XXIV. STUDIES ON COAGULATION. I. ON THE VELOCITY OF GELATION AND HYDROLYSIS OF GELATIN SOL.

BY RINNOSUKE SHŌJI.

(*From the Physiological Institute, Imperial University of Kyoto, Japan.*)

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I. THE GELATION VELOCITY OF GELATIN SOL.

GELATION of hydrophilic colloids has frequently been studied in regard to its 'gelation time' (usually called the coagulation time) *i.e.* the time necessary for the gelatinising of a sol. The definition of 'gelation time,' however, is somewhat arbitrary and differs with the observer. Some observers consider a sol is gelatinised, when the vessel containing it can be inverted without spilling. Others consider it gelatinised, when it adheres as an amorphous mass to a rod inserted in it. Still others consider it gelatinised, when a small glass bead thrown into it stops half-way down. Gelation, however, is not a sudden change of state, but a kinetic process with respect to time. Therefore it is more important and fundamental to study the course of a whole process of gelation than to study simply the gelation time.

It is not yet known exactly, what change of state the colloidal constituents undergo in the process of gelation. The process is called gelation only when a hydrophilic sol, separating into two phases, gradually increases its viscosity until it becomes an amorphous solid mass throughout. Thus the degree of gelation can be estimated by measuring the increment of viscosity, and the rate at which the viscosity increases is called the 'gelation velocity.'

Von Schröder [1903] studied this problem as follows. He heated a gelatin sol at 100° for a certain time, and then cooled it suddenly to 25°. He now kept the sol at this latter temperature, and measured its viscosity twice, first, after a lapse of five minutes, and again, after sixty minutes. The second value was of course larger than the first one. He called the difference of these two viscosity values $\Delta\eta$, and the time interval between the measurements (55 minutes) Δt , and assumed that $\frac{\Delta\eta}{\Delta t}$ represented the coagulability of the sol. He found that the longer the sol was kept at 100°, the smaller were both the viscosity at the first measurement and $\frac{\Delta\eta}{\Delta t}$.

Levites [1908] later studied this problem in the same way. He measured the viscosity of a sol several times in the course of its gelation, and found that the gelation velocity, $\frac{d\eta}{dt}$, was a constant independent of the time, so that the viscosity is a linear function of the time. He studied the process, however, only during the first 1.5 hours of a gelation, which is a relatively brief period when it is remembered that the whole process, according to his own statement, occupied from 11 to 24 hours. His conclusion, therefore, is necessarily somewhat insufficiently supported by experiment.

The present writer took the same problem. The method and procedure followed by him were as follows. A weighed amount of dried commercial gelatin is put into water in such proportions as to have a desired percentage solution when dissolved. This mixture is kept in a cool place in a flask for a certain time in order to allow the solid gelatin to swell sufficiently. It is then placed in a thermostat at 70° or 80°, and by thorough shaking is brought to a homogeneous sol in a few minutes. The flask is fitted with a condenser to prevent the sol from evaporating. At successive intervals after the beginning of heating 5 cc. of the sol are taken out of the flask, and put into an Ostwald viscosimeter kept in another thermostat at 18° and allowed to gelatinise at this temperature. Its viscosity coefficient is then determined frequently over a considerable period of time. The first determination is made at the end of the first six minutes, preliminary experiments showing that the temperature of the sol brought into the 18° thermostat falls to this temperature in five minutes. The initial viscosity coefficient, *i.e.* the viscosity coefficient at the initial time of gelation is found by extrapolation, assuming that the process of gelation begins regularly as soon as the sol is brought into the 18° thermostat.

Since the successive portions are taken out of one and the same sol, they differ only in the length of time they have been previously heated, and the whole course of gelation of each of them is studied in detail, since it is desired to study the influence of previous heating on the process of gelation, as well as the process of gelation itself. The observations give the relative viscosity coefficient, that of water at 18° being taken as unity. The absolute viscosity coefficient can then be easily calculated if desired.

The results of experiments with a 3 per cent. gelatin sol are shown in Fig. 1. The quantities $\eta - \eta_i$ are taken as ordinates and the time t as abscissa, η and η_i being the viscosity coefficients at the time t and at the initial time of gelation respectively. Curves 1, 2, 3, 4, 5 and 6 are viscosity-time curves for portions previously heated for six minutes, 1, 3, 6, 11 and 20 hours respectively at 80°. Fig. 2 is another example of a 3 per cent. sol which was heated at 70° instead of 80°, curves 1, 2, 3, 4, 5, 6 and 7 corresponding to portions heated for 6 minutes, 2, 6, 16, 20, 30 and 39 hours respectively.

It is seen clearly from these figures that the longer the sol is previously heated, the smaller is the initial gelation velocity, a result in agreement with

that found by von Schröder. This disagrees, however, with Levites since the viscosity fails to be a linear function of the time in all cases. When the sol is heated for a relatively short time, the gelation velocity, $\frac{d\eta}{dt}$, increases with the time, so that the curve is convex towards the t -axis (Fig. 1, Nos. 1 and 2). For the sake of convenience let us call this the first case. On the contrary,

Fig. 1. Gelation of 3 per cent. gelatin sol. (previously heated at 80°).

when the sol is heated relatively longer, the gelation velocity decreases with the time, so that the curve is concave towards the t -axis (Fig. 1, Nos. 4, 5 and 6), which we may call the second case. At some intermediate 'critical' stage the gelation velocity is constant, so that the curve is a straight line. Fig. 1, No. 3 approximates to this case.

It is generally believed that α -glutin, the actual gelatinising constituent of gelatin, is gradually hydrolysed, by heating, to β -glutin which has no tendency to gelatinise even at low temperatures, and as a matter of fact, the longer the sol is heated, the further the hydrolysis goes. Adopting this point of view, therefore, we may say that the higher the concentration of α -glutin, the larger the initial gelation velocity; that when its concentration is higher than a certain critical value, the gelation velocity increases with the time until the viscosity grows beyond bounds; and that when the concentration is lower than this critical value, the gelation velocity decreases with the time, until the viscosity ultimately reaches a finite, limiting value. It is not clear whether the concentration of β -glutin affects these facts or not.

Fig. 2. Gelation of 3 per cent. gelatin sol. (previously heated at 70°).

These conclusions are supported by similar experiments with a 1 per cent. gelatin sol represented in Fig. 3. Curves 1, 2, 3 and 4 are viscosity-time curves for portions previously heated at 80° for 0.1, 1.2, 4 and 11 hours respectively. We see that the gelation velocity decreases with the time even when the sol has been heated for only a short period. That is to say, the gelation belongs to the second, and never to the first case. Obviously the concentration of α -glutin in this case has been lower than the critical concentration from the beginning.

The numerical value of the critical concentration of α -glutin cannot be found, since we do not know the concentration of α -glutin in solid gelatin.

The curves of Figs. 1, 2 and 3 suggested the empirical equation

$$\eta - \eta_i = \frac{\mu t}{1 + \frac{\mu}{\lambda} t} \quad \text{.....(1)}$$

both μ and λ being constants. To test this equation we may write it as

$$\frac{1}{\eta - \eta_i} = \frac{1}{\mu} \frac{1}{t} + \frac{1}{\lambda} \quad \text{.....(2)}$$

a linear equation in $\frac{1}{\eta - \eta_i}$ and $\frac{1}{t}$. It is then found that equation (2) is a good fit. The straight line (the figure is not given here) for the critical case $\lambda = \infty$ passes through the origin in each case, the straight lines below it ($\lambda < 0$) corresponding to samples heated for a shorter period, and the straight lines above it ($\lambda > 0$) corresponding to samples heated for a longer period.

Fig. 3. Gelation of 1 per cent. gelatin sol. (previously heated at 80°).

The constant μ is plainly the value of $\frac{d\eta}{dt}$ at $t = 0$, *i.e.* the initial gelation velocity; we may regard it as increasing with the concentration of α -glutin. It ranges from 0 to ∞ . As to the constant λ we may regard it as increasing with the concentration of α -glutin up to the critical concentration where it becomes infinite. For slightly higher concentrations λ is large and negative and decreases through negative values to a definite limit. This is more or less equivalent to regarding $\frac{1}{\lambda}$ as given by $\frac{1}{c} - \frac{1}{C}$, where c and C are respectively the concentration of α -glutin and the critical concentration. In terms of the curves we may say that λ , when positive, is the value of $\eta - \eta_i$ attained after a long interval of time, while, when λ is negative, the $\eta - \eta_i$ increases beyond bounds after a time given by $t = -\frac{\lambda}{\mu}$. In this latter case it is reasonable to speak of a 'gelation time' but not in the former case. As we see from equation (2) the constants $\frac{1}{\mu}$ and $\frac{1}{\lambda}$ may be taken directly from the straight lines of its graph; $\frac{1}{\mu}$ represents the tangent slope and $\frac{1}{\lambda}$ the intercept on the vertical axis.

Equation (1) may be looked upon as the solution of the differential equation

$$-\frac{d}{dt}[\lambda - (\eta - \eta_i)] = \frac{\mu}{\lambda^2} [\lambda - (\eta - \eta_i)]^2 \dots \dots \dots (3).$$

Now it may be shown that not only the equation (2), but also the solutions of the equations of more general type

$$-\frac{d}{dt}[\lambda - (\eta - \eta_i)] = \frac{\mu}{\lambda^n} [\lambda - (\eta - \eta_i)]^n,$$

where n is an integer, represent curves of the same general character as those given by the above experiments; the significance of μ and λ in these new equations being the same as before. Two solutions of this differential equation of general type are

$$(a) \quad \eta - \eta_i = \lambda (1 - e^{-t}), \quad \text{when } n = 1,$$

$$\text{and, } (b) \quad \frac{1}{[\lambda - (\eta - \eta_i)]^2} = \frac{2\mu}{\lambda^3} t + \frac{1}{\lambda^2}, \quad \text{when } n = 3.$$

Tests were made with these solutions and it was found that they accorded with the observations only for the first shorter period of gelation, and therefore they may reasonably be rejected in favour of equation (1).

Comparison of the values observed and calculated by equation (1) is to be seen in Tables 1, 2 and 3 which correspond to Figs. 1, 2 and 3 respectively.

It is seen from these tables that equation (1) holds for the first four or five hours of gelation, but that at later periods, the viscosity observed increases more rapidly than is given by this equation. Moreover, as can be seen in Fig. 1, curve 3, a gelation starting as a second case, but very near the critical case, may change gradually into the first case, after a certain lapse of time, so that the curve has an inflexion point. Therefore, the statements given above, although holding exactly for earlier periods of gelation, do not hold for later periods. An equation which holds for the whole course of gelation has not yet been found.

The equation (3) is an equation of the second order reaction with respect to the term $\lambda - (\eta - \eta_i)$. If it is assumed that this term is directly proportional to the concentration of α -glutin, the nature of gelation can be discussed as follows.

From the kinetic theory point of view, the particles of a sol are continuously colliding with each other, and gelation can be regarded as being due to the fact that the particles, or at least a certain proportion of them, unite to form an aggregate particle on coming into contact with each other. In the earlier periods of gelation such a union would occur mainly between two individual particles, the reaction thus being of the second order, as given by equation (3). Later, however, when the number of such aggregate particles becomes larger, the probability of union between an aggregate particle and a single particle, as well as between two aggregate particles, increases, so that the viscosity increases more rapidly than indicated by equation (1). These aggregate particles again unite with others, and become larger and larger

Table 1. *Gelation of 3 per cent. gelatin sol at 18° (Fig. 1).*
(Previously heated at 80°.)

t		η	$\eta - \eta_i$		t		η	$\eta - \eta_i$		
(hours)			obs.	calc.	(hours)			obs.	calc.	
					$\mu = 3.2$					
					$\lambda = -8.6$					
No. 1 (Curve 1) Heated for 6 minutes	0	2.15	0	0	No. 4 (Curve 4) Heated for 6 hours	0	1.75	0	0	
	0.1	2.47	0.32	0.33		0.1	1.83	0.08	0.08	
	0.3	3.22	1.07	1.08		0.2	1.90	0.15	0.15	
	0.5	4.10	1.95	1.96		0.5	2.11	0.36	0.35	
	0.7	5.20	3.05	3.03		1.0	2.37	0.62	0.62	
	1.0	7.28	5.13	5.10		1.6	2.62	0.87	0.87	
	1.2	9.10	6.95	6.95		2.0	2.74	0.99	1.00	
	1.4	11.52	9.37	9.37		3.0	3.02	1.27	1.27	
	1.6	14.75	12.6	12.6		4.0	3.32	1.57	1.47	
	1.8	19.05	16.9	17.5		5.0	3.50	1.75	1.61	
2.05	29.5	27.4	27.7	6.0	3.77	2.02				
					$\mu = 2.2$					
					$\lambda = -14.7$					
No. 2 (Curve 2) Heated for 1 hour	0	2.01	0	0	No. 5 (Curve 5) Heated for 11 hours	0	1.66	0	0	
	0.1	2.23	0.22	0.22		0.1	1.70	0.04	0.04	
	0.2	2.48	0.47	0.45		0.3	1.78	0.12	0.12	
	0.4	2.96	0.95	0.94		0.5	1.84	0.18	0.18	
	0.6	3.48	1.47	1.45		1.0	1.96	0.30	0.30	
	0.8	4.02	2.01	2.00		2.0	2.11	0.45	0.45	
	1.0	4.58	2.57	2.59		4.0	2.26	0.60	0.60	
	1.3	5.57	3.56	3.55		7.0	2.48	0.82	0.70	
	1.7	7.05	5.04	5.02		9.0	2.56	0.90		
	2.0	8.25	6.24	6.27		10.0	2.61	0.95		
	2.3	9.61	7.60	7.71		12.0	2.73	1.07		
	2.8	12.3	10.3	10.4		14.0	2.83	1.17		
	3.0	14.0	12.0	12.0		18.0	2.95	1.29		
	3.3	15.9	13.9	14.3		22.0	3.04	1.38		
	3.55	19.3	17.3	16.6						
4.0	27.7	25.7	21.9							
					$\mu = 1.27$					
					$\lambda = 20.0$					
No. 3 (Curve 3) Heated for 3 hours	0	1.87	0	0	No. 6 (Curve 6) Heated for 20 hours	0	1.57	0	0	
	0.2	2.12	0.25	0.25		0.2	1.60	0.03	0.03	
	0.4	2.40	0.53	0.50		0.5	1.64	0.07	0.07	
	0.6	2.60	0.73	0.73		1.0	1.69	0.12	0.12	
	0.8	2.84	0.97	0.97		2.0	1.76	0.19	0.19	
	1.0	3.07	1.20	1.19		3.0	1.80	0.23	0.23	
	1.3	3.43	1.56	1.53		5.0	1.86	0.29	0.29	
	1.7	3.83	1.96	1.95		6.0	1.89	0.32	0.31	
	2.0	4.12	2.25	2.25		9.0	1.94	0.37	0.35	
	2.5	4.60	2.73	2.74		13.0	1.98	0.41		
	3.0	5.06	3.19	3.20						
	4.0	5.98	4.11	4.05						
	5.0	6.96	5.09	4.82						
	6.0	8.09	6.22	5.51						
	7.0	9.45	7.58							
8.0	10.77	8.90								
9.0	11.96	10.09								
11.0	14.75	12.88								

Table 2. Gelation of 3 per cent. gelatin sol at 18° (Fig. 2).
(Previously heated at 70°.)

$\eta - \eta_i$				$\eta - \eta_i$					
t	η	obs.	calc.	t	η	obs.	calc.		
(hours)				(hours)					
$\begin{cases} \mu = 3.52 \\ \lambda = -7.9 \end{cases}$				$\begin{cases} \mu = 1.00 \\ \lambda = 1.95 \end{cases}$					
No. 1 (Curve 1) Heated for 6 minutes	0	2.00	0	0	0	1.70	0		
	0.1	2.36	0.36	0.37	0.1	1.80	0.10	0.095	
	0.3	3.23	1.23	1.22	0.3	1.96	0.26	0.26	
	0.5	4.27	2.27	2.26	0.5	2.10	0.40	0.40	
	0.7	5.55	3.55	3.58	1.0	2.36	0.66	0.66	
	1.0	8.35	6.35	6.35	2.0	2.69	0.99	0.99	
$\begin{cases} \mu = 2.50 \\ \lambda = -10.4 \end{cases}$				No. 5 (Curve 5) Heated for 20 hours	3.0	3.03	1.33	1.18	
No. 2 (Curve 2) Heated for 2 hours	0	1.93	0		0	5.0	3.53	1.83	
	0.1	2.18	0.25		0.26	8.0	4.19	2.49	
	0.3	2.76	0.83		0.81	10.0	4.55	2.85	
	0.5	3.35	1.42		1.42	13.0	5.11	3.41	
	0.7	4.03	2.10		2.10	15.0	5.48	3.78	
	1.0	5.18	3.25	3.29	17.0	5.85	4.15		
1.4	7.20	5.27	5.27	19.0	6.21	4.51			
2.0	11.53	9.60	9.61	25.0	7.20	5.50			
$\begin{cases} \mu = 1.63 \\ \lambda = -30.0 \end{cases}$				No. 6 (Curve 6) Heated for 30 hours	28.0	7.64	5.94		
No. 3 (Curve 3) Heated for 6 hours	0	1.84	0		0	0	1.63	0	
	0.1	2.01	0.17		0.16	0.1	1.71	0.08	0.08
	0.3	2.33	0.49		0.50	0.3	1.85	0.22	0.21
	0.5	2.69	0.85		0.84	0.5	1.95	0.32	0.32
	0.7	3.01	1.17		1.19	1.0	2.14	0.51	0.51
	1.0	3.56	1.72	1.72	2.0	2.37	0.74	0.74	
1.5	4.50	2.66	2.66	3.0	2.53	0.90	0.86		
2.0	5.49	3.65	3.66	5.0	2.79	1.16			
2.5	6.58	4.74	4.72	7.0	2.99	1.36			
4.0	11.37	9.53	8.34	9.0	3.21	1.58			
$\begin{cases} \mu = 1.10 \\ \lambda = 4.5 \end{cases}$				No. 7 (Curve 7) Heated for 39 hours	11.0	3.39	1.76		
No. 4 (Curve 4) Heated for 16 hours	0	1.72	0		0	13.0	3.56	1.93	
	0.1	1.83	0.11		0.11	17.0	3.83	2.20	
	0.3	2.04	0.32		0.31	20.0	4.04	2.41	
	0.5	2.21	0.49		0.49	24.0	4.27	2.64	
	0.7	2.37	0.65		0.66	32.0	4.72	3.09	
	1.0	2.60	0.88	0.88	38.0	5.04	3.41		
2.0	3.20	1.48	1.48	44.0	5.30	3.67			
3.0	3.62	1.90	1.90	48.0	5.50	3.87			
4.0	4.08	2.36	2.22	$\begin{cases} \mu = 0.83 \\ \lambda = 0.97 \end{cases}$					
5.0	4.48	2.76		No. 7 (Curve 7) Heated for 39 hours	0	1.61	0	0	
6.0	4.90	3.18			0.1	1.69	0.08	0.08	
7.0	5.28	3.56			0.3	1.81	0.20	0.20	
9.0	6.08	4.36			0.5	1.90	0.29	0.29	
11.0	6.93	5.21			1.0	2.05	0.44	0.45	
14.0	8.19	6.47			2.0	2.22	0.61	0.61	
16.0	8.98	7.26		4.0	2.43	0.82	0.75		
17.0	9.37	7.65		8.0	2.76	1.15			
				11.0	2.95	1.34			
				15.0	3.16	1.55			
				23.0	3.47	1.86			
				30.0	3.74	2.13			
				34.0	3.87	2.26			
				39.0	4.02	2.41			
				50.0	4.26	2.65			

Table 3. *Gelation of 1 per cent. gelatin sol at 18° (Fig. 3).*
(Previously heated at 80°.)

t (hours)				η	$\eta - \eta_i$ obs. calc.		t (hours)				η	$\eta - \eta_i$ obs. calc.		
					$\begin{cases} \mu = 0.21 \\ \lambda = 0.57 \end{cases}$							$\begin{cases} \mu = 0.10 \\ \lambda = 0.23 \end{cases}$		
No. 1 (Curve 1) Heated for 6 minutes	0	1.26	0	0	No. 3 (Curve 3) Heated for 4 hours	0	1.22	0	0	No. 4 (Curve 4) Heated for 11 hours	0	1.20	0	0
	0.1	1.28	0.02	0.02		0.1	1.23	0.01	0.01		0.3	1.21	0.01	0.01
	0.2	1.30	0.04	0.04		0.3	1.25	0.03	0.03		0.6	1.22	0.02	0.02
	0.5	1.35	0.09	0.09		0.6	1.27	0.05	0.05		1.0	1.23	0.03	0.03
	0.8	1.39	0.13	0.13		1.0	1.29	0.07	0.07		2.0	1.25	0.05	0.05
	1.0	1.42	0.16	0.15		1.5	1.31	0.09	0.09		3.5	1.27	0.07	0.07
	1.5	1.46	0.20	0.20		2.0	1.33	0.11	0.11		6.0	1.29	0.09	0.09
	2.0	1.50	0.24	0.24		3.0	1.35	0.13	0.13		10.0	1.32	0.12	0.11
	3.0	1.56	0.30	0.30		4.0	1.37	0.15	0.15		15.5	1.35	0.15	0.12
	4.0	1.60	0.34	0.34		6.0	1.41	0.19	0.17		22.5	1.38	0.18	
	5.0	1.64	0.38	0.37		8.0	1.44	0.22	0.18		30.0	1.40	0.20	
	8.0	1.75	0.49	0.43		13.0	1.49	0.27			40.0	1.42	0.22	
	10.0	1.81	0.55			17.0	1.55	0.33						
	13.0	1.90	0.64			22.0	1.58	0.36						
	17.5	2.01	0.75			29.0	1.63	0.41						
	21.0	2.10	0.84			37.0	1.67	0.45						
26.0	2.20	0.94		43.0	1.71	0.49								
33.0	2.29	1.03		47.0	1.72	0.50								
41.0	2.39	1.13		52.0	1.74	0.52								
47.0	2.45	1.19												
51.0	2.50	1.24												
57.0	2.55	1.29												
					$\begin{cases} \mu = 0.17 \\ \lambda = 0.40 \end{cases}$							$\begin{cases} \mu = 0.037 \\ \lambda = 0.15 \end{cases}$		
No. 2 (Curve 2) Heated for 1.2 hours	0	1.244	0	0	No. 3 (Curve 3) Heated for 4 hours	0	1.22	0	0	No. 4 (Curve 4) Heated for 11 hours	0	1.20	0	0
	0.1	1.26	0.016	0.016		0.1	1.23	0.01	0.01		0.3	1.21	0.01	0.01
	0.3	1.29	0.046	0.045		0.3	1.25	0.03	0.03		0.6	1.22	0.02	0.02
	0.6	1.325	0.08	0.08		0.6	1.27	0.05	0.05		1.0	1.23	0.03	0.03
	0.8	1.34	0.10	0.10		1.0	1.29	0.07	0.07		2.0	1.25	0.05	0.05
	1.0	1.36	0.12	0.12		1.5	1.31	0.09	0.09		3.5	1.27	0.07	0.07
	1.5	1.39	0.15	0.15		2.0	1.33	0.11	0.11		6.0	1.29	0.09	0.09
	2.0	1.42	0.18	0.18		3.0	1.35	0.13	0.13		10.0	1.32	0.12	0.11
	3.0	1.46	0.22	0.22		4.0	1.37	0.15	0.15		15.5	1.35	0.15	0.12
	4.0	1.50	0.26	0.25		6.0	1.41	0.19	0.17		22.5	1.38	0.18	
	6.0	1.55	0.31	0.29		8.0	1.44	0.22	0.18		30.0	1.40	0.20	
	9.0	1.62	0.38	0.32		13.0	1.49	0.27			40.0	1.42	0.22	
	10.0	1.64	0.40			17.0	1.55	0.33						
	12.0	1.69	0.45			22.0	1.58	0.36						
	16.5	1.77	0.53			29.0	1.63	0.41						
	20.0	1.83	0.59			37.0	1.67	0.45						
25.0	1.90	0.66		43.0	1.71	0.49								
32.0	1.98	0.74		47.0	1.72	0.50								
40.0	2.05	0.81		52.0	1.74	0.52								
46.0	2.12	0.88												
50.0	2.16	0.92												
56.0	2.20	0.96												

with the lapse of time. They contain, of course, a certain amount of water, gelatin being a hydrophil colloid.

This hypothesis seems very probable, its only weakness being the assumption stated above. It can, indeed, be reasonably regarded that the term $\lambda - (\eta - \eta_i)$ is an increasing function of the concentration of α -glutin. But there is no theoretical or experimental basis for the assumption that the former is directly proportional to the latter.

Therefore the only conclusion which can be definitely deduced from the results of these experiments is that the gelation is, in its early stage at any rate, a second order reaction with respect to the term $\lambda - (\eta - \eta_i)$.

II. ON THE HYDROLYSIS OF GELATIN BY HEATING.

Gelatin sol undergoes an irreversible change when it is heated at a high temperature. This change is believed to be a hydrolysis of α -glutin, producing β -glutin, as already mentioned in the foregoing section. Commercial gelatin contains to begin with a certain amount of β -glutin, for heat is applied in its production. Moreover, when it is brought to a sol, heat is again applied, so that a part of the α -glutin changes to β -glutin. Hence the concentration of α -glutin in a gelatin sol of known percentage is quite unknown and varies with the sample used and the conditions of its preparation.

The dynamic study of the hydrolysis of gelatin is merely a study of the variation of the concentration of the α -glutin or its hydrolysis products with the time. However, we have as yet no method of determining the concentration of α -glutin or of β -glutin separately. Moreover, β -glutin may reasonably be regarded, not as a definite substance, but as a mixture of the products at various stages of the hydrolysis caused by heating.

The determination of the viscosity of the sol might be regarded as a method for studying its hydrolysis. But, even when β -glutin is assumed to be a single substance, a gelatin sol is still a mixture of two colloids, namely α -glutin and β -glutin. Now the viscosity of a mixture is not yet known as a definite function of the viscosities and concentrations of its constituents; at least it is not a linear function of the concentrations of the constituents, except in the case of dilute solutions. Therefore the hydrolysis of gelatin cannot be determined by measuring changes in its viscosity. In fact we do not know as yet of any measurable properties of a gelatin sol whose rate of change is proportional to the rate of change of the concentration of α -glutin in the process of its hydrolysis caused by heating.

Now, as a by-product of the experiments of the foregoing chapter, a study was made of the change of viscosity of the sol during the course of its hydrolysis. This study was made, however, for its own intrinsic interest, and not for its bearing on the process of the hydrolysis.

The initial viscosities η_i of the previous chapter are merely the viscosities of a mixture of α -glutin and β -glutin at successive periods of its hydrolysis, measured, however, at a lower temperature, viz. 18°. We shall, in what

follows, represent the time of heating by τ , to distinguish it from the time t in the course of subsequent gelation.

Von Schröder [1903] stated that the change in the viscosity of the hydrolysing gelatin sol, which he measured at 25°, was represented by an equation of the first order reaction, viz.:

$$-\frac{d\eta_i}{d\tau} = k_1(\eta_i - \eta_{i\infty}),$$

i.e.
$$k_1 = \frac{1}{\tau} \ln \frac{\eta_{i0} - \eta_{i\infty}}{\eta_i - \eta_{i\infty}},$$

where η_{i0} and $\eta_{i\infty}$ are respectively the values of η_i at the beginning of the heating and after a long period of heating, while k_1 is a constant usually called the velocity coefficient.

Levites [1908], on the other hand, stated that this equation did not hold for his experiments with gelatin, agar and the sodium salt of α -thymonucleic acid. This equation fails, too, to represent correctly the results of the present experiments, whereas the equation of the third order reaction

$$-\frac{d\eta_i}{d\tau} = k_3(\eta_i - \eta_{i\infty})^3$$

i.e.
$$k_3 = \frac{1}{2\tau} \left[\frac{1}{(\eta_i - \eta_{i\infty})^2} - \frac{1}{(\eta_{i0} - \eta_{i\infty})^2} \right]$$

or
$$k_3 = \frac{1}{2(\tau_1 - \tau_2)} \left[\frac{1}{(\eta_{i1} - \eta_{i\infty})^2} - \frac{1}{(\eta_{i2} - \eta_{i\infty})^2} \right] \quad \dots\dots\dots(4)$$

where k_3 is a velocity coefficient varying with the temperature of heating and the concentration of α -glutin is found to be satisfactory. This can be seen from Tables 4, 5 and 6, in which the η_i (calc.) column is calculated from equation (4) using a mean value of k_3 , and k_2 is the velocity coefficient corresponding to the equation of the second order reaction, i.e.

$$k_2 = \frac{1}{\tau_1 - \tau_2} \left[\frac{1}{\eta_{i1} - \eta_{i\infty}} - \frac{1}{\eta_{i2} - \eta_{i\infty}} \right].$$

Table 4. *Hydrolysis of 3 per cent. gelatin sol heated at 80°.*
(Data of η_i taken from Table 1.)

τ (hours)	η_i	η_i (calc.)	k_3	k_2	$\cdot 434k_1$
0.1	2.15	—	—	—	—
1.0	2.01	2.02	0.33	0.26	0.088
3.0	1.87	1.86	0.29	0.20	0.060
6.0	1.75	1.75	0.30	0.18	0.047
11.0	1.66	1.65	0.29	0.15	0.034
20.0	1.57	1.57	0.31	0.13	0.025
∞	1.30	—	—	—	—
Mean			0.304	—	—

Table 5. *Hydrolysis of 3 per cent. gelatin sol heated at 70°.*
(Data of η_i taken from Table 2.)

τ (hours)	η_i	η_i (calc.)	k_3	k_2	$\cdot 434k_1$
0.1	2.00	—	—	—	—
2.0	1.93	1.935	0.126	0.083	0.024
6.0	1.84	1.843	0.118	0.072	0.019
16.0	1.72	1.719	0.114	0.060	0.014
20.0	1.70	1.689	0.106	0.054	0.012
30.0	1.63	1.635	0.119	0.053	0.011
39.0	1.61	1.602	0.108	0.046	0.009
∞	1.30	—	—	—	—
Mean			0.115	—	—

Table 6. *Hydrolysis of 1 per cent. gelatin sol heated at 80°.*
(Data of η_i taken from Table 3.)

τ (hours)	η_i	η_i (calc.)	k_3	k_2	$\cdot 434k_1$
0.1	1.26	—	—	—	—
1.2	1.244	1.244	10.4	1.16	0.057
4.0	1.22	1.221	11.1	1.07	0.045
11.0	1.20	1.198	9.6	0.76	0.028
∞	1.14	—	—	—	—
		Mean	10.4		

CONCLUSIONS.

1. The change of viscosity η of gelatin sol with respect to time t in the early stages of its gelation is represented by the equation

$$-\frac{d}{dt}[\lambda - (\eta - \eta_i)] = \frac{\mu}{\lambda^2}[\lambda - (\eta - \eta_i)]^2,$$

i.e.
$$\eta - \eta_i = \frac{\frac{\mu t}{\lambda}}{1 + \frac{\mu}{\lambda} t},$$

μ being the rate of increase of viscosity at the initial moment of gelation, increasing with the initial concentration of the α -glutin. The constant λ is also larger, the larger the initial concentration of α -glutin, being positive or negative according as the initial concentration is below or above a certain critical concentration. When positive, λ is the asymptotic value of the viscosity attained after a long time. When λ is negative, gelation reaches its final stage after a finite time given by $t = -\frac{\lambda}{\mu}$.

The bearing of the above equation on the nature of gelation is discussed at some length.

2. The change of viscosity η_i of gelatin sol with respect to time τ in the course of its hydrolysis caused by heating is found to be represented by the equation,

$$-\frac{d\eta_i}{d\tau} = k(\eta_i - \eta_{i\infty})^3,$$

i.e.
$$2k\tau = \frac{1}{(\eta_i - \eta_{i\infty})^2} - \frac{1}{(\eta_{i0} - \eta_{i\infty})^2}.$$

The writer wishes to express his thanks to Dr Yoshio Ishida for some valuable suggestions which assisted him in finding the empirical gelation-formula adopted. Further studies on the process of gelation with respect to concentration and temperature will be reported in a following paper.

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