LXXVI. THE PENETRATION OF ELECTROLYTES INTO GELS.

IV. THE DIFFUSION OF SULPHATES IN GELS.

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INTRODUCTION.

It is a curious fact relating to the nutrition of plants that plant tissue appears to absorb chlorides and nitrates to a considerably greater extent than sulphates. This phenomenon appears to be very general. Thus Wodehouse [1917] found chloride abundant in the marine alga *Valonia*, whereas sulphate was absent from it, although abundant in the sea water in which the alga was growing. Stiles and Kidd [1919] found that sulphates were absorbed to a much less extent than chlorides and nitrates by potato tuber and carrot root. The investigations of Pantanelli [1915, 1918] on a large number of plants point to the same conclusion with regard to root absorption. This state of affairs is the more surprising as sulphur is an essential element for the plant, whereas many plants are able to thrive if unprovided with chlorine in any form.

It would appear to be significant in regard to the apparent difficulty of absorption of sulphates by plants as compared with the absorption of chlorides, that a similar difference has been observed in the matter of the penetration of these salts through precipitation membranes [Traube, 1867; Tammann, 1892; Walden, 1892] and membranes of collodion [Brown, 1915].

It thus would seem possible that the small quantity of sulphate that enters living plant tissue as compared with the quantity of chloride and nitrate, might be due to the different degrees of difficulty of sulphates on the one hand, and chlorides and nitrates on the other, in passing through colloidal membranes, of the protoplast [*see* Stiles, 1921]. It becomes of interest, therefore, to determine whether the diffusion of sulphates in gels presents any anomalous features similar to those presented in their diffusion through membranes, which might help to explain the unexpected phenomenon of their comparatively slight absorption by plant tissue.

The only recorded observations on the diffusion of sulphates in gels appear to be those of von Fürth and Bubanović [1918] who used agar-agar containing barium nitrate as an indicator. They did not calculate coefficients of diffusion

from their results, nor do they provide the data to enable this to be done absolutely, but instead they calculate a quantity called by them the "invasion factor," which should be approximately proportional to the square root of the coefficient of diffusion.

From the data of earlier workers von Fürth and Bubanović have calculated the coefficients of diffusion in water at 18° of the substances with which they worked. In Table I are collected the numbers they quote for sulphates together with the invasion factors they found for the same substances and the coefficients of diffusion obtained by taking the squares of the invasion factors.

Table I. Coefficients of diffusion at 18° of some sulphates in water and in 2 % agar-agar containing barium nitrate. (Calculated from the data of von Fürth and Bubanović, the coefficient of diffusion of sodium chloride being taken as unity.)

Sulphate	Invasion factor in gel	Coefficient of diffusion in gel	Coefficient of diffusion in water
Hydrogen sulphate	0.98	0.96	1.33
Potassium sulphate	1.06	1.12	0.74
Zinc sulphate	0.74	0.55	0.48
Magnesium sulphate	0.67	0.45	0.50
Ammonium sulphate	0.67	0.45	0.76

These results exhibit no sort of relation between the coefficients of diffusion in the gel and in water. It has, however, already been pointed out in the first paper in this series [Stiles, 1920], that von Fürth and Bubanović neglect the influence of the concentration of the indicator in their experiments, although this influences very considerably the invasion factor, and consequently the coefficient of diffusion calculated from it. A fresh series of determinations of the coefficients of diffusion of a number of sulphates in gels of gelatin and agar-agar has therefore been made; the values obtained are recorded in a subsequent section of this paper.

METHOD.

The method employed was that outlined in the third paper in this series [Stiles and Adair, 1921]. Gels of 0.5 % agar-agar and 10 % gelatin were employed, and barium chloride in 0.01 *N* concentration by weight was used as the indicator in the gel. The solutions of sulphates employed were in normal concentration. The experiments were carried out in thermostats maintained at 0° and about 20.5°.

In calculating the coefficients of diffusion from the experimental data, the more exact of the two formulae obtained by Adair [1920] was employed. For this purpose the coefficient of diffusion of barium chloride was assumed to be 0.76×10^{-5} c.g.s. units under the experimental conditions. Although exact data of this constant do not exist, such values for the coefficient of

diffusion of barium chloride as have been obtained indicate the value used as approximately correct. Even a 50 % error in the value of the constant introduces only a very slight error in the calculated coefficient of diffusion, and it is safe to conclude that any error arising from an assumption of an incorrect value for the coefficient of diffusion of barium chloride is negligible.

EXPERIMENTAL RESULTS.

The sulphates employed were those of ammonium, potassium, sodium, magnesium and copper. The experimental data are summarised in Table II.

Table II. Penetration of various sulphates from a *N* solution into gels of agar-agar and gelatin containing barium chloride as indicator. (Concentration of barium chloride in the gel, 0.01 *N*; time in hours; penetration in centimetres of precipitate; diffusion coefficient *k* in c.g.s. units $\times 10^5$.)

Diffusing salt	Gel	Temperature ° C.	Time	Penetration	<i>k</i>
(NH ₄) ₂ SO ₄	0.5 % agar	0	22.36	2.220	0.474
"	"	20.3	23.45	3.202	0.920
"	"	"	47.68	4.599	0.932
"	10 % gelatin	20.5	22.66	2.748	0.706
"	"	"	46.87	3.955	0.706
K ₂ SO ₄	0.5 % agar	0	22.28	2.218	0.475
"	"	20.3	23.44	3.200	0.918
"	10 % gelatin	20.5	22.67	2.745	0.704
"	"	"	46.90	3.924	0.695
Na ₂ SO ₄	0.5 % agar	0	22.45	1.920	0.355
"	"	20.3	23.69	2.937	0.770
"	"	"	47.60	4.213	0.787
"	10 % gelatin	20.5	22.70	2.515	0.593
"	"	"	46.90	3.615	0.593
MgSO ₄	0.5 % agar	0	22.12	1.657	0.269
"	"	20.0	20.39	2.192	0.502
"	"	"	45.30	3.316	0.517
"	10 % gelatin	20.5	22.60	2.002	0.384
"	"	"	46.80	2.872	0.382
CuSO ₄	0.5 % agar	0	22.20	1.793	0.314
"	"	20.0	20.25	2.276	0.545
"	"	"	45.23	3.439	0.557
"	10 % gelatin	20.5	22.74	1.796	0.311
"	"	"	46.95	2.592	0.314

A first glance at these results as they stand shows that the coefficient of diffusion is considerably raised with increase of temperature from 0° to 20°; that at the same temperature diffusion is much more rapid in 0.5 % agar than in 10 % gelatin, and that the coefficients of diffusion of different substances in the gels are roughly parallel to the coefficients of diffusion in water. Each one of these questions will now be considered more in detail.

1. *Influence of temperature.*

If we assume, as is usually done, that the coefficient of diffusion increases with rise of temperature according to a linear relation between diffusivity and temperature, we have the following equations for the coefficient of diffusion of the various salts examined at any temperature θ lying between 0° and 20° .

Salt	Coefficient of diffusion at θ° C.
Ammonium sulphate	$0.474 (1 + 0.0463 \theta)$
Potassium sulphate	$0.475 (1 + 0.0463 \theta)$
Sodium sulphate	$0.355 (1 + 0.0592 \theta)$
Magnesium sulphate	$0.269 (1 + 0.0446 \theta)$
Copper sulphate	$0.314 (1 + 0.0382 \theta)$

The increase in the rate of diffusion for rise of temperature of 1° relative to the coefficient of diffusion at 0° thus varies somewhat with different salts, being least for copper sulphate and greatest for sodium sulphate. The numbers are however all of the same order. The value of this quantity in the case of the diffusion of sodium chloride in 0.5 % agar at temperatures between 0° and 20° is however much the same, namely 0.0385, as that for copper sulphate. It is clear that the influence of temperature on the diffusion of sulphates in agar gels presents no unusual features.

2. *Influence of gel concentration.*

In the previous paper of this series the influence of the concentration of the gel on the diffusion of sodium chloride was investigated over a wide range of gel concentrations. In order to determine whether the effect is similar in the case of sulphates it was considered sufficient to carry out experiments with a thin gel of low concentration (0.5 % agar) and a stiff gel of moderately high concentration (10 % gelatin). The values previously obtained with sodium chloride indicate that with that salt the coefficient of diffusion in 0.5 per cent. agar is about 1.3 times that in 10 % gelatin at the same temperature. The ratios of the coefficients of diffusion of the sulphates examined in 0.5 % agar and 10 % gelatin at 20.5° are as follows:

Ammonium sulphate ...	1.31	Magnesium sulphate ...	1.34
Potassium sulphate ...	1.31	Copper sulphate ...	1.78
Sodium sulphate ...	1.32		

With the exception of copper sulphate, the relation between the coefficients of diffusion in 0.5 % agar and in 10 % gelatin is much the same in all the sulphates examined, and in sodium chloride. Copper sulphate forms a very conspicuous exception to the rule in that the coefficient of diffusion is relatively much greater in 0.5 % agar than would be expected from the rate of diffusion in 10 % gelatin.

3. *Comparison of the coefficients of diffusion in gels and in water.*

The observations that have been made in the past on the diffusion of sulphates in pure water have been made at a number of differing temperatures

and with very varied concentrations of diffusing salts. A comparison between the actually observed rates of diffusion in gels and water cannot therefore be made. However from the results obtained for the coefficient of diffusion of sulphates in 0.5 % agar at 0° and 20°, it is at once possible to obtain by interpolation the values for the coefficient of diffusion in this gel at the temperatures used in earlier investigations on diffusion in pure water. In the following Table are shown, for the sulphates examined in this investigation, the values of the coefficients of diffusion in pure water and in 0.5 % agar-agar at the same temperature. The concentrations of the diffusing salts are not always the same, but the coefficients of diffusion in pure water tabulated are those for the concentration of salt nearest to normal, that used in the experiments with gels. Observations made by Öholm [1905] on other salts suggest that generally decrease in concentration results in an increase in the coefficient of diffusion, but the influence of concentration is not very great over small ranges of concentration.

Table III. Comparison of the coefficients of diffusion of various sulphates in water and in 0.5 % agar-agar. (Coefficient of diffusion, k , in c.g.s. units $\times 10^5$; concentration of salt in diffusion in gels N in all cases; concentration of salt in diffusion in water given in normalities in fifth column.)

Diffusing salt	Temperature °C.	k in gel	k in water	Concentration in normalities of salt in diffusion in water	Observer of k in water
$(\text{NH}_4)_2\text{SO}_4$	18	0.869	0.880	2.0	{ Lang—Hedin— von Fürth and Bubanović
K_2SO_4	19.6	0.903	{ 0.995 0.914	{ 0.56 1.9	
Na_2SO_4	10.4	0.574	0.567	2.58	Graham-Stefan
MgSO_4	{ 5.5 10	{ 0.335 0.389	{ 0.37 0.394	{ 1.08 0.80	Scheffer
CuSO_4	17	0.518	0.336	1.00	
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The numbers presented in this Table show conclusively that, with the exception of copper sulphate, the values for the coefficient of diffusion of the sulphates in 0.5 % agar are very close to those for diffusion of the same salts in pure water. The evidence is that the coefficient in agar is slightly less than in pure water, as would be expected from the increased viscosity in the gel.

CONCLUSION.

From the results of this study of the diffusion of a number of sulphates in gelatin and agar-agar gels, it appears evident that, with the single exception of copper sulphate, the diffusion of sulphates in gels presents the same features as that of sodium chloride. Diffusion proceeds almost as rapidly in 0.5 % agar-agar as in pure water, while in 10 % gelatin the diffusion coefficient is reduced about 25 %. The influence of temperature is similar to that on the coefficient of diffusion of sodium chloride. Copper sulphate, on the other hand, shows

an abnormally large coefficient of diffusion in 0.5 % agar-agar, although the coefficient of diffusion of this salt in 10 % gelatin bears more nearly, though not exactly, the same relation to the coefficient of diffusion in water as the other salts examined. This is a very curious phenomenon for which at present no explanation can be offered, but which certainly deserves further investigation.

A reference to Table I of this paper shows that the results of von Fürth and Bubanović indicate that the coefficients of diffusion of potassium sulphate and zinc sulphate are greater, and that of ammonium sulphate considerably less, in a 2 % agar-agar gel than in pure water. The more exact determinations recorded in this paper show clearly that such a divergence between diffusion of these sulphates in water and in gels does not exist.

The comparatively small intake of sulphates by plant tissue is therefore not to be explained on account of any abnormal behaviour of these salts in diffusing through colloidal systems. Further evidence in this direction is forthcoming from the observations of Stiles and Kidd [1919] in which it was shown that the plant tissue examined absorbs sulphates *initially* faster than either chlorides or nitrates, but that the rate of absorption of sulphate falls off very much more rapidly than that of chloride or nitrate. It would thus appear that it is a question of equilibrium in a chemical combination, or in adsorption, that limits the intake of sulphates, rather than any retardation owing to a particularly slow rate of diffusion, or to a change brought about by the sulphate on the colloidal system as such which renders it much more resistant to the passage of the ions.

SUMMARY.

The coefficients of diffusion of a number of sulphates in 0.5 % agar-agar and 10 % gelatin have been determined by the indicator method. In the cases of the sulphates of ammonium, potassium, sodium and magnesium the coefficient of diffusion in 0.5 % agar-agar is very close to, though slightly less than, that in pure water at the same temperature and for the same concentration of diffusing salt, while the coefficient of diffusion in 10 % gelatin is about 25 % less than in 0.5 % agar-agar. The diffusion coefficient of copper sulphate in 0.5 % agar-agar is considerably greater than in water, but in 10 % gelatin it is smaller than in water but yet somewhat higher than the values obtained for other sulphates would indicate. Increase of temperature from 0° to 20° increases the diffusion coefficient about 1.76 to 2.2 times according to the salt. These effects are of the same order as in the case of sodium chloride.

Except in the case of copper sulphate the diffusion of sulphates in the gels examined proceeds normally and the results of von Fürth and Bubanović indicating the contrary are not confirmed.

The comparatively small uptake of sulphates by plant tissue is not to be explained on the basis of retarded diffusion through a gel.

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