

# THE RATE OF COAGULATION AS A MEASURE OF THE STABILITY OF SILVER IODIDE SOLS

BY H. REERINK\* AND J. TH. G. OVERBEEK  
van't Hoff Laboratory, University of Utrecht

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The form of the energy barrier between two sol particles is calculated from the electrical repulsion and the van der Waals attraction. Flocculation is retarded by this barrier, and the retardation factor  $W$  of the slow coagulation as compared to the rapid coagulation of the same sol is connected to it.

It follows from numerical computations for monodisperse sols with spherical particles:

- (a) the value of  $W$  is mainly determined by the height  $V_m$  of the energy barrier;
- (b) there is a nearly linear relationship between  $\log W$  and  $\log c_e$ ,  $c_e$  being the concentration of electrolyte.

Approximate equations are derived for the relation between  $W$  and  $V_m$ , and between  $W$  and the concentration and valency of the electrolyte, the van der Waals constant, the surface potential and the particle radius.

Experiments were performed to test the theory. Various silver iodide sols were mixed with various electrolytes. By means of different sol and electrolyte concentrations a range of  $10^4$  in  $W$  was covered.

The change in turbidity was used to measure the rate of coagulation. This method worked well with polyvalent gegenions while there were some complications with monovalent ions.

The theory is confirmed by our own experimental results and by work of other authors as far as the linear relationship between  $\log W$  and  $\log c_e$  is concerned. For small particles absolute values of the surface potential and the van der Waals constant as derived from the slow coagulation agree reasonably well with other estimates. With coarser sols the calculated value of the surface potential was definitely too low.

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The stability of lyophobic colloids depends upon the energy of interaction between two approaching particles. According to Verwey and Overbeek<sup>1</sup> this energy is composed of a long range electrical repulsion and a long range van der Waals attraction. For a given colloid the attraction is assumed to be constant while the repulsion changes with the electrolyte content of the system. With decreasing repulsion the stability decreases.

When there is no repulsion every collision of two colloidal particles leads to coagulation (rapid coagulation). When the repulsive energy is not zero only a fraction  $1/W$  of the collisions leads to coagulation (slow coagulation). With increasing repulsion the value of  $W$  increases. Therefore  $W$  can be used as a quantitative measure of the stability, and we will call  $W$  the stability factor.

No lyophobic sol is absolutely stable against coagulation; that is  $W$  is always finite. However  $W$  may be so large, e.g.  $W > 10^9$  that a sol in this state does not change perceptibly in many years.

A relation between the stability factor  $W$  and the energy of interaction can be derived from the theory of Verwey and Overbeek. It is the purpose of this paper to test this relation and some of its implications.

\* Present address: Koninklijke/Shell Laboratory, Amsterdam.

## I. THEORETICAL PART

1. INTERACTION OF COLLOIDAL PARTICLES. The energy of interaction has been calculated for the models of infinite plane particles and of spherical particles. In our experiments we used silver iodide sols with relatively small particles which from electronmicrographs<sup>2</sup> were shown to be nearly spherical. Therefore we chose the spherical model.

(i) *Structure of the double layer.*

As far as the stability is concerned the following model of the double layer will suffice.<sup>3</sup> The particle surface acquires a surface charge by adsorption of potential determining ions. A layer of gegenions adheres to the surface forming an ionic condenser, the Stern layer.<sup>4</sup> From here the diffuse part of the double layer extends into the solution.<sup>5, 6</sup>

The repulsive energy depends upon the potential across the diffuse part of the double layer,  $\psi_\delta$  (Stern potential), and the concentration and valency of the gegenions in the solution.<sup>1</sup>

(ii) *Interaction of spherical diffuse double layers.*

The electrical energy of interaction between the overlapping double layers on two spherical particles of equal size  $V_R^{aa}$ , calculated according to Verwey and Overbeek, appears to be positive which means that the particles repel each other. An approximate expression reads<sup>7</sup> (at 25° C in water as a solvent):

$$\begin{aligned} V_R^{aa} &= 4.62 \times 10^{-6} (\alpha\gamma^2/v^2) \exp(-\kappa H_0) \\ &= 4.62 \times 10^{-6} (\alpha\gamma^2/v^2) \exp(-\tau u) = C \exp(-\tau u), \end{aligned} \quad (1.1)$$

$$\gamma = (e^{z/2} - 1)/(e^{z/2} + 1), \quad z = v e \psi_\delta / kT,$$

$v$  = valency of gegenions,

$H_0$  = shortest distance between particle surfaces,

$\kappa = (8\pi n v^2 e^2 / \epsilon kT)^{1/2}$  is the familiar expression in the theory of Debye and Hückel<sup>8</sup>;  $1/\kappa$  is a measure of the thickness of the diffuse double layer.

$$\tau = \kappa a,$$

$$u = H_0/a,$$

$$a = \text{particle radius.}$$

An equation for the repulsion between two unequal spheres of radii  $a$  and  $b$  can be derived in the same way as (1.1).

$$V_R^{ab} = 2b/(a+b) \times V_R^{aa} = q V_R^{aa}; \quad b > a, \quad (1.2)$$

(iii) *Forces of attraction.*

The concept of long range van der Waals forces was first introduced in colloid chemistry by Kallmann and Willstätter,<sup>9</sup> and theoretically developed by de Boer<sup>10</sup> and Hamaker.<sup>11</sup> In the stability theory of Verwey and Overbeek these forces play an important role. Sparnaay<sup>12</sup> succeeded in measuring directly forces of the predicted order of magnitude.

An approximate expression for the attraction potential between two spheres for short distances ( $u \ll 1$ ) is given by Hamaker

$$V_A^{ab} = -2b/(a+b) \times A/12u = -q A/12u = q V_A^{aa}, \quad (1.3)$$

where  $A$  is the van der Waals constant.

iv) *Total energy of interaction.*

The total energy  $V$  is the sum of the repulsive and attractive potentials

$$V(u) = V_R(u) + V_A(u) \quad (1.4)$$

Fig. 1 shows the influence of electrolyte concentration  $c_e$  on  $V$ , calculated with complete expressions for attraction and repulsion and with the approximations (1.1) and (1.3). It appears that the approximate curves are much too low. The main cause for this is a failure of eqn. (1.3) in this region of  $u$  values. Notwithstanding this systematic error the approximate equations are still quite useful as will be pointed out in § 4 (ii).

## 2. THE RATE OF COAGULATION.

The kinetics of rapid coagulation of monodispersed sols have already been described in 1916 by von Smoluchowski,<sup>13</sup> who considered the process as a diffusion of the colloidal particles towards each other. It has been shown by Müller<sup>14</sup> that normal polydispersity has little influence on the results.

With regard to the slow coagulation von Smoluchowski assumed that the stability factor  $W$  remained constant during the whole process. Experiments show that this is by no means true: <sup>15, 16</sup> the rate of coagulation decreases in the course of slow coagulations.

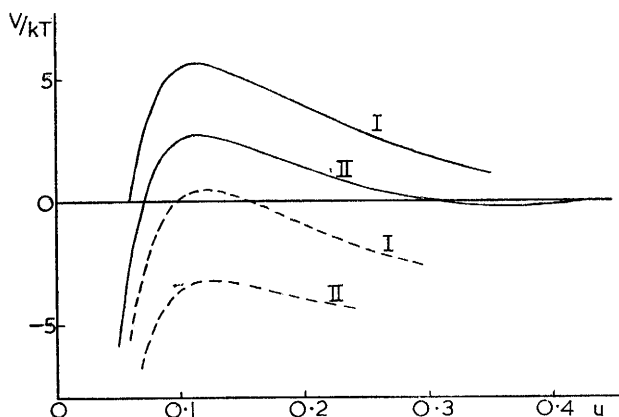


FIG. 1.—Energy of interaction as a function of particle distance for equal spheres. Drawn curves: exact calculations according to Verwey and Overbeek, and Hamaker. Dashed curves: approximated with (1.1) and (1.3)

$$a = 10^{-6} \text{ cm}, \quad A = 10^{-12} \text{ erg}, \quad v = 1, \quad z = 3.$$

Curves I:  $c_e = 59.5$  mmole/l.      Curves II:  $c_e = 93$  mmole/l.

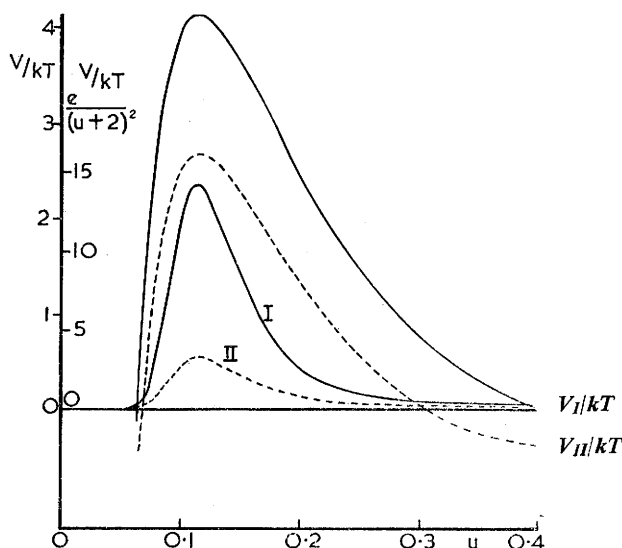


FIG. 2.—Energy of interaction and corresponding values of  $\exp(V/kT)/(u+2)^2$ .

$$a = 10^{-6} \text{ cm}, \quad A = 10^{-12} \text{ erg}, \quad v = 1, \quad z = 3.$$

Drawn curves:  $c_e = 75$  mmole/l.      Dashed curves:  $c_e = 93$  mmole/l.

This is explained by the fact that, other conditions being equal, the repulsion between aggregates is larger than that between single particles. Since we want to characterize the stability of the original sol and not of the aggregates, the value of  $W$  must be extrapolated to zero time.

Considering the slow coagulation as a diffusion process in a potential field Fuchs<sup>17</sup> derived a relation between the energy of interaction  $V$  and the stability factor  $W$ .

$$W = 2 \int_0^{\infty} \exp(V/kT) \frac{du}{(u+2)^2} \quad (2.1)$$

From potential curves of the type given in fig. 1 the value of  $W$  can be evaluated by graphical or numerical integration. In fig. 2 two potential curves and the corresponding values of  $\exp(V/kT)/(u+2)^2$  are given. It appears that the value of  $W$  is mainly determined by the maximum  $V_m$  in the potential curve, the width and shape of the exponential curves being about the same.

From plots of  $\log W$  against  $\log c_e$  a nearly linear relationship is found (see fig. 3). At high electrolyte concentrations the repulsion is zero and  $W = 1$ . The bend in the curves lies in the region where  $V_m/kT = 1$ .

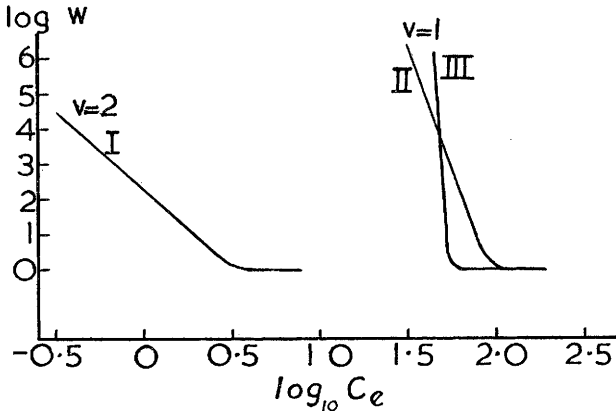


FIG. 3.—Relation between stability factor and electrolyte concentration  $c_e$  (mmole/l.)

Curve I :	$a = 10^{-6}$ cm.	$A = 2 \times 10^{-12}$ erg.	$v = 2,$	$z = 6,$
Curve II :	$a = 10^{-6}$ cm.	$A = 2 \times 10^{-12}$ erg.	$v = 1,$	$z = 5,$
Curve III :	$a = 5 \times 10^{-6}$ cm.	$A = 2 \times 10^{-12}$ erg.	$v = 1,$	$z = 5,$

### 3. INFLUENCE OF POLYDISPERSITY AND STERN POTENTIAL.

It can be shown<sup>18</sup> that polydispersity tends to stability curves which are slightly concave towards the axes. On the other hand the Stern potential  $\psi_\delta$  decreases somewhat with increasing electrolyte concentration, which effect tends to give convex curves. Both influences are difficult to estimate. Since they are opposite to each other and from experiments nearly straight curves are obtained we neglected both effects and used the theory for mono dispersed sols with constant  $\psi_\delta$ .

### 4. DERIVATION OF APPROXIMATE RELATIONS.

To avoid the laborious computations of the exact Verwey and Overbeek theory two approximate equations were derived. One has the form  $W = k \exp V_m$ , indicating that the stability factor  $W$  is determined by the maximum  $V_m$  in the potential curve. The other starts from the approximate equations (1.1) and (1.3) and leads to a linear relationship between  $\log W$  and  $\log c_e$ .

#### (i) The maximum in the potential curve.

For  $V_m > kT$  only the values of  $\exp(V/kT)/(u+2)^2$  which lie in the neighbourhood of the maximum contribute to the integral in (2.1). In this region  $(u+2)$  only changes a few per cent. Therefore we write  $(u_m+2)$  instead of  $(u+2)$ , where  $u_m$  corresponds to the maximum  $V_m$ . From (2.1) we obtain :

$$W = 2/(u_m+2)^2 \int_0^{\infty} \exp(V/kT) du \quad (4.1)$$

Expanding  $V(u)$  in the neighbourhood of  $V_m$  in a Taylor series gives

$$V = V_m + V_m'' (\Delta u)^2/2 + \dots \quad (4.2)$$

as  $V_m' = 0$ .

Using (4.2) and neglecting higher terms the exponential curve is replaced by a Gauss curve with the same height and the same curvature in the maximum.

$$\begin{aligned} W &= \frac{2 \exp(V_m/kT)}{(u_m + 2)^2} \int_0^\infty \exp \left[ \frac{V_m'' (\Delta u)^2}{2kT} \right] du \\ &= \frac{2 \exp(V_m/kT)}{(u_m + 2)^2} \int_{-\infty}^\infty \exp [-p^2 (\Delta u)^2] d(\Delta u); \quad p = (-V_m''/2kT)^{1/2}. \end{aligned} \quad (4.3)$$

Replacing the lower limit of integration by  $-\infty$ , which introduces only a negligible error, we obtain:

$$W = 2\pi^{1/2}/p(u_m + 2)^2 \times \exp(V_m/kT) \quad (4.4)$$

In the appendix it will be shown that  $p(u_m + 2)^2$  is practically constant. Thus  $W$  is determined by  $V_m$ .

With the help of eqn. (4.4),  $W$  can be evaluated from the potential curves without the tedious graphical integration of the exponential curves. In fig. 4 this procedure is compared to the complete calculation. It appears that eqn. (4.4) is rather a good approximation, except evidently in the region where  $W_{\text{exact}}$  approaches the value 1.

(ii) *The linear relation between  $\log W$  and  $\log c_e$ .*

Starting with the approximate equations (1.1) and (1.3) the following relation can be derived (see appendix):

$$\begin{aligned} \log W &= - (A/24 u_m kT) \log c_e - (A/24 u_m kT) \log (8\pi N v^2 e^2 a^2 10^{-6}/\epsilon kT) \\ &\quad + (3/2 - A/12 u_m kT) \log u_m + \frac{1}{2} \log 96\pi kT/A \\ &\quad - \frac{1}{2} \log (2 - \tau u_m) (u_m + 2)^4 \\ &= - k_1 \log c_e + k_2 \end{aligned} \quad (4.5)$$

where  $k_1$  and  $k_2$  are constants, and  $N$  is the Avogadro number.

In fig. 4 curves calculated from eqn. (4.5) are shown together with the exact curves and the approximation (4.4).

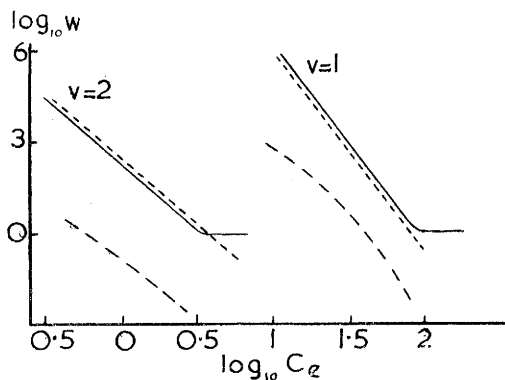


FIG. 4.—Relation between  $W$  and  $c_e$  for different approximations.

Left set of curves:  $a = 10^{-6}$  cm.  $A = 2 \times 10^{-12}$  erg.  $z = 6$ .  $v = 2$ .

Right set:  $a = 10^{-6}$  cm.  $A = 10^{-12}$  erg.  $z = 3$ .  $v = 1$ .

Drawn curves: exact calculations.

Dashed curves: approximation (4.4).

Interrupted curves: approximation (4.5).

At first sight eqn. (4.5) appears to be a bad approximation. In the first place the curves lie much too low. This is readily explained, because the approximate energy curves lie much lower than the exact ones (see fig. 1). As the absolute values of the approximations for the repulsive and attractive energies are both too large a nearly exact compensation of errors occurs for certain combinations of  $\psi_\delta$  and  $A$  (for instance  $a = 10^{-6}$ ,  $A = 3 \times 10^{-13}$ ,  $z = 3$ ,  $v = 1$ ). Secondly, the curves are not straight. This is explained in the appendix.

Nevertheless eqn. (4.5) is useful to calculate the slope of the stability curve. This slope is given by (see appendix) (at 25° C in water as a solvent):

$$\frac{d \log W}{d \log c_e} = - 2.15 \times 10^7 a \gamma^2 / v^2 \quad (4.6)$$

If one point of the curve is obtained with the exact theory or with eqn. (4.4) the remainder can be calculated conveniently with (4.6). Table 1 shows that exact and approximate slopes are in reasonable agreement. It may be remarked that according to both calculations the value of  $A$  has no influence on the slope of the stability curves. The slope is proportional to the radius of the particles and increases with increasing surface potential.

TABLE 1.—COMPARISON OF EXACT AND APPROXIMATE SLOPE.

$a$ cm	$A$ erg	$z$	$v$	$\frac{d \log W}{d \log c_e}$	
				exact	approximation (4.6)
10 <sup>-6</sup>	10 <sup>-12</sup>	3	1	— 6.6	— 8.6
10 <sup>-6</sup>	2 × 10 <sup>-12</sup>	3	1	— 6.6	— 8.6
10 <sup>-6</sup>	2 × 10 <sup>-12</sup>	5	1	— 14.0	— 15.3
5 × 10 <sup>-6</sup>	2 × 10 <sup>-12</sup>	5	1	— 72	— 76
10 <sup>-6</sup>	2 × 10 <sup>-12</sup>	6	2	— 4.9	— 4.4

### 5. EVALUATION OF STERN POTENTIAL AND VAN DER WAALS CONSTANT FROM EXPERIMENTAL STABILITY CURVES.

The slope of the stability curves immediately leads to  $\gamma$  and to the Stern potential  $\psi_\delta$  with the help of eqn. (4.6) and (1.1).

With  $\psi_\delta$  as determined in this way stability curves are constructed for a number of values of the van der Waals constant  $A$ . These curves are all parallel. The value of  $A$  belonging to the experimental curve can now be determined by interpolation.

### 6. APPENDIX.

*The linear relationship between  $\log W$  and  $\log c_e$*

For two particles of equal size the total energy of interaction follows from (1.1) and (1.3):

$$V(u) = C \exp(-\tau u) - A/12u. \quad (6.1)$$

The maximum of  $V(u)$  is obtained when

$$C \exp(-\tau u_m) = A/12\tau u_m^2. \quad (6.2)$$

Combination of (6.1) and (6.2) gives

$$V_m = A/12u_m \times (1/\tau u_m - 1). \quad (6.3)$$

In practical cases the values of  $\tau u_m$  lie in the neighbourhood of 1 and  $u_m$  changes only very slowly with  $\tau$ .

Eqn. (6.3) shows that for  $V_m = 0$  the value of  $\tau u_m$  exactly equals 1 and by differentiating eqn. (6.2) it is found that

$$\frac{du_m}{d\tau} = -\frac{u_m(1 - \tau u_m)}{\tau(2 - \tau u_m)} \quad (6.4)$$

which is zero for  $\tau u_m = 1$ .

As the flocculation conditions are always close to the case where  $V_m = 0$ , we may consider  $\tau u_m \approx 1$  and  $u_m$  as a constant.

We thus may write

$$1/\tau u_m - 1 = -\ln \tau u_m. \quad (6.5)$$

From (4.4), (6.3) and (6.5) we obtain

$$\log W = - (A/12u_m kT) \log \tau - (A/12u_m kT) \log u_m + \log 2\pi^{\frac{1}{2}} - \log p (u_m + 2)^2 \quad (6.6)$$

And from (4.3) and (6.1),

$$p^2 = -V_m''/2kT = A/24kT \times (2 - \tau u_m)/u_m^3. \quad (6.7)$$

Combination of (6.6) and (6.7), with the help of the definitions in (1.1), leads to:

$$\log W = - (A/24u_m kT) \log c_e - (A/24u_m kT) \log (8\pi N v^2 e^2 a^2 10^{-6}/\epsilon kT) \\ + (3/2 - A/12u_m kT) \log u_m + \frac{1}{2} \log 96\pi kT/A - \frac{1}{2} \log (2 - \tau u_m) (u_m + 2)^4, \quad (6.8)$$

where  $c_e$  is expressed in mmoles/l., and  $N$  is the Avogadro number.

Since on changing  $c_e$  the changes in  $(2 - \tau u_m)$  and  $u_m$  are small compared to the changes in  $c_e$  all terms in (6.8) except the first one may be considered to be constant. Therefore,

$$\log W = -k_1 \log c_e + k_2, \quad (6.9)$$

see eqn. (4.5).

It is clear that eqn. (6.5)-(6.9) only hold in a relatively small region of  $\tau$ -values. Application of (6.8), outside this region and taking the non-constancy of  $u_m$  into account will result in curved stability curves (see fig. 4).

The slope  $k_1$  still contains  $u_m$ . This may be eliminated by calculating  $u_m$  from eqn. (6.2) using the condition that  $\tau u_m = 1$ . This leads to

$$u_m = Ae/12C. \quad (6.10)$$

Inserting this value into eqn. (6.8) the slope of the stability curve is found to be (at 25° C and using water as a solvent)

$$d \log W / d \log c_e = -C/2ekT = -2.15 \times 10^7 \alpha \gamma^2 / v^2. \quad (6.11)$$

## II. EXPERIMENTAL TEST OF THE THEORY

The theory has been tested by specially designed experiments on silver iodide sols and by using data already present in the literature.

### 7. PREPARATION AND CHARACTERIZATION OF AgI-SOLS.

Details of our experiments on AgI will be reported elsewhere. We will restrict ourselves here to the bare outlines.

In order to test the influence of particle size, five sols were used.

*Sol A* was prepared by mixing dilute solutions of  $\text{AgNO}_3$  and KI, followed by electro-dialysis and electrodecantation using the methods described by de Bruyn and Troelstra.<sup>19</sup>

*Sol B* consisted of the fine particles of sol A, that did not settle after centrifuging during 3 hours at about 2000g.

*Sol C* consisted of the coarse particles of sol A obtained by careful sedimentation.

*Sol D* was obtained from sol A by ageing at 95° during 50 hours.

*Sol E* was prepared following Troelstra<sup>20</sup> by pouring a solution of AgI in concentrated KI into water under vigorous stirring.

All the sols used were brought to  $p_1 = 4$  with KI.

Particle sizes were determined by sedimentation, turbidity measurements (using Rayleigh's law) or from electronmicrographs. Although none of these methods gives very accurate results, table 2 shows a reasonable agreement between different methods.

TABLE 2.—PARTICLE RADIUS IN Å OF DIFFERENT AgI SOLS

	sol A	sol B	sol C	sol D	sol E
rate of sedimentation (minimum value)	—	250	550	—	1560
turbidity (weight average)	520	205	520	650	—
electronmicroscope (number average)	—	—	—	—	2000

### 8. DETERMINATION OF RATE OF COAGULATION AND STABILITY FACTOR.

In most cases the rate of coagulation was determined from turbidity. In the case of coagulating hydrophobic systems, light scattering is not suited to determine absolute values for the number of particles because the scattered light is not in a simple way related to the size of the aggregates. It may be assumed, however, that the scattering is uniquely determined by the state of coagulation, irrespective of the rate at which it is reached. Therefore rates of coagulation can be compared with each other by measuring the times after which a certain amount of scattering is obtained. This comparison is simplified by the fact that extinction-time curves all start with a linear part in agreement with calculations and observations by Troelstra<sup>21</sup> and Oster.<sup>22</sup> Fig. 5 gives a few of our observations on the flocculation of Sol A with  $\text{Ba}(\text{NO}_3)_2$ .

The slopes of the curves for zero time are proportional to the rate of coagulation or inversely proportional to the stability factor  $W$ ,

$$dE/dt \propto 1/W. \quad (8.1)$$

In order to cover a large range in  $W$  without getting involved in measurements at very short or inconveniently long times the sol concentration was varied. As coagulation is essentially a "bimolecular" process the rate of change of extinction is given by

$$dE/dt \propto C_s^2 d/W, \text{ or } 1/W \propto (dE/dt)/(C_s^2 d), \quad (8.2)$$

where  $C_s$  is the sol concentration and  $d$  the length of the light-path in the sol. It was verified that the Lambert-Beer law holds up to extinctions of about 1.2.

This method of determining  $W$  from eqn. (8.2) was very successful for flocculations with bi- and trivalent ions. With monovalent ions some complications arose. The extinction was too high, probably due to a rearrangement of the primary particles in the aggregates. The stability curves ( $W$  against  $c_e$ ) were therefore extrapolated to infinite sol concentration where the rate of this secondary rearrangement could be neglected compared to the rate of flocculation.

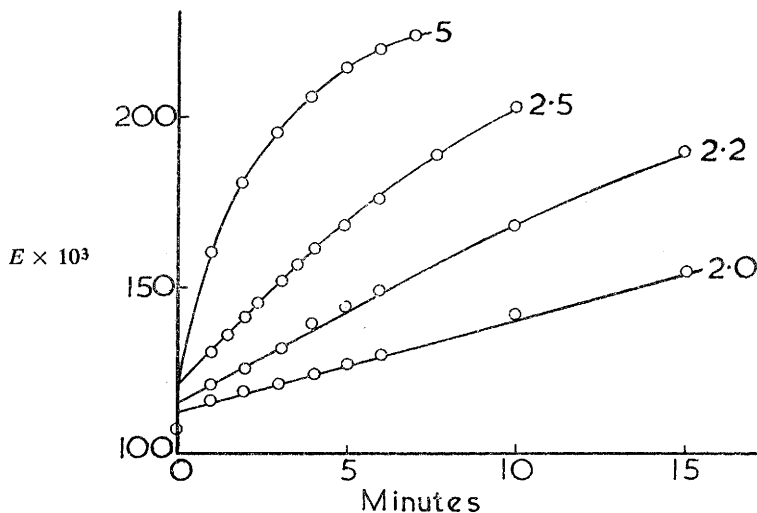


FIG. 5.—Extinction against time for different  $\text{Ba}(\text{NO}_3)_2$  concentrations indicated by the numbers (in mmole/l.). Sol A. Concentration 0.1 mmole/l. AgI.

For the very coarse sol E the extinction changed only very little during flocculation. In this case the rates of flocculation were evaluated by counting the particles in the ultra-microscope.

For a single example (sol C with  $\text{Ba}(\text{NO}_3)_2$ ), table 3 shows all the values of the stability factor obtained at different sol concentrations and electrolyte concentrations.

TABLE 3.—VALUES OF  $10^3/C_s^2 d \times dE/dt = \text{const}/W$  FOR SOL C AS A FUNCTION OF  $\text{Ba}(\text{NO}_3)_2$  CONCENTRATION. ALL CONCENTRATIONS IN MMOLE/L.  $p_1 = 4$

	$c_e = 5.0$ rapid flocculation	2.5	2.2	2.0	1.8	1.65	1.5	1.4	1.2
$C_s = 1.16$	—	—	—	—	28	14	6.2	2.8	0.52
0.58	—	285	137	74	25	12	5.9		
0.29	—	—	143	—					
0.145	2040	238	—	71					

The proportionality constant is evaluated from rapid flocculations, where  $W = 1$ .



## 9. DISCUSSION OF THE STABILITY CURVES

Stability curves for the AgI sols A-E are pictured in fig. 6. The linear relationship required by the theory is confirmed.

In fig. 7 stability curves are given which are calculated from coagulation measurements by other authors. In addition it may be mentioned that already in 1912 Paine<sup>23</sup> gave an empirical relation:  $\log W = k - p \log c_e$ , with  $p$  as a constant between 5 and 6. The slopes in fig. 7 range from -2 to -14.

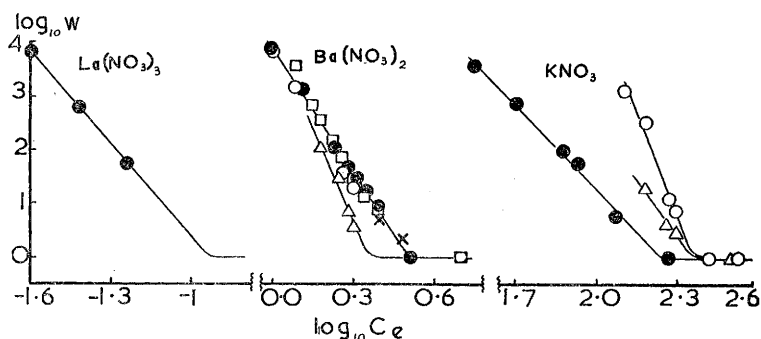


FIG. 6.—Stability curves for silver iodide sols. Electrolyte concentration in mmole/l.

● sol A; ○ sol B; □ sol C; × sol D; △ sol E.

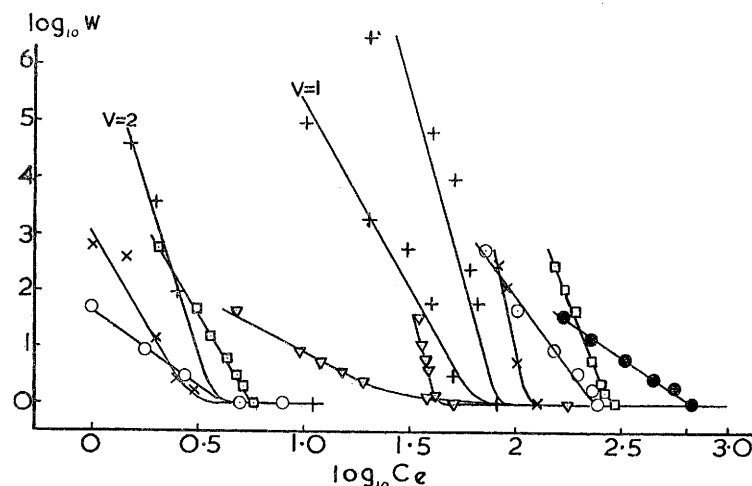


FIG. 7.—Stability curves for various sols.

- |  |   |
|--|---|
| □ AgI sol, Lepin and Bromberg; <sup>24</sup>       | ○ AgI sol, Hermans; <sup>25</sup>                                       |
| ▽ gold sol (steep curve), Tuorila; <sup>16</sup>   | ▽ gold sol (flat curve), Westgren; <sup>26</sup>                        |
| ● WO <sub>3</sub> sol, Hermans; <sup>25</sup>      | × As <sub>2</sub> S <sub>3</sub> sol, Hofmann and Wannow; <sup>27</sup> |
| + selenium sol, Van Arkel and Kruyt. <sup>15</sup> |   |

Although the linear relationship is in accord with theory, eqn. (6.11) is not confirmed as far as the proportionality between slope and particle radius is concerned. For Ba(NO<sub>3</sub>)<sub>2</sub> there is no significant difference between the fine sol B on the one hand and sols A, C and D on the other. The coarse sol E shows qualitatively the predicted effect that its stability curve is steeper than and intersects the curve

of the finer sols but the slopes  $d \log W/d \log c_e$  are not proportional to  $a$ . For  $\text{KNO}_3$  the results are still worse, the fine sol B having the steepest slope.

There are only very few older publications on the influence of particle size on slow coagulations. Westgren<sup>26</sup> measured rates of coagulation of three monodisperse gold sols with particle radii of 490 Å, 770 Å and 1200 Å at various electrolyte concentrations, and could not find any difference between them.

Tuorila<sup>16</sup> on the other hand showed that in a mixture of two gold sols ( $a = 20$  Å and 250 Å) at a rather high electrolyte concentration the coarse particles coagulated at a much higher rate than the small ones. It may be assumed that  $\psi_\delta$  had the same value for both kinds of particles in this mixture, while in Westgren's experiments  $\psi_\delta$  may have had different values for the various sols.

Holliday<sup>28</sup> demonstrated a higher stability for larger particles. In a very fine gold sol the primary particles became unstable upon dialysis (low  $c_e$ ) and coagulated, forming aggregates of two primary particles which did not flocculate any further. Application of the theory of Verwey and Overbeek leads to the plausible value of  $\psi_\delta \approx 100$  mV.

The results of van Arkel and Kruyt<sup>15</sup> on selenium sols show rather large differences in coagulating rate at nearly the same particle size. Here, too, nothing was known about  $\psi_\delta$ .

It seems permissible to draw the conclusion that there is an influence of particle size, but this influence is over-estimated by eqn. (6.11). Possible reasons for this discrepancy may be deviations from spherical shape, or imperfections of the theory of interaction of spherical double layers.

Yet we have used eqn. (6.11) to evaluate  $\psi_\delta$  and Å (see § 5). The results are given in table 4 for our silver iodide sols and in table 5 for those sols of fig. 7 for which particle sizes are known.

TABLE 4.—VALUES OF STERN-POTENTIAL AND VAN DER WAALS CONSTANT

electrolyte	sol	$a$ Å	$\frac{d \log W}{d \log c_e}$	$\psi_\delta$ mV	$A \times 10^{12}$ erg
$\text{KNO}_3$	A	520	— 5.9	— 24	0.05
	B	250	— 10.6	— 48	0.2
	E	2000	— 7.3	— 14	0.02
$\text{Ba}(\text{NO}_3)_2$	A	520	— 8.0	— 30	0.4
	B	250	— 8.0	— 53	0.9
	C	520	— 8.0	— 30	0.4
	D	650	— 8.0	— 26	0.3
	E	2000	— 11.0	— 12	0.2
$\text{La}(\text{NO}_3)_3$	A	520	— 5.8	— 28	1.0

TABLE 5.—VALUES OF STERN-POTENTIAL AND VAN DER WAALS CONSTANT

sol	electrolyte	$a$ Å	$\frac{d \log W}{d \log c_e}$	$\psi_\delta$ mV	$A \times 10^{12}$ erg	authors
gold	LiCl	350	— 14	— 48	0.6	Tuorila <sup>16</sup>
	KCl	350	— 14	— 48	0.6	
	CsCl	350	— 14	— 48	0.6	
gold	LiCl	900	— 4.0	— 15	0.1	Westgren <sup>26</sup>
	NaCl	900	— 2.0	— 10	0.05	
selenium	KCl	500	— 13.0	— 37	0.2	Van Arkel and Kruyt <sup>15</sup>
		520	— 4.7	— 20	0.05	
		620	— 5.8	— 20	0.1	
selenium	$\text{BaCl}_2$	560	— 5.0	— 21	0.2	Van Arkel and Kruyt <sup>15</sup>
		560	— 6.2	— 24	0.2	
		620	— 11.8	— 35	0.5	

The values of  $\psi_0$  have the expected order of magnitude (10-100 mV) although as a rule they are rather on the low side. This is especially striking for the coarse sol E and Westgren's gold sol. On the other hand the rule of Schulze and Hardy is obviously obeyed in all cases mentioned and this points to (see ref. (1), p. 119) a rather high value of the surface potential ( $> 25$  mV).

It may be that the particle radius  $a$  has been over-estimated in so far that it is rather the radius of curvature at protrusions on the particle than half its diameter that determines its interaction with other particles.

Tables 4 and 5 also give the van der Waals constant  $A$  calculated in the way described in § 5. The values are in agreement with other estimates derived from flocculation values and from London's theory. The great scatter in  $A$  for one sol shows that there are still serious shortcomings in the theory, but the assumption of a lower value for the effective particle radius  $a$  as indicated above would bring the van der Waals constants more in line with the values found for the smallest sol particles.

Our results might be summarized in the following way. Taking into account the comparative crudeness of the theoretical approach the agreement with experiments is satisfactory. The straight line relationship and the fact that we find the correct order of magnitude of surface potential and van der Waals constant confirm the present picture of the stability of hydrophobic colloids. It certainly is desirable to improve both theory and experiments. Good experiments with truly spherical particles (e.g. with emulsions) are especially desirable.

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