*.

Table XIII. Values of $P/\sqrt{t}$ for different concentrations of sodium chloride and silver nitrate.

Mean values of the four sets of determinations recorded above.

	5 <i>N</i> NaCl	2 <i>N</i> NaCl	<i>N</i> NaCl	0.5 <i>N</i> NaCl	0.2 <i>N</i> NaCl	0.1 <i>N</i> NaCl
<i>N</i> AgNO ₃	4.37	2.65	1.19	0	-2.36	-3.79
0.5 <i>N</i> „	5.53	3.91	2.51	1.48	-1.13	-0.261
0.2 <i>N</i> „	6.75	4.65	3.745	2.70	1.32	-0.437
0.1 <i>N</i> „	7.18	5.475	4.615	3.63	2.335	0.967
0.05 <i>N</i> „	7.43	6.185	5.22	4.355	3.15	1.89

Table XIV. Values of $P/\sqrt{t}$ for different concentrations of sodium chloride and silver nitrate.

(a) 0.5 per cent. agar.

	1.2 <i>N</i> NaCl	0.5 <i>N</i> NaCl
0.05 <i>N</i> AgNO ₃	6.08	5.56
0.025 <i>N</i> „	6.96	6.29
0.005 <i>N</i> „	8.44	8.12

(b) 0.5 per cent. agar.

	1.2 <i>N</i> NaCl	<i>N</i> NaCl	0.2 <i>N</i> NaCl	0.1 <i>N</i> NaCl	0.05 <i>N</i> NaCl
0.005 <i>N</i> AgNO ₃	8.44	8.27	6.63	5.82	4.86
0.001 <i>N</i> „	10.02	9.88	8.41	7.72	6.94
0.0005 <i>N</i> „	10.71	9.96	9.17	8.56	7.84

From an examination of these tables certain facts are made clear. In the first place it is evident that the rate of penetration depends very much on the ratio of the concentrations of the penetrating sodium chloride and the silver nitrate in the gel. When the concentration of the latter is higher than that of the former the sodium chloride does not penetrate into the gel, but the silver nitrate on the contrary diffuses out into the sodium chloride solution, and if the experimental tubes remain unshaken, an advancing boundary of silver chloride is seen in contact with the pure sodium chloride solution. This is indicated in the tables by the minus sign. This being the case it might be expected that when the initial concentration of the penetrating liquid is only slightly higher than the concentration of silver nitrate in the gel penetration would only take place to a slight extent, for when withdrawal of sodium chloride by the silver nitrate has taken place to such an extent that its average concentration is reduced to that of silver nitrate in the unaltered part of the gel, no further penetration is possible. This is actually found to be the case. It is perfectly clear that such cases as these are not allowed for in the equation of von Fürth and Bubanović. It is also evident that with decrease of the silver nitrate content of the gel the relative difference in the penetration factor due to differences in concentration of the invading salt rapidly decreases. Thus with 0.1*N* silver nitrate the ratio of the penetration factors of 0.2*N* and

0.1*N* sodium chloride is 2.335 : 0.967. With 0.0005*N* silver nitrate this becomes 9.17 : 8.56. Earlier in this paper it has been pointed out that von Fürth and Bubanović's equation connecting time, distance, penetration and initial concentration of the penetrating salt cannot be accepted.

An approximate relation between the concentration, penetration and time becomes clear however on inspection of Fig. 4. Here the data given in Tables XIII and XIV (*b*) are represented graphically, the values of $P/\sqrt{t}$ being plotted against the logarithms of the concentrations. It will be observed that the relation between $P/\sqrt{t}$ and $\log c$ is approximately linear in the case

Fig. 4. The relation between the penetration factor ($P/\sqrt{t}$) and the initial concentration (c) of the penetrating salt in the case of a number of agar gels containing various concentrations of silver nitrate as indicated on the diagram.

of all the gels examined, these containing quantities of silver nitrate varying from *N* to 0.0005*N* and the initial concentrations of sodium chloride varying from 5*N* to 0.05*N*. This approximately linear relation between $P/\sqrt{t}$ and $\log c$ is thus of wide applicability. It must however only be regarded as a working approximation.

The equation connecting the penetration (that is the distance a definite concentration of sodium chloride has reached), time, and initial concentration of salt may therefore be written in the form

$$\frac{P}{\sqrt{t}} = k \log c + k',$$

where k and k' are constants for any particular gel, in which is involved the factor depending on the concentration of silver nitrate in the gel. It is almost unnecessary to point out that although the penetration factor is dependent on the initial concentration of the penetrating salt this has no bearing on the question whether the coefficient of diffusion is influenced by concentration. For the penetration means no more than the distance between the starting-point of diffusion and a layer of a certain definite, if low, concentration. If the coefficient of diffusion is uninfluenced by concentration, the penetration will obviously be greater in the case of an initially high concentration of penetrating salt than in one of low concentration.

SUMMARY.

1. The penetration of sodium chloride into agar gels has been followed by the indicator method. When silver nitrate is present in the gel the entrance of sodium chloride into the gel is marked by the formation of silver chloride, and the progress of the chloride into the gel is indicated by the movement forward of the sharp line of demarcation between the silver chloride in the gel and the unprecipitated silver salt. The distance this line of demarcation has moved forward in any time is called the penetration. It marks the position of a definite concentration of chloride, namely, the saturation concentration of silver chloride.

2. The penetration of sodium chloride into agar gels containing silver nitrate is within wide limits proportional to the square root of the time. If P is the penetration in a time t , the value $P/\sqrt{t}$ is thus a constant for any particular gel and any particular concentration of penetrating salt, and may be called the *penetration factor*.

3. The rate of penetration is dependent upon the initial concentration of the penetrating salt, the higher the concentration of salt the more rapid the penetration.

4. The rate of penetration depends also on the concentration of the silver nitrate in the gel; the higher the concentration of silver nitrate, the lower the rate of penetration.

5. The concentration of the gel itself appears to exercise little influence on the rate of penetration, but owing to the probability of actions between the silver salt and the gel and hence doubt as to the real active concentration of silver salt in the gel, which, as stated in the preceding paragraph, influences the rate of penetration, the influence of concentration of the gel must be left an open question. In any case the influence cannot be great in gels containing between 1 and 4 per cent. agar.

6. The expression obtained by von Fürth and Bubanović to indicate the relation between the penetration, time, and concentration of penetrating salt only holds in very special cases and between very narrow limits, and is then only a crude approximation.

7. An empirical relation between these quantities of more general application is

$$\frac{P}{t^{\frac{1}{2}}} = k \log c + k',$$

where P is the penetration, t the time and c the initial concentration of the penetrating salt. The value of the constant k depends principally on the nature of the penetrating salt, and also, although to a slight extent, on the nature of the gel contents, while the value of k' depends principally on the concentration of silver nitrate in the gel.

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