DIFFUSION OF IONS THROUGH SOME INDIAN TIMBERS

BY D. NARAYANAMURTI AND R. S. RATRA
(*Forest Research Institute, Dehra Dun*)

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DIFFUSION processes play an important part in various timber industries, *e.g.*, the treatment of veneers with resins or resin forming systems, preservatives like boric acid, etc. For efficient treatment it is essential that the fundamental laws governing the movement of ions, molecules, etc., through wood are established. A knowledge of these factors is also of interest to the wood seasoning, textile, leather, and paper technologists and the plant physiologist.

Cady and Williams (1935) studied the diffusion of urea, glycerol and lactose into several species of water-saturated soft woods relative to their diffusion in water. More recently the diffusion of salts through green timber has been extensively studied by Christensen in Australia.

THEORETICAL

Fick's law of diffusion can be mathematically expressed as follows:—

$$q = k\frac{dc}{dx}, \tag{1}$$

where q is the quantity of the substance flowing through in gm./cm.^{2} sec. at the steady state, k the diffusion constant and $\frac{dc}{dx}$ the concentration gradient. k has the dimensions cm.^{2}/sec. This applies to capillary systems. In the case of space energy systems (pores of molecular dimensions) the concentration at the two surfaces of the membrane are not the same as that in the reservoir and a relation between reservoir and surface concentrations depending on a Henry distribution exists and $\frac{dc}{dx} = \mathrm{T}\frac{dc'}{dx}$ where T is the distribution coefficient.

APPARATUS

The apparatus employed is shown in Fig. 1. In essentials it consists of 2 chambers made from perspex sheeting with flanges between which the specimen under investigation is fixed, rubber washers being used between the

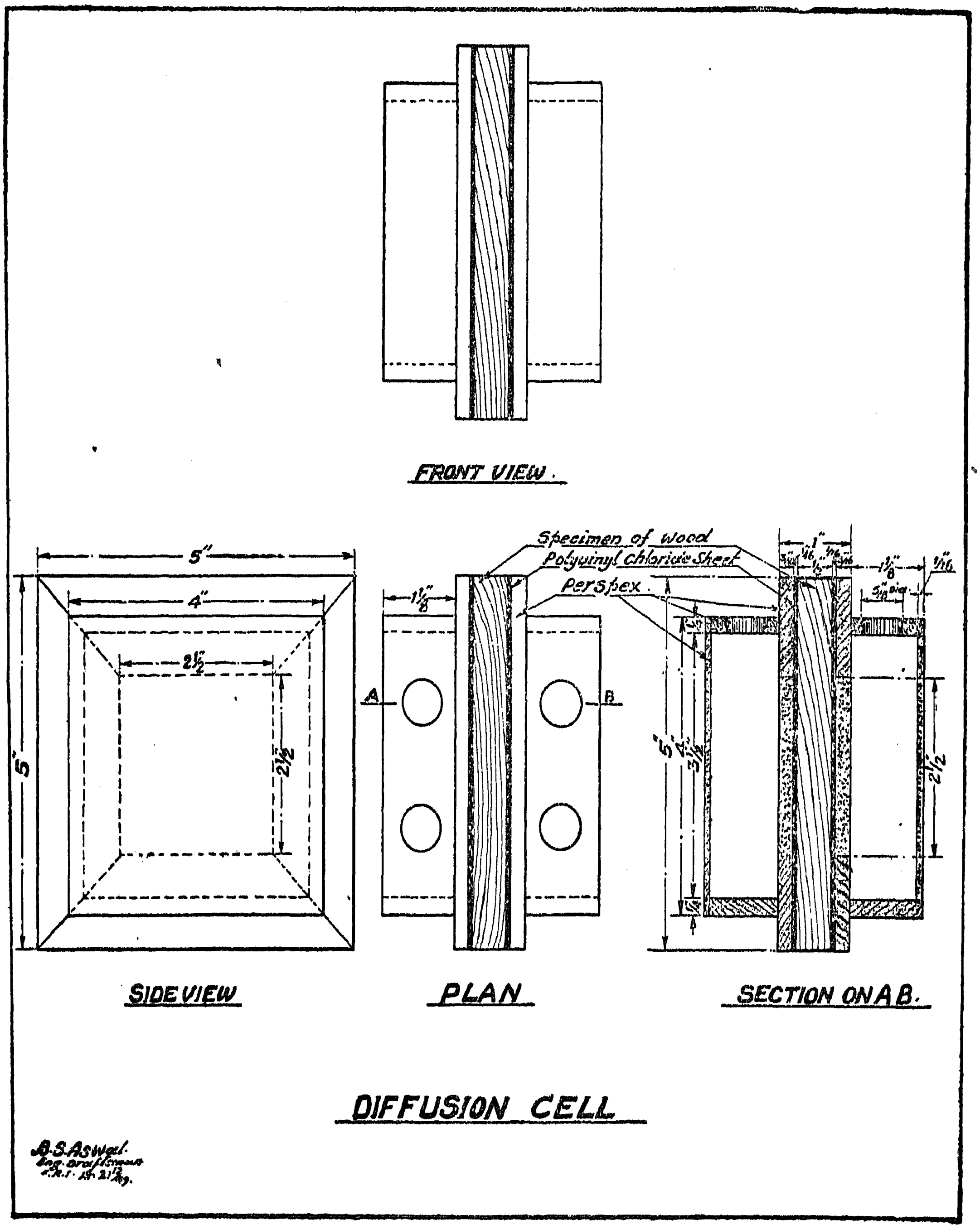

FIG. 1

flanges and the specimen. The tops of the two halves of the diffusion cells were provided with two holes for receiving or emptying the solution or water used in the cells. These were stoppered with a fine capillary to avoid evaporation during the test.

The specimen was placed between the flanges of the cell and the whole assembly was held in a wooden frame fitted with nuts and bolts. Rubber packing between the cell walls and wooden frame helped to prevent damage to the cells.

MATERIALS AND PREPARATION OF THE SPECIMENS

Canarium strictum (dhup) and *Cullenia excelsa* (karani) were used for most of the experiments.

Specimens were prepared from different locations in 8″ thick discs of the timbers.

They were cut and planed to the size required and were kept under water till wanted for use. Before fitting in the cells, the outer half inch of the edges of the specimens were given three coats of shellac varnish to prevent end leakage. They were further given a coat of paraffin and in other cases thin aluminium foil was used.

In addition to wood, cellophane was also studied.

PROCEDURE OF CARRYING OUT THE TESTS

After installation of the test specimen in the diffusion cell both compartments of the cell were first filled with distilled water and kept in an air thermostat for a day; the next day the cells were emptied and then one side was filled with distilled water and the other side with the solution of the salt. It is necessary, especially with axial specimens, to pour both the solution and water at the same time and at the same rate, otherwise there is a danger of flow from one side to the other. The holes in the top were then lightly corked and the cells kept in the air thermostat.

At intervals of 24 hours the cells were emptied (again care being taken to empty both sides simultaneously and at the same rate) and analysed according to standard practice. This was continued till the steady state was reached.

From the analytical and other data the diffusion coefficient was calculated according to equation (1).

RESULTS AND DISCUSSION

The results of all the experiments are given in Tables I–III and Figs. 2 and 3.

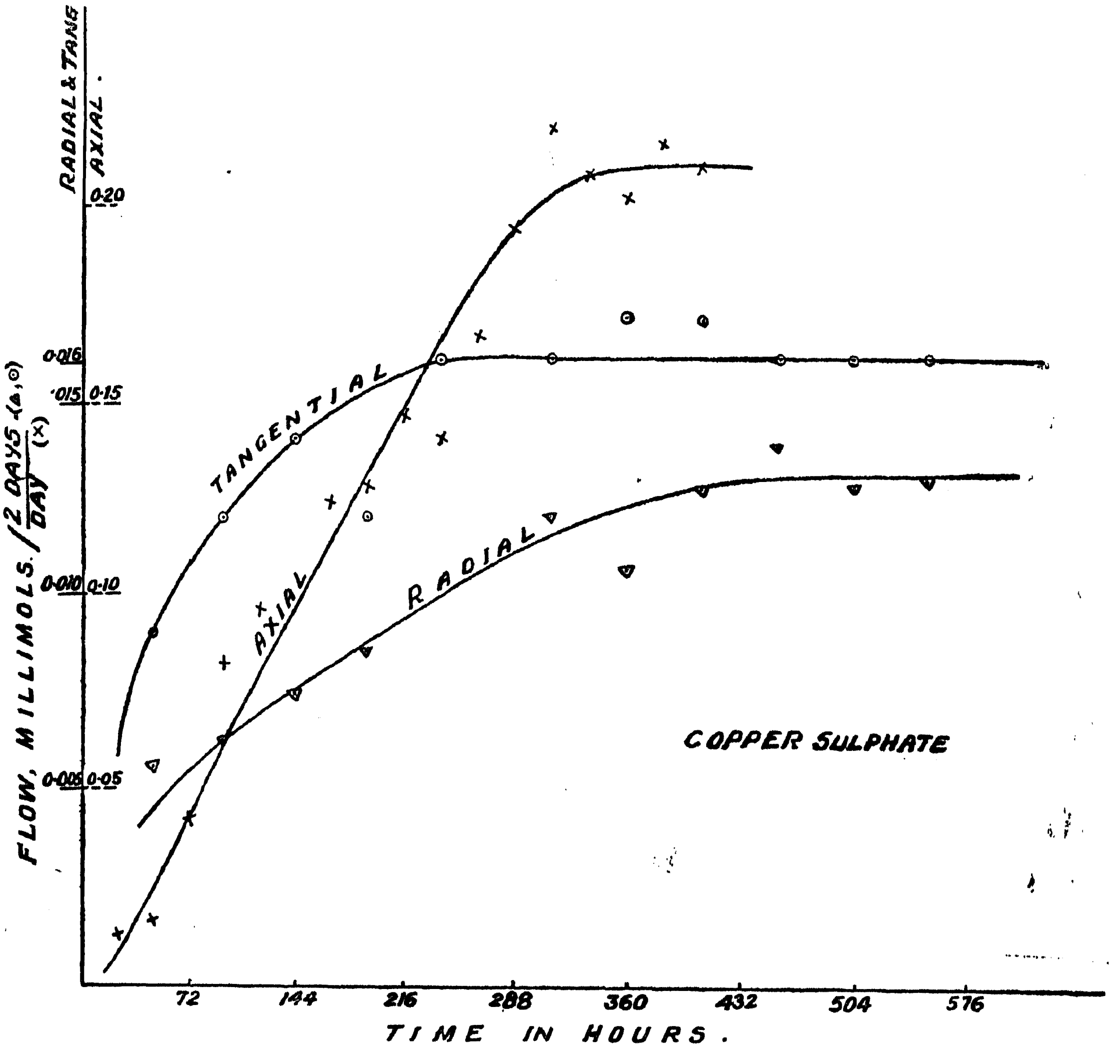

FIG. 2

Time taken to reach steady state.

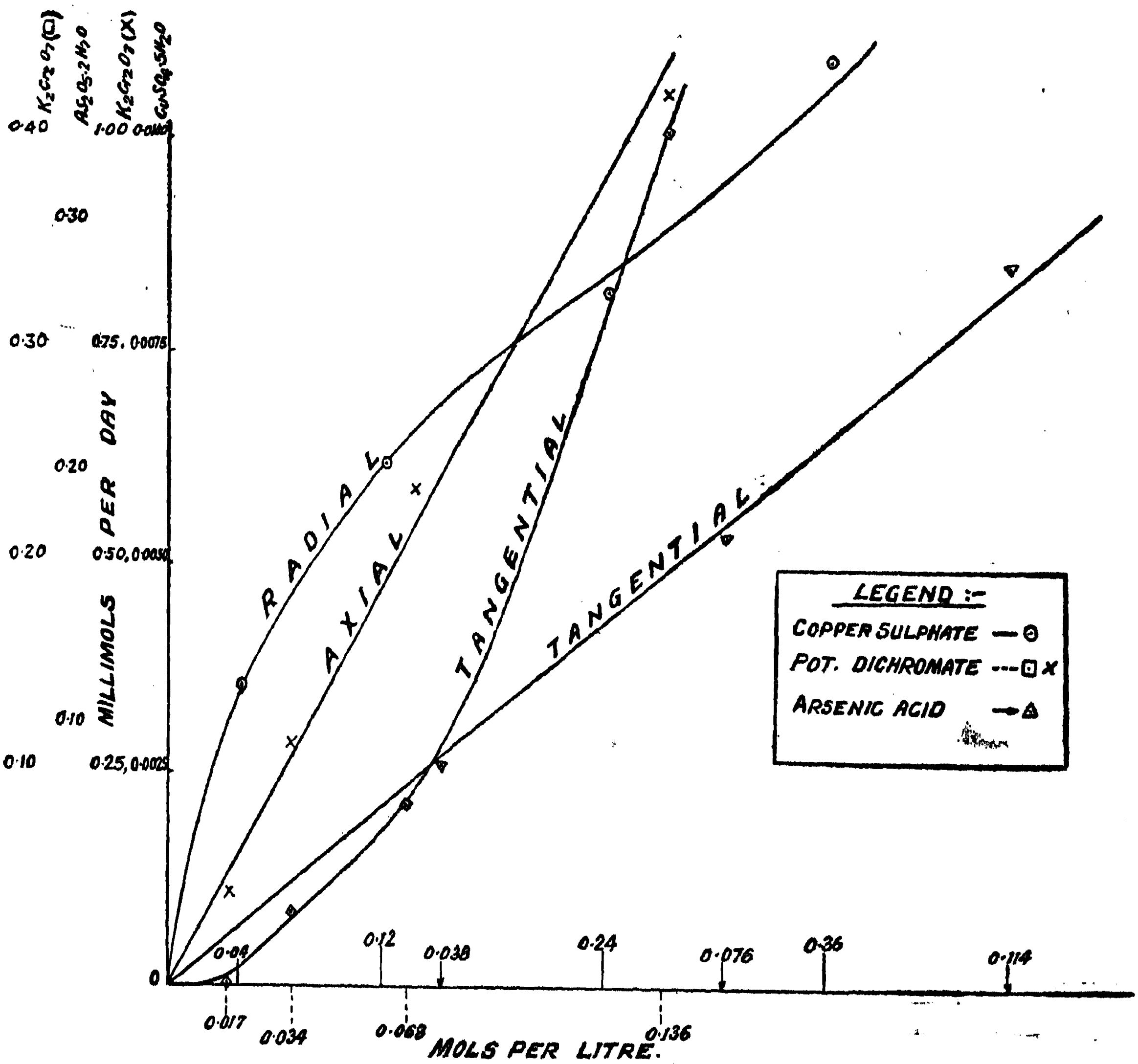

FIG. 3.

Y – AXIS - Quantity diffusing through per day at the steady state.

X - AXIS - Concentration difference across the membrane.

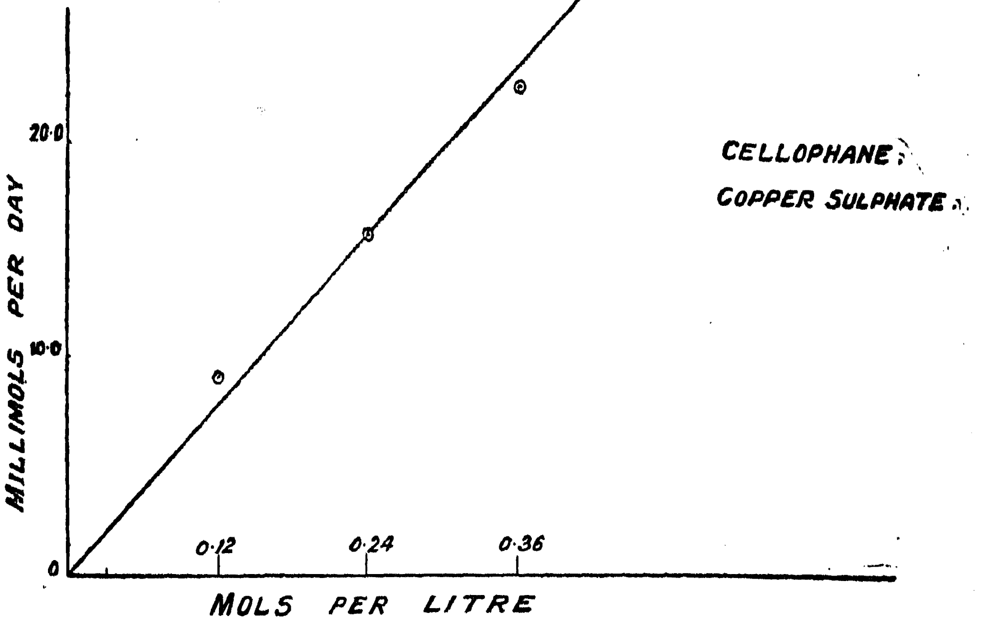

Table I illustrates the influence of increasing concentration gradient on the diffusion constant.

TABLE I

Species and direction of flow	Concentration difference mols./litre	K cm.^{2}/day
1	2	3
	Sodium chloride	
1 *Canarium strictum* Axial II (10)	0·2, 0·4, 1·0, 2·0, 4·0	0·229, 0·380, 0·349, 0·320, 0·267 Mean = 0·309
do I (10)	do	0·233, 0·350, 0·349, 0·326, 0·281 Mean = 0·308
2 *Boswellia serrata* Radial	1·0	0·00136
	Copper sulphate	
3 *Canarium* sp. Axial I (11)	0·04, 0·12, 0·24, 0·36	0·474, 1·235, 0·523, 1·105 Mean = 0·834
4 *Canarium* sp. Axial II (10)	do	*Nil, 0·039, 0·031, 0·112 Mean = 0·061
5 *Canarium* sp. Axial III Unleached (9)	do	0·0398, 0·0607, 0·0663, 0·134 Mean = 0·0752
6 *Canarium* sp. Radial I (3)	do	*Nil, 0·00019, 0·00013, 0·00011 Mean = 0·00014
7 Do II (4)	do	*Nil, 0·00023, 0·00015, 0·00019 Mean = 0·00019
8 *Canarium* sp. Radial III (7) unleached	do	0·00039, 0·00023, 0·00015, 0·00014 Mean = 0·00023
9 *Canarium strictum* Tangential I (12)	do	*Nil, 0·00014, 0·00012, 0·00013 Mean = 0·00013
do II (15)	do	*Nil, 0·00016, 0·00017, 0·00016 Mean = 0·00016
	Potassium dichromate	
10 *Canarium strictum* Axial I (10)	0·017, 0·034, 0·068, 0·136	0·0094, 0·036, 0·059, 0·034 Mean = 0·0346
do II (11)	do	0·261, 0·299, 0·344, 0·309 Mean = 0·303
11 *Cullenia excelsa* Radial I (7)	do	0·0152, 0·0196, 0·0175, 0·0168 Mean = 0·0173
do II (2)	do	0·00156, 0·00525, 0·00759, 0·00525 Mean = 0·00491
12 *Cullenia excelsa* Tangential I (3)	do	0·00048, 0·00668, 0·00798, 0·0188 Mean = 0·00849
do II (8)	do	0·00013, 0·0024, 0·0025, 0·0036 Mean = 0·00216
	Arsenic acid	
13 *Canarium strictum* Axial I (11)	0·038, 0·076, 0·114	0·409, 0·425, 0·414 Mean = 0·416
do II (9)	do	0·205, 0·208, 0·218 Mean = 0·210
14 *Cullenia excelsa* Radial I (6)	do	0·059, 0·0645, 0·070 Mean = 0·0645
do II (7)	do	0·0658, 0·0663, 0·0709, Mean = 0·0677
15 *Cullenia excelsa* Tangential I (5)	do	0·0255, 0·0249, 0·0245 Mean = 0·025
do II (4)	do	0·0161, 0·0148, 0·0157 Mean = 0·0155

* The nil values hove not been considered for the mean.

The agreement between duplicates is satisfactory in the case of sodium chloride (No. 1). The diffusion coefficient is within the limits of experimental error independent of the concentration gradient excepting for the lowest and highest gradients. In the former case the rather low values may be due to the low amounts diffusing through, with consequent inaccuracies in determination, and in the latter case the large amounts diffusing and thus bringing the real gradient to less than 4·0 and also the noticeable osmotic effects in this case.

From the results (Table II, item 2) given it will be seen that unlike the diffusion of moisture in wood (*vide* Martley, Egner, Narayanamurti) and diffusion of dyestuffs in cellulose (Neale, *et al.*, 1938), the diffusion of salt is independent of the salt concentration as far as sodium chloride is concerned.

To investigate the influence of thickness, the same specimen was used for all the four thicknesses investigated. At the end of the experiment with the largest thickness the specimen was planed down to the next thickness, this procedure being repeated for the other thicknesses. The results (Table II) show the validity of Fick's law.

TABLE II

Sodium Chloride—Effect of Thickness

Species and direction of flow	Thickness cm.	K cm.^{2}/day
	Effect of thickness	
1 *Canarium strictum* Axial I (10)	1·241, 1·146, 0·958, 0·745	0·349, 0·361, 0·352, 0·392 Mean = 0·363

Effect of constant gradient

	Concentration			
	Higher	Lower	1	2
2 *Canarium strictum* Axial (10)	1·0	0·5	0·458	0·490
	1·5	1·0	0·442	0·430
	2·0	1·5	0·447	0·467
	2·5	2·0	0·465	0·478
			Mean = 0·453	0·466

Christensen obtained a diffusion constant of $3 \cdot 38 \times 10^{-3}$ cm.^{2}/day at 70° F. and $6 \cdot 84 \times 10^{-3}$ cm.^{2}/day at 110° F. for *Eucalyptus obliqua* across the grain, no results for diffusion along the grain being available. *Salai* (Table I, 2) appears to be less permeable than *Eucalyptus*.

Influence of the type of ion diffusing

The results for copper sulphate axial flow (Table I, 3, 4 and 5) are irregular and show wide variation with different concentration gradients. Whether this is due to precipitation, swelling, adsorption, pH changes, etc., that may be caused, only further experiments can say. In the case of tangential flow the constants agree within 15% in one case and 7% in the other. The variation is higher for radial flow.

The closer agreement for tangential flow may be due to the extremely low permeability of these specimens. The unleached specimen for radial flow, however, shows erratic results, the diffusion constant decreasing with increasing gradient. Possible reaction of the solution with wood constituents may be one of the major causes of this deviation from Fick's law (*vide* Christensen). Stiles (1920, etc.) also found that the diffusion coefficient decreases with concentration of reacting ions in gels.

This is further strengthened by results obtained with cellophane in place of wood. The results are shown in Fig. 3. The constancy of the diffusion coefficient is good. Cellophane is more permeable than *Canarium* across the grain.

The erratic behaviour noticed with potassium dichromate (Table I, 10 to 12) also is possibly due to the reaction and precipitation of chromium.

As can be seen from the results reported, Fick's law is obeyed irrespective of species and direction of flow with arsenic acid (Table I, 13, 14, 15). This is probably due to the fact that unlike copper sulphate and potassium dichromate this substance is not precipitated in wood. The high value of the diffusion coefficient may be due to the high acidity. Christensen's work showed increased diffusion of sodium chloride with decreasing pH. It would be interesting to study the diffusion of H_3AsO_4; or H_2NaAsO_4; Na_2HAsO_4 and Na_3AsO_4 to see the influence of pH.

Ascu

With Ascu (Table III) the tendency of the constant to increase with the concentration can be noticed in the case of copper sulphate and potassium dichromate, even though not to the same extent as with the pure chemicals.

TABLE III

Ascu

Species and direction of flow	Concentration difference in mols./litre w.r.t.			K cm.^{2}/day w.r.t.		
	KCr_2O_7	$CuSO_4 5H_2O$	$As_2O_5 2H_2O$	$K_2Cr_2O_7$	$CuSO_4 5H_2O$	$As_2O_5 2H_2O$
Cullenia excelsa	0·068	0·06	0·019	0·058	0·056	0·068
Radial (7)	0·136	0·12	0·038	0·112	0·127	0·136
Do II (6)	do	do	do	0·023	0·016	0·025
				0·038	0·035	0·037
Cullenea excelsa	do	do	do	0·0008	Nil	Nil
Tangential I (4)				0·002	Nil	Nil
Do II (5)	do	do	do	0·0015	Nil	Nil
				0·003	0·0025	Nil
Canarium strictum	do	do	do	0·31	0·31	0·31
Axial I (9)				0·47	0·46	0·36
Do II (9)	do	do	do	1·12	1·11	1·41
				1·25	1·35	1·35

Another interesting point to note is that the diffusion constant for the three constituents is almost the same.

Influence of temperature

The results for 3% copper sulphate at three temperatures are given below:

Species and direction of flow	Temperature °C.	K cm.^{2}/day	Temperature coefficient	
			30/20	40/30
Canarium sp.				
Axial I (9)	20, 30, 40	0·327, 0·388, 0·438	1·19	1·13
			Mean = 1·16	
Do II (9)	do	0·176, 0·214, 0·248	1·22	1·16
			Mean = 1·19	
Cullenia excelsa				
Tangential I	do	0·0082, 0·0114, 0·0143	1·39	1·25
			Mean = 1·32	
Do II	do	0·0094, 0·012, 0·015	1·28	1·25
			Mean = 1·27	

As is to be expected, the diffusion constant increases with temperature, the increase being greater with *Cullenia* specimens than with *Canarium* specimens. Christensen found a temperature coefficient of 1·38 for 10° C. for sodium chloride and *Eucalyptus* which was constant between 70° F. and 150° F.

In the present tests there is a slight decrease in the temperature coefficient with rise in temperature, which may be due to the fact that any reaction of the constituents of wood with copper sulphate is likely to be more, the higher the temperature.

Influence of direction of flow, etc.

The species investigated being hardwoods the longitudinal permeability, as is to be expected, is much more than that across the grain.

Copper sulphate diffuses through *Canarium* in the axial direction several hundred times that in the direction across the grain. The radial permeability is higher than the tangential. Christensen found the radial diffusion to be 2 to 4 times the tangential for some Australian species. With *Cullenia excelsa* the radial permeability is about 5–10 times the tangential permeability for potassium dichromate and 3–4 times for arsenic acid.

In contrast to Christensen, who believes that there is no difference between heartwood and sapwood, our results indicate that specimens near or in the heartwood are less permeable than those running into the sapwood. For example, the diffusion of copper sulphate in the axial direction is several times more in the sapwood (Table I, 3) than in the heartwood (Table I, 4). In the radial and tangential directions also the specimens nearer the heart are more resistant. Similar behaviour is noticeable with potassium dichromate and arsenic acid.

Comparison with the results of other investigators

As earlier remarked, apart from the work of Christensen very little work has been done on the subject. The present results point to the extreme complexity of the problem. While with substances like sodium chloride and arsenic acid, which do not react with the constituents of wood, it is easy to predict the depth of diffusion under definite conditions, it will not be so with various wood preservatives and other chemicals, which chemically undergo transformation in wood. The study of various individual chemicals and mixtures of chemicals may help in the selection of chemicals for diffusion treatments. Work on various organic molecules, resin forming substances, etc., is in progress in this laboratory.

SUMMARY

A simple diffusion cell (which can be easily constructed from perspex sheeting) for studying the passage of molecules, ions, gases, vapours and liquids through wood and other membranes is described.

The diffusion of ions through some species of Indian timbers under variety of conditions has been studied and the results reported.

The results show that the diffusion of ions through wood obeys Fick's law as long as the ion does not react with any constituents of the wood. In other cases there is deviation from this law. The diffusion constant is largest in the axial direction and smallest in the tangential direction. As against other claims, for the species tested, ionic diffusion is higher through sapwood than through heartwood. Temperature increases the rate of diffusion of ions. Diffusion of copper sulphate through cellophane is in conformity with Fick's law and is of the same order as for some timbers.

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