

*The Rate of Absorption of Various Phenolic Solutions by Seeds of Hordeum vulgare, and the Factors Governing the Rate of Diffusion of Aqueous Solutions across Semipermeable Membranes.*

By ADRIAN J. BROWN, F.R.S., and FRANK TINKER, M.Sc.

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It has been pointed out previously\* that the seeds of *Hordeum* (barley) are enclosed by a membrane which exhibits the exceptional property of differential permeability, and that use may be made of this property of the seeds for the purpose of investigating some of the obscure phenomena associated with osmosis.†

When the dry seeds are immersed in aqueous solutions of most inorganic acids and salts, sugars, etc., water only passes through the containing membrane and moistens their starchy contents; with other classes of solutes, however, such as the phenols, fatty acids, and monohydric alcohols, the solute enters the seeds together with water. A dry seed of *Hordeum* may be regarded, therefore, as a diffusion system consisting of a mass of solid material capable of absorbing moisture, enclosed within a differentially permeable membrane. In the presence of those solutes which do not enter the seed-diffusion-system along with the solvent the action of its membrane is comparable to that of a copper-ferrocyanide membrane in contact with sugar solution. On the other hand, in the presence of those solutes which do enter the seed-diffusion-system together with the water, its membrane evidences a property of selective permeability only recognised to any extent with living protoplasm, and with the coverings of certain seeds.

Previous investigations carried out by methods of experiment already described have demonstrated that when seeds of *Hordeum* are immersed in solutions of solutes to which the seeds are impermeable, less water enters the seeds than from pure water, and that the actual amount entering is

\* A. J. Brown, "On the Existence of a Semipermeable Membrane enclosing the Seeds of some of the Gramineæ," 'Annals of Botany,' vol. 21, p. 79 (1907); "The Selective Permeability of the Coverings of the Seeds of *Hordeum vulgare*," 'Roy. Soc. Proc.,' B, vol. 81, p. 82 (1909); A. J. Brown and F. P. Worley, "The Influence of Temperature on the Absorption of Water by Seeds of *Hordeum vulgare*," 'Roy. Soc. Proc.,' B, vol. 85, p. 546 (1912).

† The seed of the sub-species of *Hordeum* (barley) known as *Hordeum vulgare* has been found especially suitable for experimental purposes, and has been employed in the following investigation.

regulated, in the main, by the osmotic pressure of the solution in which the seeds are immersed—a condition normal to the behaviour of any semi-permeable diffusion system.

On the other hand it has been demonstrated that with solutions of those solutes which are able to diffuse through the seed membrane there is a general tendency not only for more moisture to enter the seeds than from pure water itself, but also for the rate of entry of the moisture to be accelerated to an extent varying with both the nature of the solute and the concentration of its solution.

The factors controlling the rate of entry of moisture into the seeds provide a promising subject for investigation, but so far the influence of temperature only has been studied. It has been shown in a previous communication\* that the rate of entry of moisture into the seeds from both pure water and solutions of permeable and impermeable solutes is an exponential function of the temperature with a very high coefficient closely approximating that of vapour pressure, and also of a number of chemical reactions occurring in solution. But this conclusion provides no explanation of the interesting observation that the rate of entry of moisture into the seeds from solutions of permeable solutes varies with the nature of the solute when the solutions are at constant temperature and of equimolecular concentration. Presumably the explanation of this is to be found in the variation in the physical properties of the different solutes when in solution, and it was with the object of discovering, if possible, with which of the physical properties of the solutions the rate of absorption is associated, that the present research was undertaken. Such properties as are likely to exert an influence on the absorption rate are evidently ionisation, osmotic pressure, vapour pressure, viscosity, and surface tension.

Preliminary experiments showed that the phenols would form a most suitable series of solutes for the purpose of the present comparative study. The membrane of the barley seed is permeable to them all; they show striking differences among themselves with regard to some of their physical properties, whilst other of their properties are almost equal, and they have a negligible ionisation when in solution, so that consideration of this latter factor is eliminated when dealing with them. The solutions chosen for the present research accordingly comprised those of phenol, catechol, resorcinol, quinol, and pyrogallol.

Three series of comparative experiments were made with the above phenolic solutions:—

(a) In the first series samples of seed were steeped in seminormal

\* Brown and Worley, *loc. cit.*

solutions of phenol, catechol, resorcinol, quinol, and pyrogallol at 19° C. Thus the nature only of the steeping solution was different, the temperature and molecular concentration being the same in each case.

(b) The second series of solutions was exactly similar to the above, except that the steeping temperature was increased to 32.2° C. This series was chosen in order to determine what difference would be made to the relative rates of absorption by increasing the temperature, whilst keeping all the other factors the same.

(c) In the third series the various samples were steeped in solutions of ordinary phenol of various strengths at 22.6° C., in order to determine the effect of altering the concentration of a given solution at a constant temperature.

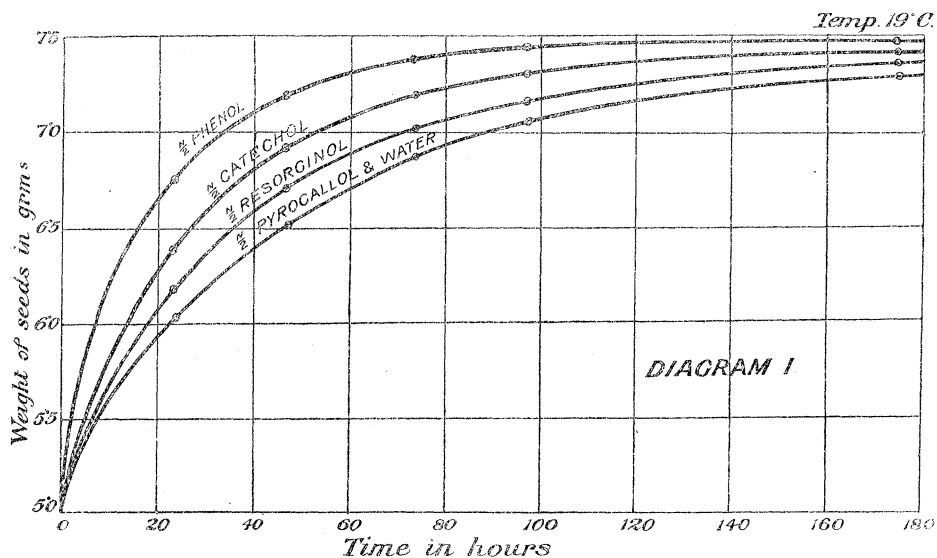
*Experimental Determination of the Increase in Weight when the Seeds are Immersed in the Various Solutions.*

(a) *Seeds in Seminormal Phenolic Solutions at 19° C.*—In this series the solutions were made of equivalent strength (half molar by volume in each case). Since they contained equal numbers of solute molecules their osmotic pressures were consequently equal.\* Notwithstanding this fact, however, the rate at which the solution is absorbed varies greatly. This is shown in Table I and its corresponding curve, expressing the weight of the original 5 gramm. of seeds after stated intervals.

Table I.—Temperature 19° C.

Time from beginning of experiment.	Weight of seeds immersed in					
	Water.	N/2 phenol.	N/2 catechol.	N/2 resorcinol.	N/2 quinol.	N/2 pyrogallol.
0 hours	5.00	5.00	5.00	5.00	5.00	5.00
1 "	5.11	5.13	5.12	5.10	5.13	5.16
24 "	6.08	6.73	6.31	6.11	6.15	6.08
48 "	6.56	7.22	6.91	6.66	6.69	6.58
72 "	6.94	7.38	7.24	7.07	7.06	6.96
96 "	7.15	7.44	7.33	7.25	7.29	7.21
7 days	7.31	7.50	7.37	7.39	7.40	7.38

\* Assuming, of course, that dilute solutions of equal molecular concentration have equal osmotic pressures. This is only so absolutely when the solutions have also equal heats of dilution and evaporation and equal surface tensions, and when the degree of association of the solvent is the same in each case (Findlay, 'Osmotic Pressure,' Chap. V).



An inspection of the above Table, and its corresponding curve, shows that the rate of absorption gradually falls off in each case as the equilibrium point is reached. But it will be seen also that the time in which equilibrium is attained is considerably shorter for the phenolic solutions than for water. Each of the phenols, with the exception of pyrogallol, exerts a marked accelerating effect on the rate at which its solution is absorbed, the order in which they do this being—(1) phenol, (2) catechol, (3) resorcinol and quinol, (4) pyrogallol and water. The rates of absorption for solutions of resorcinol and quinol, on the one hand, and pyrogallol and water on the other, are practically identical.\*

(b) *Seeds in Seminormal Phenolic Solutions at 32.2° C.*—In this series all the essential factors were kept the same as in the previous series, with the exception that the temperature was raised from 19° C. to 32.2° C. A small rise in temperature is accompanied by a great increase in the velocity of moisture absorption. This greatly increased rate is shown in Table II. Whereas the equilibrium is attained only after six or seven days at a temperature of 19° C., it is reached after two or three days at 32.2° C.†

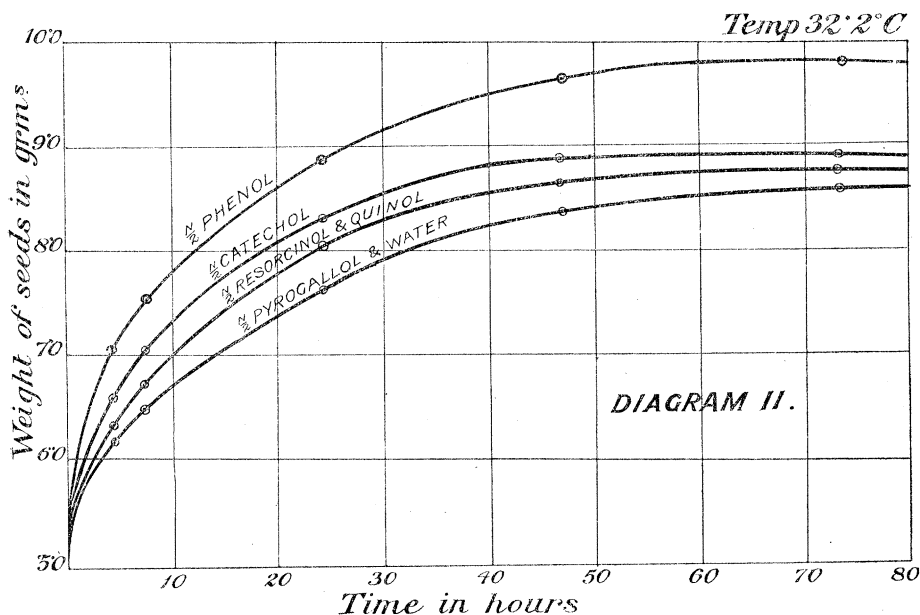
\* It is also worthy of note that a high rate of absorption also seems to be accompanied by a slight raising of the equilibrium point; for instance, the weight of phenol absorbed by the seeds when these are in equilibrium with the surrounding solution is 0.2 gm. greater than the weight of water absorbed at equilibrium. This figure is too great to be accounted for by the slightly greater density of seminormal phenol solution.

† The comparison is only a rough one, since the samples of seeds were different ones in the two cases, and the initial moisture-content different also. But it has been shown elsewhere (Brown and Worley, *loc. cit.*) that the velocity of absorption is an exponential function of the temperature, which increases very rapidly.

But, in spite of this general increase in the velocity of absorption, the relative rates at which the solutions are taken up remains the same at 32·2° C. as at the lower temperature. All the phenolic solutions, with the exception of pyrogallol, are absorbed at a greater rate than pure water.

Table II.—Temperature 32·2° C.

Time from beginning of experiment.	Weight of seeds immersed in					
	Water.	N/2 phenol.	N/2 catechol.	N/2 resorcinol.	N/2 quinol.	N/2 pyrogallol.
hours.	gram.	gram.	gram.	gram.	gram.	gram.
0	5·00	5·00	5·00	5·00	5·00	5·00
2	5·99	6·36	6·08	5·99	5·99	5·95
5	6·41	7·03	6·53	6·49	6·49	6·41
8	6·74	7·52	6·94	6·88	6·84	6·74
15	7·26	8·29	7·55	7·45	7·46	7·27
24½	7·77	8·85	8·12	8·04	8·03	7·78
48	8·43	9·30	8·72	8·62	8·65	8·48
72	8·69	9·37	8·86	8·80	8·80	8·71

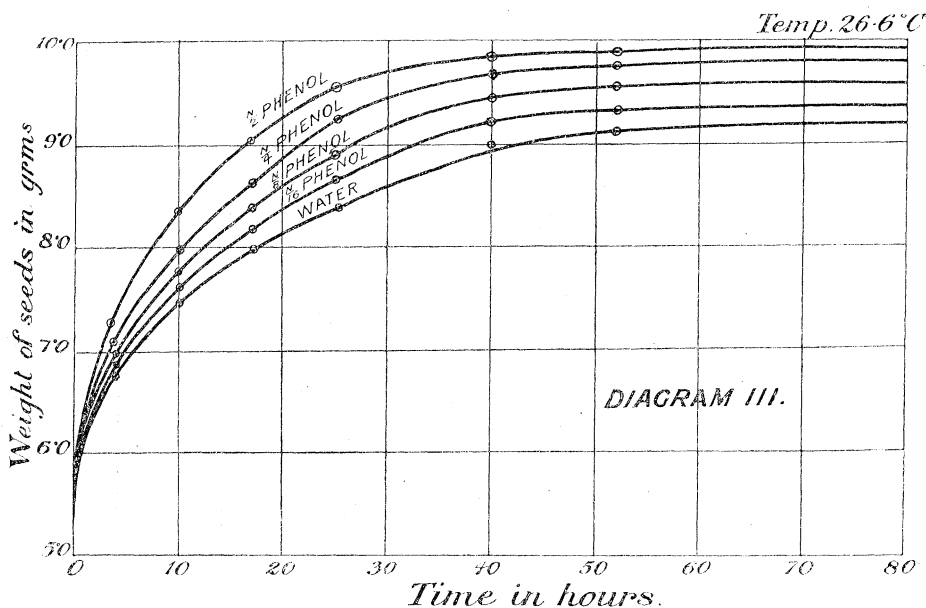


(c) *Seeds in Solutions of Ordinary Phenol of Various Concentrations at 26·6° C.*—As might be expected, the accelerating effect of phenol on the rate of absorption is diminished when the amount dissolved is diminished. This is shown in Table III and the corresponding diagram. The accelerating effect is most marked in the case of seminormal phenol, and the rate of

absorption gradually approaches that of water as the dilution is increased. When the concentration has been reduced to thirty-secondth normal, the velocity of absorption of the solution is practically equal to the rate at which pure water is taken up.

Table III.—Temperature 26·6° C.

Time from beginning of experiment.	Weight of seeds immersed in					
	N/2 phenol.	N/4 phenol.	N/8 phenol.	N/16 phenol.	N/32 phenol.	Water.
hrs.	gm.	gm.	gm.	gm.	gm.	gm.
0	5·00	5·00	5·00	5·00	5·00	5·00
4	7·18	7·03	6·93	6·85	6·78	6·75
10	8·22	7·97	7·80	7·68	7·50	7·46
18	8·95	8·66	8·52	8·34	8·10	8·04
25½	9·35	9·02	8·90	8·72	8·41	8·39
40	9·71	9·38	9·24	9·13	8·96	8·92
51½	9·86	9·47	9·35	9·26	9·19	9·15



*The Accelerating Effect of the Phenols on the Rate of Absorption is not due to Disruption of the Membrane.*

It might be argued that the remarkably high velocity of absorption of the phenolic solutions by the barley seeds, as compared with water, is due to the

complete or partial disruption of the semipermeable membrane by the solutions. That this is not so was shown in the following way:—

After each sample of seeds had attained fulness in the various seminormal phenolic solutions at 19° C., they were slowly and carefully dried in air at about 30° C. The samples were next immersed in pure water in each case, and the rate of absorption of the pure water determined in the same way as when the seeds were in the phenolic solutions. It is evident that, if any sample had been damaged, it would have absorbed water more quickly than the sample originally in pure water. It was found, however, that the rate of absorption was almost exactly the same in every case as the rate for the sample originally in pure water. A comparison of the corresponding weights, after stated intervals of the two samples originally in water and seminormal phenol, is given in Table IV.

Table IV.—Temperature 19° C.

Time from beginning.	Weight in pure water of seeds originally immersed in		Difference.
	Water.	N/2 phenol.	
days.	gm.	gm.	gm.
0	4·71	4·74	0·03
1	6·10	6·25	0·15
2	6·61	6·71	0·10
3	6·92	6·95	0·03
4	6·97	7·02	0·05
7	6·97	7·10	0·13

It is apparent that the weight differences between the seeds originally in N/2 phenol and water respectively are comparatively small, and within the experimental error involved in prolonged manipulation—losses in weight being caused by numerous dryings with a cloth.

*Discussion of the Absorption Curves.*

(1) *Equation to the Absorption Curves—*

It has been pointed out already that the rate at which the seeds absorb any solution is dependent on the amount of solution which has previously entered them (their degree of fulness), as well as on the nature of the solution. In order to find the mathematical relationship existing between the absorption rate and the degree of fulness, tangents were drawn to each of the curves in Diagrams 1, 2, and 3 at points where the seeds had attained definite weights

*e.g.* 6·5, 7·0, 7·5, 8·0 gm.\* Table V shows the rate of entry of each of the solutions, in grammes per hour, when the original 5 gm. of seeds have increased in weight to the given extent.

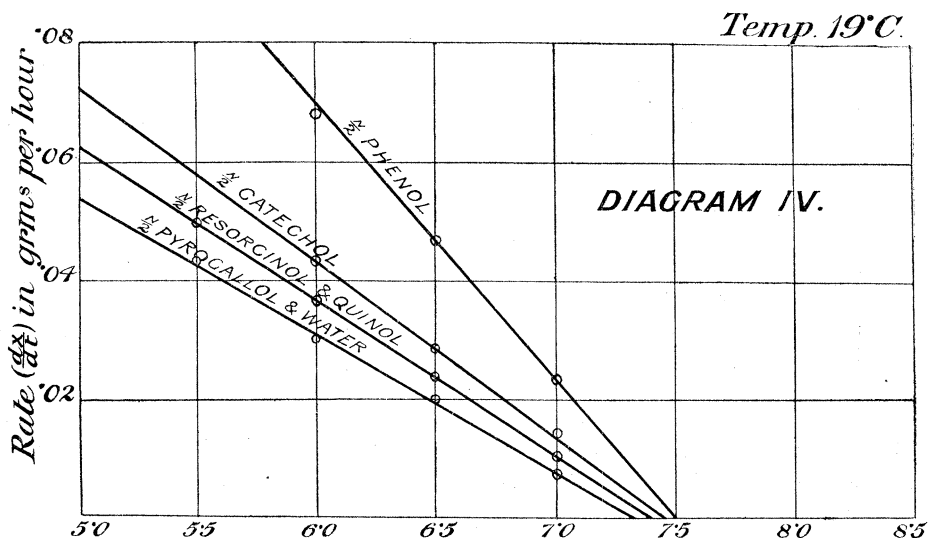
Table V.—Showing the Rate of Absorption (in grammes per hour) of the Various Solutions when the Seeds have attained given Weights.

Weight to which original 5 gm. seeds have attained.	Rate of entry (in grammes per hour) of—					
	Pure water.	N/2 phenol.	N/2 cate- chol.	N/2 resor- cinol.	N/2 quinol.	N/2 pyro- gallol.
(a) Seminormal Phenolic Solutions at 19° C.						
gram. 5·5	0·044	—	—	0·050	0·050	0·046
6·0	0·031	0·068	0·042	0·036	0·035	0·031
6·5	0·020	0·047	0·026	0·022	0·022	0·020
7·0	0·009	0·021	0·015	0·012	0·014	0·011
(b) Seminormal Phenolic Solutions at 32·2° C.						
6·5	0·100	0·245 ?	0·140	0·131	0·130	0·100
7·0	0·075	0·182	0·105	0·099	0·099	0·075
7·5	0·053	0·147	0·078	0·068	0·068	0·053
8·0	0·032	0·105	0·050	0·039	0·032	0·032
8·5	—	0·070	0·026	0·015	0·015	—
(c) Ordinary Phenol Solutions at 26·6° C.						
Weight to which original 5 gm. seeds have attained.	Rate of entry (in grammes per hour) of—					
	N/2 phenol.	N/4 phenol.	N/8 phenol.	N/16 phenol.	Water.	
gram. 7·0	0·245	0·205	0·170	0·155	0·120	
7·5	0·195	0·160	0·135	0·115	0·090	
8·0	0·150	0·115	0·105	0·085	0·060	
8·5	0·105	0·075	0·070	0·055	0·035	
9·0	0·065	0·035	0·030	0·025	0·010	

Diagram 4 shows graphically the results for the seminormal phenolic solutions at 19° C. The diagrams for the other solutions are exactly similar in form.

\* The rate of entry of the solution also falls off as the time proceeds, but this is obviously because they are all the while getting fuller. It is evident that the time is only a secondary factor ; the degree of fulness, as indicated by the weight to which the seeds have attained, being the fundamental one.





In the case of every solution studied, there is evidently a straight line relationship existing between the absorption rate and the degree of fulness. The rate of entry at any given time is therefore given by an equation of the type

$$dx/dt = k(a-x),$$

where

$dx/dt$  = rate of increase in weight (in grammes per hour) when the seeds have attained the weight  $x$ ;

$x$  = weight of the seeds after the interval  $t$ ;

$a$  = weight of the seeds at equilibrium;

$k$  = a constant for the solution at the given temperature and concentration.

The values of the constants  $k$  and  $a$  are given in Table VI.

Table VI.

	Temp. 19° C		Temp. 32·2° C.	
	$k$ .	$a$ .	$k$ .	$a$ .
(a) Seminormal Phenolic Solutions.				
Water .....	0·024	7·34	0·045	8·7
N/2 phenol .....	0·047	7·50	0·076	9·4
N/2 catechol .....	0·029	7·42	0·055	8·9
N/2 resorcinol .....	0·026	7·37	0·052	8·8
N/2 quinol .....	0·026	7·37	0·052	8·8
N/2 pyrogallol .....	0·024	7·34	0·045	8·7

Table VI—*continued*.

(b) Ordinary Phenol Solutions of Various Strengths at 26·6° C.		
	<i>k</i> .	<i>a</i> .
N/2 phenol .....	0·090	9·8
N/4 „ .....	0·082	9·5
N/8 „ .....	0·073	9·4
N/16 „ .....	0·064	9·3
Water .....	0·054	9·2

Since the relationship between the absorption rate and the degree of fulness is a linear one, it follows that the original experimental absorption curves are logarithmic.

Integration of the equation

$$dx/dt = k(a-x),$$

between the limits  $x$  and  $x_1$ , gives

$$\log_e \frac{a-x_1}{a-x} = k(t-t_1).$$

Taking  $x_1$  as the initial weight (5 gm.), this becomes (since  $t = 0$ )

$$\log_e \frac{a-5}{a-x} = kt.$$

This equation represents the experimental absorption curves with a high degree of accuracy. If the weight of the original 5 gm. of seeds after any given interval is calculated from it, there is rarely a difference exceeding two or three tenths of a gramme between the calculated and the actual experimental value. Table VII gives this comparison for the seeds immersed in water at 19° C., and also those steeped in N/2 phenol at the same temperature. The differences between the calculated and the experimental values are well within the experimental errors involved in weighing and drying the seeds.

The absorption equation for water at 19° C. is

$$\log_e \frac{2\cdot34}{7\cdot34-x} = 0\cdot024 t,$$

and for N/2 phenol

$$\log_e \frac{2\cdot5}{7\cdot5-x} = 0\cdot045 t.$$

Table VII.

Time from beginning of experiment.	Seeds in water at 19° C.			Seeds in N/2 phenol at 19° C.		
	Calculated.	Experimental.	Difference.	Calculated.	Experimental.	Difference.
hours.	gm.	gm.		gm.	gm.	
0	5·00	5·00	—	5·00	5·00	—
24	6·03	6·08	+0·05	6·64	6·73	+0·09
48	6·59	6·56	—0·03	7·20	7·22	+0·02
72	6·93	6·94	+0·01	7·40	7·38	—0·02
96	7·11	7·14	+0·03	7·46	7·44	—0·02

(2) *The Absorption Constant  $k$ , and the Interpretation of the Absorption Equation.*

The equation  $dx/dt = k(a - x)$  is worthy of consideration in more detail. It shows that the rate of absorption of a solution by the barley at any given instant is the product of two factors—the constant  $k$ , which depends on the nature of the solution, its temperature and concentration; and the degree of dryness ( $a - x$ ) of the seeds. These two separate factors are considered more fully below.

(a) *Effect of the Degree of Hydration of the Internal Contents of the Seeds on the Absorption Rate.*—The term  $a - x$  represents the difference between the equilibrium weight and the weight  $x$  at any given instant. It follows therefore, from the above equation, that when the seeds are surrounded by a solution of constant concentration and temperature, the rate of absorption of the solution by the barley is proportional to the weight of the solution which the seeds are still capable of absorbing before equilibrium is reached. For convenience this weight might be termed the degree of dryness of the seeds. The rate of absorption is a maximum when the seeds contain no moisture at all, and zero when the seeds are full.

The gradual falling off of the rate of absorption as the degree of fulness gets greater seems to be caused by the operation of a backward pressure,\* for it is evident that the solution would of itself tend to diffuse into the seeds at a constant rate, since its temperature and concentration remain the same throughout. But as it flows into the seeds, the gradually increasing vapour pressure of the hydrated starchy contents of the seeds opposes to a

\* The existence of this backward diffusion pressure is amply proved by the fact that wet seeds gradually give up their moisture in dry air, or when immersed in anhydrous alcohol, sulphuric acid, or other media to which the membrane is impermeable. The rate of diffusion of the moisture outwards gets less as the seeds get drier, and finally becomes zero.

progressively greater extent the forward diffusion pressure of the solution outside. The rate of absorption of the solution is at a maximum when the seeds are absolutely dry, because the backward pressure tending to make the solution diffuse out again is then zero. It is zero at equilibrium because the backward diffusion pressure has then become equal to the forward diffusion pressure of the solution outside.

(b) *Effect of the Nature of the Solution, etc., on the Absorption Rate: the Absorption Constant.*—It has been indicated already that, in order to compare the relative rates at which various solutions are absorbed by the seeds, equal degrees of fulness  $x$  should be chosen. But if  $x$  is given a constant value for all the solutions in any series, the value  $a-x$  for all the solutions will be the same also, since the magnitude of the equilibrium weight  $a$  is practically the same in every case (see Table VII). It would follow, therefore, that the relative rates of absorption of the various solutions at any given degree of fulness ( $x$ ) are proportional to their constants  $k$ . The constant  $k$  might hence be termed the absorption constant for the given solution. It gives a measure of the relative rate at which the solution will enter the seeds at all degrees of fulness. Thus, whatever weight the seeds may have attained, seminormal phenol always enters the seeds with about twice the velocity that water enters, since its absorption constant is about twice that of water.

An inspection of Table VI shows that the absorption constants of all the phenolic solutions are greater than that of water, with the exception of pyrogallol, which has a constant practically the same as that of water. The constant increases greatly in value with a slight rise in temperature. This increase is an exponential one rather than linear, being like vapour pressure in this respect. Indeed it has been shown\* that the curves showing the relationship between the rate of entry of water into the seeds and the temperature can almost be superposed on the vapour pressure-temperature curves for water, either being represented by the equation

$$v = ce^{\kappa\theta},$$

where  $v$  represents either the velocity of absorption of water or the vapour pressure, and  $\theta$  the temperature,  $k$  and  $c$  being constants.

Since it has now been shown that the rate of absorption is always proportional to the absorption constant, it follows that the latter is an exponential function of the temperature, *i.e.*

$$k \propto ce^{\kappa\theta},$$

where  $\kappa$  has the same value as in the temperature-vapour pressure curves. In other words, if a series of temperatures be chosen, the absorption

\* A. J. Brown and F. P. Worley (*loc. cit.*).

constants of any solution at those temperatures are approximately proportional to the corresponding vapour pressures. This result would seem to suggest that there is intimate relationship between the absorption constant and the vapour pressure of a solution. It will be shown later that there is also a close connection between the absorption constant and the surface tension. Apparently the absorption constant is one of the most important constants for a solution in contact with a selectively permeable membrane.

*Relation between the Rate of Diffusion of the various Phenolic Solutions across the Barley Membrane and the Physical Properties of the Solutions.*

It appeared to be of interest to correlate the rate of absorption with the common physical properties which might exert an influence on the rate of diffusion of a solution across the barley membrane. Such properties were evidently osmotic pressure, vapour pressure, viscosity and surface tension. Accordingly these properties were measured for the solutions in question, with the exception of osmotic pressure. The latter was taken as being practically identical for the seminormal phenolic solutions.\* Any slight differences there might be in them were obviously unable to account for the great variations noticed in the magnitude of the absorption constants. Further, if the osmotic pressure of the solution were the predominating factor in determining the rate of diffusion across the membrane, the osmotic pressures of the phenolic solutions ought to be negative, since they diffuse across the membrane at a greater rate than pure water. The existence of a solution with a negative osmotic pressure is most unlikely.†

(a) *Surface Tensions of the Solutions.*—The surface tensions of the solutions were measured by the capillary tube method, using a similar apparatus to that employed by R. P. Worley in the determination of the surface tensions of aqueous solutions of aniline and phenol.‡ The correct temperature was attained by immersing the solutions in a thermostat with glass sides for a few hours. The capillary rise was measured by means of a vertical cathetometer reading to 1/10 mm., whilst the capillary diameter was measured on the microscope stage by means of a graduated eyepiece. Instead of determining the average diameter of the capillary it was thought advisable to determine this at the point where the meniscus had been, a procedure which

\* See also footnote on p. 121.

† The equality of the partial vapour pressure of water in solutions of ordinary phenol to the vapour pressure of pure water (Table XI) would indicate that the osmotic pressures of phenol solutions are zero.

‡ R. P. Worley, 'Chem. Soc. Journ.,' vol. 105, p. 260 (1914).

was very simply done by cutting the capillary tube at that point. The formula employed was

$$s = \frac{ghrd}{2},$$

where  $g = 981$  cm./sec.<sup>2</sup>,  $h$  = capillary rise in cm.,  $r$  = capillary radius in cm.,  $d$  = density of solution,  $s$  = surface tension of the solution in dynes/cm.

For the sake of brevity the results only are given. They are correct to the nearest one or two units only, since the error in the determination of the capillary rise and the capillary radius might have amounted to 1 per cent. in each case. But a greater accuracy than this was not necessary for the present purpose.

Table VIII.—Showing Surface Tensions of the Phenolic Solutions.

	Surface tension.			Surface tension at 26·6° C.
	Temp. 19° C.	Temp. 32·2° C.		
	dynes/cm.			
Water .....	71·8	70·6	N/2 phenol.....	43·8
N/2 phenol.....	43·3	41·7	N/4 „ .....	49·5
N/2 catechol .....	56·3	56·3	N/8 „ .....	55·2
N/2 resorcinol ...	63·8	60·0	N/16 „ .....	64·8
N/2 quinol .....	63·7	59·3	N/32 „ .....	69·6
N/2 pyrogallol ...	69·8	69·2	Water .....	71·5

If the surface tensions in the above Table are compared with the corresponding absorption constants given in Table VI it will be seen that there is a remarkable relationship between the two. The order in magnitude of the absorption constants is the same as the inverse order of the surface tensions in the case of all three series. When the surface tension is abnormally low the absorption constant is abnormally high. Seminormal phenol solution, for example, has a surface tension about half that of water, and an absorption constant about twice as large. Indeed, the absorption constant is approximately inversely proportional to the surface tension of the solution, and this holds whatever the temperature may be. The product of the surface tension and the absorption constant is therefore practically constant. This is shown for the seminormal phenolic solutions at 19° C. in Table IX.

Table IX.

	Absorption constant $k$ at 19° C.	Surface tension at 19° C.	Product constants at 19° C. $k \times$ surface tension.
Water .....	0·024	71·8	1·72
N/2 phenol .....	0·045	43·3	1·94
N/2 catechol .....	0·029	56·3	1·64
N/2 resorcinol .....	0·026	63·8	1·66
N/2 quinol .....	0·026	63·7	1·65
N/2 pyrogallol.....	0·024	69·8	1·68

In the same way the product constant for the seminormal phenolic solutions at 32·2° C. has an approximate value of 3·1, and for the solutions of ordinary phenol of various strengths a value of about 4·0.\*

(b) *Viscosity*.—The viscosity of the solutions was measured by means of an Ostwald viscometer of about 20 c.c. capacity, the correct temperature being maintained by immersing it in the same thermostat as was used for the surface tension determinations. The relative viscosity only was found, in terms of water at the same temperature, the usual formula

$$\eta = t'd'/td$$

being employed;  $t'$  and  $d'$  being the time of flow and density for the solution;  $t$  and  $d$  representing the same for water.

The results are given in Table X. An inspection of them shows that the variation in viscosity of the solutions between themselves is too slight to account for the large variations in the absorption rates. Apparently, the viscosity of the solution is a factor of no importance; and even if it exerts a small effect on the rate of diffusion across the membrane, it is completely masked by other factors. Indeed, all the phenolic solutions, which have a slightly greater viscosity than water, tend to diffuse across the membrane more rapidly than the latter.

Table X.

	Viscosity.			Viscosity at 26·6° C.
	Temp. 19° C.	Temp. 32·2° C.		
Water .....	1·000	1·000	N/2 phenol.....	1·110
N/2 phenol.....	1·111	1·099	N/4 „ .....	1·066
N/2 catechol .....	1·122	1·119	N/8 „ .....	1·051
N/2 resorcinol ...	1·119	1·118	N/16 „ .....	1·012
N/2 quinol .....	1·120	1·117	N/42 „ .....	1·001
N/2 pyrogallol ...	1·129	1·130	Water .....	1·000

\* Since the samples of seeds were different and the initial moisture-content not the same, these constants are not comparable with one another.

(c) *Vapour Pressure*.—In view of the predominance which has been given to vapour pressure in various theories of the mechanism of osmosis, it seemed of interest to obtain data with respect to the vapour pressures of aqueous phenolic solutions. Owing to the experimental difficulties, and the somewhat complicated apparatus required, it was not possible to measure these in the present research. The nearest results available are those given by Schreinemakers,\* which refer to aqueous solutions of phenol at 56.3° C. This temperature is considerably higher than those worked with in the case of barley, and on this account the results are not absolutely comparable. The surface tensions of the solutions are given side by side, for purposes of comparison.†

Table XI.—Vapour Pressures and Surface Tensions of Solutions of Phenol at 56.3° C.

Percentage of phenol.	Total vapour pressure.	Partial vapour pressure of water.	Surface tension.
	mm.	mm.	
0.0	125	125	66.7
2.0	125	125	52.5
5.58	127	125.5	42.0
7.42	126.5	125	39.4

Since the law that the absorption constant is inversely proportional to the surface tension seems to hold for all temperatures,‡ it would follow that, even at 56.3° C., the absorption constant for phenol would be large relative to water, since the surface tensions are still widely different at that temperature (see above Table). On the other hand, both the total and partial vapour pressures of the phenol solutions of all concentrations differ very slightly from the vapour pressure of pure water, and it will be seen that, although the total vapour pressures of the phenol solutions are very slightly greater than the vapour pressure of pure water, they are by no means great enough to account for the large differences in the rates of absorption.

#### *Conclusions.*

It is apparent from what has preceded that the variations in the rate at which phenolic solutions diffuse across the differentially permeable membrane of barley are primarily associated with differences in the surface tensions of the solutions. In the case of the phenolic solutions studied, the surface tension is the only physical property whose variation is great enough to

\* Schreinemakers, 'Roy. Acad. Amsterdam Proc.,' vol. 3, pp. 1 and 701.

† The surface tensions are taken from R. P. Worley's paper (*loc. cit.*).

‡ See p. 132.



account for the relative differences in the absorption constants. At any given temperature the magnitudes of the other physical properties of the aqueous phenolic solutions are practically the same. This does not mean that these factors have no influence at all on the rate of absorption. Indeed, they must exert a more or less pronounced influence on the rate of diffusion of a solution across a semipermeable membrane. Bartrell, for instance, has shown\* that solutions diffusing through copper ferrocyanide and other membranes obey Poiseuille's law, according to which the rate of diffusion of a solution across a membrane would be inversely proportional to its viscosity. It has also been shown in the case of barley that if a series of temperatures are chosen, the rate of diffusion of moisture into the seeds is proportional to the corresponding vapour pressures.

The only legitimate conclusion to draw from the preceding work is that when the osmotic pressures, vapour pressures, and viscosities of a series of solutions of *permeable* solutes are equal, their rates of diffusion across the barley membrane are inversely proportional to their surface tensions.

A close relationship between the rate of diffusion of solutions of permeable solutes and their surface tensions might be anticipated. When a solution has a lower surface tension than the pure solvent, it has also a lower intrinsic pressure. In terms of the Laplace theory of capillarity this implies that, by some means or another, the solute molecules have diminished the attractive power of the solvent molecules for one another. The solvent molecules will therefore tend to diffuse over the surface of the barley membrane all the more readily, and from thence on to the surfaces of the solid particles of absorbent material within the seeds.†

These considerations must be confined, however, to solutions of solutes which are permeable to the membrane, and not extended to osmotic phenomena as a whole, as I. Traube has attempted to do.‡ Driving forces due to differences in osmotic pressure on the two opposite sides of the membrane must be eliminated. This is not the case when the membrane is impermeable to the solute and pure water alone enters the seed.

\* Bartrell, 'J. Phys. Chem.,' vol. 15, p. 659 (1911).

† The relationship between the intrinsic pressure, or "attraction pressure," and other physical properties such as surface tension, lowering of vapour pressure, compressibility of solution, etc., has been worked out in detail by I. Traube ('J. Phys. Chem.,' vol. 14, p. 452 (1910), and many other papers). In particular low surface tension, and therefore low intrinsic pressure, is accompanied by abnormally high vapour pressure. For instance, it has been shown in Table XI on p. 134 of the present paper that the partial vapour pressure of water in phenol solutions is equal to that of pure water. The fact that it is not *greater*, however, shows incidentally that the moisture does not pass across the membrane as vapour.

‡ I. Traube, *loc. cit.*