

AN INVESTIGATION OF SMOLUCHOWSKI'S EQUATION AS APPLIED TO THE COAGULATION OF GOLD HYDROSOL.

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INTRODUCTION.

As regards the kinetics of coagulation of colloidal solutions the Smoluchowski equation is the only one which has a theoretical basis. Freundlich,¹ working with aluminium hydroxide sols, deduced an equation, based on measurements of the variation of the viscosity of a sol during coagulation, which gives the relationship between the time and the amount of precipitated colloid. It has the drawback, however, that no definite relationship is known to exist between the size of particles and the viscosity of a colloidal solution.

Smoluchowski² was led to the theoretical treatment of the problem of coagulation from a consideration of certain experiments of Zsigmondy on colloidal gold. Zsigmondy found that, on coagulating a gold sol by means of electrolyte, the speed of coagulation increased with increasing electrolyte concentration until a maximum speed was obtained. This maximum speed is independent of all further increase in electrolyte concentration. This fact formed the basis of Smoluchowski's theory of "rapid coagulation."

In the absence of electrolyte, the electrical double layer on the particles prevents coalescence taking place on impact of one or more particles. Addition of electrolyte to the colloid system diminishes the electrical double layer on the particles, and a force of attraction comes into play. The region of "rapid coagulation," as formulated by Smoluchowski, corresponds to a state of complete electrical discharge of the particles and consequently of maximum attractive forces between them.

*Smoluchowski's Theory.*³—According to this theory each particle in a homogenous sol is supposed to possess a sphere of attraction R , within which the attraction is so strong that any other particle, whose centre enters this sphere, is firmly held.

In an originally uniform sol, whose particles have been completely discharged, the initial number of particles whose centres are less than R apart is vanishingly small.

In course of time, Brownian movement brings the particles into all possible configurations. In consequence of Brownian movement and of

¹ Freundlich, *Trans. Faraday Soc.*, **9**, 66, 1913.

² Smoluchowski, *Zeitschr. physikal. Chem.*, **92**, 129, 1917.

³ *Ibid.*

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the existence of "spheres of attraction" an irreversible state of coagulation is finally set up. It would be futile to merely give the deduction of Smoluchowski's equation; that will be found in the original paper.

Smoluchowski, combining probability considerations and the laws of diffusion, derives a series of equations which give the rate of disappearance of the particles in a colloid solution during "rapid" coagulation. The following equation which gives the rate of disappearance of primary particles is the one used for the following investigation:

$$v_1 = \frac{v_0}{(1 + \beta t)^2}$$

where v_0 is the number of primaries at zero time, v_1 is the number of primaries at a time t , and β is a constant equivalent to $4\pi DRv_0$, where D is the diffusion coefficient and R is the radius of the sphere of attraction.

Smoluchowski also attempts to extend his theory to *slow* coagulation. In this case owing to incomplete discharge of the electric layers, the attractive forces between the particles are not at their maximum and hence only a fraction of the collisions result in union. A probability factor ϵ is therefore introduced to allow for this. The resulting equations obtained by Smoluchowski are identical in form with those obtained for rapid coagulation except that the term β is now replaced by $\epsilon\beta$. Thus the equation $v_1 = \frac{v_0}{(1 + \beta t)^2}$ becomes $v_1 = \frac{v_0}{(1 + \epsilon\beta t)^2}$. The probability factor ϵ is assumed by Smoluchowski to be constant throughout the course of coagulation.

A fundamental assumption of Smoluchowski's theory is that the rate of disappearance of primaries is greater than that of a simple "bimolecular" reaction. As a corollary to the above it would follow that if coagulation were treated as a bimolecular process, the bimolecular velocity "constant" k_{bi} should *always* increase with time for both slow and rapid coagulation. In the case of slow coagulation, however, a rapid fall in the Smoluchowski constant and also in k_{bi} is obtained experimentally, although theoretically the former should remain constant and the latter should rise.

PREVIOUS INVESTIGATIONS OF SMOLUCHOWSKI'S EQUATION.

Smoluchowski's equations have been tested by Zsigmondy, by Westgren and Reitstötter, and more recently by Kruyt and Arkel, and by Mukherjee and Papaconstantinou. These investigators, with the exception of the last named, used an ultramicroscopic method and followed the coagulation by making a count of the number of particles present at various intervals of time. The experiments of Zsigmondy¹ gave reasonable constants for β (variation of about 50 per cent.) when rapid coagulation was studied. Westgren and Reitstötter² worked with coarse gold sols, and found the ratio of $\frac{R}{r}$, i.e. the radius of the sphere of attraction, divided by the radius of the primary particles. The values of $\frac{R}{r}$, which of course should be constant, varied in some cases by 100 per cent.

¹ Zsigmondy, *Zeitschr. physikal. Chem.*, **92**, 600, 1917.

² Westgren and Reitstötter, *Zeitschr. physikal. Chem.*, **92**, 750, 1917.

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Using the data of Westgren and Reitstötter,¹ the values of β have been calculated by the present writer using the equation

$$\Sigma v = \frac{v_0}{(1 + \beta t)}$$

DATA OF WESTGREN AND REITSTÖTTER.

Series 1.			Series 2.		
<i>t</i> Secs.	Σv (Relative).	β (Calculated).	<i>t</i> Secs.	Σv (Relative).	β (Calculated).
0	10.0	—	0	10.0	—
60	8.70	0.149	30	6.63	1.0
120	8.36	0.098	60	5.45	0.834
240	7.51	0.083	120	3.92	0.775
420	6.29	0.083	180	3.12	0.735
600	5.46	0.083	300	2.39	0.645
900	5.06	0.065	420	1.84	0.635
1320	4.46	0.057	600	1.42	0.604

It will be observed that the tendency of β to fall is quite marked in spite of the fact that in series 2 the speed of coagulation is such that the total number of particles is halved in the first minute. Kruyt and Arkel,² working with selenium sol, find that Smoluchowski's equation holds in the rapid region but that β falls rapidly for coagulation at intermediate speed. Mukherjee and Papaconstantinou³ measured the variation in the optical absorption coefficient, which accompanied the change of colour of colloidal gold in presence of electrolyte. If t_1 , t_2 , and t_3 are the times required by the coagulating sol to reach the same absorption coefficient, using a different concentration of electrolyte in each case, it can be deduced from Smoluchowski's equation that

$$\frac{t_1}{T_1} = \frac{t_2}{T_2} = \frac{t_3}{T_3} \text{ or } t_1 : t_2 : t_3 = T_1 : T_2 : T_3$$

where

$$T_1 = \frac{1}{\beta_1}, T_2 = \frac{1}{\beta_2}, T_3 = \frac{1}{\beta_3}.$$

Mukherjee and Papaconstantinou obtained data which gave reasonable constants for the ratio of $T_1 : T_2 : T_3$.

The act of coagulation of colloidal gold involves a change of colour from red to blue. The red is supposed to be due to primary particles. On the assumption that the percentage of red remaining is proportional to the change in the absorption coefficient, the values of β were calculated by the writer from Mukherjee and Papaconstantinou's data, using the

$$\text{equation } v_1 = \frac{v_0}{(1 + \beta t)^2}.$$

In the case of potassium chloride and potassium nitrate as electrolyte, the value of β calculated on the above basis showed good constancy for β . However, in the case of barium chloride (the speed of coagulation being slower than in the two previous cases) the value of β calculated

¹ *Ibid.*

² Kruyt and Arkel, *Rec. Trav. Chim. Pays Bas.*, **39**, 656, 1920.

³ Mukherjee and Papaconstantinou, *Phil. Mag.*, **44**, 305, 1922.

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from the data of Mukherjee and Papaconstantinou was found to fall as coagulation proceeded. This is shown in the following table:—

DATA OF MUKHERJEE AND PAPACONSTANTINOI.

Electrolyte—BaCl₂.

Conc. BaCl ₂ .	Time in Minutes.	Absorption Coefficient.	Per Cent. Red (Calc.).	β (Calc.).
0.00075 N	0	0.0453	100.0	—
	1	0.1603	71.56	0.182
	2	0.2007	61.57	0.137
	4	0.2687	44.76	0.123
	5	0.3051	35.73	0.134
	7	0.3237	31.15	0.113
	9	0.3527	23.93	0.116
	13	0.3700	19.70	0.096
	16	0.3732	18.91	0.081
	—	0.4497	—	—

In the last column the value of β falls by more than one-half. It is certain that the alteration in the value of β is real, as will be shown later.

In addition to the above investigations, attention must be drawn to those of Hatschek,¹ who devised a colorimetric method of testing the applicability of Smoluchowski's equation. The details of the method will be found in the original paper. The principle of the method is as follows: A rectangular cell divided by an oblique partition contains, in one half red gold sol and in the other half blue sol in suspension stabilised by gelatin. This cell when viewed from the front shows a colour range varying from 100 per cent. red to 100 per cent. blue. A second cell, similar to the first, is placed on top and into it is poured the coagulating sol which is being examined. The colour of the sol in the upper cell varies gradually, with time, from 100 per cent. red to blue. By direct comparison of the tints in the upper and lower cells, the percentage of red remaining at any instant can be estimated directly.

Using this method, Hatschek tested the applicability of the equation

$$v_1 = \frac{v_0}{(1 + \beta t)^2}$$

where

v_0 = 100 per cent. red.

v_1 = the percentage of red at time t .

The following values are taken from Hatschek's paper:—

DATA OF HATSCHKE.

Electrolyte—Hydrochloric Acid.

Conc. HCl.	Time in Minutes.	Per Cent. Red.	β .	Conc. HCl.	Time in Minutes.	Per Cent. Red.	β .
0.0075 N	0	100.0	—	0.00826 N	0	100.0	—
	2.0	60	0.145		1.5	40	0.380
	3.0	50	0.138		3.0	25	0.333
	4.5	40	0.130		5.5	15	0.287
	8.0	30	0.103		16.0	5	0.280
	14.0	20	0.088				
	28.0	10	0.077				

¹ Hatschek, *Trans. Faraday Soc.*, **17**, 499, 1921.

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The constancy of β is not satisfactory although in the faster reaction the fall in β is much less marked. Hatschek also gives instances in which coagulation does not go to completion, *i.e.* no further colour change takes place even after many hours. It follows from this that β ultimately becomes zero and consequently a fall of β from the initial value is inevitable.

The work to be recorded in the present paper consists of a further and more detailed examination of the Smoluchowski equation using the method of Hatschek.

It is convenient to divide the various cases encountered into three divisions, namely :—

- (i) Rapid coagulation.
- (ii) Intermediate speed of coagulation.
- (iii) Slow coagulation.

PREPARATIVE.

Preparation of Colloidal Gold.—The water used for this purpose was conductivity water which had been redistilled from a silver-lined copper vessel. All standard solutions used (electrolytes, etc.) were made up with this redistilled water. The gold sols themselves were made by three methods.

(a) *Sodium Citrate Method.*—To 240 c.c. of redistilled water are added 2.5 c.c. of a 0.6 per cent. solution of gold chloride and the whole heated to boiling. Three cubic centimetres of a 1 per cent. solution of sodium citrate are then added. The solution turns a clear port red and then a further 2.5 c.c. of gold chloride are added and the solution again boiled.

(b) *Method of Hatschek.*—300 c.c. of redistilled water are placed in a flask together with 0.06 grams of white dextrin and 2 c.c. of a normal caustic soda solution. The whole is heated. Five c.c. of a 0.6 per cent. solution of gold chloride are added and the mixture slowly heated to boiling. Between 95° C. and 100° C. the whole turns ruby red.

(c) *The Formaldehyde Method.*—480 c.c. of redistilled water are brought to boiling-point and 10 c.c. of a 0.6 per cent. gold chloride solution together with 14 c.c. of 0.18N potassium carbonate solution are added. When the solution is boiling vigorously a 0.3 per cent. solution of formaldehyde is slowly added as recommended by Elliott.¹ The addition of formaldehyde is continued until no further change in colour occurs.

The sols prepared were dialysed in collodion dialysers against distilled water. The specific conductivity of the dialysed sols ranged from 0.8×10^{-5} to 2×10^{-5} mhos. The dialysed gold sols contained 56 milligrams of gold per litre.

Method of Procedure.—All glass and quartz vessels were cleansed, for each fresh sol, with chromic acid and aqua regia, washed out with distilled water and finally with steam from redistilled conductivity water. The concentration of colloid in the comparison sol was in all cases identical with that of the coagulating sol. In all cases the sol was poured into the electrolyte and rapidly mixed. Hydrochloric acid, potassium chloride, barium chloride and aluminium chloride² were used as coagulating agents and the comparison sol was made by using the electrolyte, which was being examined.

¹ Elliott, *Journ. Indus. and Eng. Chem.*, 13, 699, 1921.

² Note.—The present investigation was already partly completed before the writer became aware of the results obtained by Mukherjee and Papaconstantinou by the absorption coefficient method. It is entirely accidental, therefore, that the same precipitating electrolytes were used in both cases.

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EXPERIMENTAL RESULTS.

In the following tables, selected from numerous results, β was calculated, using the equation

$$v_1 = \frac{v_0}{(1 + \beta t)^2}$$

where $v_0 = 100$ per cent. red, and $v_1 =$ the per cent. red at time t . In several cases the value of k_{bi} has been calculated assuming that the primaries (*i.e.* the percentage red) disappear simply by union with each other. In the results recorded below, only those experiments which gave concordant results, after two or more repetitions have been utilised.

A. CONDITIONS APPROXIMATING TO RAPID COAGULATION.

1. *Electrolyte—Hydrochloric Acid.*

Sol 12A (Formaldehyde).
HCl = 0.00833 N.

Sol 12A. HCl = 0.01 N.

Time (Secs.).	Per Cent. Red.	β .	$k_{bi} \times 10^3$.	Time (Secs.).	Per Cent. Red.	β .	$k_{bi} \times 10^3$.
0	100.0	—	—	0	100.0	—	—
35	25.6	1.54	5.0	25	25.0	2.34	7.0
57	19.2	1.25	2.44	35	16.6	2.48	12.4
95	12.8	1.06	4.10	50	12.8	2.15	7.10
150	6.4	1.17	8.5	90	6.4	1.98	11.8

2. *Electrolyte—Potassium Chloride.*

Sol 45 (Formaldehyde).—KCl = 0.033 N.

Time. (Secs.).	Per Cent. Red.	β .
0	100.0	—
17	60.0	0.928
45	40.0	0.748
60	29.3	0.848
84	20.0	0.884
160	12.9	0.930
240	6.4	0.737

3. *Electrolyte—Barium Chloride.*

Sol 22 (Formaldehyde).
BaCl₂ = 0.00332 N.

Sol 19 (Formaldehyde).
BaCl₂ = 0.00166 N.

Time. (Secs.).	Per Cent. Red.	β .	Time (Secs.).	Per Cent Red.	β .
0	100.0	—	0	100.0	—
15	46.6	1.860	20	53.3	1.11
25	33.3	1.760	40	38.6	0.915
45	20.0	1.650	55	29.3	0.925
80	9.3	1.710	80	24.0	0.777
130	4.3	1.850	115	16.0	0.782
			150	10.6	0.828
			190	6.6	0.913

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The constancy of β in the above tables is good, especially in the case of barium chloride as electrolyte. Analogous behaviour was observed with aluminium chloride. The results may be taken as indicating that the Smoluchowski equation is holding in the region observed. In fact, the values of β in the case of barium ion are apparently more concordant than have been previously obtained.

B. CONDITIONS OF INTERMEDIATE SPEED OF COAGULATION.

Electrolyte—Hydrochloric Acid.

Sol 7 (Formaldehyde). HCl = 0.00847 N.

Sol 10 (Formaldehyde).
HCl = 0.0053 N.

Time. (Secs.).	Per Cent. Red.	β .	$k_{bi} \times 10^2$.	Time. (Secs.).	Per Cent. Red.	β .
0	100.0	—	—	0	100.0	—
30	56.4	0.662	1.5	30	67.9	0.428
70	38.4	0.526	1.26	60	59.0	0.302
120	25.5	0.490	0.87	110	51.3	0.212
270	19.4	0.282	0.50	180	44.9	0.164
420	12.7	0.258	1.08	360	25.6	0.162
840	6.4	0.211	1.11	540	20.5	0.134

Electrolyte—Potassium Chloride.

Sol 45 (Formaldehyde). KCl = 0.03166 N.

Time. (Secs.).	Per Cent. Red.	β .	$k_{bi} \times 10^2$.
0	100.0	—	—
30	60.0	0.582	1.33
80	33.3	0.550	1.60
130	26.0	0.449	1.07
180	22.6	0.368	0.70
360	13.3	0.290	1.50

*Electrolyte—Barium Chloride.*Sol 19 (Formaldehyde). BaCl₂ = 0.00134 N.

Time. (Secs.).	Per Cent. Red.	β .	$k_{bi} \times 10^2$.
0	100.0	—	—
30	73.3	0.336	0.72
55	60.0	0.317	0.72
100	46.6	0.279	0.63
220	33.3	0.200	0.43
560	13.3	0.187	0.60
1080	3.3	—	—

In the above tables it will be observed that the value of β falls continuously as coagulation proceeds, indicating that the Smoluchowski equation is not depicting the true rate of coagulation.

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C. SLOW COAGULATION.

Electrolyte—Hydrochloric Acid.

Sol 7 (Citrate Method).—HCl = 0.00508 N.

Time (Minutes).	Per Cent. Red.	β .	$k_{bi} \times 10^3$.
0	100.0	—	—
1	76.0	0.146	3.1
2	66.7	0.112	1.8
4	53.3	0.117	1.8
6	44.0	0.085	2.0
8.25	40.0	0.070	1.0
11.5	35.9	0.060	0.88
24	26.7	0.039	0.77
35	22.5	0.031	0.63

The change to 100.0 per cent. blue was incomplete after 2 hours.

Electrolyte—Potassium Chloride.

Sol 45 (Formaldehyde Method).—KCl = 0.0266 N.

Time (Secs.).	Per Cent. Red.	β .	$k_{bi} \times 10^2$.
0	100.0	—	—
45	73.3	0.214	0.48
94	60.0	0.166	0.34
165	50.8	0.147	0.26
270	44.0	0.113	0.17
380	37.3	0.100	0.22
720	30.7	0.067	0.10

*Electrolyte—Barium Chloride.*Sol 19 (Formaldehyde Method).—BaCl₂ = 0.001 N.

Time (Minutes).	Per Cent. Red.	β .	$k_{bi} \times 10^3$.
0	100.0	—	—
1	86.7	0.074	1.53
2.33	73.3	0.071	1.58
3.75	66.6	0.060	0.96
5.66	60.0	0.051	0.86
24.50	46.6	0.018	0.20
36.0	33.3	0.020	0.74
67.5	28.0	0.013	0.18
107.0	17.3	0.008	0.056

It will be seen in the above tables that β and even k_{bi} fall rapidly—the more so the slower the speed of coagulation. Although in nearly all the results quoted the sols used were made by the formaldehyde method, experiments were conducted using sols made by the other methods mentioned previously. The results obtained show that the value of β for a given concentration of electrolyte varies with the mode of preparation of the sol. A lesser degree of variation occurs when sols are prepared in an identical manner. Probably this is a question of difference in size of the particles and possibly also of their structure.

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In addition to a fall in β , it is possible to arrange the electrolyte concentration so that the sol never reaches 100 per cent. blue after standing many hours.

It would perhaps be of interest to compare the values of β for slow coagulation with hydrochloric acid as electrolyte, with those obtained by other workers cited in the Introduction. In series 1 of Westgren's data the value of β fell from 0.149 at the end of the first minute to 0.057 after 22 minutes. In the recalculation of Mukherjee and Papaconstantinou's data, using barium chloride as electrolyte, the value of β fell from 0.182 after the first minute to 0.081 after 16 minutes. In the first table for slow coagulation by the author, given above, the value of β fell from 0.146 after the first minute to 0.060 after 11.5 minutes. Although the data are obtained by three totally different methods, the rate of fall of β is about the same in each case. This is evidence in favour of the general applicability of the various experimental methods employed.

DISCUSSION OF RESULTS.

The experiments indicate that for the coagulation of gold sols, by means of the electrolytes chosen, there is a "rapid" region in which Smoluchowski's equation holds reasonably well. The constancy of β is quite good, especially in the case of barium chloride as electrolyte. In a region of smaller electrolyte concentration than the above, an excessive slowing down in the speed of coagulation with time is observed. This is in agreement with the data of Kruyt and Arkel and also with the one case (incidentally the slowest speed) of Mukherjee and Papaconstantinou in which the value of β , calculated by the writer, was shown to fall.

The general conclusion arrived at by the writer is that the Smoluchowski equation is strictly limited in its application.

Smoluchowski asserts that the curves depicting slow and rapid coagulation should have a similar form, the only varying factor being the probability that an impact will give union. For so-called "rapid" coagulation this probability factor is unity and for non-rapid coagulation it is ϵ , where $\epsilon < 1$. This factor ϵ is assumed by Smoluchowski to be constant throughout the course of any one coagulation, but this is not found to be the case. The factor ϵ depends upon, and must be some function of, the residual nett charge on the particle. When two charged particles unite, the surface density of the charge on the complex is different from that on the original particle and therefore different repulsive forces come into play. It is therefore very probable that the factor ϵ for union between a charged primary and a charged complex, is less than the factor ϵ for union between two primaries.

Let us assume that each primary particle has a radius r and possesses a nett charge E .

When two primaries approach one another, a force of repulsion comes into play, reaching a maximum value of

$$F = \frac{E^2}{4r^2K},$$

where K is the dielectric constant of the medium.

Before two such particles can unite, their relative velocity must be such that this force of repulsion is overcome.

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If W_{11} is the work done in overcoming this force of repulsion, the probability that any two particles will possess the necessary critical velocity is given by

$$P_{11} = e^{-\frac{W_{11}}{kT}}.$$

This probability factor P_{11} is the factor ϵ .

Let us now consider a union between a primary and a secondary particle. For simplicity consider the latter to be a sphere. If the density is constant, the radius of the secondary will be $r\sqrt[3]{2}$ and its charge $2E$. The force of repulsion between a primary and a secondary will now be

$$F_{12} = \frac{2E^2}{r^2(1 + \sqrt[3]{2})^2K}.$$

The work W_{12} to be done before union can take place is now greater and the probability of union becomes

$$P_{12} = e^{-\frac{W_{12}}{kT}}.$$

$$\text{Where } W_{12} = \frac{8}{(1 + \sqrt[3]{2})^2} W_{11}.$$

It is thus evident that the probability factor is varying continuously as the complexes become larger. The falling value of ϵ would partly account for the falling value of β observed in this region, since the β calculated in the previous tables implicitly contains ϵ . However even if this modification were introduced into the Smoluchowski equation, the rate of disappearance of primaries would, theoretically, always be greater than that obtained by a bimolecular process, assuming primaries simply united with each other. The data obtained however show that in some cases the value of k_{bi} falls, *i.e.* coagulation is proceeding even more slowly than would be expected on the basis of a bimolecular process. Furthermore, if primaries did disappear simply by union with each other it would follow that once coagulation has commenced it should proceed until no more primaries are left. On this basis incomplete colour change from red to blue should not be possible, since any red colour remaining would indicate unchanged primaries (attributing the red colour to the latter). However, as we have seen, incomplete colour change does occur and simply depends upon the concentration of the electrolyte present. This phenomenon admits of two explanations:

1. It may be due to the possibility that the rate of disappearance of primaries is counterbalanced by an opposing effect: that is, primaries are being reformed either by spontaneous disruption of complexes or by collision of complexes with each other. Such reversibility however would seem to entail a behaviour, on dialysis, of incompletely coagulated sol which has not yet been observed.

2. A more probable explanation would seem to be that the initial primary particles (giving the red colour) are *unequally* charged. In the case of slow and eventually incomplete coagulation very small amounts of electrolyte are used and it is conceivable that the amount adsorbed is not sufficient to reduce the charge of some of the particles (which initially carry an excessive charge) below the critical limit which will permit coagulation to take place.

If this conception of unequal charge is correct, the Smoluchowski equation could not be expected to be applicable in general.

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In reviewing the whole problem of coagulation, it would appear that the Smoluchowski equation in its present form is limited in its application. Before it can be applied to all types of coagulation it apparently requires modification to allow for the two factors:

- (a) The decrease of the probability factor as coagulation proceeds.
- (b) The existence of incomplete coagulation as a consequence of unequal, and in some cases therefore, of excessive initial electrical charge on the primary particles.

SUMMARY.

1. A survey of investigations bearing on the Smoluchowski equation has been given.
2. Colorimetric determinations of the rate of coagulation of gold sols by hydrochloric acid, potassium chloride, barium chloride and aluminium chloride have been carried out, using the method of Hatschek.
3. In agreement with previous investigators, a region of rapid coagulation is found in which Smoluchowski's equation holds fairly well. The equation holds most satisfactorily in the case of a certain concentration range of barium chloride as coagulant.
4. A slower region of coagulation is found in which the equation is inapplicable.
5. Possible explanations of (4) have been suggested.
6. It is concluded that, on the whole, the Smoluchowski equation in its present form is strictly limited to rapid coagulation.
7. Certain of the results obtained can be interpreted as indicating considerable variations in magnitude of the charge on individual primary particles of the sol.

Addendum.—Since the above paper was written the author has found that Kruyt and Arkel¹ working with selenium sol have investigated the Smoluchowski equation, by the method of counting the particles. These observers find that the theory of Smoluchowski holds in the region in which the velocity of coagulation does not differ greatly from the velocity for completely discharged particles. At lower electrolyte concentration the coagulation takes place more slowly than the theory demands. This is in agreement with the results obtained in the above work.

The investigation described in the Paper was carried out under the direction of Professor W. C. M. Lewis.

¹ Kruyt and Arkel, *Koll. Zeitsch.*, **32**, 29, 1923.

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