

VII. KINETICS OF FLOCCULATION

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§ 1. VON SMOLUCHOWSKI'S THEORY OF RAPID COAGULATION

In the introduction to Chapter VI it has been mentioned that the stability of hydrophobic colloids is to be judged by their rate of coagulation. A further consideration of the flocculation process is therefore necessary.

The course of the coagulation with time is determined by two factors, the BROWNIAN motion of the particles and their interaction when they are close together. The simplest case is then obtained when so much electrolyte has been added to the sol that the repulsion may be completely neglected. As a further simplification the remaining attraction can be represented by a sphere of action surrounding each particle. If a second particle enters this sphere of action, the two particles coalesce irreversibly. This means that we replace the LONDON-VAN DER WAALS attraction v by an infinitely deep potential well with a vertical wall. Fig. 1.

In this form of coagulation every encounter between particles leads to a permanent contact. The rate of this so-called *rapid coagulation* is thus completely determined by BROWNIAN motion alone. VON SMOLUCHOWSKI¹ has given an admirable analysis of the rate of this process.

He assumes that initially ν_0 spherical particles of equal size are present per unit of volume and that at $t = 0$ the repulsion between the particles is suddenly removed (for instance by addition of electrolyte) so that coagulation sets in. Now the number of encounters between the particles has to be determined, a problem which can be conveniently solved by considering it as a diffusion problem².

Considering first one particle as fixed in the origin of coordinates, we ask how many of the other particles will collide with it in the course of time. The other particles are now in a diffusion field characterized by the conditions that

$$\left. \begin{array}{ll} \text{at } t = 0 & \nu = \nu_0 \quad \text{for } r > R \\ \text{for } t > 0 & \nu = 0 \quad \text{for } r = R \end{array} \right\} \quad (1)$$

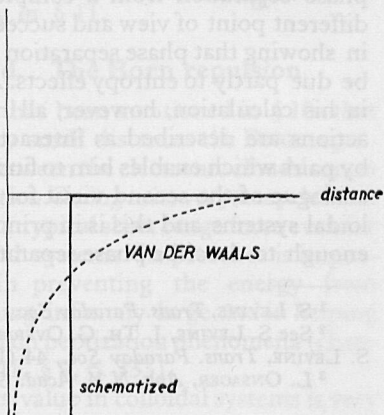


Fig. 1. Replacement of the VAN DER WAALS attraction by a sphere of action.

¹ M. VON SMOLUCHOWSKI, *Physik. Z.*, 17 (1916) 557, 585; *Z. physik. Chem.*, 92 (1917) 129.

² See also S. CHANDRASEKHAR, *Revs. Mod. Phys.*, 15 (1943) 59.

r is the distance from the centre of coordinates, R is the distance between the centres of two particles at which a lasting contact is formed. In the simplest case R is equal to $2a$, a being the radius of one particle.

The changes in number of particles anywhere in the diffusion field are given by the second equation of FICK

$$\frac{\partial \nu}{\partial t} = D \Delta \nu \quad (2)$$

in which D is the diffusion constant of the particles, and Δ the Laplace operator.

The solution of this equation subject to the conditions (1) is

$$\nu = \nu_0 \left\{ 1 - \frac{R}{r} \left(1 - \frac{2}{\sqrt{\pi}} \int_0^{(r-R)/2\sqrt{Dt}} e^{-x^2} dx \right) \right\} \quad (3)$$

This seems a rather complicated equation and perhaps a clearer insight into the physical state of affairs may be gained by directing the attention to the nearly stationary state of diffusion which is reached very soon (for $t \gg R^2/D$, see below).

In the stationary state the number (J) of particles diffusing through any closed surface in the direction of the central particle must be constant and equal to the number of particles colliding with the central one.

This can be expressed by the first equation of FICK which, for a sphere around the origin, runs

$$J = D \cdot 4 \pi r^2 \cdot \frac{\partial \nu}{\partial r} \quad (4)$$

The solution of this equation satisfying the condition

$$\nu = \nu_0 \text{ for } r = \infty \quad (5)$$

$$\text{is: } \nu = \nu_0 - \frac{J}{D} \cdot \frac{1}{4 \pi r} \quad (6)$$

With the aid of the condition

$$\nu = 0 \text{ for } r = R \quad (7)$$

the number of collisions with the central particle is found to be

$$J = 4 \pi D R \nu_0 \quad (8)$$

If the central particle is also subject to BROWNIAN motion, the diffusion constant in (8) should now describe the relative motion of two particles. As the motions of the two particles are completely independent of each other, the suitable diffusion constant is now

$$D_{12} = D_1 + D_2 \quad (9)$$

or when the particles are of equal size

$$D_{11} = 2 D_1 \quad (10)$$

The diffusion constant is related to the mean square of the displacement in one direction by the equation

$$D = \frac{\overline{x^2}}{2t} \quad (11)$$

The relative displacement of two particles is given by $x_1 - x_2$ and so the relative diffusion constant by

$$D_{12} = \frac{\overline{(x_1 - x_2)^2}}{2t} = \frac{\overline{x_1^2}}{2t} - \frac{2\overline{x_1 x_2}}{2t} + \frac{\overline{x_2^2}}{2t} = D_1 + D_2 \quad (12)$$

as the average value of $x_1 x_2$ is zero.

So the number of particles colliding with one individual particle is equal to $8 \pi D R v_c$ and the rate of disappearance of the primary particles is given by

$$-\frac{dv}{dt} = 8 \pi D R v^2 \quad (13)$$

which shows that coagulation proceeds as a bimolecular reaction, the reaction constant of which can be expressed in terms of known quantities.

When the concentrations in eq. (13) are expressed as molar concentrations we get

$$-\frac{dc}{dt} = 8 \pi D R N_{Av} c^2 \quad (14)$$

with a bimolecular reaction constant k equal to

$$k = 8 \pi D R N_{Av} \quad (15)$$

Substituting $R = 2a$ and $D = kT/6\pi\eta a$ we find for k

$$k = \frac{8N_{Av} kT}{3\eta} \quad (16)$$

which is about $6 \cdot 10^{12}$ for room temperature and the viscosity of water. This is just the order of magnitude we are accustomed to find for the bimolecular collision factor.

DEBYE¹ applied this idea, with refinements to be treated in § 3, to a reaction between small molecules, *viz.*, the quenching of fluorescence in ionic solutions.

Eq. (13) does not yet adequately describe the coagulation process except at the very beginning. Indeed after a certain time binary particles have been formed and it will be necessary to include the influence of collisions of primary particles with these multiple ones and those of the multiple ones amongst themselves.

The number (b) of collisions per second between primary particles follows immediately from eq. (13)

$$b_{11} = 4 \pi D R v^2 = 2 \pi D_{11} R_{11} v_1^2 \quad (17)$$

Likewise the rate of collisions between particles of type i and type j is given by

$$b_{ij} = 4 \pi D_{ij} R_{ij} v_i v_j \quad (18)$$

At a certain stage of the coagulation process let the number of primary particles per cm^3 be v_1 , that of secondary particles v_2 , generally that of i -fold particles be v_i , then

¹ P. DEBYE, *Trans. Electrochem. Soc.*, 82 (1942) 265.

the number of the k -fold particles increases by collisions of i -fold and j -fold particles in which $i + j = k$ and decreases by any collision with the k -fold particles. So

$$\frac{dv_k}{dt} = \frac{1}{2} \sum_{\substack{i=1 \\ j=k-i}}^{i=k-1} 4 \pi D_{ij} R_{ij} v_i v_j - v_k \sum_{i=1}^{\infty} 4 \pi D_{ik} R_{ik} v_i \quad (19)$$

Now $D_{ij} = D_i + D_j$, and the radius of interaction R_{ij} is about equal to $r_i + r_j$ in which r_i and r_j are the radii of the multiple particles. Moreover the diffusion constant D_i will be inversely proportional to r_i . Consequently

$$D_{ij} R_{ij} = (D_i + D_j) (r_i + r_j) = D_i r_1 \left(\frac{1}{r_i} + \frac{1}{r_j} \right) (r_i + r_j) \quad (20)$$

When r_i and r_j are not too widely different, the product $(r_i + r_j) (r_i^{-1} + r_j^{-1})$ will have a value slightly larger than 4, and SMOLUCHOWSKI therefore introduces the approximation

$$D_{ij} \cdot R_{ij} = 4 D_1 r_1 \quad (21)$$

or, if one wants to acknowledge the fact that the distance of interaction (R) between primary particles may be different from $2 r_1$

$$D_{ij} R_{ij} = 2 D_1 R \quad (22)$$

In section 4 on the coagulation of polydispersed sols a better approximation than (22) will be introduced.

With eq. (22) the fundamental eq. (19) can now be simplified to

$$\frac{dv_k}{dt} = 4 \pi D_1 R \left\{ \sum_{\substack{i=1 \\ j=k-i}}^{i=k-1} v_i v_j - 2 v_k \sum_{i=1}^{\infty} v_i \right\} \quad (23)$$

The rate of change of the total number of particles irrespective of their size is then given by

$$\begin{aligned} \frac{d}{dt} \sum_{k=1}^{\infty} v_k &= 4 \pi D_1 R \left\{ \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} v_i v_j - 2 \sum_{k=1}^{\infty} \sum_{i=1}^{\infty} v_k v_i \right\} = \\ &= -4 \pi D_1 R \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} v_i v_j = -4 \pi D_1 R \left(\sum_{k=1}^{\infty} v_k \right)^2 \end{aligned} \quad (24)$$

So also the total number of particles decreases according to a bimolecular equation which can be easily integrated. Remembering that the original number of particles is v_0 , we find

$$\sum_{k=1}^{\infty} v_k = \frac{v_0}{1 + 4 \pi D_1 R v_0 t} = \frac{v_0}{1 + \frac{t}{T}} \quad (25)$$

in which $T = \frac{1}{4 \pi D_1 R v_0}$ is called the time of coagulation, giving the time in which the

number of particles is just halved. With the help of (25), eq. (23) which gives the number of k -fold particles can be solved now too, starting with the equation for the primary particles, which leads to

$$\left. \begin{aligned} v_1 &= \frac{v_0}{\left(1 + \frac{t}{T}\right)^2} \\ v_2 &= \frac{v_0 t/T}{\left(1 + t/T\right)^3} \\ v_k &= \frac{v_0 \left(\frac{t}{T}\right)^{k-1}}{\left(1 + \frac{t}{T}\right)^{k+1}} \end{aligned} \right\} \quad (26)$$

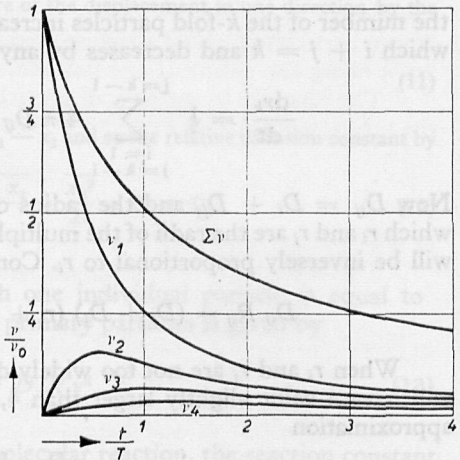


Fig. 2. Number of particles as a function of time in rapid coagulation.

Fig. 2 illustrates the course of the flocculation as a function of time. For experimental confirmation of eq. (25) we refer to § 7 and § 8.

Incidentally we may remark that if the diffusion constant D , is put equal to $kT/6\pi\eta r_1$, the time of flocculation becomes

$$T = \frac{1}{8\pi D r_1 v_0} = \frac{3\eta}{4kTv_0} \quad (27)$$

which for water as the medium of dispersion and $T = 298^\circ$ is equivalent to

$$T \sim 2 \cdot 10^{11}/v_0$$

and depends only on the number of particles.

The influence of the dimensions of the particles on the collision number drops out because the influence on the mobility (D) is just equal and opposite to the influence on the region of contact (R).

In a very concentrated AgI sol, (1 mol/l, $r_1 = 30 \text{ m}\mu$) the number of particles is $4 \cdot 10^{14}/\text{ml}$. So $T \sim 1/2000$ sec. In a sol of normal concentration, as usually applied for determination of the flocculation, value, T (for rapid flocculation) varies from a second to a minute.

It is now possible to discuss the effect made in substituting the approximate solution (eq. (4) — (8)) for the exact solution (3) of the diffusion equation (2). Instead of eq. (8)

$$J = 4\pi D R v_0 \quad (8)$$

the exact solution would have given the number of collisions on one resting particle

$$J = 4\pi D R v_0 \left(1 + \frac{R}{\sqrt{\pi Dt}}\right) \quad (28)$$

a correction which is unimportant when

$$t \gg R^2/\pi D$$

or, substituting again $R = 2a$

$$t \gg 8\varphi T \quad (29)$$

where φ is the volume fraction of the colloid.

Now it is already difficult to prepare hydrophobic colloids with a concentration larger than 1% and in experiments on coagulation the concentration is usually much smaller (e.g., $10^{-3}\%$). This means that after only a very small fraction of the coagulation time T has passed, the situation is adequately described by the simplified equations (4) and following¹.

§ 2. SLOW COAGULATION AS A CONSEQUENCE OF THE PARTIAL EFFECTIVITY OF COLLISIONS (SMOLUCHOWSKI)

Although of course the rapid coagulation is important as an application of the theory of BROWNIAN motion, it scarcely gives us any information on the stability of colloids.

In rapid coagulation we study the decomposition of the corpse of a colloid, which is as dead as the traditional doornail.

Slow coagulation on the contrary could be compared to a degeneration process leading finally to death but in which we may study still very interesting parts of the processes of living.

Curiously enough the interpretation of slow coagulation which has been given by VON SMOLUCHOWSKI rests on very formal grounds and only very much later has it been tried to connect the slowness of coagulation with the interaction between particles.

SMOLUCHOWSKI'S theory of slow coagulation is derived very simply indeed from the theory of the foregoing section. He assumed that the difference between rapid and slow coagulation is given by the fact that in the former every encounter between particles leads to permanent coalescence but in the latter only a fraction α of the encounters is successful.

The course of coagulation is then fully described by eq. (25) and (26), only the time of coagulation now becomes

$$T = \frac{1}{4 \pi D_1 R n_0 \alpha} \quad (30)$$

Consequently all coagulation-time curves, whether rapid or slow should be transformable into each other simply by a change of the time scale.

Unfortunately, however, there is no theory giving the connection between the quantity α and magnitudes like the double layer potential, concentration of electrolytes, etc.

Here, the theory of FUCHS, originally developed for coagulations of smokes or mists, gives a new starting point.

§ 3. SLOW COAGULATION AS A CONSEQUENCE OF A SMALLER NUMBER OF COLLISIONS DUE TO REMAINING ENERGY BARRIERS (FUCHS)²

The theory of rapid coagulation may be extended to the case of appreciable interaction between the particles by substituting for the diffusion equation (4) a diffusion in a field of force.

¹ F. C. COLLINS and G. E. KIMBALL, *J. Colloid Sci.*, 4 (1949) 425, published a detailed investigation on this point, in view of its application to diffusion-controlled reaction rates.

² N. FUCHS, *Z. Physik*, 89 (1934) 736.

Calling $V(r)$ the potential energy of two particles as a function of their distance r , the stationary diffusion current to one (resting) particle is given by

$$J = 4 \pi r^2 \left(D_1 \frac{\delta v}{\delta r} + \frac{v}{\rho} \frac{dV}{dr} \right) \quad (31)$$

in which ρ is the frictional constant of a particle ($= 6 \pi \eta a$)

When the central particle is also free to move the diffusion constant D_1 in (31) has to be replaced by $D_{11} = 2 D_1$ (cf. eq. (10)) but at the same time the relative displacement of two particles subject to the potential energy V is also doubled, which may be expressed by taking

$$\frac{1}{\rho_{11}} = \frac{2}{\rho_1} \quad (32)$$

Further, EINSTEIN¹ has deduced that the general relation between ρ and D is

$$\rho D = kT \quad (33)$$

With these substitutions eq. (31) is transformed into

$$J = 8 \pi r^2 \left(D_1 \frac{\delta v}{\delta r} + \frac{v D_1}{kT} \frac{dV}{dr} \right) \quad (34)$$

which equation has to be solved for the boundary conditions

$$v = 0 \text{ at } r = 2a$$

$$\text{and } v = v_0 \text{ at } r = \infty.$$

When the particles are very far apart there is no interaction or $V_\infty = 0$ whereas $V(2a) = -\infty$

The solution of (34) is then given by

$$v = v_0 \exp(-V(r)/kT) + \frac{J \exp(-V(r)/kT)}{8 \pi D_1} \int_{\infty}^r \frac{\exp(V(x)/kT)}{x^2} dx \quad (35)$$

$$\text{with } J = \frac{8 \pi D_1 v_0}{\int_{2a}^{\infty} \frac{\exp(+V(x)/kT)}{x^2} dx}$$

giving the number of collisions with one particle.

Comparing this equation with eq. (13) of § 1 and putting $R = 2a$, we see that

¹ A. EINSTEIN, *Z. Elektrochem.* 14 (1908) 235; *Ann. Physik*, 17 (1905) 549; 19 (1906) 371.

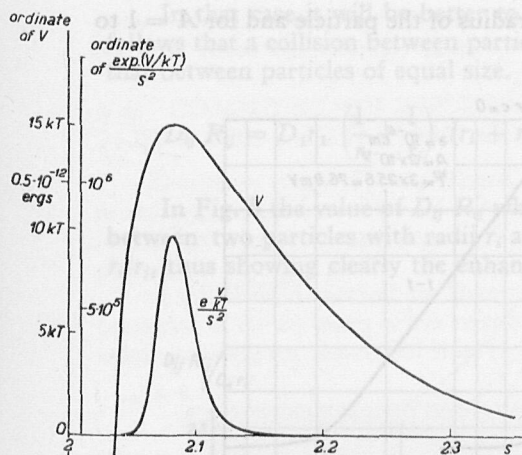


Fig. 3. Curves of potential energy of interaction (V) and of the quantity $\frac{\exp(V/kT)}{s^2}$.

Interaction of two spherical particles with radius $a = 10^{-5}$ cm; electrolyte $\kappa = 10^6$; LONDON-VAN DER WAALS constant $A = 10^{-12}$ erg; surface potential $\psi = 28.2$ mV.

by the presence of the potential energy V the coagulation has been slowed down by a factor¹

$$W = 2a \int_{2a}^{\infty} \exp(V/kT) \frac{dr}{r^2} = 2 \int_2^{\infty} \exp(V/kT) \frac{ds}{s^2} \quad (36)$$

where $s = r/a$.

Although it would be desirable to extend the theory given in this section also to collisions between multiple particles it would not be possible to introduce in a simple way an analogue of eq. (22) and the general theory would become very complicated; on the other hand eq. (36) describes exactly the retardation of the flocculation in the first stages when not many secondary particles have been formed.

The application of (36) to practical cases demands an evaluation of the integral of $1/s^2 \exp(V/kT)$, which usually has to be done by graphical or numerical integration. An approximation which is useful as a first orientation is given by

$$2 \int_2^{\infty} \exp(V/kT) \frac{ds}{s^2} \sim \frac{1}{2 \kappa a} \exp(V_{\max}/kT) \quad (37)$$

where V_{\max} is the maximum in the potential curve.

The method for evaluating V has been described in Ch. VI, § 12, p. 271.

Fig. 3 gives the interesting parts of a curve of potential energy and the values of $1/s^2 \exp(V/kT)$. For the evaluation of the integral only the part of the potential curve near the maximum is important which simplifies the calculation quite appreciably.

Fig. 4 shows how the stability ratio W depends on the electrolyte concentration for two different values of the valency.

Over a great part of the graph there is a nearly linear relation between $\log W$ and $\log c$, a relation that could be confirmed experimentally. (See chapter VIII, § 5, p. 320).

For large concentrations of electrolyte W becomes independent of c . We have to do with rapid coagulation. That the stability ratio is somewhat smaller than 1 is to be explained by the presence of the LONDON attraction which indeed accelerates the coagulation by about a factor 2. In the terminology of SMOLUCHOWSKI this means that the

¹ See E. J. W. VERWEY and J. TH. G. OVERBEEK, *Theory of the stability of lyophobic colloids*.

distance of interaction R is larger than twice the radius of the particle and for $A = 1$ to $2 \cdot 10^{-12}$ we find about $R = 3$ to $4 r_1$

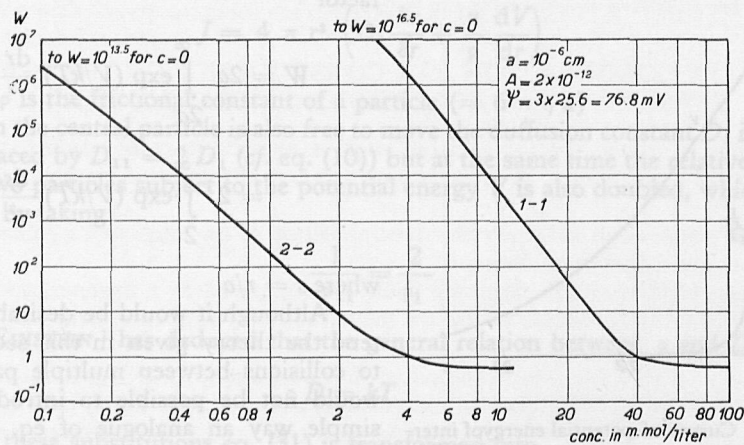


Fig. 4. Stability ratio W as function of the concentration of electrolyte for 1-1 and 2-2 valent electrolytes.

In § 1 we already mentioned DEBYE's¹ application of the theory of coagulation to a case of rate of reaction in ionic solution. As the reacting particles were supposed to be charged, an energy barrier, determined by the charge of the particles and the ionic strength impeded the reaction.

The formalism used by DEBYE is completely analogous to the treatment given above.

In the field of lyophobic colloids the theory of FUCHS was first applied by DERJAGUIN².

§ 4. RAPID COAGULATION OF ESSENTIALLY POLYDISPERSED SYSTEMS

In a flocculating system containing particles of very different sizes it is observed that the smaller particles disappear much more quickly than the larger ones.³

This effect has been explained by MÜLLER⁴ who used an extension of SMOLUCHOWSKI's theory of coagulation. Without introducing any new assumptions the existence of the WIEGNER effect may be understood qualitatively. In the coagulating sol collisions occur between small particles among themselves, between large and small particles and between large particles among themselves. As the complex of a small and a large particle is still a large one, collisions between small and large particles do not change the number of the large particles but they do decrease that of the small ones. Thus one gets the impression that the small particles are caught by the larger ones.

In addition to this, MÜLLER showed that the assumption that the collisions between particles of whatsoever size are equally probable as is expressed in eq. (22) is probably a bad approximation when the sol is strongly heterodispersed.

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In that case it will be better to retain the more accurate eq. (20) from which it follows that a collision between particles of different size is always more probable than that between particles of equal size.

$$D_{ij} R_{ij} = D_1 r_1 \left(\frac{1}{r_i} + \frac{1}{r_j} \right) (r_i + r_j) = D_1 r_1 \left\{ 4 + \left(\sqrt{\frac{r_i}{r_j}} - \sqrt{\frac{r_j}{r_i}} \right)^2 \right\} > 4D_1 r_1 \quad (38)$$

In Fig. 5 the value of $D_{ij} R_{ij}$ which is proportional to the probability of collision between two particles with radii r_i and r_j is plotted against the logarithm of the ratio r_i/r_j , thus showing clearly the enhanced probability of collision when $r_i \neq r_j$.

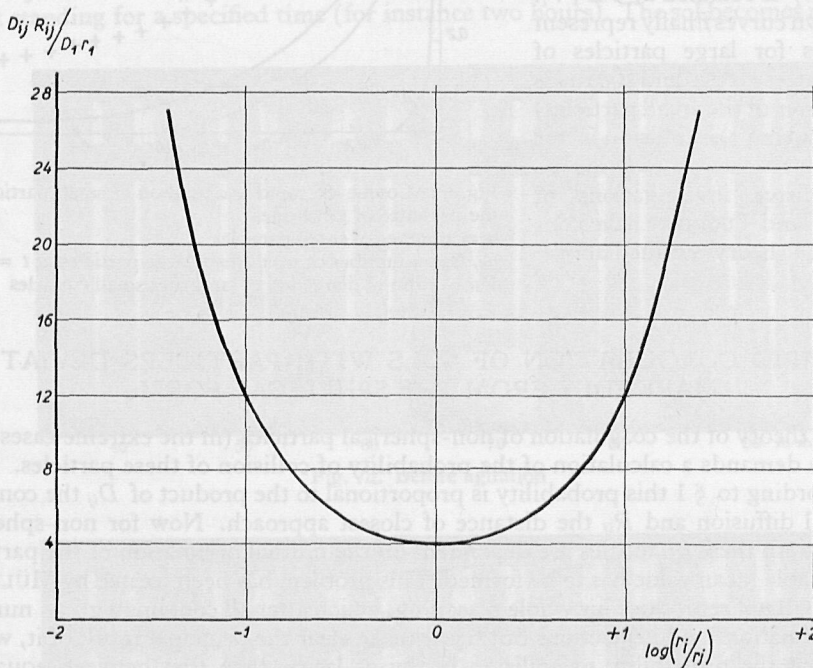


Fig. 5. Probability of collision between particles of different sizes.

MÜLLER worked out the theory of rapid coagulation for the case of sols containing originally two kinds of particles of widely different dimensions. His basic assumptions are the same as those of SMOLUCHOWSKI'S theory except for the fact that the probability of collision between a small particle (or a complex of small particles) with a large one is taken proportional to (cf. eq. 38)

$$\left[4 + \left(\sqrt{\frac{r_i}{r_j}} - \sqrt{\frac{r_j}{r_i}} \right)^2 \right] D_1 r_1 \quad (39)$$

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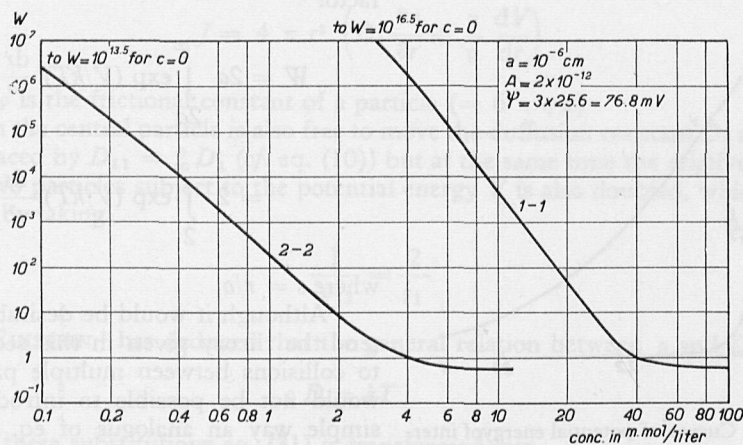


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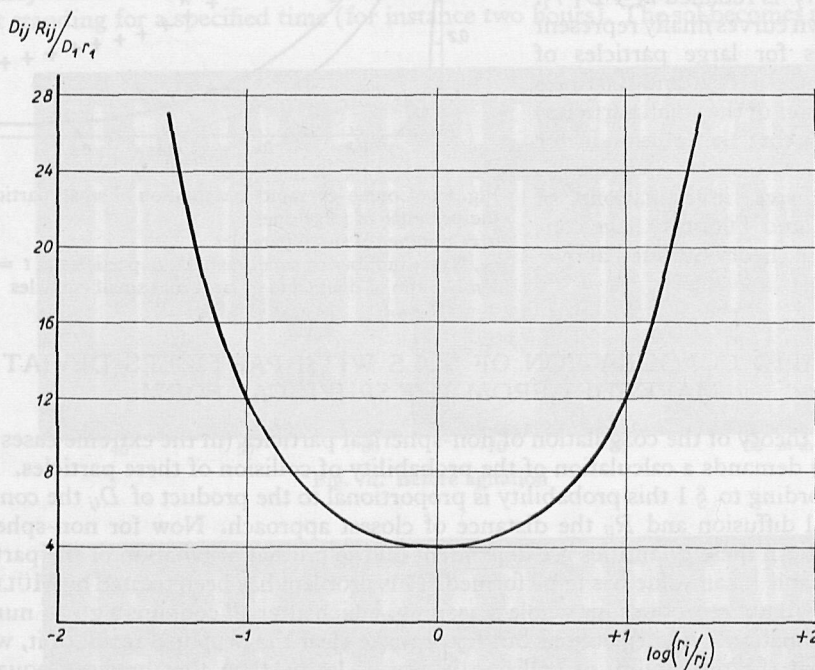


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instead of to $4 D_1 r_1$

Fig. 6 shows how the number of small particles diminishes more rapidly by the presence of an equal number of large ones.

The dotted curve gives the coagulation of the small particles should they alone be present. The curve in crosses ($V_R = 1$) gives the increase of coagulation velocity when an equal number of large particles is present but the collision probability is retained at $4 D_1 r_1$. The drawn curves finally represent the cases for large particles of different sizes (10, 20 and 100 times the diameter of the small particles) on introducing the collision factor (39).

Extensive investigations of WIEGNER and TUORILA¹ have confirmed the theory outlined above.

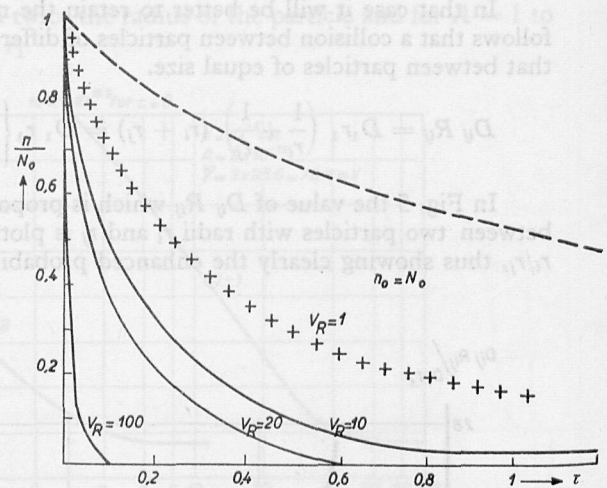


Fig. 6. Course of rapid coagulation of small particles in the presence of large ones

n = number of small particles

n_0, N_0 = number of small resp. large particles at $t = 0$

V_R = ratio of diameters of large and small particles

$\tau = t/T Smol$

§ 5. RAPID COAGULATION OF SOLS WITH PARTICLES DEVIATING MARKEDLY FROM THE SPHERICAL FORM

The theory of the coagulation of non-spherical particles (in the extreme cases rods or plates) demands a calculation of the probability of collision of these particles.

According to § 1 this probability is proportional to the product of D_{ij} the constant of mutual diffusion and R_{ij} the distance of closest approach. Now for non-spherical particles both these quantities are dependent on the mutual orientation of the particles and a suitable mean value has to be formed. This problem has been treated by MÜLLER².

We will not reproduce his whole reasoning, which after all contains a great number of approximations and neglects but try to make clear the principal result of it, which proves that the probability of collision is always larger than that between equal, or nearly equal spheres and, especially for rodlike particles, may assume large values.

As the particles are subject to rotatory BROWNIAN motion, the collision diameters will be of the order of the *largest* diameter of the particles. The diffusion constant, however, depends on a sort of *mean* diameter of the particle which, in the case of rods, may be considerably smaller than the length of the rod. Consequently anisodimensional particles have a relatively large collision diameter combined with a relatively large diffusion constant which results in a high probability of collision.

Experiments of WIEGNER and MARSHALL³ on sols with rod-like particles (vanadium

¹ G. WIEGNER and P. TUORILA, *Kolloid-Z.*, 38 (1926) 3; P. TUORILA, *Kolloidchem. Beihefte*, 22 (1926) 191.

² H. MÜLLER, *Kolloidchem. Beihefte*, 27 (1928) 223.

³ G. WIEGNER and C. E. MARSHALL, *Z. physik. Chem.*, A 140 (1929) 1, 39.

pentoxide, benzopurpurin) showed indeed a probability of collision which had more than 50 times the normal value.

§ 6. COAGULATION INFLUENCED BY SYSTEMATIC MOVEMENTS IN THE SOL (AGITATION, SEDIMENTATION OF THE PARTICLES)

Everyone, who has ever carried out a coagulation, has seen that coagulation is promoted by agitation of the sol. The agitation which seems to have little or no influence in the first stages of coagulation, is very effective when the aggregation has already proceeded for some time.

A much used method for determining the flocculation value depends upon this property. After addition of the required amount of electrolyte to the sol, the mixture is left standing for a specified time (for instance two hours). The sol becomes more and

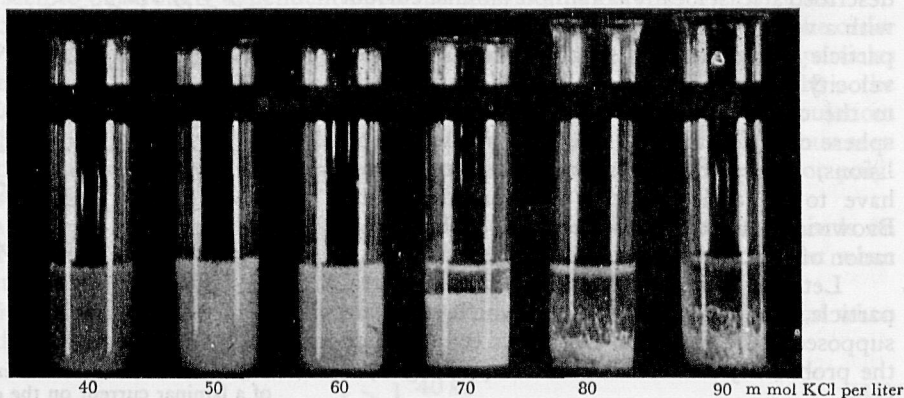


Fig. 7a. Before agitation

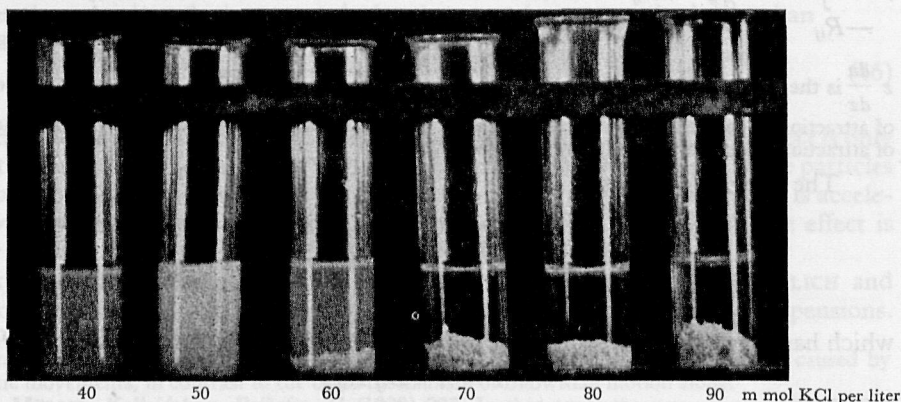


Fig. 7b. After agitation

Figs. 7a and 7b. Flocculation of an As_2S_3 -sol with KCl. Note especially the progress in flocculation after agitation in the tubes with 60 and 70 m mol KCl.

more turbid, and often part of the colloidal material separates in the form of flocks. Now the mixture is agitated and during agitation the turbidity is seen to condense in the form of big flocs which easily sediment when the stirring is stopped, leaving a perfectly clear supernatant in a short time (some minutes to half an hour).

Analogous accelerations of the coagulation have been reported as a consequence of sedimentation or centrifuging of the mixture ¹.

A theory for these effects has already been given by VON SMOLUCHOWSKI ². The theory has been extended by TUORILA ³ and MÜLLER ⁴.

We will mainly follow here VON SMOLUCHOWSKI's and TUORILA's treatment which, though less exact than MÜLLER's methods, shows the principal facts very clearly and leads to results that are not much less accurate than MÜLLER's.

Imagine in the liquid a current which can be described at least locally as a simple laminar current with a velocity gradient du/dz . Consider a certain particle in this current. As a consequence of the velocity gradient other particles will come so near to the central particle that they enter within its sphere of action and are caught by it. These collisions, caused by the movement of the liquid have to be added to the collisions caused by BROWNIAN motion and are the cause of the acceleration of the coagulation.

Let the radius of collision of the central particle, i , with a particle, j , (of which there are supposed to be ν per cm^3) be given by R_{ij} . Then the probability of these collisions is (see Fig. 8)

$$J = \int_{-R_{ij}}^{R_{ij}} 2 \nu z \frac{du}{dz} \cdot \sqrt{R_{ij}^2 - z^2} dz. \quad (40)$$

$z \frac{du}{dz}$ is the relative velocity of the liquid at the height z . $2 \sqrt{R_{ij}^2 - z^2}$ is the diameter of the sphere of attraction at height z . So (40) just represents the number of particles j that enter within the sphere of attraction of one particle i during one second.

The integration leads to

$$J = 2 \nu \frac{du}{dz} \int_0^{R_{ij}} \sqrt{R_{ij}^2 - z^2} \cdot 2 z dz = \frac{4}{3} \nu (R_{ij})^3 \frac{du}{dz} \quad (41)$$

which has to be compared with the probability of normal BROWNIAN collision (cf. eq. 8)

$$I = 4 \pi D_{ij} R_{ij} \nu$$

¹ The influence of a sonic or an A. C. field is probably more complicated. Cf. J. J. HERMANS, *Rec. trav. chim.*, 53 (1939) 139, 164, 725, 741.

² M. VON SMOLUCHOWSKI, *Z. physik. Chem.*, 92 (1917) 155.

³ P. TUORILA, *Kolloidchem. Beihefte*, 24 (1927) 1.

⁴ H. MÜLLER, *Kolloidchem. Beihefte*, 27 (1928) 223.

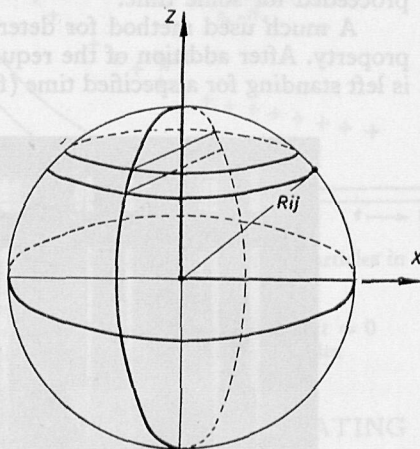


Fig. 8. To illustrate the influence of a laminar current on the collision probability.

R_{ij} = collision radius between particles i and j .

x = direction of movement.

z = direction of velocity gradient.

The ratio of the two collision probabilities is thus

$$\frac{J}{I} = \frac{(R_{ij})^3 \cdot \frac{du}{dz}}{3 \pi D_{ij}} \quad (42)$$

The mutual diffusion constant D_{ij} may be put equal to (taking account of (21))

$$D_{ij} = \frac{4 D_1 r_1}{R_{ij}} = \frac{2 kT}{3 \pi \eta R_{ij}} \quad (43)$$

Consequently J/I becomes

$$J/I = \frac{\eta (R_{ij})^3 \frac{du}{dz}}{2 kT} \quad (44)$$

and is seen to be strongly dependent upon the collision diameter of the particles.

For $du/dz = 1 \text{ sec}^{-1}$ and a particle diameter of 10^{-5} cm , the ratio J/I is of the order of 10^{-3} and completely negligible but when the diameter of at least one of the particles is larger than 1μ the ratio becomes larger than unity and for particles of 10μ the *orthokinetic*¹ flocculation is far more important than the normal *perikinetic* flocculation.

The enhanced flocculation velocity under the influence of agitation is thus seen to be present irrespective of the fact whether the system is monodispersed or polydispersed.

In the case of sedimentation, an increase in the rate of flocculation depends on the difference in sedimentation velocity of different particles and is only present when the system is polydispersed.

This case has been analysed by MÜLLER². A significant effect is only found when the radius of the sedimenting particles is larger than

$$r \geq \sqrt[4]{\frac{40 kT}{\pi g d}} \quad (45)$$

(d is the density of the particles)

whereas the particles which are caught by the central one must be larger than

$$r \geq \sqrt[4]{\frac{1.2 kT}{\pi g d}} \quad (46)$$

This means that in gold sols, at room temperature, the sedimentation effect is only present when at least some of the particles are larger than 0.7μ , whereas the particles which are notably carried away are larger than 0.3μ . When the sedimentation is accelerated by a centrifugal field of, e.g., $1000 g$ (radius 10 cm 3000 rev/min) the effect is already present for particles of the order of magnitude of about 0.1μ .

Experiments on orthokinetic flocculation have been made by FREUNDLICH and BASU³ on copper oxide sols and by TUORILA⁴ on gold sols, quartz and clay suspensions.

¹ These terms have been introduced by WIEGNER (*cf.* TUORILA *l.c.*) for coagulation caused by systematic movements, in contrast to the usual mechanism of BROWNIAN motion alone.

² H. MÜLLER, *Kolloidchem. Beihefte*, 27 (1928) 223. In this paper the movements of the liquid around a moving particle are taken more accurately into account than in the treatment of TUORILA (*l.c.*) and SMOLUCHOWSKI (*l.c.*). The results, however, are not materially changed.

³ H. FREUNDLICH and S. K. BASU, *Z. physik. Chem.*, 115 (1925) 203.

⁴ P. TUORILA, *Kolloidchem. Beihefte*, 24 (1927) 1, 27, 97.

In accordance with the theory orthokinetic flocculation presents an autocatalytic character. In the beginning when the particles are still small, the coagulation is perikinetic and its rate is slow. When a certain degree of aggregation has been reached orthokinetic coagulation comes into play and aggregation is accelerated very much.

§ 7. DETERMINATIONS OF THE RATE OF COAGULATION BY COUNTING THE PARTICLES

The most direct tests of the theories of the rate of flocculation are given by experiments in which the number of particles is counted ultramicroscopically (*cf.* chapter I and III). This type of experiment has been carried out by ZSIGMONDY¹, by WESTGREN and REITSTÖTTER² (Au-sols), by KRUYT and VAN ARKEL³ (Se-sols), by LACHS and GOLDBERG⁴ (Au-sols), by EHRLINGHAUS and WINTGEN⁵ (Au-sols in borax) and by TUORILA⁶ (Au-sols).

a. Rapid coagulation

SMOLUCHOWSKI's theory is usually tested on four points, *viz.*,

1. The flocculation should follow the course of a bimolecular reaction (eq. (25));
2. The time of coagulation T should be inversely proportional to the initial number of particles (27);
3. The absolute value of the time of coagulation should be given by (27) if indeed the interaction makes itself only felt when the particles are practically in material contact. A quicker coagulation may point to an attraction of longer range as described in the preceding chapter;
4. There should exist a region of concentrations of electrolyte where the flocculation is independent of this concentration (true rapid coagulation, all repulsion absent).

Tables 1 and 2 show that a region of rapid coagulation does indeed exist. In this region the time of coagulation T is really independent of the stage of the coagulation, that means eq. (25) is verified.

TABLE 1
EXAMPLES OF RAPID COAGULATION⁷
Gold sol $r_1 = 512 \text{ \AA}$

t (sec)	number of particles $\times 10^{-8}$		time of coagulation T (sec)
	observed	calculated with $T = 79$	
0	20.20	20.20	—
30	14.70	14.40	80
60	10.80	11.19	69
120	8.25	7.74	83
240	4.89	4.78	76
480	3.03	2.71	85
			mean 79

¹ R. ZSIGMONDY, *Z. phys. Chem.*, 92 (1917) 600.

² A. WESTGREN and J. REITSTÖTTER, *Z. phys. Chem.*, 92 (1917) 750.

³ H. R. KRUYT and A. E. VAN ARKEL, *Rec. trav. chim.*, 39 (1920) 656; 40 (1921) 169; *Kolloid-Z.*, 32 (1923) 29.

⁴ H. LACHS and S. GOLDBERG, *Kolloid-Z.*, 31 (1922) 116.

⁵ A. EHRLINGHAUS and R. WINTGEN, *Z. physik. Chem.*, 104 (1923) 301.

⁶ G. WIEGNER and P. TUORILA, *Kolloid-Z.*, 38 (1926) 3; P. TUORILA, *Kolloidchem. Beihefte*, 22 (1926) 191; 24 (1927) 1.

⁷ P. TUORILA, *Kolloidchem. Beihefte*, 22 (1926) 191.

Kaolin suspension

<i>t</i> (sec)	number of particles $\times 10^{-8}$		time of coagulation <i>T</i> (sec)
	observed	calculated with <i>T</i> = 330	
0	5.0	5.0	—
105	3.90	3.80	372
180	3.18	3.23	314
255	2.92	2.82	358
335	2.52	2.46	335
420	2.00	2.20	280
510	1.92	1.96	318
600	1.75	1.77	323
1020	1.54	1.22	(452)
2340	1.15	0.62	(699)

TABLE 2

TIME OF FLOCCULATION IN ITS DEPENDENCE ON THE CONCENTRATION OF ELECTROLYTE¹

The rapid coagulations in bold type
Se-sol

Flocculating electrolyte	Conc. of electrolyte m mol/l	Number of particles at <i>t</i> = 0	Flocculation time, <i>T</i> in sec.
KCl	20	$33.5 \cdot 10^9$	10^7
	30	"	$6 \cdot 10^6$
	40	"	$1.5 \cdot 10^6$
	50	"	$2 \cdot 10^5$
	60	"	$7 \cdot 10^3 - 14 \cdot 10^5$
	65	"	360—3000
	80	"	19.5
	100	"	20.3
	130	"	20.7
BaCl ₂	2	$33.0 \cdot 10^7$	$2 \cdot 10^5$
	3	"	$2.6 \cdot 10^4$
	4	"	7000
	10	"	1700
	40	"	1000
	100	"	1400

¹ H. R. KRUYT and A. E. VAN ARKEL, *Rec. trav. chim.*, 39 (1920) 656; 40 (1921) 169; *Kolloid-Z.* 32 (1923) 29.

Table 3 shows that T is inversely proportional to v_0 .

TABLE 3¹
COAGULATION OF SE - SOLS OF DIFFERENT CONCENTRATIONS BY KCl, 180 millimols/l

Dilution of the sol	time of observation in sec.	number of particles, v	time of coagulation, T	Mean T	Tv_0
1 : 1	0	$32.2 \cdot 10^9$	—	22.7	$7.1 \cdot 10^{11}$
	7	24.1 "	16.5		
	15.0	19.9 "	24.7		
	20.2	16.7 "	21.8		
	28.0	14.2 "	22.0		
	57	10.1 "	25.4		
	167	4.3 "	25.6		
1 : 2	0	$16.0 \cdot 10^9$	—	44.0	$7.0 \cdot 10^{11}$
	7.4	13.2 "	35		
	18.6	10.2 "	31.6		
	42.5	6.4 "	(28)		
	125	4.8 "	52.7		
	278	2.6 "	40.9		
	592	1.5 "	61.0		
1 : 10	0	$3.22 \cdot 10^9$	—	214.2	$6.9 \cdot 10^{11}$
	32.4	2.52 "	116		
	98.0	1.44 "	(79)		
	288	1.33 "	200		
	595	0.98 "	260		
	908	0.67 "	260		
	1190	0.53 "	230		

TABLE 4
RADII OF INTERACTION FOR DIFFERENT SOLS

Sol	r_1 in Å	R/r_1	Author
Au	242	3.12; 2.63	ZSIGMONDY ²
"	960	2.39	WESTGREN AND REITSTÖTTER ³
"	29	2.80—3.02	TUORILA ⁴
"	54	3.11	"
"	320	2.71	"
"	498	3.33	"
"	516	2.33	"
"	598	2.06	"
Kaolin	heterodispersed	5.15 (beginning)- 1.09 (end)	"
Clay	nearly isodispersed	1.95; 2.05	"
Clay		4.95—2	"

¹ H. R. KRUYT and A. E. VAN ARKEL, *Rec. trav. chim.*, 39 (1920) 656; *Kolloid-Z.*, 32 (1923) 29.

² R. ZSIGMONDY, *Z. physik. Chem.*, 92 (1918) 623.

³ A. WESTGREN and J. REITSTÖTTER, *Z. physik. Chem.*, 92 (1918) 750.

⁴ P. TUORILA, *Kolloidchem. Beihefte*, 22 (1926) 191.

Table 4 gives some experimentally determined values of the radius of interaction R as compared with the radius of the primary particles r_1 , for rapid coagulations. With a LONDON-VAN DER WAALS constant of 1 or $2 \cdot 10^{-12}$, R is expected to be 3 or 4 r_1 . Experimentally the ratio R/r_1 is found between 2 and 3 showing that there is an attraction with a range of about one particle radius though perhaps somewhat smaller than the calculated one.

Also the influence of polydispersion and of agitation is quite well confirmed by experiments.¹

From this material, although not very extensive, we may conclude that SMOLUCHOWSKI'S theory describes the rapid coagulation satisfactorily.

b. Slow coagulation

In the case of slow coagulation the situation is less uniform. In some experiments (Table 5) SMOLUCHOWSKI'S idea of a uniform retardation of the coagulation as expressed by eq. (22) seems to hold rather well.

TABLE 5²
SLOW FLOCCULATION OF SE-SOL BY KCl, 50 millimols/l

t time in hours	$10^{-9} \times$ number of particles per cm^3	T in hours
0	33.5	—
0.25	32.3	—
22.5	28.6	(131)
42.5	19.1	55
67.5	14.6	52
187.5	7.5	54
239	7.5	68
335	4.7	55
1008	1.46	48
	mean	55 hours
	Time of rapid coagulation	20 seconds

TABLE 6²
SLOW FLOCCULATION OF SE-SOL. Particles of 52μ . Coagulated by KCl, 59 m mols/l. Sol of $29.7 \cdot 10^3$ particles per cm^3 .

t time in hours	$10^{-3} \times$ number of particles per cm^3	T in hours
0	29.70	—
0.66	20.90	1.5
4.25	19.10	7.6
19	14.40	18
43	10.70	24
73	7.70	25
167	6.45	46

¹ P. TUORILA, *Kolloidchem. Beihefte*, 22 (1926) 191.

² H. R. KRUYT and A. E. VAN ARKEL, *Rec. trav. chim.*, 39 (1920) 656; *Kolloid-Z.*, 32 (1923) 29.

In other cases, however, the coagulation does not follow SMOLUCHOWSKI'S equation. In the course of the coagulation the rate slows down more and more and may even lead to a fairly stable system not coarsening any further. Tables 6 and 7.

TABLE 7¹Gold sol. Particles of $r_1 = 120 \text{ m } \mu$.Coagulated by NaCl, 4.8 millimols per litre. Sol of $4.35 \cdot 10^8$ particles per cm^3 .

t time in hours	$10^{-3} \times$ number of particles per cm^3	T in hours
0	4.35	—
0.5	4.01	59
1	3.74	61
2	3.32	65

3	3.28	94?
5	3.33	160?
9	3.35	300?
28	3.20	670?

Coagulation seems to have stopped after 2 hours.

This behaviour may very well be explained by the application of the ideas in slow coagulation described in § 3. In slow coagulation a certain potential barrier is left and the height of this barrier will be the larger, the larger the particles.

Consequently the factor W by which the coagulation is slowed down as compared with rapid coagulation, is not constant but increases as the particles grow during coagulation and finally the barrier may become so high as to prevent any further agglomeration.

It is impossible to work out this idea quantitatively because the agglomerates will have a very complicated form so that exact calculations on the energy of interaction are not feasible.

As to the influence of factors like the surface potential, concentration of electrolyte, specific properties of the sol, they will be discussed in the next chapter.

§ 8. DETERMINATIONS OF THE RATE OF COAGULATION BY MEASUREMENT OF TYNDALL LIGHT AND EXTINCTION

As the counting of colloidal particles is a very time-consuming business, researches on coagulation are usually performed with other methods. Among these, optical methods, *viz.*, measurements of TYNDALL scattering or light absorption, are the most frequently used. Indeed, also the usual visual determination of the flocculation value depends upon a certain specified degree of turbidity remaining in the sol after a specified time.

The basis for these optical methods is found in RAYLEIGH'S law (*cf.* chapter III) which states that the TYNDALL scattering is proportional to the *square* of the volume of the particles. Therefore, although the number of particles decreases during flocculation,

¹ A. WESTGREN, *Arkiv Kemi Mineral. Geol.*, 7 (1918) nr. 6.

the total scattering increases. Of course, this law of RAYLEIGH needs to be modified when the sol particles are coloured and when they are not very small, but even after these modifications the fact remains that the coagulated system has a light scattering and light absorption different from those of the original system.

The theory of extinction methods has been well described by TROELSTRA¹. As a very simple example we shall treat the case of a white sol (in which light is scattered but not absorbed) and where the particles are so small that RAYLEIGH'S law holds accurately. Moreover we assume that the multiple particles formed during the coagulation scatter as much as a massive spherical particle of the same weight.

Starting with an isodispersed sol with n_0 particles, each of volume v_1 , the scattered light will be given by (see chapter III)

$$I_R = I_0 \cdot K \cdot n_0 \cdot v_1^2 \quad (47)$$

After a certain time t , the number of primary, secondary and other multiple particles will be described by the theory of VON SMOLUCHOWSKI, that is by the eq. (26).

The light scattering is now given by

$$I_R = I_0 K \sum_{i=1}^{\infty} n_i v_i^2 = I_0 K v_1^2 \sum_{i=1}^{\infty} i^2 n_i \quad (48)$$

When the values of n_i from eq. (26) are introduced in (48) we find

$$I_R = I_0 K v_1^2 n_0 \sum_{i=1}^{\infty} \frac{\left(\frac{t}{T}\right)^{i-1} i^2}{\left(1 + \frac{t}{T}\right)^{i+1}} = \frac{I_0 K n_0 v_1^2}{\left(1 + \frac{t}{T}\right)^2} \sum_{i=1}^{\infty} i^2 \alpha^{i-1} \quad (49)$$

in which $\alpha = \frac{t}{t+T}$

The sum $\sum i^2 \alpha^{i-1}$ can be calculated by transforming

$$\begin{aligned} \sum_{i=1}^{\infty} i^2 \alpha^{i-1} &= \sum_{i=1}^{\infty} \alpha^{i-1} \sum_{j=1}^{\infty} (2j-1) = \sum_{j=1}^{\infty} (2j-1) \sum_{i=j}^{\infty} \alpha^{i-1} = \sum_{j=1}^{\infty} (2j-1) \frac{\alpha^{j-1}}{1-\alpha} = \\ &= \frac{1}{1-\alpha} \left\{ \sum_{j=1}^{\infty} \alpha^{j-1} + 2 \sum_{k=1}^{\infty} k \alpha^k \right\} = \frac{1}{1-\alpha} \left\{ \frac{1}{1-\alpha} + 2 \sum_{k=1}^{\infty} \sum_{x=k}^{\infty} \alpha^x \right\} = \\ &= \frac{1}{(1-\alpha)^2} \left\{ 1 + 2 \sum_{k=1}^{\infty} \alpha^k \right\} = \frac{1}{(1-\alpha)^2} \left\{ 1 + \frac{2\alpha}{1-\alpha} \right\} = \frac{1+\alpha}{(1-\alpha)^3} \end{aligned}$$

So

$$I_R = I_0 K n_0 v_1^2 \left(1 + \frac{2t}{T}\right) \quad (50)$$

which means that the scattered light increases linearly with time and is three times the original value after the time of coagulation T .

¹ S. A. TROELSTRA, *Thesis*, Utrecht 1941; S. A. TROELSTRA and H. R. KRUYT, *Kolloid-Beihfte*, 54 (1943) 225.

Usually it has been found easier to measure the extinction E than the amount of scattered light. The extinction E is defined as $\ln I_0/I$ in which I is the intensity of the transmitted light, I_0 that of the incident light. When there is no consumptive absorption and multiple scattering is avoided by using small scatterings, the extinction is given by

$$E = K n_0 v_1^2 \left(1 + \frac{2t}{T} \right) d \quad (51)$$

in which d is the length of the light path in the sol.

TROELSTRA showed that even when there is a certain consumptive absorption and when the sol is not monodispersed but polydispersed, it may nevertheless be expected that the extinction is a linear function of time given in general by

$$E = \text{const.} \left(1 + \frac{\alpha t}{T} \right) \quad (52)$$

where α is a constant of the order of magnitude of 2 or 3.

Practically, however, the extinction curve is not straight but concave to the time-axis (see Fig. 9¹). For a coagulation which has proceeded very far this was to be expected on account of the restricted validity of RAYLEIGH'S law. But even at the start of flocculation the increase of extinction is much smaller than expected from eq. (51). This must be attributed to the fact that agglomerates of particles scatter much less than a massive particle of the same weight, and thus extinction measurements allow us some insight into the structure of the agglomerates.

A typical case is given in Fig. 10 for the flocculation of AgI-sol with KNO_3 . The abscissa gives the concentration of KNO_3 . The time during which the coagulation has proceeded is introduced as a parameter. For concentrations below 150 m mol/l the coagulation is clearly accelerated by increasing amounts of electrolyte. It seems however, as if for concentrations of the order of 250 m mol/l a decrease of the rate of coagulation is found. Now this is completely contrary to all other experimental evidence and the conclusion from Fig. 10 must be that at very high KNO_3 concentrations the flocculation though very rapid ($T \sim$ some seconds!) gives rise to agglomerates that scatter the light less than agglomerates found at smaller concentrations.

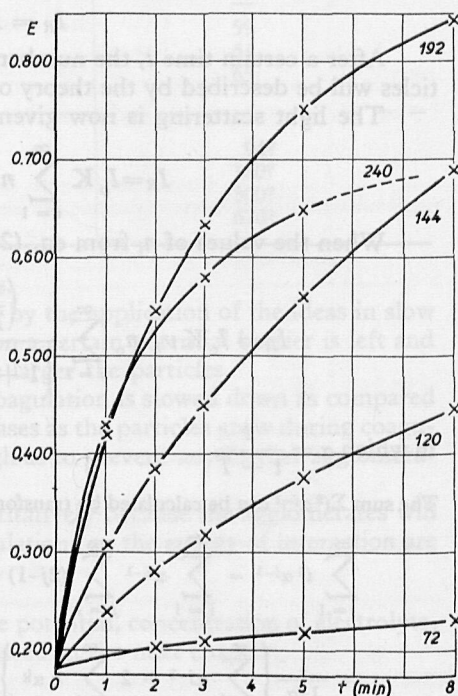


Fig. 9. Extinction-time curves for a silver iodide sol (0.4 m mol/litre) flocculated with KNO_3 . The concentration of KNO_3 in m mol/litre is indicated beside the curves.

¹ This figure and the following ones are taken from S. A. TROELSTRA, *Thesis*, Utrecht 1941; S.A. TROELSTRA and H. R. KRUYT, *Kolloid. Beihefte*, 54 (1943) 225.

The physical interpretation given by TROELSTRA is that the flocs are relatively dense, resembling more the highly scattering RAYLEIGH particles, when the repulsive action of the double layer is not completely discarded.

When the repulsion is completely absent, the flocs are very irregular, rather loose

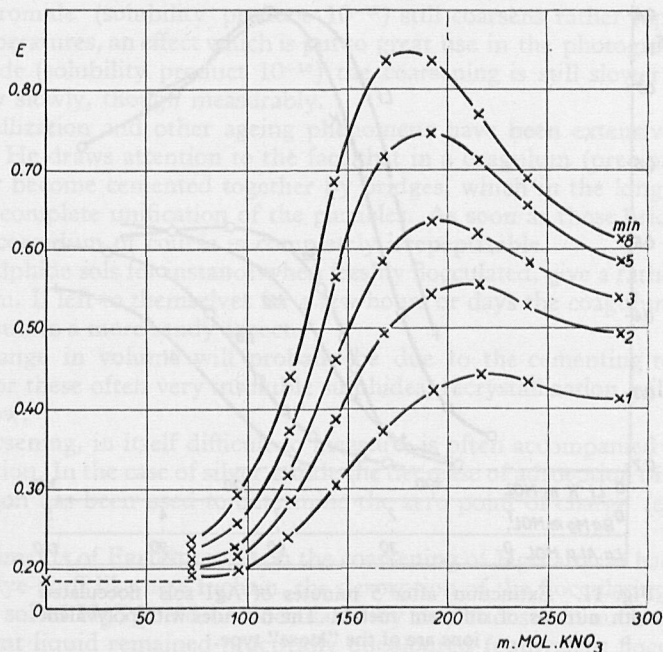


Fig. 10. Extinction-concentration curves for different times of flocculation (AgI sol with KNO₃). The low extinction at high concentrations corresponds to a loose floccule.

and scatter little light. Fig. 11 shows that the maximal extinction after 5 minutes is much larger for monovalent cations than for polyvalent ions which can be explained in the same way. The flocs formed by coagulation with polyvalent ions are always less dense than those formed by monovalent ions. In the same way a coagulum formed after a complete discharging of the surface by addition of potential-determining ions has a very low density.

In the very rapid coagulations, the primary particles are connected in the completely haphazard way in which they first touched each other. If there is just a little repulsion left, rearrangements in the positions are still possible which will be expected to lead to a lower energy, better contact and thus a denser structure. The polyvalent ions seem to act as cementing centres, preventing this type of stabilization.

The increase of turbidity although simple is not the only optical means of following coagulation. Several sols show a distinct change in colour during coagulation. The best known example is the gold sol which from red in the stable state turns blue during coagulation. (Congorubin shows an analogous effect).

The change of colour can be explained by the theory of MIE (*cf.* chapter III) and is due fundamentally to a much larger real consumptive absorption than that of the white or weakly coloured sols.

Because for a normal gold sol this change of colour is produced in a short time

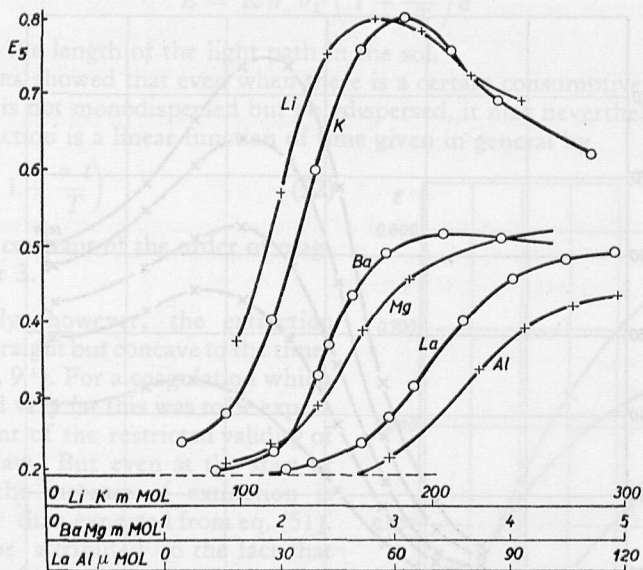


Fig. 11. Extinction after 5 minutes of AgI sols flocculated with nitrates of different metals. The floccules with polyvalent ions are of the "loose" type.

(5 minutes) coagulation experiments with colloidal gold have received much attention. An accurate estimation of a coagulation value is possible here because the change of colour is rather abrupt at a certain stage of coagulation and can be clearly distinguished without waiting for the sedimentation, which takes hours, as is often necessary in other systems.

§ 9. COARSENING AND DESORPTION DURING COAGULATION

A phenomenon which takes place in many sols and during which the number of particles decreases and the light absorption increases is coarsening or recrystallization. It is necessary to distinguish it quite clearly from the coagulation treated in the foregoing sections.

A sol is, as has already been pointed out in chapter I, never a stable system in the thermodynamical sense, because the large interface of sol particles and dispersion medium are a source of surface free energy. This free energy tends to a minimum which can only be reached by replacing the many small particles by a few (in the limit a single) large ones. By coagulation this aim is not accomplished because in the coagulum the particles retain a certain independence. Only small parts of the surface (if any) are

The total surface, however, can be decreased by recrystallization, a phenomenon which of course is more pronounced the higher the solubility of the colloid. So with metal sols this form of coarsening is very weak but in silver-chloride sols it is so pronounced that AgCl sols (solubility product 10^{-10}) cannot be preserved for a very long time.

Silver-bromide (solubility product 10^{-13}) still coarsens rather rapidly at slightly elevated temperatures, an effect which is put to great use in the photographic industry. In silver iodide (solubility product 10^{-16}) the coarsening is still slower and these sols age only very slowly, though measurably.

Recrystallization and other ageing phenomena have been extensively studied by KOLTHOFF¹. He draws attention to the fact that in a coagulum (precipitate) different particles may become cemented together by bridges, which in the long run may even result in the complete unification of the particles. As soon as those bridges have been formed, the coagulum of course is completely irrepeptizable.

Many sulphide sols for instance when freshly flocculated, give a rather voluminous jelly coagulum. If left to themselves for a few hours or days the coagulum shrinks very much and assumes a more sandy aspect.

This change in volume will probably be due to the cementing together of the particles as for these often very insoluble sulphides, recrystallization will be expected to be very slow.

The coarsening, in itself difficult to measure, is often accompanied by a decrease of the adsorption. In the case of silver iodide the decrease of adsorption of the potential-determining ion has been used to determine the zero point of charge (cf. chapter IV, § 6a, p. 160).

In experiments of FREUNDLICH² on the coarsening of HgS after it had been coagulated with a dye-stuff like new fuchsin, the desorption of the flocculating ion was very marked. The sol of HgS could be flocculated by new fuchsin in such quantities that the supernatant liquid remained practically uncoloured (equivalent flocculation).

After some time the surface of the precipitate decreased, the dyestuff ion returned to the liquid phase and the supernatant liquid became distinctly coloured³.

P. STOLL⁴ could establish a coarsening of flocculated gold by X-ray measurements. In the sol and the fresh coagulum the X-ray diffraction lines are broadened because the particles are so very small. After coagulation the lines become sharper.

¹ See e. g., I. M. KOLTHOFF, *Proc. Koninkl. Nederland Akad. Wetenschap*, 40 (1937) 82; *Chem. Weekblad*, 29 (1932) 362; 31 (1934) 526, and a long series of papers "Studies on aging and formation of precipitates" in *J. Am. Chem. Soc.*, and *J. phys. Chem.*, started in 1934, I. M. KOLTHOFF and CH. ROSENBLUM, *J. Am. Chem. Soc.*, 56 (1934) 1264.

² H. FREUNDLICH and H. SCHUCHT, *Z. phys. Chem.*, 85 (1913) 660; H. FREUNDLICH and E. HASE, *Z. phys. Chem.*, 89 (1915) 417.

³ Many examples of the adsorption method to determine the surface of a precipitate are given by KOLTHOFF. *l.c.*

⁴ P. STOLL, *Arch. sci. phys. et nat.*, (5) 3 (1921) 547.