

Physics. — *Formation and properties of the silver bromide sol.* By G. H. JONKER, H. R. KRUYT and L. S. ORNSTEIN.

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1. Introduction.

If we mix strongly diluted solutions (10^{-4} — 10^{-6} N) of AgNO_3 and KBr , an AgBr sol is formed which originally is transparent but in the course of a few hours becomes gradually more turbid, until a certain degree of turbidity is reached, dependent upon various factors.

According to JABLZYNSKI¹⁾, the increasing turbidity is due to coarsening as the result of recrystallization, while SCHNELLER²⁾ mainly considers the process as a flocculation phenomenon.

We have once more examined in detail which changes take place in the sol, by measuring the conductivity, extinction, Br^- ion concentration and electrophoretic velocity.

2. Conductivity.

The measurements of the conductivity were carried out with an apparatus built according to the directions of JONES³⁾. 25 cc of $2 \cdot 10^{-4}$ N AgNO_3 solution and 25 cc of $2,2 \cdot 10^{-4}$ N KBr solution were during 20 minutes heated in a thermostat of $25^\circ,00$ C. These solutions were quickly mixed and poured into 3 flocculation glasses hung in the thermostat. In the first glass the conductivity cell was placed during 2 minutes in order to be brought into adsorption equilibrium. Subsequently the cell was placed alternately in the 2nd and 3rd glass and each time the resistance was determined, till after a few hours it remained constant.

Immediately after mixing there are present in the solution Ag^+ , NO_3^- , K^+ and Br^- ions. The conductivity of this mixture can be calculated. It is about $30 \cdot 10^{-6} \text{ Ohm}^{-1} \text{ cm}^{-1}$. The greater part of the Ag^+ and Br^- ions disappear from the solution. Consequently it is to be expected that the conductivity will be lowered to about one half.

The first measurement was made 3 to 5 minutes after mixing. From the fact that the conductivity then already had reached half the calculated initial value and even began to increase it follows that within this time all the AgBr had crystallized and that consequently the sols further contained a constant quantity of AgBr .

In fig. 1 the course of the conductivity has been drawn. The drawn part of the curve has been really measured. The further course is not easily

¹⁾ C. JABLZYNSKI, Bull. Soc. Chim. France [IV] 33, 1392 (1923).

²⁾ H. SCHNELLER, Koll. Zeit. 71, 180 (1935).

³⁾ G. JONES, J. Am. Chem. Soc. 50, 1049 (1928).

interpreted, since the two parts of the conductivity, of electrolyte and of colloid, may change separately.

3. Extinction.

The extinction measurements of sols with 10^{-4} mol AgBr per liter were performed with an extinction meter with vacuum thermo-elements, according to Moll.

For the more strongly diluted sols we took a photo-electric selenium cell.

For all extinction measurements white light was used. 100 cc of AgNO_3 solution were mixed with 100 cc of KBr solution and poured into a cuvette with a thickness of 30 mm. The extinction was calculated in percentages of the light transmitted by the water.

There were the following influences upon the extinction of the sol:

a. Impurities caused by dust. Dust particles serve as nuclei for the crystallization and consequently have a large influence upon the number of the first formed crystals.

This influence is clearly apparent from the extinction curves in fig. 2. For sol a the solutions were filtered through a g_3 glass filter, for sol b through the denser g_4 filter and for sol c through a membrane filter.

Owing to the dust, the extinction curves could not be well reproduced. We tried to correct this by beforehand introducing a certain large amount of particles into the solution, viz. by adding some cc of a similar sol to the KBr solution. The influence of this on the extinction curves was very large, as may be seen in fig. 3. However, this was not the right way to examine the sol formation, for an important part, the formation of nuclei

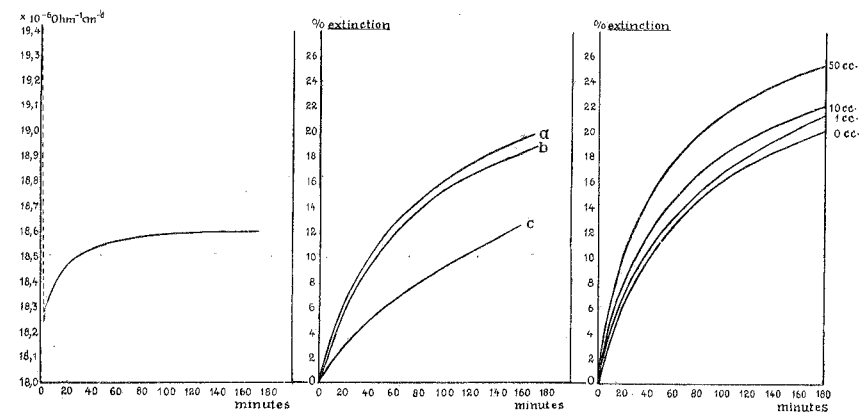


Fig. 1

Fig. 2

Fig. 3

of their own accord during crystallization was eliminated here. For the following measurements, therefore, the solutions were made as pure as possible.

b. The temperature had a large influence upon the rate of increase and on the final value of the extinction. The constant temperature, which consequently was necessary, was obtained by placing a glass tube in the

cuvette, through which water was pumped from a thermostat. The measurements were carried out at 25°.

c. The extra concentration of KBr was the factor which proved to have the largest influence. As the result of this, for the sols with 10^{-4} mol AgBr per liter the extinction curve of the sol with equivalent quantities of AgNO_3 and KBr could not be determined accurately, owing to small errors made during pipetting.

Owing to greater excess of KBr the extinction curve was constantly lower. This has been reproduced for the sols with 10^{-4} mol AgBr per liter in fig. 4 and for the sols with $2 \cdot 10^{-5}$ mol AgBr per liter in fig. 5.

d. The sol concentration influenced the shape of the curve. While for the sols with 10^{-4} mol AgBr per liter it has a monotonous course, for those with $2 \cdot 10^{-5}$ and $2 \cdot 10^{-6}$ mol AgBr per liter the S-form occurs. See figs. 4 and 5.

From the increase of the extinction it follows that either the particles grow constantly larger or the number of particles grows smaller.

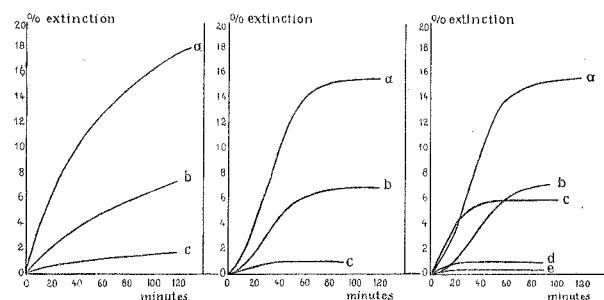


Fig. 4

Fig. 5

Fig. 6

Fig. 4. a. 10^{-6} mol KBr/liter
b. 10^{-5} " " "
c. 10^{-3} " " "

Fig. 5. a. $2 \cdot 10^{-6}$ mol KBr/liter
b. $2 \cdot 10^{-5}$ " " "
c. $2 \cdot 10^{-4}$ " " "

Fig. 6. a. 0 mg
b. 0.5 "
c. 3 "
d. 50 "
e. 500 "

According to RAYLEIGH, the dispersion of the light by a particle is proportional to the square of the volume a , e.g. ka^2 . The dispersion by n particles is then kna^2 . If the total volume of the solid is v , then is $n = \frac{v}{a}$, so that the dispersion is kva . According to the conductivity test v is constant, so that the extinction is proportional to the average size of the particles. When the particles are no longer small with regard to the wavelength of the light and not globular, this relation is no longer applicable, but yet the extinction remains a criterion for the size of the particles.

4. Gelatin tests.

From the measurements mentioned sub 3 it does not yet follow in what way the particles grow larger.

By means of experiments with gelatin we could make a decision between recrystallization and flocculation. Recrystallization, i.e. the dissolving of small particles and the developing of larger ones, is a diffusion process. This cannot be retarded by gelatin. Flocculation, however, may be completely prevented by gelatin.

From our experiments it appeared that even small quantities of gelatin (0.5 to 3 mg per 100 cc of sol) strongly lower the extinction curve and that higher concentrations (500 mg) almost completely prevent turbidity (fig. 6). This proves that the coarsening consists of a flocculation, although to a small extent recrystallization may take place as well.

It is now evident why the extra concentration of KBr so strongly influences the rate of flocculation and its final value. The KBr, namely, regulates the stability of the particles.

It seems that for the explanation of this flocculation the theory of KRUYT and DE HAAN⁴) on the retarded flocculation may be applied. Immediately after formation of the sol the total surface of the particles is so large that the added quantity of KBr is not sufficient for the formation of a complete double layer. Moreover, this double layer may be distributed irregularly owing to the rapid formation, so that the particles show charged and uncharged spots. Upon collision of two particles with uncharged spots, adhesion may easily take place. Thus floccules are formed, which are gradually more completely surrounded by charged spots, so that the flocculation proceeds constantly more slowly and finally comes to a stop. Simultaneously the electrophoretic velocity must increase.

According to the researches by KRUYT and VERWEY⁵), the surface decreases in size as the result of internal recrystallization. Owing to this, a peptizing electrolyte is liberated, involving greater density of charge and consequently greater stability.

5. Br^- -concentration measurements.

In order to find out whether during the extinction of the AgBr sol really a peptizing electrolyte was liberated, Br^- -ion concentrations were determined at different times.

For this purpose was measured the potential difference between an AgBr electrode in the sol and a calomel electrode saturated with KCl, which by means of a liquid junction ($1.7\text{N KNO}_3 + 0.3\text{N NaNO}_3$) was connected with the sol. The potential difference was measured with a lamp voltmeter. The Br^- -concentration was found by interpolation between the E.M.F.'s belonging to standard solutions with 10^{-4} , 10^{-5} and 10^{-6} g. equiv. Br^- per liter.

For these measurements sols were prepared with 10^{-4} g. mol AgBr/liter and different quantities of KBr.

⁴) H. R. KRUYT, These Proceedings 32, 857 (1929); H. R. KRUYT and E. F. DE HAAN, Koll. Zeit. 51, 61 (1930).

⁵) E. J. W. VERWEY and H. R. KRUYT, Z. physik. Chem. A 167, 137 (1933).

In most cases the Br^- conc. was lowered during some minutes, then remained constant for a long time and finally began to rise.

Sol + $0,5 \cdot 10^{-4}$ g mol KBr/l.		Sol + $0,1 \cdot 10^{-4}$ g mol KBr/l.		Equivalent sol	
Time	Br^- conc.	Time	Br^- conc.	Time	Br^- conc.
1 min	$3,8 \cdot 10^{-5}$ mol/l.	2 min	$0,95 \cdot 10^{-6}$ mol/l.	1 min	$0,21 \cdot 10^{-6}$ mol/l.
26 "	$3,8 \cdot 10^{-5}$ "	5 "	$0,78 \cdot 10^{-6}$ "	5 "	0,26 "
$2\frac{1}{2}$ hrs	$4,0 \cdot 10^{-5}$ "	6 hrs	$0,78 \cdot 10^{-6}$ "	30 "	0,34 "
21 "	$4,6 \cdot 10^{-5}$ "	23 "	$1,40 \cdot 10^{-6}$ "	42 "	0,34 "
		29 "	$2,40 \cdot 10^{-6}$ "	6 hrs	0,92 "
				23 "	3,40 "

The course of the Br^- conc. is remarkable in the equivalent sol. The solubility of AgBr in water is at 18°C . $0,7 \cdot 10^{-6}$ g. mol/l. The Br^- conc. of the equivalent sol, however, is immediately after preparation $0,21 \cdot 10^{-6}$. Consequently Br^- has been adsorbed originally. After 6 hours the concentration of the bromine ions had increased to $0,92 \cdot 10^{-6}$ and after 20 hours even to $3,40 \cdot 10^{-6}$, i.e. far above the value corresponding to the solubility. The sol consequently showed a reversed adsorption; now Ag^+ -ions were adsorbed.

6. Electrophoretic measurements.

It became now necessary to examine the change in stability of the sol. For this purpose was used the apparatus for electrophoretic measurements according to VAN GILS⁶⁾. Sols with $2 \cdot 10^{-5}$ g. mol AgBr were immediately fit for measuring.

The first measurements were made on a sol with $0,2 \cdot 10^{-5}$ g. mol KBr per liter extra. The sol showed a negative electrophoretic velocity, which during the extinction increased. Also after the period required for reaching

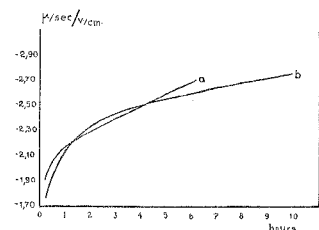


Fig. 7

the final value of the turbidity the increase in velocity continued (Fig. 7a). Sols with greater excess of KBr showed the same. For the equivalent sol, considering the course of the Br^- conc., it was to be expected that it would change from negative to positive. However, this was not the case. Like the sols with excess of KBr, it became increasingly negative (Fig. 7b).

Similarly a sol with $0,4 \cdot 10^{-5}$ mol/liter excess AgNO_3 , which according to § 5 will adsorb Ag^+ still more strongly, was immediately after formation negative and became more strongly negative. A sol with greater

⁶⁾ G. E. VAN GILS and H. R. KRUYT, Koll. Beihefte 45, 60 (1936).

excess, $2 \cdot 10^{-5}$ g. mol AgNO_3 per liter, was immediately after mixing positive. This sol caused a surprise. The electrophoretic velocity decreased rapidly and after $1\frac{1}{2}$ hours the sol had become negative. This was likewise the case with sols with $8 \cdot 10^{-5}$ and $18 \cdot 10^{-5}$ g. mol AgNO_3 per liter. With these sols the reversal set in after 10 and 20 hours respectively.

Consequently, in spite of the Ag^+ adsorption, all examined sols have turned negative (Fig. 8).

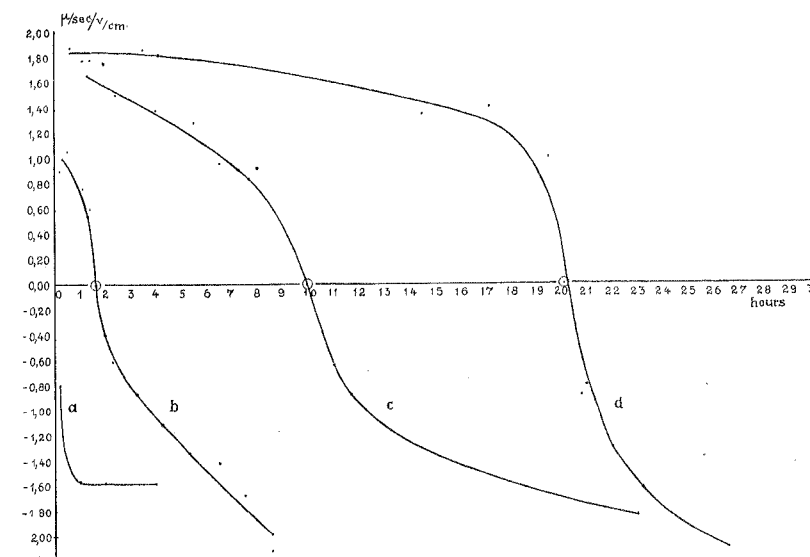


Fig. 8.

The same phenomenon was found in a different way by JULIEN⁷⁾. JULIEN measured flow potentials on AgBr capillaries. It proved impossible to give the wall of the capillary a positive charge with AgNO_3 solutions. Only if on the wall fresh AgBr was precipitated, he succeeded but when the precipitate was some hours old it could no longer be done. JULIEN expected that a smooth AgBr surface like most substances in water would acquire a negative charge.

This may be a good explanation for the behaviour of the AgBr sols. It has to be assumed then that on the crystal surfaces, which during extinction grow constantly larger, a new double layer is formed by the side of the normal one on the edges and angles.

This new double layer has such a large influence that originally positive sols turn negative.

7. Influence of electrolytes.

In order to demonstrate the existence of these two double layers by the side of each other, we also examined the influence of various neutral

⁷⁾ P. F. J. A. JULIEN, Thesis. Utrecht 1933.

electrolytes on the electrophoretic velocity of a 12 hours old, so negative sol with $2 \cdot 10^{-5}$ g. mol AgNO_3 per liter in excess. The negative ions influence the normal double layer, the positive ions the new double layer of the crystal surfaces.

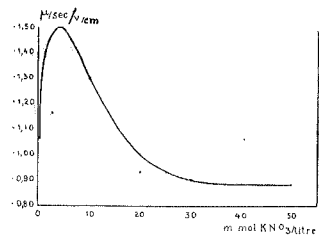


Fig. 9

10. KNO_3 . Small quantities of KNO_3 strongly increased the electrophoretic velocity of the sol. A maximum set in at about 3 m. mol/liter. At higher concentrations the velocity again became smaller (Fig. 9).

This has been frequently observed. We have to deal here with a relaxation effect. Owing to the fact that there are so few ions in the solution, the layer of counter ions of the particles cannot be replenished sufficiently rapidly during electrophoresis, so that the particles are inhibited electrostatically by the counter ions moving in the opposite direction. Only little electrolyte is required to neutralize this effect.

The same effect was observed on a positive hydrophobic Fe_2O_3 sol. Here the electrophoretic velocity was about doubled by 5 m. mol KNO_3 .

20. BaNO_3 . The Ba^{++} -ion had such a preponderantly lowering influence that here no maximum was found.

30. K_2SO_4 and $\text{CH}(\text{SO}_3\text{K})_3$. In these salts again a maximum set in. At higher concentrations the electrophoretic velocity was not so strongly lowered by K_2SO_4 as by KNO_3 . The influence of $\text{CH}(\text{SO}_3\text{K})_3$ was still smaller.

Conc.	KNO_3	K_2SO_4	$\text{CH}(\text{SO}_3\text{K})_3$
0 m. equiv./l.	-1.22 $\mu/\text{sec}/\text{V}/\text{cm}$	-1.22 $\mu/\text{sec}/\text{V}/\text{cm}$	-1.22 $\mu/\text{sec}/\text{V}/\text{cm}$
20 " " "	-1.27 " "	(-1.17) " "	-1.57 " "
30 " " "	-0.88 " "	-1.01 " "	-1.57 " "

The K^+ -ions compress the unknown double layer equally strongly in all salts. The ions of higher valency SO_4^{--} and $\text{CH}(\text{SO}_3)_3^{---}$, however, compress the normal double layer much more strongly than the NO_3^- -ion, so that altogether the electrophoretic velocity is not so strongly reduced.

In this sol, consequently, a double rule of SCHULZE-HARDY is observed.

8. Summary.

A dilute AgBr sol becomes rapidly extinct. During a few hours a flocculation takes place, which slowly comes to an end, owing to increasing stability of the sol. Sols with excess of AgNO_3 adsorb Ag^+ -ions, but finally become negative under the influence of a new double layer, the construction of which is yet unknown, on the crystal surfaces formed by internal recrystallization.

Mathematics. — Une inégalité relative aux sommes de WEYL. Par J. G. VAN DER CORPUT.

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Dans cet article X désigne un entier $\equiv 2$.
 P désignant un entier et

$$f(y) = \frac{a}{n!} y^n + a_1 y^{n-1} + \dots + a_n$$

un polynôme à coefficients réels, chaque somme de la forme

$$\sum_{y=P+1}^{P+X} e^{2\pi i f(y)}$$

s'appelle une somme de WEYL. Dans la théorie analytique des nombres nous avons besoin d'une borne supérieure pour le module de

$$S = X^{-1} \sum_{y=P+1}^{P+X} e^{2\pi i f(y)}$$

Supposons que n soit > 1 , que τ soit un nombre $\equiv 1$ et $\frac{a}{q}$ une fraction irréductible à dénominateur positif, tels que nous ayons $\left| a - \frac{a}{q} \right| \equiv \frac{\tau}{q^2}$.

Comme il est connu, dans ces conditions à tout nombre positif ε correspond un nombre c_1 , dépendant uniquement de ε et n tel que

$$|S|^{2^{n-1}} < c_1 X^\varepsilon \left(\tau + \frac{q \log q}{X} \right) \left(\frac{1}{q} + \frac{1}{X^{n-1}} \right) \dots \quad (1)$$

Cette formule, qui a été appliquée à plusieurs reprises dans la théorie additive des nombres, n'a pas d'intérêt quand l'ordre de grandeur de q est moins élevée que celui de chaque puissance de X à exposant fixe; en effet, dans ce cas le membre de droite de (1) tend vers l'infini avec X . C'est précisément ce désavantage qui rend jusqu'à présent la formule inutile dans la théorie additive des nombres premiers. Cette difficulté provient du facteur X^ε . M. VINOGRADOW¹⁾ a remplacé l'inégalité par une

¹⁾ Einige allgemeine Primzahlsätze. Travaux de l'Institut mathématique de Tbilissi, 3, 35-67 (1938); voir p. 36, Hilfssatz 2.