

THE SWELLING OF ISOELECTRIC GELATIN IN WATER.

II. KINETICS.

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Measurements of the osmotic pressure and of the swelling of gelatin in salt solutions and of the swelling pressure of gelatin have led the writers¹ to assume that gelatin was a mixture of two substances or groups of substances, one of which is soluble and the other insoluble. Solid gelatin was therefore pictured as a network of the insoluble material holding a solution of the soluble protein in its meshes. The osmotic pressure of this soluble material was assumed to be the force which caused the block to swell. According to this mechanism the swelling of gelatin should be a special case of diffusion and should be fundamentally similar to osmosis. The peculiarity of swelling lies in the fact that the block of gelatin is both membrane and solution. Swelling differs from osmosis then in that the thickness of the membrane, *i.e.* the gelatin itself, increases during the course of the experiment, and the osmotic pressure is opposed by the elasticity of the gelatin rather than by the hydrostatic pressure. It might be expected therefore that the equation for the kinetics of the process while similar to that for osmosis would differ from it in some respects. This has been found to be the case.

As pointed out in the discussion of the kinetics of osmosis, the equation is of the same form whether the water is assumed to dissolve in and diffuse through the membrane or whether it is assumed to flow through capillary pores in the membrane. The only difference lies in the physical significance of the constants. There is some evidence that the flow of water through gelatin is also through pores and since this mechanism may be more easily analysed, it has been assumed in the present paper.

¹ Northrop, J. H., and Kunitz, M., *J. Gen. Physiol.*, 1926-27, x, 161.

Formulation of the Equation.

According to Poiseuille's law the rate of flow of water through fine capillaries is proportional to the pressure times the fourth power of the radius and inversely proportional to the length of the capillary and the viscosity of the liquid. If the gelatin is assumed to consist of n pores per unit surface, then the total rate of flow of the water will be given by the expression

$$\frac{dv}{dt} = \frac{C'r^4nSP}{\eta h} \quad (1)$$

in which r is the radius of the pores, P the pressure, S the surface of the gelatin, h the length of the capillaries which is assumed to be the thickness of the gelatin, and η the viscosity of water. In order to use this expression the variable terms must be expressed as functions of v or t . In general, since the volume changes, the surface and thickness will also change. In the case of thin films of gelatin on glass, however, the surface may be assumed constant and the thickness therefore is equal to the volume divided by the surface, or $h = v/S$. The average distance traversed by the water in the case of swelling is half the thickness, so that $h/2$ must be used in place of h in equation (1).

Evaluation of P .—Since we are interested only in the amount of water which passes the outside surface of the gelatin it is not necessary to consider the pressure gradient in the gelatin, and the pressure may be assumed² equal to the average pressure. The pressure driving the water into the gelatin will be the difference between the swelling (osmotic) pressure which tends to cause the water to flow in and the elastic pressure of the gelatin which tends to force it out. Equilibrium is attained when these two pressures are equal. It was shown in the previous paper³ that the swelling pressure at 5°C. from 0.14 to 0.4 gm. gelatin per gm. of water could be represented by the empirical formula

$$OP = \frac{1330 - 140V}{V},$$

² The validity of this assumption is discussed in the preceding paper, Northrop, J. H., *J. Gen. Physiol.*, 1926-27, x, 883.

³ Northrop, J. H., *J. Gen. Physiol.*, 1926-27, x, 893.

where V is the volume of water per gm. of gelatin, and the elastic pressure by

$$EP = \frac{K_e(V - V_f)}{V_f},$$

where K_e is the bulk modulus and V_f is the volume when under no strain. Therefore

$$P = \frac{1330 - 140V}{V} - \frac{K_e(V - V_f)}{V_f}. \quad (2)$$

At equilibrium these two pressures are equal, *i.e.*

$$\frac{1330 - 140V_e}{V_e} = \frac{K_e(V_e - V_f)}{V_f} \quad \text{or} \quad K_e = \frac{1330(1 - .105V_e) V_f}{(V_e - V_f) V_e}. \quad (3)$$

Evaluation of the Radius.—In the case of most membranes the radius of the pores would be constant, but in the case of gelatin this is probably not the case. If a block of gelatin is considered in any way analogous to a mass of separate fine particles of gelatin, then it is evident that the size of the pores which corresponds to the space between the particles will decrease rapidly as the particles swell. The exact function cannot be foretold as there is not sufficient evidence in regard to the actual structure of the gelatin. The simplest assumption, however, is that the radius of the pores between the particles would decrease as the radius of the particles increased or, approximately, $r^4 = c/V$. It will be assumed that the number of pores is constant. The size of the pores will also vary with the original concentration of the gelatin, but since this is constant for any one experiment it need not be taken into account here.

It is much more convenient to express the results in terms of the volume of water per gm. of gelatin rather than as the total volume. If g is the gm. of dry gelatin and V the volume of water per gm., then Vg equals the total volume of water, v , and $dv = gdV$.

As in the case of osmotic pressure, the equation may be solved in various ways depending upon which constants are used. The simplest expression is obtained in terms of K_e ,⁴ the bulk modulus, V_e the equi-

⁴ Since V_e may be expressed in terms of K_e and V_f it would theoretically be possible to express the equation in terms of V_f and K_e alone. Actually, however, this can only be done if a number of swelling curves are made with similar

librium volume, and V_f the volume when under no strain. In order to obtain the equation in this form equations (1) and (3) are added and the resulting equation solved for P .

Substituting these values of h , P , r^4 and v in equation (1) and simplifying and collecting the constant terms, equation (1) becomes

$$\frac{dV}{dt} = \frac{2CS^2 1330(bV + V_f)(V_o - V)}{V^2 g^2 V_e V_f},$$

where $b = K_e V_e / 1330$; on integration, this becomes

$$C = \frac{g^2 V_e V_f}{2 \times 1330 S^2 t} \left[\frac{V_o^2 - V^2}{2b} + \frac{(bV_e - V_f)(V_o - V)}{b^2} + \frac{2.3 V_e^3}{(bV_e + V_f)} \log \left(\frac{V_e - V_o}{V_e - V} \right) - \frac{2.3 V_f^3}{b^2 (bV_e + V_f)} \log \left(\frac{V_f + bV}{V_f + bV_o} \right) \right] \quad (4)$$

In these experiments the last term is negligible in most cases. If K_e , the bulk modulus, is small, however, the last term becomes significant. C is the rate of flow of water under unit pressure through unit thickness and unit area of gelatin of concentration V_f . In the units used in these experiments it is cc. per hour, per sq. cm. surface, per cm. thickness per mm. mercury pressure.

In order to test this equation a number of experiments were performed with films of gelatin of various concentrations on glass slides. The gelatin was heated to 40°C., the slides weighed and then dipped in the gelatin. They were then cooled and weighed again and placed at 5°C. in stoppered tubes with wet filter paper. It was shown in the preceding paper³ that the pressure changes for the first 3 days and then remains constant, so that in order to obtain reproducible results and also since the pressure-concentration curve is based on the value of the equilibrium pressure, the slides were usually allowed to remain at this temperature for 3 days before immersing in water. They were

films and the results averaged before applying the equation. This is due to the fact that the value of V_e , and hence of K_e , varies slightly in individual experiments and the value of C is very sensitive to small differences in the value of V_e , especially near the end of the curve. It is therefore necessary in the calculation of individual curves such as those given to use the value of K_e and V_e determined from the particular experiment in question.

TABLE I.
Swelling of Films of Gelatin on Glass.

Experiment	S	g	V _f	V _e	t	V	C × 10 ⁶
	sq. cm.	gm.	cc.	cc.	hrs.	cc.	
2/2 a	25	.05	6.1	6.9	0	6.12	
					.05	6.50	1.15
					.10	6.65	1.00
					.20	6.77	.80
1/13 a	25	.045	6.0	6.75	0	6.0	
					.05	6.32	.63
					.10	6.48	.61
					.20	6.66	.49
2/2 b	25	.12	6.1	6.9	0	6.12	
					.32	6.50	1.05
					.55	6.65	1.03
					1.00	6.75	.85
c	25	.14	6.0	6.75	0	6.0	
					.2	6.27	1.22
					.4	6.45	1.30
					.8	6.62	1.30
1/24 a	25	.063	5.9	6.75	0	2.45	
					.10	5.0	.40
					.20	5.82	.48
					.40	6.42	.56
1/20	27	.16	5.0	5.4	0	5.0	
					.5	5.15	.140
					1.0	5.225	.123
					1.5	5.275	.120
1/24 b	27	.052	3.80	5.0	0	1.55	
					.05	3.3	.120
					.10	4.0	.118
					.20	4.45	.119
1/13 b	25	.10	3.35	4.20	0	3.35	
					.05	3.70	.360
					.10	3.82	.284
					.20	3.95	.235
12/29	42	.31	2.35	3.4	0	2.23	
					.125	2.62	.125
					.25	2.82	.122
					.50	3.0	.110

then weighed again and placed in water at 5°C. They were removed at intervals, the excess water removed with soft filter paper and weighed in air at the same temperature. This is necessary since even slight warming destroys the elasticity and greatly increases the swell-

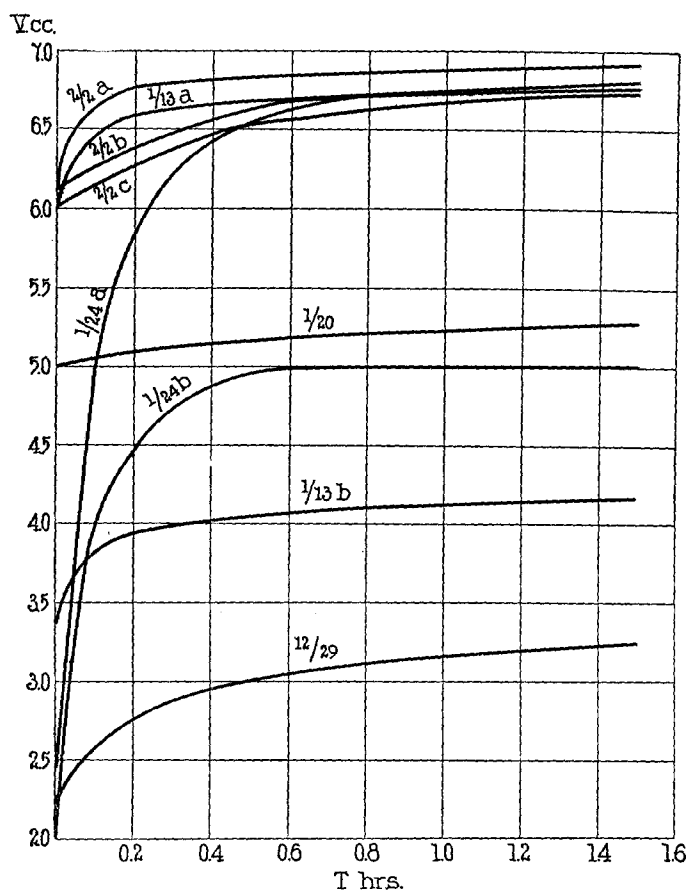


FIG. 1. Swelling films of gelatin on glass.

ing. It is also important to be sure that no change in weight has occurred before the slides and gelatin are weighed for the first time, since in the calculations it is assumed that the gelatin is of the same concentration as the solution of gelatin in which they were dipped. In some experiments the gelatin was allowed to dry partially at 5°

before placing in water. In this case the gelatin swells much more than the same concentration of gelatin which had been solidified at that concentration. It was shown in the preceding paper³ that the equilibrium reached could be calculated by assuming that the concen-

TABLE II.

Swelling of Gelatin Spheres and Plates.

13.9 per cent gelatin heated to 40° and allowed to drop slowly into 200 cc. cold toluene in 250 cc. graduate. 20 spheres used for experiment.

13.9 per cent gelatin solidified in test-tubes. 5°, 3 days. Gelatin removed by warming and sections cut.

Spheres					
g	V_f	V_e	t	V	$C \times 10^6$
<i>gm./sphere</i>	<i>cc.</i>	<i>cc.</i>	<i>hrs.</i>	<i>cc.</i>	
.002	6.4	7.7	0	6.4	
			1.0	6.8	.85
			2.0	7.06	.84
			4.0	7.40	.92
.005	6.4	7.7	0	6.4	
			1.5	6.8	1.02
			2.8	7.06	1.10
			7.0	7.40	0.97
Sections cut from cylinder 2.0 cm. diameter					
.037	6.3	7.5	0	6.2	
			.5	6.9	2.00
			1.0	7.13	1.75
			2.0	7.35	1.65
.10	6.3	7.5	0	6.2	
			3.0	6.9	2.45
			5.75	7.13	2.20
			11.0	7.35	2.15

tration when under no strain, V_f , was the concentration when the gelatin solidified. That is, the gelatin will swell to the same final value as though it had not been dried. This is strictly true only within certain limits and provided too long a time has not elapsed after drying,

as otherwise the gelatin becomes fatigued and V_f assumes a different value.

The results of some of these experiments are shown in Table I and in Fig. 1. The value of C varies slightly, but as a whole the equation appears to fit the experiment in a satisfactory way. The value of C is greater the greater the value of V_f , that is the more dilute the gelatin. This means that water flows more easily through dilute gelatin, which is a reasonable result. It can be confirmed, as will be shown

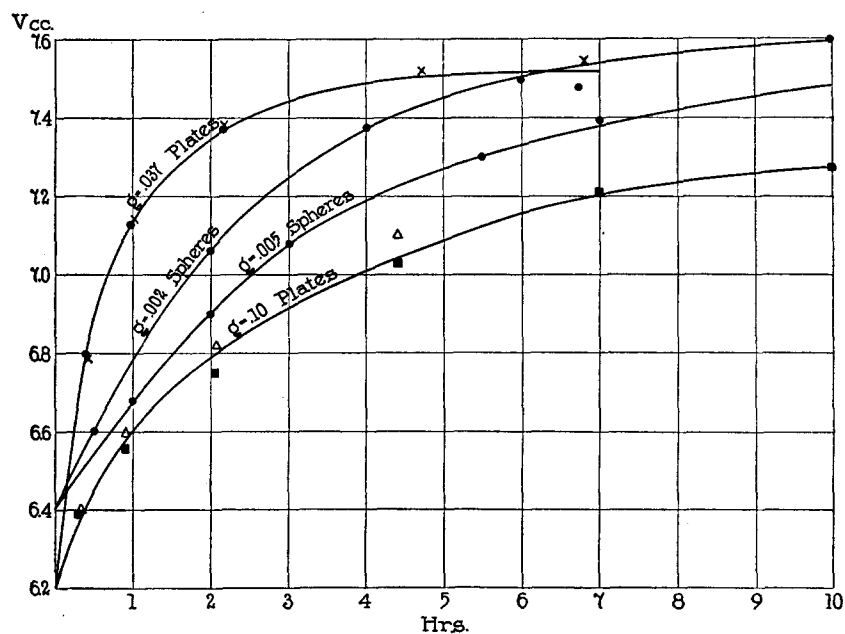


FIG. 2. Swelling of gelatin plates and spheres.

below, by direct measurement. In spite of the precautions noted some of the experiments show an anomalous course in that the gelatin swells either more or less than others of the same series. Experiment 1/20 is an example. The swelling in this case was very much less than would be expected from the average bulk modulus, and therefore the value of C although reasonably constant for this one experiment does not fit in with the other experiments. If the gelatin is placed in water immediately after solidifying, the opposite result is obtained, the gelatin swelling much more. This was ascribed to the fact that the pres-

sure is too high since it is assumed that the block is a saturated solution of one of the constituents and it requires time for the equilibrium concentration to be reached. In such cases also it was found that the value of C would be constant for that particular experiment but would differ from the other values.

Plates of Gelatin.—In the case of thin plates cut transversely from a cylinder of gelatin conditions are approximately the same as in the case just considered, since here also the greatest change in dimension is an increase in thickness and the surface may be considered constant. The results of some experiments with such plates are shown in Fig. 2 and Table II. The results have been calculated by formula (4) as before.

Spheres.—In the case of spheres the thickness instead of increasing directly as the volume increases only as the cube root of this value. The average distance which the water has to move is $1/6$ the radius, which is $1/2$ the ratio of volume to surface or

$$h/2 = r/6.$$

In these experiments the volume increases less than 20 per cent, so that the cube root of the volume may be considered constant for any one sphere and h assumed equal to $r_0/3$. This assumption is made in order to avoid the mathematical difficulties attendant on the integration of the fractional power of V . The surface also increases, but since the significant factor is the total number of pores and since the number presumably remains the same during any one experiment, S will also be considered a constant for any one experiment. In any case the effect of considering S variable would be within the limit of experimental error. Therefore $S = 4\pi r_0^2$ and $S/h = 12\pi r_0$, or $24\sqrt[3]{v_0} = 24\sqrt[3]{V_0/g}$, approximately.

Substituting this value for S/h , equation (1) becomes

$$\frac{dV}{dt} = \frac{2 \times 1330 \times 24C \sqrt[3]{V_0 g} \times (bV + V_f)(V_0 - V)}{g V^2 V_0 V_f};$$

or on integration:

$$C = \frac{g^{\frac{1}{3}} V_f V_0}{2 \times 1330 \times 24 \sqrt[3]{V_0 t}} \left[\frac{V_0 - V}{b} + \frac{2.3V_0^2}{bV_0 + V_f} \log \frac{V_0 - V_0}{V_0 - V} + \frac{2.3V_f^2}{b^2(bV_0 + V_f)} \log \frac{bV + V_f}{bV_0 + V_f} \right] \quad (5)$$

The last term is again negligible except when K_e , the bulk modulus, is small, *i.e.* when b is small.

TABLE III.

Swelling of Gelatin Cylinders.

Linen thread 15 cm. long dipped into melted gelatin.

$l = 15$ cm.						
Experiment	g	V_f	V_e	t	V	$C \times 10^6$
	gm.	cc.	cc.	hrs.	cc.	
11/1	.08	5.80	6.90	0	5.8	
				.5	6.15	1.16
				1.0	6.37	1.15
				2.0	6.67	1.35
	.15	5.80	6.90	0	5.8	
				1.0	6.17	1.23
				2.0	6.40	1.22
				4.0	6.60	1.05
10/7	.25	6.0	7.8	0	6.0	
				2	6.5	1.40
				6	6.97	1.22
				16	7.50	1.18
11/2	.09	3.35	4.30	0	3.30	
				1.0	3.72	.170
				2.0	3.92	.162
				4.0	4.13	.154
11/2	.12	2.35	3.75	0	2.10	
				1	2.80	.150
				2	3.10	.145
				4	3.45	.145
10/13	1.0	2.35	4.5	0	2.35	
				10	3.20	.155
				20	3.60	.155
				40	4.00	.145

The results of the experiments are shown in Table II and Fig. 2. The values of C are again as constant as could be expected.

Cylinders.—The cylinders of gelatin were made by the repeated

dipping of a thread in liquid gelatin so that the gelatin on swelling did not increase in length but only in diameter. The average distance traversed by the water will be in this case $r/4$ and the total pore number Sn will equal $2\pi r_0 l$, where l is the length of the cylinder. In

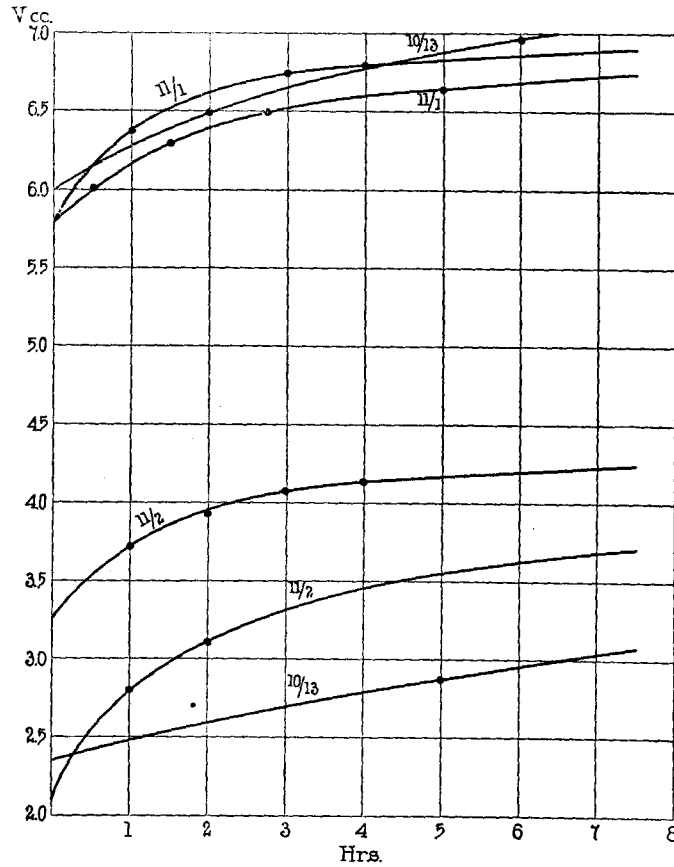


FIG. 3. Swelling of gelatin cylinders.

order to avoid fractional exponents it will be assumed again that $S = 2 \pi r l$, and therefore $S/h = 4 \pi l$. Substituting this value, equation (1) becomes

$$\frac{dV}{dt} = \frac{2 \times 1330 \times C \times 4 \pi l (bV + V_f) (V_0 - V)}{V_g V V_f V_0}$$

Integrating and collecting constant terms the equation for the rate of swelling of cylinders is therefore:

$$C = \frac{gV_fV_e}{2 \times 1330 \times 4 \pi h} \left(\frac{V_e - V}{b} + \frac{2.3V_e^2}{bV_e + V_f} \log \frac{V_e - V_e}{V_e - V} + \frac{2.3V_f^2}{b^2(bV_e + V_f)} \log \frac{V_f + bV}{V_f + bV_e} \right)$$

The effect of swelling on the rate, owing to the simplifying assumptions used, is the same as for spheres but the effect of varying the initial size is different. The results of the experiment with cylinders are given in Table III and Fig. 3.

Direct Measurement of C.—According to the derivation of the equations, C should be the rate of flow of water in cc. per hour through a cylinder of gelatin having 1 cm. cross-sectional area, 1 cm. long, under a pressure of 1 mm. mercury. This value can be determined directly by measuring the flow of water through gelatin. Gelatin was allowed to solidify in glass tubes of 0.5 cm. diameter so as to form a plug 1 cm. long.⁵ Water was then forced through these plugs under 20 cm. mercury pressure and the amount passing through measured in a pipette calibrated in 0.001 cc. The measurement was made at 5°C. Since when gelatin swells there is a loss of volume of the system as a whole, it is necessary to correct the observed rate for the change in volume when under no pressure. In the case of 14 per cent gelatin ($V_f = 6$), this correction is negligible; in the case of 23 per cent gelatin it is significant; and in the case of 30 per cent gelatin it is so large as to render the measurement uncertain. The values for the more dilute gelatin agree as well as could be expected with the value calculated from the rate of swelling measurement and show about the same effect of the original concentration. The plugs were then placed in water at

⁵ It may be noted in this connection that the membrane cannot be held in place by a rigid support since in that case the pressure at first presses water out of the membrane. This continues until the osmotic pressure of the membrane itself is equal to the applied pressure. In other words, no matter what concentration of gelatin is used to make the membrane, water will be removed or taken up so that when a steady filtration rate is reached the concentration of gelatin in the membrane is that which will give an osmotic pressure equal to the applied pressure.

5° for 24 hours and the measurement repeated. The rate of flow was now so slow as to be impossible to measure with any accuracy, thus verifying directly the assumption made in the beginning that the permeability decreased with the increase in swelling. In the case of the direct measurement the gelatin was prevented from expanding by the glass tube so that it is not surprising that the effect of swelling is much more marked than in the case of blocks not enclosed in a solid wall. A summary of the values of C is shown in Table IV.

The results as a whole show that the equations fit the time rate

TABLE IV.

Summary Value of C.

$C \times 10^5 =$ cc. per mm. Hg pressure, per hour, per sq. cm. surface per cm. thickness.

Concentration gelatin V_f	Cylinders	Plates	Spheres	Film on glass	Average	C by direct determina- tion	
						Not swollen	Swollen
6.0	1.15	1.7	.9	(.13)	1.1	1.0	<.10
	1.20	2.2	1.0	1.0			
	1.30			1.0			
				1.3			
				.60			
3.35	.16			.30	.2	.5	<.10
				.12			
2.35	.15			.12	.13		
	.15						

curves quite well. Owing to the number of constants and the uncertainty of the exact value for the equilibrium volume, this agreement might be regarded as accidental. What is much more significant, in the writer's opinion, is the fact that the equations lead to a value for the rate of diffusion of water through gelatin that has been checked by direct determination and also that they express correctly the effect on the rate of swelling of varying the initial size or shape of the block. It may be noted for instance that in the case of thin films the equation

predicts that the rate of swelling per gm. of dry gelatin decreases inversely as the square of the weight of dry gelatin, in the case of spheres it decreases approximately inversely to the $2/3$ power of the weight of dry gelatin, while in the case of cylinders the rate is inversely proportional to the first power of the weight of dry gelatin. If the rate of swelling is expressed simply as the total amount of water taken in per unit of time, then the equation predicts that in the case of thin films the rate is inversely proportional to the size of the block, or if the surface is constant, to the thickness. This is the result obtained in all work on swelling.

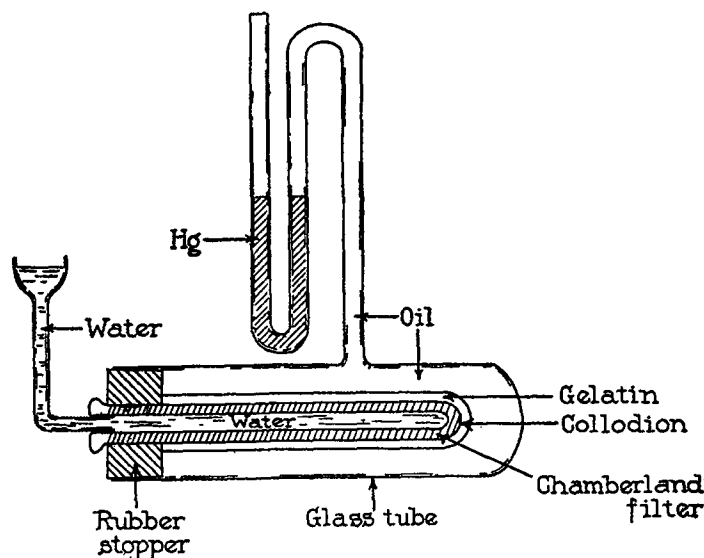


FIG. 4. Apparatus for measurement of swelling of gelatin on collodion-coated thimble.

Swelling under Experimental Conditions Which Avoid the Complicating Factors.

The preceding experiments show that the mechanism assumed for the swelling of gelatin predicts the results with considerable accuracy, but they are open to the objection that the formulas contain a number of constants and the agreement may therefore be accidental. If the mechanism is correct, however, it should be possible to predict con-

ditions under which the various secondary complications disappear or become negligible. These complications are due to the fact that the swelling pressure is opposed by the elasticity of the gelatin, a value which cannot be determined directly; and secondly to the fact that the resistance of the gelatin to the passage of the water is constantly increasing, due partly to the increase in the thickness of the layer of gelatin and partly to the decrease in the size of the pores. It was shown in the preceding paper³ that at higher temperatures the elasticity is rapidly destroyed. It was also found that the resistance offered by collodion is very much greater than that offered by gelatin. If therefore a thin film of gelatin is coated on collodion so that the water has to pass through the collodion, the resistance offered by the gelatin will be a negligible part of the total resistance. If the experiment is carried out at 25° the elasticity of the gelatin will be partially destroyed and the term representing this force will also disappear. These conditions can be fulfilled by the apparatus shown in Fig. 4. The Chamberland filter was coated with collodion and then with gelatin. The gelatin was left at 5° for 24 hours in air and the apparatus set up as shown in a constant temperature bath at 25°C.

Under these conditions all the terms in equation (1) are constant except the pressure. The pressure will be equal to the swelling pressure minus the hydrostatic pressure. The curve for the swelling pressure of gelatin at 25° may be nearly superimposed on the curve at 5° by reducing the concentration of gelatin. The gelatin used had the same swelling pressure at 25° as 23 per cent gelatin at 5°, so that the same formula will apply for the pressure as was used for the experiments at 5° provided the concentration of gelatin be assumed to be 23 per cent. The swelling pressure is now opposed by the hydrostatic pressure just as in the osmotic pressure experiments, and the total pressure may therefore be written

$$P = OP - HP = \frac{1330 - 140V}{V} - M - Kg(V - V_0),$$

where M is the initial hydrostatic pressure and K is the mm. pressure per cc. increase in volume. Substituting this value of P , equation (1) becomes

$$\frac{dV}{dt} = \frac{CSnr^4}{h\eta g} \left[\frac{1330 - 140V}{V} - M - Kg(V - V_0) \right];$$

and bringing all the constant terms together and integrating:

$$C = \frac{2.3gV_e}{(1 + bV_e) 1330 St} \left(V_e \log \frac{V_e - V_0}{V_e - V} - \frac{1}{b} \log \frac{1 + bV}{1 + bV_0} \right)$$

in which $b = KgV_e/1330$.

C in this case should be the cc. of water passing through 1 sq. cm. of the collodion-coated thimble per hour per mm. mercury pres-

TABLE V.

Swelling Gelatin on Collodion-Coated Thimble at 25°.

Experiment I. $g = 2.5$ $K = 220$ $V_e = 3.68$ $S = 103$

t	V	$C \times 10^4$
<i>hrs.</i>		
0	3.35	
.2	3.42	.45
.4	3.49	.51
.6	3.55	.57

Experiment II. $g = 2.0$ $K = 24$ $V_e = 5.3$ $S = 103$

t	V	$C \times 10^4$
<i>hrs.</i>		
0	3.35	
.4	3.78	1.05
.8	4.10	1.02
1.6	4.52	1.02
3.2	5.0	1.06

By direct determination 1.2

sure. When the swelling experiment was concluded the gelatin was removed and this value of C was determined directly. The results of this experiment are given in Table V and Fig. 5. The difference in the values of C for the two experiments is presumably due to differences in the membranes. The value for the second experiment is quite close to the figure determined directly. At this temperature and under these conditions the final amount of swelling is not determined by the concentration of the gelatin but depends only on the hydrostatic

pressure. This confirms the assumption made above that at 25° the elasticity of the gelatin does not enter into the equation.

Secondary Swelling.

Under the conditions adhered to in these experiments an apparent maximum is rapidly reached. This value has been called the equilibrium volume. If measurements are carried on over a long period of time, however, it will be found that there is a slow steady increase in volume. This is shown in Fig. 6, in which the swelling has been plotted

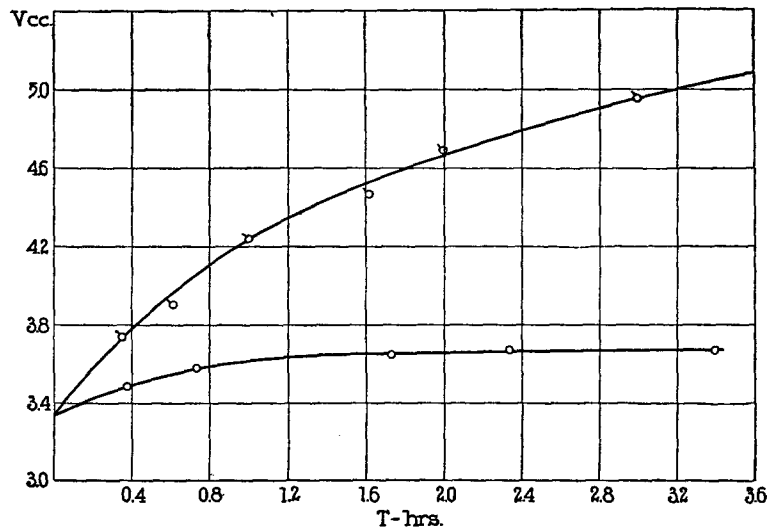


FIG. 5. Rate of swelling of gelatin on collodion-coated thimble.

against the square root of the time. This secondary swelling has been ascribed to the fatigue of the elastic force of the gelatin, and evidence was submitted in the preceding paper³ to show that this was really the case. Fig. 6 shows that the rate of this secondary swelling is independent of the size of the block while the primary swelling is inversely proportional to the square of this quantity. This also bears out the idea that the secondary swelling is due to the fatigue of the gelatin, and hence is not regulated by the rate of diffusion of the water. This fatigue effect may be ascribed to a change in the value of V_f , which tends to approach the actual volume. It is possible to gain some idea

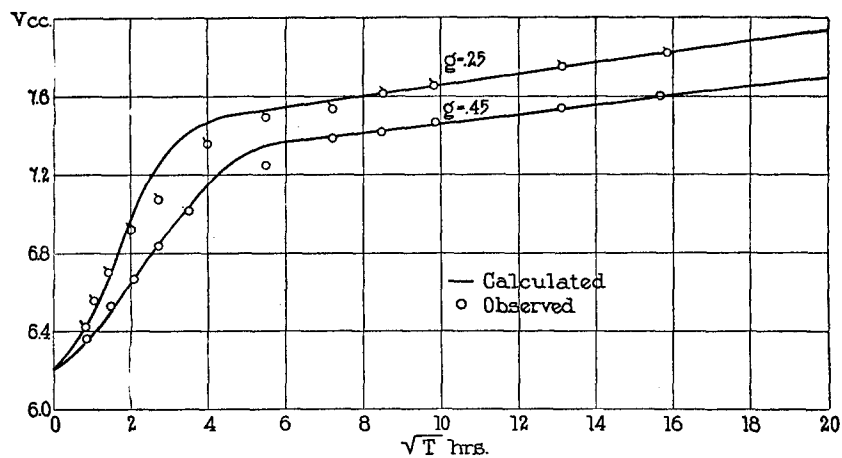


FIG. 6. Complete swelling curve of 13.5 per cent gelatin.

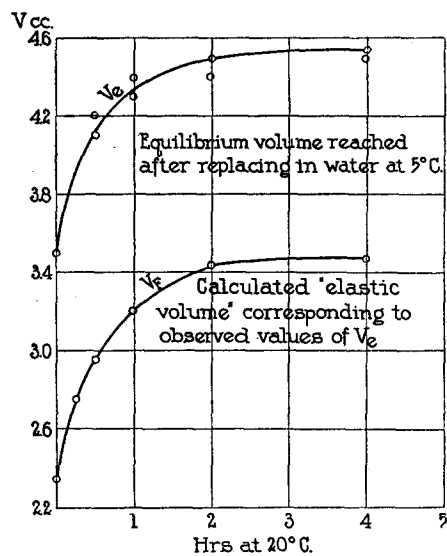


FIG. 7. Effect of time at 20° on subsequent swelling of swollen films of 30 per cent gelatin.

of the rate of change of this value by allowing swollen gelatin to remain varying lengths of time at 20° in air and then noting the swelling on returning the gelatin to water at 5°. The final volume reached in

water gives the value of V_e , and if the bulk modulus is constant the value of V_f at any time can be calculated. When these values of V_f are plotted against the time the block was kept in air, the second curve given in Fig. 7 is obtained. This curve is approximately logarithmic as might be expected and shows that the change of V_f with time is proportional to the difference between its value at time t and the equilibrium value V_{f_0} . Or

$$\frac{dV_f}{dt} = C(V_{f_0} - V_f),$$

which on integration becomes

$$C = \frac{1}{t} \log \frac{V_{f_0} - V_{f_0}}{V_{f_0} - V_f}.$$

Table VI shows that this equation holds at least as an approximation.

In this experiment the block was removed from so water that there was no change in the actual volume during the time V_f was changing,

TABLE VI.
Change of V_f with Time.

t hrs.	V_{f-t}	
	V_f	K
0	2.35	
.25	2.74	.72
.50	2.98	.72
1.0	3.20	.62
4.0	3.47	

i.e. V_{f_0} was constant. In the actual experiments however, as soon as V_f changes V_{f_0} also increases. $V_{f_0} - V_f$ may therefore be considered as approximately constant, or

$$\frac{dV_f}{dt} = C', \text{ and } V_f = C't + \text{a constant.}$$

It was shown in the previous paper³ that the equilibrium volume V_e was related to V_f by the equation $V_f = KV_e^2/1330 + V_e(K - 140)$.

The denominator of this equation may be considered constant for moderate changes in the value of V_e and the equation written

$$V_e^2 = C''V_t = C'''t; \quad (6)$$

or, since under these conditions V_e is the actual volume, $V = C\sqrt{t}$. This is the result shown in Fig. 6.

Complete Formula for Swelling.

Since the formula for the primary swelling has already been given the sum of this formula and formula (6) above will evidently represent the entire process. The equation for the primary swelling is too complicated to handle conveniently in this way, and it is necessary to omit some of the complicating factors. Since the primary swelling curve is basically logarithmic it is to be expected that it would fit the ordinary monomolecular formula provided the proper value of V_e is chosen. This of course deprives the formula of any theoretical meaning since V_e is actually determined by experiment, but may serve to give an expression for the first part of the primary swelling curve which can be used. This turns out to be the case, and it also happens that the value of V at which the secondary square root curve cuts the V axis may be used. The first part of the primary swelling may be represented therefore by the equation

$$Ct = \log \frac{V_e - V_o}{V_e - V'} \quad (7)$$

where V' is the amount of swelling due to the primary process plus the original volume, or $V' = V_e - 10^{A-Ct}$; and the secondary swelling as

$$V'' - V_e = C\sqrt{t}, \quad (8)$$

where V_e in (7) is taken arbitrarily as the value of V_e in (8) when $t = 0$.

Since V' in equation (6) is the original volume plus the increase in volume due to the primary swelling, and $V'' - V_e$ is the increase in volume due to the secondary swelling, the total volume at any time will be the sum of these quantities or

$$V = C\sqrt{t} + V_e - 10^{A-Ct}.$$

The solid lines in Fig. 6 were calculated by means of this formula and follow the general course of the actual experiment. In some of the experiments the fit was much better but there is naturally always a discrepancy near the end of the primary swelling curve.

It follows from the mechanism outlined above that if a large block is used, especially at a higher temperature, the primary swelling should be completely overshadowed by the secondary. That is, in a large block the outside layers will become fatigued and take in more water before the inside layers have swollen at all. The entire course of the

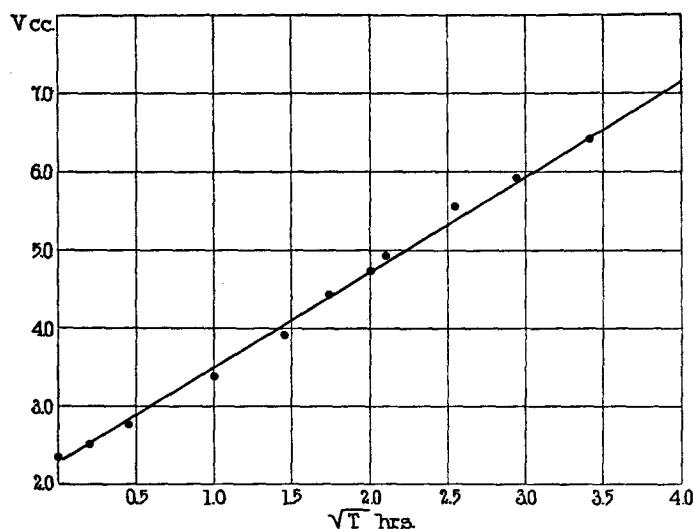


FIG. 8. Swelling of large block, 30 per cent gelatin at 27° . $g = 10$.

swelling should then be represented by the square root curve. The increase in weight of a block of 30 per cent gelatin containing about 35 cc., at 27° , is shown in Fig. 8. The process evidently follows the square root curve quite closely. According to this mechanism the gelatin should increase indefinitely or until it had taken up all the available water, and this is known to be the case.

Application to Other Types of Swelling.

If the theory of the kinetics of swelling outlined in this paper is correct it should apply in a general way to any system in which only

the solvent enters the material undergoing swelling, or in which the swelling is not affected by other substances present in solution. In the case of swelling due to a Donnan equilibrium, the pressure in the particle depends on the distribution of an electrolyte as well as on the entrance of the solvent. The theory would only apply to such systems provided conditions were such that the rate was determined by the passage of water into the solid. This condition is probably rarely if ever realized.

SUMMARY.

It has been assumed that gelatin consists of a network of an insoluble material enclosing a solution of a more soluble material.

The swelling of gelatin is therefore primarily an osmotic phenomena in that the water tends to diffuse in owing to the osmotic pressure of the soluble material. This osmotic pressure is opposed by the elasticity of the insoluble constituent, and equilibrium results when these two pressures are equal.

The rate of the entrance of water should then obey Poiseuille's law, provided the variable terms are expressed as functions of the volume. Equations have been derived in this way which agree quite well with the experimental curves and which predict the proper relation between the size and shape of the block and the rate of swelling. They lead to a value for the rate of flow of water through gelatin which has been checked by direct measurement.

The mechanism assumed predicts that at a higher temperature and under conditions such that the water has to pass through collodion before reaching the gelatin, the experiment should follow the same course as that of osmosis discussed previously. This was also found to be the case.

The slow secondary increase in swelling is ascribed to fatigue of the elastic properties of the gelatin. The rate of this secondary swelling should therefore be independent of the size of the block, in contrast to the rate of primary swelling which is inversely proportional to the size. It can further be shown that this secondary swelling should be proportional to the square root of the time, and also that with large blocks at higher temperatures the entire swelling should be of this secondary type. These predictions have also been found to be true.