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XXVIII. *An Experimental Test of Smoluchowski's Theory of the Kinetics of the Process of Coagulation.* By JNANENDRA NATH MUKHERJEE, D.Sc., Professor of Physical Chemistry, University of Calcutta, and B. CONSTANTINE PAPA-CONSTANTINOU, D.Sc., Assistant Professor of Chemistry, University of Athens*.

A short account of the Theory.

IN some experiments on the degree of dispersion of colloidal arsenious sulphide on the rate of coagulation, it has been shown (J. Amer. Chem. Soc. vol. xxxvii. p. 2026, 1915; and Sen, Trans. Chem. Soc. vol. cxv. pp. 467-8, 1919) that the finer sol is less stable. In 1915 one of us pointed out the obvious connexion with the increased facilities of coalescence. The smaller particles have a more vigorous Brownian movement due to the smaller frictional resistance of the medium. This would be clear from the well-known equation of Einstein. The diminution in the mean distance between the particles also increases the rate of collisions. It was stated that the adsorption theory does not take these factors into consideration. Recently Smoluchowski (*Zeit. Phys. Chem.* vol. xcii. p. 129, 1917) has been able to formulate the progress of the coalescence with time. His attention was drawn to the subject by Zsigmondy. Bredig (*Anorganische Fermente*, 1901, p. 15) suggested as the cause of coalescence an increase in surface tension with a decrease in the electric density on the particles. Zsigmondy (*Zeitsch. Physikal. Chem.* vol. xcii. p. 500, 1918) modified this idea in the sense that there is an attraction between the particles which increases with decrease in the electric charge. As a result of this attraction he assumes that when one particle comes within a certain distance of another, the two coalesce. This distance is taken as a measure of the force of attraction and is called the radius of the sphere of action. It has been shown by Zsigmondy that the time required for a definite colour-change in a gold sol gradually decreases with rise in electrolyte concentration till it reaches a minimum †, which does not change any further with higher

* Communicated by Prof. F. G. Donnan, F.R.S.

† Similar minimum times have been observed with cupric sulphide and mercuric sulphide sols by the writers. A copper sulphide sol gave two minutes as the time necessary for the appearance of visible clots when the concentration of the precipitating electrolyte (barium chloride) was varied from N/300 to N/20. At dilutions higher than N/300 the time was observed to increase as usual (Mukherjee and Sen, *loc. cit.*).

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concentrations. This was assumed to prove that the radius of attraction reached a maximum value.

Smoluchowski utilized this idea of a sphere of action to avoid a consideration of the forces that influence the coalescence. He considers the probability of particles coming within their mutual sphere of action when the radius of the sphere has a constant value determined by the conditions. It is assumed that as soon as a particle comes within the sphere of attraction by virtue of its Brownian movement the two particles coalesce. This discontinuous view of the obviously continuous process of coalescence was assumed to avoid a consideration of the nature and distribution of the forces that are present.

Considering the effect of the motion of each particle and also that each of the aggregates acts as a condensation centre, he derives the following equations :

$$\Sigma n = \frac{n_0}{1 + \frac{t}{T}}, \quad \dots \dots \dots (1)$$

$$n_1 = \frac{n_0}{\left(1 + \frac{t}{T}\right)^2}, \quad \dots \dots \dots (2)$$

$$n_k = n_0 \frac{(\alpha \cdot n_0 \cdot t)^{k-1}}{\left(1 + \alpha \cdot n_0 \cdot t\right)^{k+1}}, \quad \dots \dots \dots (3)$$

where “ n_0 ” denotes the total number of particles originally present per unit volume before coalescence begins. They are all assumed to be spherical and equal in size. “ t ” is the time in seconds that has elapsed since the electrolyte and the sol have been mixed. “ T ” is a constant characteristic of the rate of coagulation and is given by

$$T = \frac{1}{4 \cdot \pi \cdot D \cdot Ra \cdot n_0}, \quad \dots \dots \dots (4)$$

where “ D ”* is the diffusion constant as given by Einstein’s equation; $\alpha = 4 \cdot \pi \cdot D \cdot Ra$, and Ra is the radius of the sphere of action.

* $D = \frac{H \cdot \theta}{N_0} \frac{1}{6\pi \cdot \eta \cdot r}$, where H = the gas constant,
 θ = the absolute temperature,
 N_0 = Avogadro’s number,
 η = the viscosity,
 and r = radius of the particle.

Σn denotes the total number of particles in all stages of coalescence in unit volume when the time is "t"; n_1 denotes the number of the primary particles whose original number was n_0 at the time "t"; n_k denotes the number of particles of the k th stage of coalescence—that is, the number of aggregates each of which consists of "k" of the primary particles. "k" is evidently an integer. In 1918 Zsigmondy published the results of an investigation to test this theory. He restricted his investigation to the rate of decrease in the primary particles (green in the ultramicroscope) in a colloidal gold sol when the minimum time of coagulation has been reached. He found that $Ra = 2.2$ times r , the radius of the particles. Similar values were obtained by Westgren and Reitstötter (*Zeitschr. Phys. Chem.* vol. xcii. p. 600, 1918) with more coarsely dispersed gold sols. The value of Ra/r , however, varied in one experiment from 1.4 to 3.8. The recent experiments of Kruyt and Van Arkel (*Rec. Trav. Chim. Pays-Bas*, vol. xxxix. [4] p. 656, vol. xl. p. 169, 1920) show greater variations. They are of opinion that there is some regularity in these variations. They could not observe a maximum value of Ra/r equal to 2. They found a maximum value equal to 0.73.

Smoluchowski, assuming from the data of Zsigmondy available at that time that $Ra/r = 2$, points out that the maximum rate of coagulation is reached when each collision between two particles is successful in bringing about a coalescence. When the rate of coagulation is slower, all the collisions are not successful in bringing about a coalescence of the particles. If "ε" is the fraction of the collisions that are successful in bringing about coalescence, then "T" in equations (1) and (2) takes the form

$$T = \frac{3}{4} \frac{N_0 \cdot \eta}{Ra \cdot n_0 \cdot \theta \cdot \epsilon}, \dots \dots \dots (5)$$

where N_0 , Ra , n_0 , θ , and η have the same meaning as in equations (1) and (2).

Putting

$$\frac{3}{4} \frac{N_0 \cdot \eta}{Ra \cdot \theta \cdot n_0} = \frac{1}{\beta}, \dots \dots \dots (6)$$

we have

$$\Sigma n = \frac{n_0}{1 + \frac{T}{t}} = \frac{n_0}{1 + \beta \cdot \epsilon \cdot t} \dots \dots \dots (7)$$

Since only " ϵ " is variable, a comparison of the coagulation time " t " for the same change in the sol makes it possible to determine the variation in the percentage of successful collisions and its dependence on the conditions of experiment. When the maximum rate is reached, $\epsilon=1$ and hence a measure of the absolute value of ϵ is possible.

Problems awaiting solution.—A glance through the experimental work would show that the assumption of the constancy of " T " is not well justified. The simplicity of Smoluchowski's equations consist in that there is only one constant. The experimental limitations are great, and it is quite possible that the discrepancies are due to the defects of the ultra-microscopic method. The other possibility is that the simplifying assumptions of Smoluchowski—for example, the constancy of " T " independent of the stage of coalescence—are not true within narrow limits. It is of great interest to know the limits within which these equations are valid.

The important questions that await solution in this connexion are :

- (a) the limits within which the above equations are valid ; and
- (b) if the above equations are valid, the variation of ϵ with concentration of electrolyte ;
- (c) the dependence of ϵ on the electric charge ;
- (d) the variation of ϵ with temperature.

In the following an account of an attempt to examine these factors, with the exception of (c), is recorded.

Indirect Methods.—Variations in physical properties that occur simultaneously with the process of coagulation can be utilized to measure the rate of coalescence.

Smoluchowski pointed out that the viscosity measurements of Gann (*Koll. Chem. Beihefte*, vol. viii. p. 67 (1916)) do not satisfy the main requirements of his equations—namely, a similarity in the form of the curves (showing the variation in viscosity with time) independent of the nature of the electrolyte. He concludes that viscosity changes do not form a measure of the coagulation process. Yet he considers that the method is suitable for a quantitative comparison of the effect of various concentrations on the values of ϵ when the curves are similar.

The variation in physical properties, however, is likely

to show the validity of the fundamental equations of Smoluchowski. The fact that the curves showing the change in viscosity with time are dissimilar shows that these assumptions are not justified, and Smoluchowski thinks that "T" is dependent on the magnitude of the aggregates.

Since as yet it is not possible to express physical properties—*e. g.*, the viscosity or the absorption of light—in terms of definite functions of the number and size of particles, a quantitative comparison of different sols is not possible by indirect methods. We have, therefore, to restrict ourselves to the same sol.

Experiments with Gold Sols.—An examination of the changes in the colour of gold sols on the addition of an electrolyte showed (Mukherjee and Papaconstantinou, *Trans. Chem. Soc.* vol. cxvii. p. 1563 (1920)) that the variation in the absorption of light of gold sols affords an easy and accurate method suitable for this purpose. The gold sols prepared by the nucleus method of Zsigmondy conform very nearly to the requirements of equations (1) to (3) in so far as the particles are fairly uniform in size. It would be very convenient to work with a sol with reproducible properties, as data obtained on different dates with different preparations could be rigorously compared.

It was found that a sol on standing for some time undergoes somewhat irregular changes, which may in part be due to dust particles getting in accidentally. In spite of all precautions, one cannot be sure that there is no such variation in a particular sample. This variation is not wholly due to the fungus that grows in these sols. For this reason it is necessary to vary one factor only at a time and compare its effects.

The comparison was therefore restricted to the same sol so long as it showed no variation in its properties.

The Constancy of "T" in Equations (1) to (3) during the Process of Coalescence.

According to the simple assumptions of Smoluchowski, the progress of coalescence should be uniformly the same for various electrolytes and for their different concentrations. The constancy of "T" implies that if we assume a series of consecutive stages of coalescence of a sol—under a definite set of conditions, namely a definite electrolyte concentration

and temperature—following each other by intervals of time equal to “ δt ,” they are each characterized by a definite number and manner of distribution of particles of each category (primary, secondary, etc.). Let us indicate the stage of coalescence corresponding to the time “ t ” seconds (since the sol and the electrolyte were mixed) under the given conditions by the numbers

$$\Sigma N, N_1, N_2, N_3, \dots N_k \dots,$$

where the subscripts refer to the number of primary particles by the union of which the aggregate is composed. Thus N_k denotes the number of aggregates, each of which is composed of “ k ” primary particles. “ k ” is evidently an integer.

Similarly let us denote the stage of coalescence corresponding to the time t' ($=t + \Delta t$) by

$$\Sigma N', N_1', N_2', N_3', \dots N_k' \dots$$

These stages of coalescence are independent of external conditions so long as equations (1) to (3) are valid. The only change that external conditions can bring about is a variation in the value of T —that is, if the external conditions are varied the sol will always pass through the same consecutive stages of coalescence and only the rapidity of succession of these stages will be determined by them. Any property which varies continuously with the progress of coalescence without having any maxima or minima can be utilized to characterize the stages of coalescence; for each value of this property is characteristic of the time that has passed since the mixing of electrolyte and sol. According to the equations of Smoluchowski, the times taken to reach any particular stage depend only on the value of “ T ,” which is constant under a definite set of conditions. Let us compare two different electrolytes, A and B, of concentrations C_1 and C_2 . Let us suppose that after the time “ t ” the stage of coalescence indicated by

$$\Sigma N, N_1, N_2, N_3, \dots N_k \dots$$

has been reached when the electrolyte is “A” of concentration C_1 . This stage of coalescence has a definite value for the physical property we are considering, and is independent of the value of T . Let us assume that “ T_1 ” and “ T_2 ” are the corresponding values of “ T ” for the two cases. To be definite, we shall consider the variation in the

total number of particles of all categories, which varies continually with the progress of coalescence. Let us assume that at the times “ t_1 ” and “ t_2 ” both electrolytes have reached a state at which the total number of particles is the same. From equation (1) we have, therefore,

$$\Sigma n = \frac{n_0}{1 + \frac{t_1}{T_1}} = \frac{n_0}{1 + \frac{t_2}{T_2}} \dots \dots \dots (8)$$

or

$$\frac{t_1}{T_1} = \frac{t_2}{T_2} \dots \dots \dots (9)$$

The general equation (3) may be written as

$$n = \frac{n_0 \cdot \left(\frac{t}{T}\right)^{k-1}}{\left(1 + \frac{t}{T}\right)^{k+1}} \dots \dots \dots (10)$$

Since n_0 and k are constants, if $\frac{t}{T}$ is constant, n_k has a fixed value—that is, the condition $\frac{t_1}{T_1} = \frac{t_2}{T_2}$, which is deduced from the condition that Σn has a fixed value, also implies that the values of $n_1, n_2, n_3, \dots, n_k$ are the same in both cases. This means, in other words, that a definite value of Σn fixes unequivocally the stage of coalescence. Therefore, from the deduction that the successive stages of coalescence are always the same and depend only on the time, any property of the sol that varies continuously can be utilized to represent a fixed value of Σn or n_1 or a definite stage of coalescence. A definite value of this property is thus characteristic of the stage of coalescence. It also follows from the above considerations that all curves showing a variation of this property with time should be similar. A deviation from this similarity, in itself, would mean that equations (1) to (3) do not represent the facts.

The absorption coefficients of gold sols for different wave-lengths change on addition of an electrolyte in a complex manner. The theories of the colour of these sols as advanced by Maxwell Garnett (*Phil. Trans.* vol. cciii. A, p. 385, 1904; vol. ccv. A, p. 237, 1906) and by Mie (*Ann. der Phys.* [4] vol. xxv. p. 377) would lead one to expect that any change in the number and manner of

distribution of the particles n_1 , n_2 , etc. will produce a great change in the optical properties of the sol. This is in agreement with observations. Now, if the successive stages of coalescence were independent of the nature and concentration of the electrolyte, then the manner of variation of the complex absorption would be the same in each case. The absorption in the red region of the spectrum varies continuously, corresponding to each value of the absorption coefficient for a particular wave-length in this region; the values in the other parts should be fixed. If the contrary holds good, then the conclusion is obvious that the successive stages of coalescence are not independent of the nature and concentration of the electrolyte as assumed by Smoluchowski.

It has been found that for the stage indicated by the value of the coefficient of absorption for $683 \mu\mu = 0.4985$, the values of the coefficient for the other wave-lengths given in the following table in column II. are independent of the nature of the electrolyte.

The concentrations of the electrolytes were such as to produce rapid coagulation. In columns III. and IV. the coefficients of the "nucleus sol" have been given for the original sol and for the stage of coagulation characterized by the value of the coefficient for $683 \mu\mu = 0.4156$ (Mukherjee and Papaconstantinou, *loc. cit.*).

TABLE I.

Absorption coefficients (k).

Wave-length, in $\mu\mu$.	Absorption coefficients (k).			
	I.	II.	III.	IV.
683	0.0453	0.4985	0.0376	0.4156
602	0.1055	0.3679	0.1131	0.409
583	0.1518	0.3388	0.1595	0.3986
563	0.2076	0.3294	0.2076	0.336
547	0.2512	0.3238	0.2867	0.3732
523	0.3780	0.3780	0.3780	0.3882
506	0.4647	0.3581	0.3882	0.3780
475	0.3581	0.3198	0.3581	0.3780

*Comparison of the Values of "T" as a Test of
Smoluchowski's Theory.*

Since the absorption coefficient in the red region varies continuously with the coagulation and its magnitude is

sufficiently great, a definite value of the absorption coefficient for a fixed wave-length (683 $\mu\mu$) can be taken as representing a definite stage of the coalescence.

In the following tables the absorption coefficients at different times are given for the wave-length 683 $\mu\mu$. The tables are taken from the paper by Mukherjee and Papaconstantinou, *loc. cit.*

TABLE II.

Electrolyte : Potassium Chloride.

Time in minutes, after mixing equal volumes of electrolytes and sol.	Absorption coefficients for various concentrations.		
	N/24.	N/26.	N/28.
—	0.0453	0.0453	0.0453
0.5	0.3732	0.2867	0.1683
1	0.438	0.3630	0.2257
1.5	0.4497	0.4046	—
2	—	0.438	0.2777
3	—	0.4497	0.3431
5	—	—	0.3836
9	—	—	0.4263
13	—	—	0.438
15	—	—	0.4497

TABLE III.

Potassium Nitrate.

Times.	Concentrations.		
	N/24.	N/26.	N/30.
—	0.0453	0.0453	0.0453
0.5	0.3336	—	—
1	0.4263	0.2866	0.269
1.5	0.4497	0.3271	0.3143
2	—	0.3629	0.3336
3	—	0.4156	0.3732
4	—	0.438	0.394
5	—	0.4497	—
8	—	—	0.4263
10	—	—	0.438
16	—	—	0.4497

TABLE IV.
Barium Chloride.

Times.	Concentrations.		
	0.852N/900.	0.852N/1000.	0.852N/1100.
—	0.0453	0.0453	0.0453
1	0.2257	—	0.1603
2	0.2867	—	0.2007
4	0.3529	—	0.2687
5	0.3836	0.3051	0.3051
7	0.438	0.3431	0.3237
8	0.4497	—	0.3336
9	0.4497	0.3836	0.3529
11	—	0.4263	0.363
13	—	0.4497	0.363
16	—	—	0.3732

The limits within which the rate of coalescence could be varied were restricted by the fact that when the rate is slow the particles begin to settle, leaving a clear layer at the top, and the measurements are not reliable. Also, with time, some of the particles stick to the sides of the vessel. Lastly, it is difficult to avoid dust particles for a long time.

The values given in Tables II.-V. were plotted graphically, and the time intervals given in Tables V.-VII. below were determined from these curves.

Each of these curves is characterized by a definite value of T (or ϵ). Corresponding to the three concentrations of any one of these electrolytes, there are three intervals which must pass in order that the absorption coefficient may have the same value. These intervals are co-related by the following relation according to equations (1) to (3) or (6) :—

$$\frac{t_1}{T_1} = \frac{t_2}{T_2} = \frac{t_3}{T_3}, \dots \dots \dots (11)$$

or

$$t_1 : t_2 : t_3 = T_1 : T_2 : T_3 = \frac{1}{\epsilon_1} : \frac{1}{\epsilon_2} : \frac{1}{\epsilon_3}. \dots \dots \dots (12)$$

Since T_1 , T_2 , and T_3 are constant, the ratio of the time-parameters corresponding to the same absorption coefficient should be independent of the absolute value of the absorption coefficient. Corresponding to different values of the absorption coefficient we get different values of t_1 , t_2 , and t_3 . All these values should show a constant ratio. In the

following three tables this comparison is made for the three electrolytes mentioned in Tables II.-IV.

TABLE V.
Electrolyte : Potassium Chloride.

Values of absorption coefficient.	Time in seconds.			Ratios.
	N/24.	N/26.	N/28.	
	t_1 .	t_2 .	t_3 .	$T_1 : T_2 : T_3$.
0.370	27	65	255	1 : 2.47 : 9.44
0.400	35-40	85	345	1 : 2.3 : 9.3
0.438	60	120	780	1 : 2.0 : 13.0
0.445	75	180	900	1 : 2.4 : 12.0
	Average.....			1 : 2.3 : 11.4
	Extreme deviation from average			7.4 % 19 %

TABLE VI.
Electrolyte : Potassium Nitrate.

Absorption coefficients.	Times.			Ratios.
	N/24.	N/26.	N/28.	
	t_1 .	t_2 .	t_3 .	$T_1 : T_2 : T_3$.
0.350	25 } 27 30	105	145	1 : 3.9 : 5.4
0.400	45	165	255	1 : 3.7 : 5.7
0.425	60	210	375	1 : 3.5 : 6.2
0.445	90	300	780	1 : 3.3 : 8.6
	Average			1 : 3.6 : 6.3
	Extreme variation from average			8.8 % 33 %

TABLE VII.
Electrolyte : Barium Chloride.

Absorption coefficients.	Times.			Ratios.
	N/24.	N/26.	N/28.	
	t_1 .	t_2 .	t_3 .	$T_1 : T_2 : T_3$.
0.300	135	277	345	1 : 2 : 2.55
0.327	165	345	430	1 : 2.1 : 2.6
0.350	225	430	540	1 : 1.91 : 2.4
0.370	265	480	780	1 : 1.81 : 3.0
	Average			1 : 1.93 : 2.64
	Extreme variation from average			6 % 13 %

It will be seen from Tables V. to VII. that the agreement is as good as can be expected. The variation in T is as great as 11 times, but the ratios are constant. The agreement

shows that the ratios of the values of T are independent of the time or the stage of coalescence. The ultramicroscopic measurements so far made show even during one experiment a much greater variation in T , as will be evident from the following tables :—

TABLE VIII. (a).
(Observer : Zsigmondy.)

Values of $\beta' = \frac{1}{T}$.

Series D.	Series E.	Series F.
0.083	0.105	0.040
0.028	0.058	0.0195
0.0302	0.049	0.0183
0.0309	0.0475	0.0153
—	0.0403	0.0187
—	—	0.0126

Zsigmondy used high concentrations of electrolyte for securing a rapid rate. When the rate of coagulation is slow and the duration of experiment is greater than a few minutes, he found that impossible values of β' are obtained. He thinks that the presence of impurities in the water used in diluting the sol for ultramicroscopic observations is the cause of this irregularity. In his case the maximum time covered by the experiments is 80 secs. Similarly, Westgren and Reitstötter, working with coarse gold sols, find the following range of variation in the constant :—

TABLE VIII. (b).
(Observers : Westgren and Reitstötter.)

Values of $\frac{Ra}{r}$.

	Series I.	Series II.	Series III.	Series IV.
	3.74	2.56	2.75	3.41
	2.47	2.81	2.60	2.80
	2.07	2.33	2.17	2.60
	2.10	2.31	2.40	2.48
	2.09	2.31	2.12	2.14
	1.62	—	—	—
	1.41	2.16	2.15	2.15
	—	2.19	—	2.05
	—	—	—	—
Average	2.2	2.38	2.36	2.19
Extreme variation...	75 %	10 %	17 %	55 %

Kruyt and Arkel *, working with selenium sol and very slow rate of coagulation, find extremely wide variations in T in the same experiment.

TABLE IX.

(Observers: Kruyt and Arkel.)

Values of T (in hours).

I.	II.	III.	IV.
2.8	260	131	1.3
5.1	390	55	3.4
44	270	52	2.2
(43)	320	54	4.3
(157)	600	68	10.5
200	370	55	40
--	510	--	--
--	440	48	37
--	--	--	52
---	--	--	38

The above few instances will suffice to show the range of variations in " T " during the course of one experiment that has been observed in the ultramicroscopic measurements.

Considering that in Tables V. to VII. the ratios between the different values of T are taken, the range of variation is extremely small. *The actual deviations in the value of T in any one experiment must be much less than the extreme variations given.* This comparison leaves no room for doubt that " T " is a constant in the case of gold sols and within the limits of the rate of coagulation that have been studied. In fact, these data constitute the best evidence so far recorded in favour of the theory of Smoluchowski.

The Dependence of ϵ on the Concentration.

Tables V. to VII. show clearly how rapidly ϵ , the percentage of successful collisions, increases with concentration. A change of concentration in the ratio 24 to 28 increases the rate in the ratio 1:11 or 1:6 as the case may be. It would be extremely interesting to work with a sol which is less susceptible to impurities than these gold sols.

* *Rec. Trav. Chim. Pays-Bas*, vol. xxxix. [4] p. 656 (1920); [4] vol. xl. p. 169 (1921).

Variation of T or ϵ with Temperature.

Similarly, by determining the times required to produce a definite change in the colour of the sol for the same electrolyte concentration but different temperatures, we can determine the variation in ϵ with temperature.

From equation (3),

$$\Sigma n = \frac{n_0}{1 + \beta \cdot \epsilon \cdot t},$$

we get

$$\frac{n_0}{\Sigma n} = 1 + \beta \cdot \epsilon \cdot t. \quad \dots \quad (13)$$

Since a definite change of colour is being used, $\frac{n_0}{\Sigma n}$ is constant, or

$$1 + \beta \cdot \epsilon \cdot t = k_1, \text{ a constant.} \quad \dots \quad (14)$$

Substituting the value of β in (14), we get

$$1 + \frac{4}{3} \frac{Ra \cdot \theta \cdot n_0}{N_0 \cdot \eta} \cdot \epsilon \cdot t = k_1. \quad \dots \quad (15)$$

Since Ra, N_0 , and n_0 are constants, we have

$$\frac{t \cdot \theta \cdot \epsilon}{\eta} = k', \text{ a constant.} \quad \dots \quad (16)$$

The viscosity of colloidal gold solutions has been found to be practically equal to that of water, and the variation with temperature can be assumed to be equal to that of water. For different temperatures we have

$$\frac{t_1 \cdot \theta_1 \cdot \epsilon_1}{\eta_1} = \frac{t_2 \cdot \theta_2 \cdot \epsilon_2}{\eta_2}. \quad \dots \quad (17)$$

Since t_1 is experimentally determined and θ and η are known, variations in ϵ can be compared.

The experimental data are given below. They are taken from the same paper (pp. 1570-71).

TABLE X.

Electrolyte.	Standards*.	Temperatures.		
		15°.	30°.	50°.
N/30 Potassium chloride..	V Sol. C.	5 min.	10 min.	8 min. 30 sec.
N/30 Potassium sulphate .	„ „ D.	30 sec.	10 sec.	10 sec.
N/30 Potassium nitrate ..	„ „ D.	42 „	18 „	12 „

* These refer to the protected gold sols used as standards for comparison of colour. See *loc. cit.*

TABLE XI.

Electrolyte: Barium Chloride. Sol. E.

Con- centrations.	Standards.	Temperatures.			
		15°	30°.	40°.	50°.
0.852 N/1000	V ₂	7 min.	6 min.	4 min. 50 sec.	4 min. 20 sec.
0.852 N/1000	B ₂	34 „	23 „	—	13 „ 30 „
0.852 N/1200	V ₂	23 „	13 „	12 min. 30 sec.	6 „ 15 „
0.852 N/1200	B ₂	124 „	74 „	62 min.	—

TABLE XII.

Electrolyte: Strontium Nitrate. Sol. F.

Con- centrations.	Standards.	Temperatures.		
		15°.	30°.	50°.
N/1000	V ₃	1 min. 10 sec.	20 sec.	8 sec.
N/1000	B ₃	8 „ 15 „	1 min. 40 sec.	45 „

At 15°, 30°, 40°, and 50°, η/θ has the values 3.96×10^{-5} , 3.31×10^{-5} , 2.1×10^{-5} , and 1.7×10^{-5} respectively. The values for the viscosity are taken from the tables in Kaye and Laby's book on Physical and Chemical Constants, p. 30, 1919.

From equation (17) we have

$$\epsilon_{15^\circ} : \epsilon_{30^\circ} : \epsilon_{40^\circ} : \epsilon_{50^\circ} \\ = (\eta/t\theta)_{15^\circ} : (\eta/t\theta)_{30^\circ} : (\eta/t\theta)_{40^\circ} : (\eta/t\theta)_{50^\circ}.$$

TABLE XIII.

Electrolyte.		Temperatures.		
		15°.	30°.	50°.
N/30 KCl	N/tθ × 10 ⁷	1.32	0.50	0.33
N/30 K ₂ SO ₄	„	13.2	33	17
N/30 KNO ₃	„	9.43	18.4	14.0

TABLE XIV.

Electrolyte: Barium Chloride.

Con- centrations.	Standards.		Temperatures.			
			15°.	30°.	40°.	50°.
0.852 N/1000	V ₂	$\eta/t\theta \times 10^8$	9.43	9.2	7.24	6.54
„	B ₂	„	1.94	2.4	—	2.1
Ratio between	{	V ₂	100	: 98	: 77	: 70
$\eta/t\theta$		B ₂	100	: 123	: —	: 108
0.852 N/1200	V ₂	$\eta/t\theta \times 10^8$	2.87	4.24	2.8	4.5
„	B ₂	„	53.22	74.5	64	—
Ratio between	{	V ₂	100	: 148	: 98	: 158
$\eta/t\theta$		B ₂	100	: 140	: 106	: —

TABLE XV.

Electrolyte : Strontium Nitrate.

Concentrations.	Standards.	Temperatures.		
		15°.	30°.	50°
N/1000	V ₃ $\eta/t\theta \times 10^6$	·565	1·65	2·1
„	B ₃ $\eta/t\theta \times 10^7$	·80	3·3	3·77
Ratio between	$\left\{ \begin{array}{l} V_3 \text{} \\ B_3 \text{} \end{array} \right.$	100	291	371
$\eta/t\theta$			100	416

Since $\eta = t\theta$ is a constant for a definite electrolyte concentration and temperature according to Smoluchowski's equation, the ratios should be independent of the standard used. This is true within the limits of experimental error with ·852 N/1200 Barium Chloride. In the other two cases the variations are not great considering that we are comparing the ratios. A slight variation in each value will be magnified in the ratio. Taking into account the probable experimental error, it can be said that ϵ is roughly constant in each experiment.

On the other hand, the variation in ϵ with temperature is considerable. We have already seen that the irregularity in the variation of ϵ means that the precipitating power of the ions changes with the temperature (Mukherjee, *Trans. Chem. Soc.* vol. cxvii. p. 358, 1920).

Further experiments with arsenious sulphide are in progress on similar lines.

Summary.

(1) It has been shown that the equations of Smoluchowski on the rate of coalescence of the particles of gold sols agree with the results obtained by the writers.

(2) It has been suggested that the disagreement of the ultramicroscopic measurements with this theory may in part be due to the difficulties inherent in them.

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