

# IMPORTANCE OF DIALYSIS IN THE STUDY OF COLLOIDS.

## Part IV. Colloidal Arsenious Sulphide.

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IN previous papers we have given the results of simultaneous measurements of cataphoretic speed, stability and viscosity of colloidal solutions of ferric hydroxide,<sup>1</sup> thorium hydroxide,<sup>2</sup> and prussian blue<sup>3</sup> dialysed and diluted to different extents; in the case of prussian blue cataphoretic speed measurements on ageing and on exposure to sunlight have also been given. In the present paper the results of similar measurements of colloidal arsenious sulphide as well as of changes in its composition under different conditions are presented.

### *Experimental.*

Hydrogen sulphide gas was bubbled through four litres of distilled water till saturation. While the gas was still passing one litre of 15 per cent. solution of arsenious oxide was gradually added, stirring the mixture all the time. Hydrogen sulphide was bubbled through the mixture till it contained no free arsenious acid. The excess of hydrogen sulphide was removed by bubbling hydrogen through the sol. In the end the sol was also filtered a number of times. The colour of the sol so obtained was orange yellow with a peculiar greenish fluorescence. All exposures to light and air were avoided as far as experimental conditions could permit (see Section *E*). Dialysis was carried out in a dark room as before<sup>3</sup> and experiments with each sample were completed in as short a time as possible in order to minimise effect of ageing (see Section *D*).

The cataphoretic speed (cat. speed) was measured as before. An equi-conducting solution of HCl was found to be a satisfactory upper liquid.<sup>4</sup> The difference between the direct and reverse movements of the boundary never exceeded 3 to 4 per cent. In all the tables of results, the cat. speed (mean of direct and reverse movements) corrected for viscosity is expressed in centimetres per second per volt per centimetre  $\times 10^5$ . The concentration of the electrolytes is expressed in millimoles per litre.

The stability was measured by finding out the amount of electrolyte necessary for instantaneous coagulation. The flocculation values are expressed in millimoles of the electrolyte in total volume, *i.e.*, 30 c.c. in this case.

The composition of the sol was determined by finding out the (i) total amount of arsenic, (ii) total amount of sulphur, and (iii) free arsenious acid. For the estimation of total arsenic and sulphur the method adopted was the one used by Chaudhury and Kundu.<sup>5</sup> For the amount of free arsenious acid, the sol was first coagulated by adding an excess of KCl and the coagulum removed by filtration and washed thoroughly with conductivity water; the amount of free arsenious acid was then estimated iodometrically.<sup>6</sup> The total amount of arsenic and sulphur and the amount of free arsenious acid in terms of arsenic are expressed in all the tables in gm. per litre of the sol.

For ageing experiments the sol was kept in a resistance glass flask wrapped in black paper. Portions of sol were removed after different periods of standing and the various properties were studied after filtering the sol in order to remove precipitates formed as a result of ageing.

For light experiments equal volumes of colloidal arsenious sulphide were kept in resistance glass beakers (of the same capacity) covered with glass plates. A 500 C. P. tungsten filament lamp was used as the source of artificial light; the lamp was kept vertically above the beaker containing the sol. In the case of sunlight experiments the beakers containing the sol were directly exposed.

*Results and Discussion.*

*A. Changes in cataphoretic speed, composition and stability with progress of dialysis.*—The results of these experiments are given in Table I.

TABLE I.

Period of dialysis in days	Total As	Free arsenious acid in terms of As	Total S	Cat. speed	Flocculation values	
					KCl	MgCl <sub>2</sub>
0	2.172	0.0000	2.194	66.52	1.230	0.0202
2	2.156	0.0045	2.145	56.98	1.365	0.0190
5	2.137	0.0135	2.095	32.25	1.605	0.0172
8	2.128	0.0300	2.053	18.23	1.830	0.0156
11	2.090	0.0195	2.040	33.25	1.575	0.0166
14	2.070	0.0120	2.029	38.15	1.425	0.0180
20	2.032	0.0120	2.012	42.75	1.350	0.0187
28	2.013	0.0120	2.002	52.40	1.275	0.0193
31	1.994	0.0120	1.996	10.55	0.825	0.0080

It will be seen from the results that with the progress of dialysis

- (1) the amount of arsenic in the sol continuously decreases ;
- (2) the amount of free arsenious acid increases upto a period of 8 days after which it decreases till 14 days when it does not change any more during further dialysis ;
- (3) the amount of sulphur continuously decreases ;
- (4) the cat. speed decreases upto 8 days after which it increases till 28 days when it decreases again ;
- (5) the stability with reference to KCl increases upto 8 days and decreases continuously thereafter ;
- (6) the stability with reference to  $MgCl_2$  decreases upto 8 days after which it increases till 28 days when it decreases again.

The changes in the composition of the sol suggest that a portion of arsenious sulphide hydrolyses during dialysis giving rise to arsenious acid and hydrogen sulphide. A part of the arsenious acid passes out in the dialysate—this accounts for a decrease in the amount of arsenic in the sol (see 1 above). A portion of the hydrogen sulphide escapes as gas and of that which remains in the dissolved condition, a certain amount must also be passing out in the dialysate—these two causes account for a decrease in the amount of sulphur in the sol (see 3 above). Some of the dissolved  $H_2S$  may get oxidised giving rise to  $SO_2$  which may react with  $H_2S$  producing polythionic acids and sulphur. The sulphur might absorb polythionate ions and pass into colloidal sulphur (*cf.* Freundlich and Nathansohn<sup>7</sup>). The changes in the amount of arsenious acid suggest that upto 8 days the rate of its production by hydrolysis is greater than that of its passing out in the dialysate and that between 8 and 14 days the rate of passing out of arsenious acid in the dialysate is greater than that of its production, while after 14 days both the rates of production of arsenious acid and its passing out in the dialysate are about the same. The rate of hydrolysis is faster in the beginning and slower towards the end possibly because the sol does not contain to start with any free electrolytes and later on complications are introduced due to production of colloidal sulphur as well as changes in the distribution of the preferentially adsorbed ions on the surface of the colloidal particles as a result of introduction of electrolytes in the sol.

The amounts of total arsenic and sulphur in the freshly prepared sol are not according to the formulæ  $As_2S_3$ . This is probably due to the fact that during the preparation of the sol a portion of hydrogen sulphide gets oxidised ultimately giving rise to colloidal sulphur as stated above ; the arsenious sulphide sol thus contains some colloidal sulphur also from the

beginning. The composition of colloidal arsenious sulphide prepared in different ways has been represented as  $X_2As_2S_3$ ,  $H_2As_2S_4$  by Pauli and Semler,<sup>8</sup>  $m.As_2S_3$ ,  $H_2S$  by Linder and Picton<sup>9</sup> and  $As_2S_3$ ,  $H_2S$  by Chaudhury and Kundu<sup>5</sup> (also see Burton and Annetts<sup>10</sup> and Krestinskaya<sup>11</sup>).

The initial cat. speed changes during dialysis in this case (see 4 above) are not similar to those observed with colloidal gold,<sup>12</sup> ferric hydroxide,<sup>1</sup> thorium hydroxide<sup>2</sup> and prussian blue.<sup>3</sup> This is due to the changes in the composition of this sol during dialysis.

The fact that the amount of free arsenious acid in the sol increases upto a dialysis of 8 days and decreases thereafter upto 14 days, while the cat. speed decreases upto 8 days and increases thereafter upto 28 days suggests that the variation in the amount of free arsenious acid upto 14 days might have some bearing on the changes in the cat. speed during that period. In the following table the result of changes in the cat. speed when small increasing amounts of arsenious acid are added to the sols dialysed for different periods are presented.

TABLE II.

Sol. dialysed for 5 days		Sol. dialysed for 25 days		Sol. dialysed for 31 days	
Concentration of arsenious acid	Cat. speed	Concentration of arsenious acid	Cat. speed	Concentration of arsenious acid	Cat. speed
0.000	30.35	0.000	65.10	0.000	47.10
0.025	34.15	0.009	65.35	0.009	43.05
0.125	41.45	0.047	64.60	0.094	42.90
0.250	43.55	0.940	54.70	0.469	41.55
1.250	22.50	9.400	51.50	4.687	40.50
12.500	20.95	46.875	41.20		
170.000	15.75	139.350	35.60		

It will appear from the results that the cat. speed first increases and then decreases in the case of sol dialysed for 5 days. In the case of the sol dialysed for 25 days only a slight rise occurs in the presence of small amounts of arsenious acid, while for sols dialysed for longer periods the cat. speed continuously decreases. S. N. Mukherjee<sup>13</sup> observed that the cat. speed of

arsenious sulphide diminishes on the addition of arsenious acid, while Mukherjee, Raichaudhuri and Rajkumar<sup>14</sup> noticed that the cat. speed of  $\text{As}_2\text{S}_3$  sol increases in the presence of small amounts of  $\text{H}_3\text{AsO}_3$  although it decreases when larger amounts of the acid are added to the sol. Our results support both the observations. The difference in the behaviour in different cases is due to a difference in the composition of the sol, the preferential adsorption of the ions being affected to different extents on account of differences in the nature and amounts of electrolytes present in each sol.

From Table II, it will appear that the initial rise of cat. speed increases with a decrease in the period of dialysis. A greater initial rise of cat. speed on addition of small increasing amounts of arsenious acid is therefore likely to occur in the case of the freshly prepared sol containing no free arsenious acid than that of the sol dialysed for 5 days and containing some free arsenious acid from the beginning. The fact that the cat. speed of the freshly prepared sol first increases and then decreases on the addition of small increasing amounts of arsenious acid will incline one to the view that the cat. speed of the sol might have increased immediately after keeping the sol for dialysis and before 2 days, *i.e.*, as soon as traces of arsenious acid were produced as a result of hydrolysis—this might have occurred during the first couple of hours of dialysis and hence not noticed in the experiments described here. Leaving aside this particular point, it is clear that the decrease in the cat. speed upto 8 days is due to an increase in the amount of arsenious acid in the sol. Between 8 and 14 days the cat. speed has increased and this is due to a decrease in the amount of arsenious acid (Table I) during that period. Thus the cat. speed changes upto 14 days' dialysis are primarily due to changes in the amount of arsenious acid in the sol which affect the preferential adsorption of the ions on the surface of the colloidal particles.

The cat. speed changes between 14 and 31 days, *i.e.*, first an increase (between 14 and 28 days) and then a decrease (between 28 and 31 days) can be explained as done by Desai and co-workers<sup>1,2,3</sup> by considering the process of dialysis as a reverse of the case of adding small increasing amounts of the peptising electrolyte to the colloid. In the present case, the sol is probably peptised by sulphide and hydrosulphide ions. Although it has not been possible to take measurements of cat. speed of  $\text{As}_2\text{S}_3$  sol on adding small increasing amounts of hydrogen sulphide, it is highly probable that, as in the case of other peptising agents and sols, in this case also the cat. speed will first increase and then decrease on adding small increasing amounts of hydrogen sulphide. The amount of total sulphur has continuously decreased between 14 and 31 days as before 14 days. This decrease is due to escape of  $\text{H}_2\text{S}$  as gas and in the dialysate as stated earlier. The amount of the

peptising ions must therefore be continuously decreasing between 14 and 31 days and therefore the cat. speed should first increase and then decrease as stated by Desai and co-workers.<sup>1,2,3</sup> Thus the cat. speed changes between 14 and 31 days of dialysis are primarily due to changes in the amount of the peptising ions in the sol which alter the distribution of the ions on the surface of the particles.

Upto a dialysis of 8 days stability has increased although cat. speed has decreased. This might perhaps be due to replacement of arsenious acid from the surface of the particles by KCl, which process will increase the cat. speed (from a comparison of the results given in Table II with those for KCl given in Section C, it will appear that the initial increase in the cat. speed is greater in the presence of KCl than arsenious acid) and hence a larger amount of KCl would be required for coagulation of sols dialysed for relatively long periods than in the beginning when the amount of arsenious acid is relatively small. The stability changes with reference to KCl (Table I) between 8 and 28 days might be primarily due to preferential adsorption of similarly charged ions (Cl-ions) as in the cases of ferric and thorium hydroxide and prussian blue where the stability also decreased in spite of increase of cat. speed. The stability changes between 28 and 31 days are primarily due to changes in cat. speed during that period.

The stability changes with reference to  $MgCl_2$  are primarily due to changes in the cat. speed—greater cat. speed greater stability and *vice versa* because the preferential adsorption of the similarly charged ions is probably not allowed to take place in the presence of bivalent coagulating ions.<sup>1,2,3</sup> The productions of slight turbidity on the addition of  $MgCl_2$  to the sol containing free arsenious acid does not seem to have any marked influence on the stability of the sol.

*B. Changes in cataphoretic speed and stability of arsenious sulphide sol dialysed and diluted to different extents.*—Sols of different concentrations were prepared by adding requisite amounts of conductivity water to the original sol. The original sol has dilution 1 ; dilutions of other sols have been obtained from the value of the ratio  $\frac{\text{total volume of the diluted sol}}{\text{actual volume of the original sol}}$ . The results of these experiments are given in the following table :—

TABLE III.

Period of dialysis in days	Dilution												
	1		1.33		2		4		8				
	Cat. speed	Flocculation values		Cat. speed	Cat. speed	Flocculation values		Cat. speed	Flocculation values		Cat. speed	Flocculation values	
		KCl	MgCl <sub>2</sub>			KCl	MgCl <sub>2</sub>		KCl	MgCl <sub>2</sub>		KCl	MgCl <sub>2</sub>
0	50.65	1.620	0.016	40.75	33.60	1.89	0.020	21.70	2.40	0.023	17.40	3.15	0.028
4	34.15	1.935	0.012	30.30	24.85	2.52	0.016	17.55	3.37	0.017	14.35	4.26	0.021
8	26.10	2.160	0.010	24.05	20.85	2.84	0.011	15.65	3.96	0.012	13.25	5.25	0.012
17	39.25	1.635	0.016	38.30	36.15	2.40	0.022	33.30	3.06	0.025	33.45	4.02	0.030
23	45.70	1.530	0.020	45.80	46.10	2.02	0.024	48.30	2.58	0.030	54.25	3.30	0.039
29	36.00	1.260	0.014	33.30	28.40	1.62	0.017	31.80	1.95	0.019	43.70	2.34	0.022
31	21.40	0.610	0.007	22.65	24.80	0.81	0.009	29.00	0.93	0.009	41.20	1.05	0.010

It will be seen from the table that on diluting the sol the cat. speed (horizontal rows), (a) continuously decreases for sols dialysed for 0, 4 and 8 days, (b) first decreases and then shows a tendency of increase for sol dialysed for 17 days, (c) continuously decreases for sols dialysed for 23 and 31 days and (d) first decreases and then increases for sol dialysed for 29 days; however in all the cases, the stability with reference to KCl and MgCl<sub>2</sub> continuously increases (horizontal rows) on diluting the sol. For all the samples of the sol having different dilutions, the cat. speed during dialysis first decreases and then increases after which it again decreases (vertical columns) (*cf.* Section A); the results of stability with reference to KCl and MgCl<sub>2</sub> (vertical columns) are also exactly similar to those given before in Section A.

From the above results, it is quite clear that in the case of arsenious sulphide sol the changes in cat. speed on dilution of sols dialysed for different periods are not regular as in the case of colloidal ferric and thorium hydroxide and prussian blue.<sup>1,2,3</sup> This is due to the fact that the composition of the sol continuously changes during dialysis which affects distribution of the ions adsorbed on the surface of the colloidal particles as shown in Section A; hydrolysis of arsenious sulphide will also perhaps increase with dilution of the sol, the size of the particles decreasing at the same time. Peculiar changes in cat. speed on dilution of As<sub>2</sub>S<sub>3</sub> sol observed by Mukherjee and co-workers<sup>15</sup> are also probably due to a difference in the composition of the various samples tried by them. Mukherjee and Ganguly<sup>16</sup> also observed as

has been done by us that the stability as determined by flocculating values with electrolytes increases on dilution. It may be concluded that the results of stability and cat. speed measurements of colloidal arsenious sulphide should not be utilised either to prove or disprove any of the existing ideas about coagulation of colloids in view of considerable differences that are likely to be produced as a result of changes in the composition of different samples of the sol.

*C. Measurements of cat. speed of arsenious sulphide sol (dialysed for different periods) from the point of view of critical potential.*—The results of these experiments are given in the following table :—

TABLE IV.

Electrolyte	Period of dialysis	Initial cat. speed	Initial rise in cat. speed	Cat. speed at which sol begins to coagulate	Concentration of electrolyte at which sol begins to coagulate
HCl ..	5 days	28.60	33.80	15.90	25.00
	25 "	65.50	24.00	26.90	12.50
	31 "	46.80	nil	28.50	17.50
KCl ..	5 "	29.20	22.40	25.40	50.00
	25 "	63.10	23.75	25.85	37.50
	31 "	45.35	nil	29.50	25.00
MgCl <sub>2</sub> ..	5 "	26.25	nil	12.80	0.25
	25 "	63.70	nil	14.15	0.37
	31 "	45.35	nil	18.20	0.25
K <sub>2</sub> SO <sub>4</sub> ..	5 "	17.30	36.20	27.65	25.00
	25 "	62.40	14.35	25.00	18.75
MgSO <sub>4</sub> ..	5 "	15.95	nil	10.40	0.37

It will be seen from the results that the initial rise in the cat. speed when small increasing amounts of electrolytes are added to the sol does not occur in those cases where the electrolyte contains a bivalent coagulating ion.<sup>1,2,3</sup> Further, even in the case of electrolytes with univalent coagulating ions, the initial rise is not noticed with those samples of the sol which are dialysed for long periods. The initial increase in the cat. speed is due to preferential adsorption of the similarly charged ions and this may not be noticed when the coagulating ion is multivalent. The non-observance of initial rise even with the univalent coagulating ions for sols dialysed for longer periods is due to changes in the composition of the sol as stated before.



Mukherjee and co-workers<sup>17</sup> observed that the cat. speed of  $As_2S_3$  sol continuously decreases on adding small increasing amounts of HCl, while Nanitski and Proskurnin<sup>18</sup> got first an increase and then a decrease with HCl. Freundlich and Zeh<sup>19</sup> observed that when KCl is added to  $As_2S_3$  sol the cat. speed continuously decreases, while Kruyt and co-workers<sup>20</sup> got a continuous increase with this electrolyte; Mukherjee and co-workers<sup>21</sup> got with KCl results similar to those of Freundlich and Zeh as well as of Kruyt and co-workers and further observed that in some cases the cat. speed with KCl first decreases and then increases. From what has been stated above it is clear that the differences in the results of different investigators working with the same electrolytes are probably due to differences in the composition of the  $As_2S_3$  sols tried by them.

From the table it will appear that the value of cat. speed at which coagulation takes place lies between 10.40 and 29.50. It would thus appear that these results as a whole do not support the idea of critical potential.<sup>22</sup> The variation in the value of critical cat. speed for individual electrolytes is, however, generally small. The results show that generally the value of critical cat. speed at which coagulation begins is lower for bivalent coagulating ions than for univalent ones (*cf.* Powis<sup>23</sup> and Chaudhury<sup>24</sup>).

The variation in the value of the critical cat. speed in different cases is due to preferential adsorption of the stabilising ions which is considerably modified by the valency of the coagulating ions as suggested by Desai and co-workers.<sup>1,2,3</sup> In the case of colloidal  $As_2S_3$  the differences are further increased as a result of changes in the composition of the sol—varying amounts of arsenious acid,  $H_2S$  and colloidal S.

*D. Influence of ageing on the cataphoretic speed, stability and composition of the arsenious sulphide sol.*—The precipitates formed as a result of ageing were removed by filtration before studying the various properties. The results of these experiments are given in the following table:—

TABLE V.

Age in days	Total As	Free arsenious acid in terms of As	Total S	Cat. speed	Flocculation values	
					KCl	MgCl <sub>2</sub>
0	1.306	0.00263	1.426	37.05	1.70	0.0252
15	1.287	0.03300	1.412	34.95	2.02	0.0228
30	1.191	0.04175	1.379	29.35	2.22	0.0189
45	1.110	0.05228	1.341	20.50	1.86	0.0168
60	1.093	0.05689	1.282	18.15	1.66	0.0153
90	1.026	...	1.148	16.30	1.60	0.0147

It will appear from the results that the amount of total As and S continuously decreases on ageing, the amount of free arsenious acid in the sol increasing at the same time. These changes are due to decomposition of the arsenious sulphide sol as stated in Section A. The decrease in the total amount of As and S (besides that due to escape of H<sub>2</sub>S as gas) is due to removal of the precipitate. Arsenious acid and polythionate ions will have stabilising as well as destabilising effect on both colloidal As<sub>2</sub>S<sub>3</sub> and S; the formation of precipitate is due to latter effect.

The decrease in the cat. speed is due to an increase in the amount of arsenious acid with an increase in the age of the sol.

The initial increase in the stability with reference to KCl in spite of a decrease of cat. speed is due to preferential adsorption of the stabilising ions as stated in Section A. In the case of MgCl<sub>2</sub> the stability has continuously decreased with cat. speed as the preferential adsorption of the similarly charged ions has not been probably allowed to take place as a result of bi-valency of the coagulating ion.

*E. Effect of artificial light and sunlight on the cat. speed and composition of the arsenious sulphide sol dialysed for different periods.*—In these experiments also as in the ageing experiments the precipitate formed on exposing the sol to light was removed by filtration before all measurements were made. Any decrease in volume on exposure was made good by adding conductivity water. The results of these experiments are given in Tables VI, VII and VIII.

TABLE VI.  
*Artificial Light.*

Period of exposure in minutes	Total As	Free Arsenious acid in terms of As	Total S	Cat. speed	Flecculation values	
					KCl	MgCl <sub>2</sub>
0	1.306	0.0028	1.482	37.05	1.70	0.025
50	1.306	0.0214	1.473	31.05	1.76	0.024
100	1.306	0.0337	1.462	27.20	1.85	0.023
150	1.296	0.0416	1.456	23.60	1.72	0.022
200	1.290	0.0484	1.448	21.85	1.60	0.021
300	1.286	0.0536	1.431	19.50	1.18	0.019
500	1.284	0.0623	1.405	17.00	0.86	0.013
900	1.283	.	1.371	15.38	0.58	0.008

TABLE VII.  
Sunlight.  
Undialysed Sol.

Period of exposure in minutes	Total As	Free arsenious acid in terms of As	Total S	Cat. speed
0	1.529	0.0000	1.467	50.10
30	1.519	0.0024	1.458	51.25
70	1.514	0.0362	1.450	48.35
150	1.500	0.0569	1.425	43.80
300	1.452	0.0825	1.338	34.05
450	1.422	0.1075	1.326	32.05
1,200	1.403	0.1781	1.312	29.85

TABLE VIII.  
Sunlight.

Values in columns 1 and 2 refer to sols dialysed for 25 and 35 days respectively.

Period of exposure in minutes	Total As		Free arsenious acid in terms of As		Total S		Cat. speed	
	1	2	1	2	1	2	1	2
0	1.471	1.413	0.0437	0.0437	1.422	1.390	41.40	36.20
60	1.442	1.374	0.1000	0.1812	1.373	1.308	35.20	30.05
300	1.307	1.219	0.2256	0.5563	1.222	1.120	21.45	17.40
600	1.258	1.132	0.2751	0.4625	1.169	1.049	18.85	14.25
1,200	1.210	1.074	0.4282	0.6437	1.100	0.967	17.15	11.45

It will appear that on exposing the sol to light the amount of total As and S decreases while that of free arsenious acid continuously increases. These changes are due to hydrolysis of a part of  $As_2S_3$  into arsenious acid and  $H_2S$ .  $H_2S$  is photochemically oxidised to  $SO_2$  which further reacts

with  $H_2S$  giving rise to polythionic acids and S. The latter adsorbs polythionate ions and passes into colloidal sulphur (Freundlich and Nathansohn<sup>7</sup>).

The cat. speed decreases on exposure as the amount of arsenious acid increases except for the undialysed sol where it first increases slightly and then decreases. As stated before (Section A) the cat. speed first increases and then decreases on adding small increasing amounts of arsenious acid in the case of sols dialysed for short periods and the initial increase in the cat. speed of the undialysed sol is due to this effect.

The stability with reference to KCl first increases and then decreases on exposing the sol to artificial light (same changes were also noticed with sunlight) (*cf.* Miss Shila Roy<sup>25</sup>), while that with reference to  $MgCl_2$  continuously decreases. The stability changes on exposure to light are thus exactly similar to those observed on ageing (Section D) and can be explained in the same manner.

#### *Summary.*

The cat. speed of colloidal arsenious sulphide with the progress of dialysis decreases upto 8 days after which it increases till 28 days when it decreases again; the amount of total arsenic and sulphur continuously decreases, while that of free arsenious acid increases at first and then remains constant. The stability with reference to KCl first increases and then decreases, while that with reference to  $MgCl_2$  changes exactly as the cat. speed. It is shown that changes in cat. speed are as a result of changes in the composition of the sol with the progress of dialysis which in turn affect to different extents the preferential adsorption of the ions on the surface of the colloidal particles.

The changes in cat. speed on dilution of sols dialysed for different periods are not regular as in the case of colloidal ferric and thorium hydroxide and prussian blue. The stability with reference to KCl and  $MgCl_2$  increases regularly on dilution.

The idea of critical potential is not supported in the case of this sol.

The cat. speed decreases generally on ageing and exposure to light; the amount of total arsenic and sulphur (excluding that in the precipitate) decreases, while that of free arsenious acid increases at the same time. The stability with reference to KCl first increases and then decreases, while that with reference to  $MgCl_2$  regularly decreases both during ageing and exposure to light.

It is shown that the results with  $As_2S_3$  sol should not be utilised either to prove or disprove any of the existing ideas about coagulation of colloids because changes in the composition of the sol introduce considerable complications.

In the end it may be mentioned that our cataphoretic speed measurements given in the four papers of this series support the physical point of view (based on the adsorption of the ions of the peptising electrolytes by the colloidal particles)<sup>26</sup> about the origin of charge ; the chemical point of view<sup>27</sup> about the origin of charge which is based on the dissociation of the ionogenic complex is not supported by our results. These points will be discussed in detail in a later publication (Paper to be published in September 1936 number of the *Journal of the Bombay University*).

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