IMPORTANCE OF DIALYSIS IN THE STUDY OF COLLOIDS

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IMPORTANCE OF DIALYSIS IN THE STUDY OF COLLOIDS.

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IMPORTANCE OF DIALYSIS IN THE STUDY OF COLLOIDS.

Introduction.

Dialysis has been utilised since the time of Graham for freeing a colloidal solution from the impurities introduced into it at the time of its preparation viz., the peptising agent and the other electrolytes formed as a result of double decomposition. The importance of the influence of dialysis on the various properties of colloidal solutions has not, however, been generally realised and as a result of this different investigators trying the same experiments on the same colloid and with the same electrolytes have frequently obtained apparently conflicting results. Thus Dhar and Ghosh[1]* working on prussian blue sol found that it showed abnormal behaviour to the dilution rule viz., that the greater the concentration of a colloid, the greater is the amount of an electrolyte necessary for coagulating it, when coagulated with KCl, while Weiser and Nicholas[2] observed that the same sol when coagulated by the same electrolyte was normal to the dilution rule. Desai[3] however showed that it is erroneous to classify colloids into two divisions according to their behaviour to the dilution rule as done by Dhar and collaborators[4] because a suitable adjustment of the amount of the

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* References are given on pages 101 to 103.

the peptising agent (by subjecting it to dialysis) seems to make a colloid normal or abnormal to the dilution rule.

It is a general belief that the stability of a sol decreases with the progress of dialysis except in the case of colloidal gold where the stability with reference to KCl first increases and then decreases[5]. Further it is customary to explain the decrease in stability on dialysis as being due to a decrease in the charge on the colloid particles although no direct measurements of charge are made to support this generalisation.

According to v. Smoluchowski[6] a sol with greater electric charge should show greater viscosity than a sol containing particles of feeble electric charge. The results of viscosity measurements of a number of colloids with the progress of dialysis and in the presence of electrolytes have however been explained by Dhar and co-workers[7] on the assumption that the viscosity is related to the charge on the colloid and that the smaller the charge on the colloidal particles, the greater their hydration and the greater the viscosity of the sol.

No systematic investigations seem to have been made to determine simultaneously the relation between the charge on the particles and the stability, viscosity and other related properties of colloidal solutions dialysed and diluted to diferent extents. In what follows

follows is given a connected account and a discussion of the experimental results obtained with various colloidal solutions in the Physical Chemistry Laboratory of the Wilson College, Bombay (India) to show how changes in the purity of colloidal solutions and their concentration alter the charge on their particles and their stability, viscosity and conductivity. In addition simultaneous measurements of charge, stability and conductivity for certain of these colloidal solutions when dialysed for different periods and allowed to age or exposed to sunlight are also given.

EXPERIMENTAL.

(a) Preparation of colloidal solutions.

Ferric hydroxide sol - 100 gm. of hydrous ferric chloride were dissolved in 300 c.c. of water. About 50 c.c. of ferric chloride solution were added to 500 c.c. of boiling distilled water drop by drop, the mixture being stirred all the time. The resulting brown red sol was further boiled for half an hour.

Thorium hydroxide sol - 25 gm. of thorium nitrate were dissolved in about 300 c.c. of warm water and the hydroxide precipitated by adding excess of ammonia. The precipitate was washed till free from ammonia and suspended in two litres of water. The suspension was heated nearly to the boiling point and N/20 HCl was added in quantities of 2 c.c. at intervals till an opalescent sol

sol was obtained.

Prussian blue sol - Prussian blue was precipitated by adding slowly and without stirring a 2% solution of $K_4Fe(CN)_6$ to a 2% solution of ferric chloride. The precipitate was allowed to stand for about 15 minutes, filtered, washed and peptised by shaking with a 2% oxalic acid solution.

Arsenious sulphide sol - Hydrogen sulphide was bubbled through four litres of distilled water till saturation. While the gas was still passing 1 litre of 15% 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.

Gold sol - Gold sol was prepared by Zsigmondy's nucleus method in batches of 100 c.c.

Vanadium pentoxide sol - The sol was prepared by the method of Biltz. A known weight of ammonium vanadate was made into a pasty mass in a mortar by adding small increasing amounts of water. Thereafter an equivalent amount of HCl was added to it drop by drop mixing the paste all the time with pestle. The red precipitate obtained was removed to a filter paper and washed with water till it showed a tendency to pass into colloidal solution. The precipitate was then removed to a flask and vigorously shaken with the addi-

addition of a small quantity of water till a clear deep red sol was obtained.

(b) Dialysis of colloidal solutions.

All the sols were filtered after preparation and dialysed against distilled water in parchment paper bags which were previously kept soaked in distilled water for 3 to 4 days. The dialysis was carried out in a dark room in order to avoid effect of light as far as possible. The outer water was changed twice a day.

The following were detected in the dialysate during dialysis in the case of different sols:-

Sol.	Ions or electrolytes detected in dialysate.
1. Ferric hydroxide	$FeCl_3$ and HCl.
2. Thorium hydroxide	$ThCl_4$ and HCl.
3. Prussian blue	Oxalic acid and $Fe^{\cdots}$ ions, also traces of Cl' ions.
4. Arsenious sulphide	Arsenious acid and traces of S'' ions.
5. Gold	Cl', $K^{\cdot}$ and OH' ions.
6. Vanadium pentoxide	Vanadate ions, also some NH_4Cl.

The concentration of the colloid did not change appreciably with the progress of dialysis except in the case of colloidal As_2S_3 and V_2O_5 which will be discussed later. Samples of sols were withdrawn after different periods of dialysis for experiments on the variation of its properties with progress of dialysis. From changes

changes in turbidity or colour it appeared that the size of colloidal particles increased during dialysis.

As As_2S_3 decomposes during dialysis, ageing and exposure to light, the composition of the sol in different cases was determined by finding out the (i) total 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 Choudhury and Kundu[8]. 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 in the filtrate was then estimated iodometrically. 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.

(c) Determination of charge.

As discussed by Mukherjee[9] the variations in the density of the charge on the surface of the colloidal particles are given directly by the variations in the cataphoretic speed (cat. speed). The cat. speed measurements therefore can enable one to follow the changes in the charge on the colloidal particles.

The cat. speed was measured by Mukherjee's[10] improved U-tube method. In order to get reliable results it is necessary as pointed out by Mukherjee to have the upper liquid such that the direct and reverse boundary movement as well as the potential gradient before and after the experiment will be the same. Desai, Nabar and Barve[10(A)] found that dialysate could be used as a satisfactory upper liquid under certain circumstances in the case of colloidal ferric hydroxide. In all the cases the upper liquid was so selected that the requirements of the constancy of the potential gradient both before and after the experiment as well as a close agreement between the direct and reverse movements were satisfied. The following upper liquids were used in different cases:-

Sol	Upper liquid.
1. Ferric hydroxide	Dialysate made equiconducting with the sol by addition of concentrated solution of $FeCl_3$.
2. Thorium hydroxide	Dialysate made equiconducting with the sol by addition of suitable amounts of HCl.
3. Prussian blue	Dialysate made equiconducting with the sol by addition of suitable amounts of KCl in the initial stages of dialysis and of oxalic acid later.
4. Arsenious sulphide	Equiconducting solution of HCl.
5. Gold	Equiconducting solution of KCl.
6. Vanadium pentoxide	Dialysate made equiconducting with the sol by addition of NH_4Cl.

The electrodes were placed in the side bulbs attached to the two limbs of the U-tube (Fig. A) instead

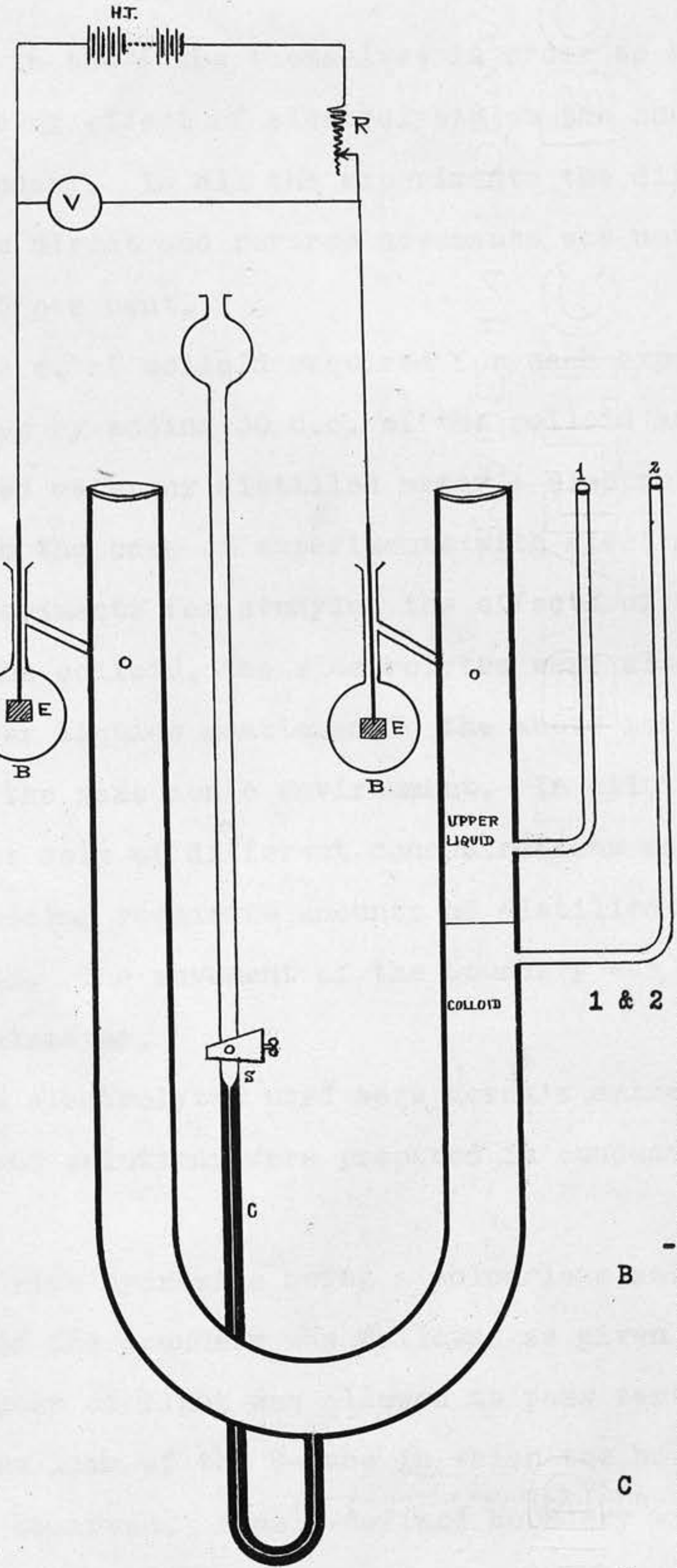


FIG- A

1 & 2 = Side-tubes attached to the limb of the U-tube in which measurement of boundary is followed. The boundary is always kept between these two side-tubes. The side-tubes are used to measure potential gradient across the boundary.

B = Side-bulb attached to the limb of the U-tube for keeping electrode; this prevents disturbing effect of electrolysis on the sharpness of the boundary.

C = Capillary for slow filling to get a sharp boundary.

E = Electrode.

H. T. = High Tension cells.

R = Adjustible resistance.

S = Stop-cock.

V = Voltmeter.

instead of in the limbs themselves in order to avoid the disturbing effect of electrolysis on the sharpness of the boundary. In all the experiments the difference between the direct and reverse movements was never found to exceed 5 per cent.

40 c.c. of colloid required for each experiment were made up by adding 30 c.c. of the colloid and 10 c.c. of distilled water or distilled water + electrolytic solution in the case of experiments with electrolytes. In the experiments for studying the effects of electrolytes on the colloid, the electrolytes were also added to the upper liquids mentioned in the above table so as to get the same ionic environment. In dilution experiments sols of different concentrations were prepared by adding requisite amounts of distilled water to the colloid. The movement of the boundary was followed by a cathetometer.

The electrolytes used were Merck's extra pure reagents and solutions were prepared in conductivity water.

Thorium hydroxide being a colourless sol, the movement of the boundary was followed as given below:-

A beam of light was allowed to pass vertically down in the limb of the U-tube in which the boundary was to be observed. A well-defined boundary was observed between the colloid and the upper liquid in concentrated sols due to Tyndall phenomenon. As

As difficulty was experienced in following the movement of boundary even by this method in the case of very dilute sols, 0.5 c.c. of 0.1 per cent solution of Neutral Red (amino-dimethylamino-toluphenazonium chloride, P_H 6.8-8.0) was added to 100 c.c. of upper liquid in all dilution experiments for sake of uniformity. Cat.speed was determined both in the presence and absence of the Neutral Red in the case of concentrated sols, and it was found that the mean cat.speed obtained in the two cases agreed within 2 per cent. Also the boundary obtained between the colloid and the coloured upper liquid was always very sharp, there being practically no diffusion of the dye into the colloid.

In all the tables of results, the cat.speed (mean of the direct and reverse movements) corrected for viscosity is expressed in centimetres per second per volt per centimetre X 10^5. The concentration of the electrolyte added is expressed in millimoles per litre of the mixture colloid + water + electrolyte. In all dilution experiments, dilution is expressed in terms of the value of the ratio $\frac{\text{total volume of the diluted sol}}{\text{actual volume of the original sol}}$; thus the original sol has dilution 1 in each case.

(d) Determination of stability.

The stability was determined by finding out the amount of electrolyte necessary for giving a definite blue colour in the case of colloidal gold and for instantaneous

instantaneous coagulation (to attain same turbidity as the standard immediately on mixing the sol with the electrolyte) for other colloidal solutions. The volume of the mixture colloid + electrolyte + water was kept constant throughout and the flocculation values (F.V.) are expressed in millimoles of the electrolyte per litre of the mixture.

(e) Viscosity measurements.

Viscosity was determined by using an Ostwald viscometer. The same volume (10 c.c.) of the colloid or the mixture colloid + electrolyte + water was taken in all the experiments. The time of flow was measured by a stop watch reading to one tenth of a second. The results have been expressed in terms of viscosity of distilled water at the temperature of the experiment as unity.

(f) Conductivity measurements.

The conductivity was measured by the usual method using an amplifying circuit similar to the one used by Lorenz and Klauer[11], the details of the method being the same and those given by Desai, Naik and Desai[12].

(g) Ageing experiments.

For these experiments sols dialysed for different periods were removed and stocked in resistance glass flasks (covered with black paper) for different periods before taking measurements. In the case of As_2S_3 the precipitate which formed on ageing was removed by by filtration before studying the various properties.

(h) Experiments on exposure to light.

For these experiments equal volumes of sol were removed in resistance glass beakers (of same capacity) which were kept covered with glass plates and exposed directly to sunlight for different periods. Any loss due to evaporation was made good by addition of conductivity water.

In the case of As_2S_3 the sol was also exposed to artificial light. In this case the source of light was a 500 C.P. Tungsten fillament lamp, the lamp being kept vertically above the beaker containing the sol.

The precipitate which formed on exposure to light in the case of As_2S_3 sol was removed by filtration before studying the various properties.

(i) Temperature of experiments.

All the measurements of cat. speed, stability, viscosity and conductivity were made at a temperature of 30°C. For this purpose an electrically controlled thermostat with two opposite glass sides was used. The temperature could be maintained correct to within ± 0.1°C.

RESULTS.

SECTION I - Changes during dialysis.

TABLE I.

(a) Ferric hydroxide.

Period of dialysis -days.	Cat.speed.	F. V. with KCl
3	27.24	550
6	43.80	375
9	55.65	250
12	71.85	100
15	68.69	25
18	63.84	15
21	51.17	11

(b) Ferric hydroxide.

Period of dialysis -days.	Cat.speed.	Viscosity.
2	39.53	1.042
4	46.15	1.034
6	49.57	1.031
8	50.31	1.023
10	51.48	1.013
12	52.24	1.025
15	51.81	1.030
18	49.25	1.035
21	48.51	1.042
24	47.75	1.045

TABLE II.

Thorium hydroxide.

Period of dialysis -days.	Cat. speed.	F. V. with KCl.	Viscosity.
0	29.72	-	1.0240
2	35.47	2185.0	1.0279
4	39.38	580.0	1.0311
6	41.04	252.5	1.0372
8	37.37	85.0	1.0463
10	31.97	35.5	1.0541
12	28.65	11.0	1.0682
14	24.88	2.3	1.1316

TABLE III.

(a) Prussian blue.

Period of dialysis - days.	Cat. speed.	F. V. with KCl.	Viscosity.
4	39.00	161.0	1.014
9	41.10	140.0	1.009
14	44.10	88.0	1.004
18	43.60	43.0	1.005
27	38.00	-	1.012
30	27.00	-	1.014
34	19.50	-	-

TABLE III. (Contd.)

(b) Prussian blue.

Period of dialysis -days.	Cat. speed.	Sp. conductivity $\times 10^6$
3	38.70	31630.0
8	40.60	8780.0
13	43.20	2156.0
17	42.50	1116.0
21	41.05	554.4
26	37.10	270.9

TABLE IV.

(a) Arsenious sulphide.

Period of dialysis -days.	Total As.	Free As_2O_3 in terms of As.	Total S.	Cat. speed.	F. V. with	
					KCl	$MgCl_2$
0	2.172	0.0000	2.194	66.52	41.0	0.67
2	2.156	0.0045	2.145	56.98	45.5	0.63
5	2.137	0.0135	2.095	32.25	53.5	0.57
8	2.128	0.0300	2.053	18.23	61.0	0.52
11	2.090	0.0195	2.040	33.25	52.5	0.55
14	2.070	0.0120	2.029	38.15	47.5	0.60
20	2.032	0.0120	2.012	42.75	45.0	0.62
28	2.013	0.0120	2.002	52.40	42.5	0.64
31	1.994	0.0120	1.996	10.55	27.5	0.27

TABLE IV. (Contd.)

(b) Arsenious sulphide.

Period of dialysis -days.	Cat. Speed.	Sp. Conductivity X 10^6
0	50.65	226.3
4	34.15	181.1
8	26.10	167.0
17	39.25	284.5
23	45.70	213.1
29	36.00	209.6

TABLE V.

Gold.

(a)

Period of dialysis -days.	Cat. speed.	F. V. with NaCl.
3	65.75	19.67
6	92.50	22.00
10	105.25	23.67
13	116.50	26.33
18	128.50	32.00
21	109.50	24.00
24	75.00	21.00
26	53.75	17.32

(b)

Period of dialysis -days.	Sp. Conductivity X 10^6
0	240.0
4	163.8
8	53.9
10	33.6
13	24.8
17	16.6
21	11.4
25	5.9

TABLE VI.

(a) Vanadium pentoxide.

(Dilute sol)

Period of dialysis -days.	Concentration of V_2O_5 per litre.	Cat. speed.	F. V. with NaCl	Viscosity.	Sp.Conductivity X 10^6
0	2.75	28.92	10.01	1.401	490.6
2	2.67	35.84	9.22	1.386	373.4
4	2.21	39.48	9.01	1.350	365.2
6	2.06	30.20	8.00	1.675	360.3
8	1.81	26.71	6.33	1.810	355.9
12	1.78	23.92	5.80	2.078	296.0
18	1.60	-	4.67	highly viscous.	-
20	-	-	-	Jelly formed.	

(b) Vanadium pentoxide.

(Concentrated sol).

Period of dialysis -days.	Concentration of V_2O_5 per litre.	Cat.speed.	F. V. with NaCl	Viscosity.
0	18.40	51.76	5.34	3.062
2	17.49	60.45	4.67	2.979
4	16.00	73.45	4.33	2.897
6	15.47	59.76	3.17	3.073
8	14.67	46.51	2.33	3.873
10	13.17	-	1.83	highly viscous
12	-	-	-	Jelly formed

SECTION II - Changes during dilution of sols dialysed for different periods.

TABLE VII.

Ferric hydroxide.

Period of dialysis -days.	Dilution. 1		2		4	
	Cat. speed.	F. V. KCl.	Cat. speed.	F. V. KCl.	Cat. speed.	F. V. KCl.
3	27.24	-	43.27	-	45.40	-
6	43.80	-	46.79	-	53.89	-
9	55.65	250.0	58.55	170.0	64.10	147.5
12	71.85	100.0	69.55	60.0	68.58	45.0
15	68.69	25.0	65.10	17.5	57.00	12.5
18	63.84	15.5	60.57	-	54.17	-
21	51.17	11.0	48.61	9.0	42.94	6.5

Ferric hydroxide (Contd.)

Period of dialysis -days.	Dilution. 6		10		15		20	
	Cat. speed.	F. V. KCl.	Cat. speed.	F. V. KCl.	Cat. speed.	F. V. KCl.	Cat. speed.	F.V. KCl.
3	41.43	-	42.09	-	-	-	40.70	-
6	62.61	-	51.84	-	52.72	-	52.13	-
9	57.69	115.0	44.86	85.0	48.07	75.0	45.94	60.0
12	66.88	30.0	54.17	25.0	54.45	22.0	54.98	17.5
15	56.03	11.0	49.68	7.0	48.18	6.3	45.13	5.0
18	49.95	-	44.01	-	39.69	-	36.64	-
21	38.99	5.0	37.80	4.5	37.00	4.0	36.96	3.3

TABLE VIII.

(a) Thorium hydroxide.

Period of dialysis -days.	Dilution							
	1		2		3		4	
	Cat. speed.	F. V. KCl	Cat. speed.	F. V. KCl	Cat. speed.	F. V. KCl	Cat. speed.	F. V. KCl
0	29.72	-	33.68	-	37.27	-	40.28	-
2	35.47	2185.0	36.74	1990.0	38.84	1880.0	37.27	1650.0
4	39.38	580.0	40.82	570.0	40.82	480.0	38.53	455.0
6	41.04	253.0	40.01	243.0	37.81	225.0	36.28	200.0
8	37.37	85.0	35.88	80.0	34.16	76.0	33.05	70.0
10	31.97	35.5	30.62	32.5	29.54	29.5	27.93	26.5
12	28.65	11.0	26.68	9.5	25.42	9.0	24.70	8.0
14	24.88	2.3	22.90	1.9	21.47	1.7	20.75	1.3

(a) Thorium hydroxide (Contd.).

Period of dialysis -days.	Dilution							
	8		12		16		20	
	Cat. speed.	F. V. KCl	Cat. speed.	F. V. KCl	Cat. speed.	F. V. KCl	Cat. speed.	F. V. KCl
0	33.95	3375.0	29.01	3090.0	24.85	2695.0	22.18	2205.0
2	34.58	1410.0	31.35	1300.0	27.43	1110.0	24.65	885.0
4	35.97	370.0	33.37	260.0	30.45	215.0	27.22	180.0
6	35.25	145.0	33.23	100.0	30.90	80.0	27.93	75.0
8	31.16	50.0	29.63	39.0	28.83	29.0	26.57	25.0
10	26.05	21.5	24.43	14.5	23.28	11.0	22.86	10.0
12	22.55	6.0	20.92	4.5	20.21	3.8	18.86	3.5
14	18.86	0.9	16.53	0.7	15.27	0.6	14.37	0.5

TABLE VIII (Contd.).

(b) Thorium hydroxide.

Period of dialysis -days.	Viscosity.					
	Dilution.					
	1	2	3	4	8	20
0	1.0240	1.0154	1.0120	1.0095	1.0053	1.0023
2	1.0279	1.0200	1.0128	1.0124	1.0081	1.0033
4	1.0311	1.0189	1.0161	1.0142	1.0098	1.0037
6	1.0372	1.0230	1.0195	1.0144	1.0100	1.0040
8	1.0463	1.0283	1.0226	1.0150	1.0102	1.0045
10	1.0541	1.0295	1.0235	1.0157	1.0116	1.0064
12	1.0682	1.0305	1.0264	1.0200	1.0154	1.0092
14	1.1316	1.0675	1.0457	1.0383	1.0217	1.0110

TABLE IX.

(a) Prussian blue.

Period of dialysis -days.	Dilution.					
	1		1.33		2	
	Cat.speed.	F. V. KCl	Cat.speed.	F. V. KCl	Cat.speed.	F.V. KCl
3	38.70	173.3	40.30	156.7	42.50	138.7
8	40.60	144.0	41.10	134.7	41.10	116.7
13	43.20	108.0	42.20	94.7	40.50	73.3
17	42.50	56.7	40.90	42.7	38.70	22.0
21	41.05	-	40.00	-	37.60	-
26	37.10	-	35.40	-	32.30	-
30	27.50	-	25.80	-	23.05	-

TABLE IX. (Contd.).

(a) Prussian blue (Contd.).

Period of dialysis -days.	Dilution					
	4		5.33		8	
	Cat.speed.	F. V. KCl	Cat.speed.	F. V. KCl	Cat.speed.	F.V. KCl.
3	39.00	112.0	35.75	-	30.10	105.3
8	37.70	86.0	35.00	-	30.10	73.3
13	36.10	37.3	33.80	-	28.60	12.0
17	35.00	4.7	32.50	-	27.00	-
21	33.60	-	31.30	-	25.90	-
26	24.20	-	22.30	-	21.50	-
30	21.00	-	20.60	-	-	-

(b)* Prussian blue.

Period of dialysis -days.	Sp. conductivity X 10^6				
	Dilution				
	1	2	4	8	16
3	31630.0	16020.0	9194.0	4586.0	2285.0
8	8780.0	4552.0	2442.0	1214.0	597.4
13	2156.0	1294.0	677.0	329.3	157.4
17	1116.0	578.2	280.8	138.4	68.1
21	554.4	259.1	144.7	69.8	30.2
26	270.9	119.3	72.8	33.2	14.9

* Sp. conductivity of water used for dilution = 2.50×10^{-6} mho.

TABLE IX. (Contd.)

(c) Prussian blue.

Period of dialysis -days.	Viscosity.			
	Dilution.			
	1	2	4	8
3	1.019	1.011	1.006	1.003
8	1.009	1.005	1.003	1.002
13	1.004	1.002	1.001	1.001
17	1.004	1.002	1.002	1.004
21	1.008	1.006	1.004	1.009
26	1.012	1.009	1.007	1.012

TABLE X.

(a) Arsenious sulphide.

Period of dialysis -days.	Dilution.						
	1			1.33	2		
	Cat. speed.	F. V.		Cat. speed.	Cat. speed.	F. V.	
		KCl	$MgCl_2$			KCl	$MgCl_2$
0	50.65	54.3	0.53	40.75	33.60	63.0	0.67
4	34.15	64.5	0.40	30.30	24.85	84.0	0.53
8	26.10	72.0	0.33	24.05	20.85	94.7	0.37
17	39.25	54.5	0.53	38.30	36.15	80.0	0.74
23	45.70	51.0	0.67	45.80	46.10	67.3	0.80
29	36.00	42.0	0.47	33.30	28.40	55.4	0.57
31	21.40	20.3	0.23	22.65	24.80	27.0	0.30

TABLE X (Contd.).

(a) Arsenious sulphide.(Contd.).

Period of dialysis -days.	Dilution.					
	4			8		
	Cat. speed.	F. V.		Cat. speed.	F. V.	
		KCl	$MgCl_2$		KCl	$MgCl_2$
0	21.70	80.0	0.77	17.40	105.0	0.93
4	17.55	112.3	0.57	14.35	142.0	0.70
8	15.65	132.0	0.40	13.25	175.0	0.40
17	33.30	102.0	0.83	33.45	134.0	1.00
23	48.30	86.0	1.00	54.25	111.0	1.30
29	31.80	65.0	0.63	43.70	78.0	0.74
31	29.00	31.0	0.30	41.20	35.0	0.33

(b)* Arsenious sulphide.

Period of dialysis -days.	Sp. conductivity X 10^5				
	Dilution.				
	1	1.33	2	4	8
0	22.63	17.34	11.55	5.17	2.89
4	18.11	13.61	8.37	3.80	2.60
8	16.70	12.01	7.39	3.45	2.08
17	28.45	21.17	12.02	7.18	4.33
23	21.31	16.58	12.01	6.73	4.10
29	20.96	16.00	11.02	6.18	3.30
31	21.20	15.18	10.58	4.55	3.04

* Sp. conductivity of water used for dilution = 1.97 X 10^{-6} mho.

TABLE XI.

(a) Gold.

Period of dialysis. -days.	Dilution.					
	1		1.2	1.33	2.0	
	Cat. speed.	F. V. NaCl	Cat. speed.	Cat. speed.	Cat. speed.	F. V. NaCl
3	65.75	19.67	47.50	42.00	35.50	21.33
6	92.50	22.00	74.50	47.75	42.50	24.30
10	105.25	23.66	82.50	65.00	60.75	26.66
13	116.00	26.33	95.50	86.00	70.00	28.10
18	128.50	32.00	103.75	97.50	85.50	37.35
21	109.50	24.10	95.75	76.50	67.50	26.00
24	75.00	21.00	67.00	55.50	50.00	22.47
26	53.75	17.33	43.25	39.50	35.00	20.34

(b)* Gold.

Period of dialysis -days.	Sp. conductivity X 10^6				
	Dilution.				
	1	2	4	20	40
0	240.00	171.10	95.00	24.17	14.98
4	163.80	108.10	62.44	22.12	12.77
8	53.86	30.91	19.72	7.33	5.11
10	33.62	20.53	13.88	7.04	4.86
13	24.83	14.08	9.42	6.80	4.71
17	16.61	8.86	7.86	5.97	4.52
21	11.42	6.24	5.63	5.18	4.45
25	5.89	5.24	4.99	4.68	4.21

* Sp. conductivity of water used for dilution = 2.32 X 10^{-6} mho.

TABLE XII.

(a) Vanadium pentoxide.

(Dilute sol).

Period of dialysis -days.	Dilution.								
	1			2			4		
	Cat. speed.	F. V. NaCl.	Viscosity.	Cat. speed.	F. V. NaCl.	Viscosity.	Cat. Speed.	F.V. NaCl.	Viscosity.
0	28.92	10.00	1.401	24.56	12.34	1.293	20.18	-	1.109
2	35.84	9.22	1.386	29.43	10.34	1.244	24.81	-	1.075
4	39.48	9.00	1.350	32.63	9.84	1.189	28.60	-	1.052
6	30.20	8.00	1.675	28.20	9.22	1.226	23.73	-	1.095
8	26.71	6.33	1.810	25.40	8.00	1.479	21.01	-	1.112
12	23.92	5.80	2.078	20.90	-	1.739	18.53	-	1.121

(b) Vanadium pentoxide.

(Concentrated sol).

Period of dialysis -days.	Dilution.					
	1			2		
	Cat. speed.	F. V. NaCl.	Viscosity.	Cat. speed.	F. V. NaCl.	Viscosity.
0	51.76	5.34	3.062	42.15	6.67	2.268
2	60.45	4.67	2.979	54.24	6.00	1.945
4	73.45	4.33	2.897	60.65	5.67	1.739
6	59.76	3.17	3.073	44.97	4.73	1.890
8	46.51	2.33	3.873	35.71	3.33	2.648

TABLE XII (Contd.).

(b) Vanadium pentoxide.

(Concentrated sol).

Period of dialysis. -days.	Dilution.					
	4			8		
	Cat. speed.	F. V. NaCl.	Viscosity.	Cat. speed.	F. V. NaCl.	Viscosity
0	34.68	8.20	1.523	26.93	10.67	1.263
2	40.80	7.20	1.369	30.27	9.00	1.171
4	44.16	6.33	1.287	32.17	8.00	1.123
6	32.40	5.17	1.349	28.23	7.00	1.143
8	29.35	4.20	1.817	26.35	6.10	1.478

(c)* Vanadium pentoxide.

(Dilute sol).

Period of dialysis -days.	Sp. conductivity X 10^6				
	Dilution.				
	1	2	4	6	8.
0	490.6	403.8	358.7	288.1	208.9
2	373.4	254.7	228.1	200.9	188.5
4	365.2	250.9	207.2	188.0	176.8
6	360.3	248.3	200.8	182.0	174.3
8	355.9	236.0	195.4	179.2	171.0
10	329.7	221.8	186.8	174.3	169.3
12	296.0	213.8	184.3	172.6	168.0

* Sp. conductivity of water used for dilution $= 2.05 \times 10^{-6}$ mho.

SECTION III - Changes in sols dialysed for different periods in presence of small increasing amounts of electrolytes.

The initial values of cat.speed in all the tables (b) with the same sol are different because the samples were dialysed for different periods.

TABLE XIII.

(a) Ferric hydroxide.

Sol dialysed for 8 days.		Sol dialysed for 25 days.	
Concentration of HCl.	Cat. speed.	Concentration of HCl.	Cat. speed.
0.000	38.16	0.000	53.42
0.063	43.59	0.013	56.83
0.094	45.72	0.019	59.82
0.125	44.01	0.037	55.34
0.250	39.42	0.125	47.64
0.750	36.11	0.250	46.81
1.250	35.46	2.500	45.72
25.000	33.97	50.000	42.20
150.000	33.12	100.000	34.82
		125.000	32.58

TABLE XIII(Contd.).

(b) Ferric hydroxide.

Electrolyte.	Initial cat. speed.	Initial increase of cat. speed.	Cat. speed at which coagulation begins.	Concentration of electrolyte at which coagulation begins.
HCl	38.16	7.56	33.12	150.000
	53.42	6.40	32.58	125.000
KCl	38.16	5.39	28.42	125.000
	53.42	3.76	26.50	25.000
$MgCl_2$	38.16	6.88	26.50	50.000
	53.42	4.48	25.31	1.250
H_2SO_4	38.16	nil	27.24	0.025
	53.42	nil	28.31	0.050
K_2SO_4	38.16	nil	26.17	0.250
	53.42	nil	27.35	0.250
$MgSO_4$	38.16	nil	28.70	0.050
	53.42	nil	29.06	0.025

(c) Ferric hydroxide.

Concentration of electrolyte.	Sol dialysed for 6 days.		Concentration of electrolyte.	Sol dialysed for 21 days.	
	Cat. speed.	Viscosity.		Cat. speed.	Viscosity.
<u>HCl</u>			<u>HCl</u>		
0.000	37.39	1.035	0.000	40.70	1.053
0.025	38.46	1.034	0.025	45.72	1.047
0.050	39.85	1.024	0.050	49.78	1.052
0.075	36.71	1.037	0.075	54.49	1.055
0.125	32.91	1.042	0.125	53.50	1.056
<u>KCl</u>			<u>KCl</u>		
0.000	39.39	1.035	0.000	40.70	1.053
0.013	38.24	1.030	0.025	44.86	1.040
0.025	38.46	1.020	0.050	47.11	1.036
0.050	39.10	1.024	0.075	50.20	1.043
0.075	35.04	1.031	1.250	47.00	1.048

TABLE XIV.

(a) Thorium hydroxide.

Sol dialysed for 2 days.		Sol dialysed for 5 days.	
Concentration of $ThCl_4$	Cat. speed.	Concentration of $ThCl_4$	Cat. speed.
0.0000	28.38	0.0000	35.20
0.0625	36.73	0.0625	42.88
0.1250	39.34	0.1250	45.53
0.1875	41.23	0.1875	48.62
0.2500	41.49	0.2500	49.89
0.3750	38.33	0.3750	44.01

(b) Thorium hydroxide.

Electrolyte.	Initial cat. speed.	Initial increase of cat. speed.	Cat. speed at which coagulation begins.	Concentration of electrolyte at which coagulation begins.
HCl	33.41	5.21	18.60	125.000
	24.78	6.48	16.95	0.375
KCl	33.41	4.57	18.95	125.000
	24.78	5.67	16.79	0.375
$MgCl_2$	33.41	2.33	19.04	25.000
	24.78	4.49	16.22	0.075
H_2SO_4	33.41	nil	20.52	0.375
	24.78	nil	15.86	0.125
K_2SO_4	33.41	nil	21.19	0.375
	24.78	nil	16.39	0.125
$MgSO_4$	33.41	nil	21.55	0.375
	24.78	nil	16.88	0.125

TABLE XIV. (Contd.).

(c) Thorium hydroxide.

Concentration of electrolyte.	Sol dialysed for 4 days.		Concentration of electrolyte.	Sol dialysed for 14 days.	
	Cat. speed.	Viscosity.		Cat. speed.	Viscosity.
HCl			HCl		
0.000	33.41	1.0254	0.000	24.78	1.0467
0.063	36.73	1.0255	0.013	38.07	1.0464
0.125	38.62	1.0259	0.019	29.81	1.0460
0.188	32.51	1.0261	0.025	31.16	1.0452
0.250	29.10	1.0263	0.050	29.59	1.0442
2.500	22.00	1.0275	0.125	22.90	1.0464
			0.250	17.96	1.0483
H_2SO_4			H_2SO_4		
0.000	33.41	1.0254	0.000	24.78	1.0467
0.025	30.49	1.0254	0.005	23.80	1.0465
0.050	28.96	1.0256	0.013	22.19	1.0461
0.100	26.49	1.0260	0.025	19.09	1.0466
0.250	21.51	1.0277	0.100	16.48	1.0475
			0.150	14.41	1.0490

TABLE XV.

(a) Prussian blue.

(Sol dialysed for 25 days.)

Concentration of oxalic acid.	Cat. speed.
0.000	26.95
0.013	35.00
0.037	37.50
0.125	39.40
0.250	40.80
1.250	35.70
3.750	31.90
12.500	30.70

TABLE XV.

(b) Prussian blue.

Electrolyte.	Initial cat. speed.	Initial increase of cat. speed.	Cat. speed at which coagulation begins.	Concentration of electrolyte at which coagulation begins.
HCl	38.70	3.60	27.50	0.125
KCl	37.30	7.30	26.20	2.500
$MgCl_2$	37.05 36.35	nil nil	27.85 26.75	0.075 0.750
$MgSO_4$	27.90 36.90	nil nil	22.20 24.50	0.125 1.250

TABLE XVI.

(a) Arsenious sulphide.

Sol dialysed for 5 days.		Sol dialysed for 25 days.		Sol dialysed for 31 days.	
Concentration of As_2O_3.	Cat. speed.	Concentration of As_2O_3.	Cat. speed.	Concentration of As_2O_3.	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	0.464	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		

TABLE XVI. (Contd.).

(b) Arsenious sulphide.

Electrolyte.	Initial cat. speed.	Initial increase of cat. speed.	Cat. speed at which coagulation begins.	Concentration of electrolyte at which coagulation begins.
HCl	28.60	33.80	15.90	25.00
	65.50	24.00	26.90	12.50
	46.80	nil	28.50	17.50
KCl	29.20	22.40	25.40	50.00
	63.10	23.75	25.85	37.50
	45.35	nil.	29.50	25.00
$MgCl_2$	26.25	nil	12.80	0.25
	63.70	nil	14.15	0.37
	45.35	nil	18.20	0.25
K_2SO_4	17.30	36.20	27.65	25.00
	62.40	14.35	25.00	18.75
$MgSO_4$	15.95	nil	10.40	0.37

TABLE XVII.

(a) Gold.

Sol dialysed for 2 days.		Sol dialysed for 25 days.	
Concentration of KOH.	Cat. speed.	Concentration of KOH.	Cat. speed.
0.00	60.20	0.00	90.75
6.66	74.40	1.32	122.50
11.10	122.20	1.96	131.50
13.32	97.00	3.96	117.25
15.54	65.40	6.66	105.25
37.75	31.20	16.50	57.00
		19.88	32.00

TABLE XVII. (Contd.)

(b) Gold.

Electrolyte.	Initial Cat. speed.	Initial increase of cat. speed.	Cat. speed at which coagulation begins.	Concentration of electrolyte at which coagulation begins.
KOH	60.20	62.00	31.20	37.75
	90.75	40.75	32.00	19.88
KCl	47.38	43.39	40.48	22.20
	82.57	nil.	31.74	3.33
K_2SO_4	47.38	46.92	38.64	33.00
	82.57	nil	33.58	4.11
$MgCl_2$	47.38	nil	36.80	2.46
	82.57	nil	29.21	0.41
$MgSO_4$	47.38	nil	35.42	3.89
	82.57	nil	31.28	0.53

TABLE XVIII.

(a_1) Vanadium pentoxide.

Sol dialysed for 2 days.		Sol dialysed for 10 days.	
Concentration of NH_4VO_3.	Cat. speed.	Concentration of NH_4VO_3.	Cat. speed.
0.000	28.15	0.000	31.50
0.222	33.60	0.067	36.50
0.888	37.80	0.132	41.20
1.980	42.80	0.222	44.80
2.220	35.00	0.444	36.20
2.446	24.70	1.111	32.20
2.680	22.10	1.544	25.00

TABLE XVIII. (Contd.).

(a_2) Vanadium pentoxide.

Electrolyte.	Sol dialysed for 2 days.		Sol dialysed for 10 days.	
	Concentration.	Cat. speed.	Concentration.	Cat. speed.
$BaCl_2$	0.0000	27.10	0.0000	29.50
	0.0055	23.80	0.0055	25.60
	0.0083	27.30	0.0111	24.90
	0.0247	37.50	0.0165	39.20
	0.0495	28.90	0.0222	29.20
$MgCl_2$	0.0000	27.10	0.0000	29.50
	0.0272	25.30	0.0055	27.60
	0.0333	33.80	0.0111	27.60
	0.0444	37.20	0.0222	35.70
	0.0555	29.50	0.0333	30.10
	0.0666	28.50	0.0444	26.10
$MgSO_4$	0.0000	27.10	0.0000	24.50
	0.0222	19.20	0.0088	25.00
	0.0666	28.20	0.0132	28.30
	0.0888	36.80	0.0222	38.30
	0.1110	28.40	0.0298	27.00
			0.0333	26.30

(b) Vanadium pentoxide.

Electrolyte.	Initial Cat. speed.	Initial increase in Cat. speed.	Cat. speed at which coagulation begins.	Concentration of electrolyte at which coagulation begins.
HCl	27.10	12.70	27.70	0.364
	29.50	9.80	30.10	0.200
KCl.	27.10	13.00	28.00	1.540
	29.50	14.70	28.10	1.332
NH_4Cl	28.50	15.00	21.60	1.176
	31.40	13.70	23.70	0.888
NH_4VO_3	28.50	14.30	22.10	2.680
	31.50	13.30	25.00	1.544
H_2SO_4	27.10	9.30	28.50	0.555
	29.50	8.60	28.10	0.250
K_2SO_4	27.10	11.30	29.10	3.109
	29.50	7.80	26.40	1.886

SECTION - IV - Changes in sols dialysed for different periods on ageing.

TABLE XIX.

Prussian blue.

(a) Sol dialysed for 6 days.			(b) Sol dialysed for 25 days.		
Age in days.	Cat. speed.	Sp.conductivity X10^6	Age in days.	Cat. speed.	Sp.conductivity X 10^6
0	39.20	15110.0	0	28.60	65.28
30	37.00	15110.0	20	38.30	63.61
40	36.90	15100.0	38	31.55	41.88
143	36.90	14780.0	104	27.90	34.23
216	36.60	14170.0	173	27.40	33.37
262	36.00	13820.0	218	27.20	32.70

TABLE XX.

Arsenious sulphide.

Age in days.	Total As.	Free As_2O_3 in terms of As.	Total S.	Cat. speed	Sp.conductivity X 10^6	F. V.	
						KCl	$MgCl_2$
0	1.306	0.00263	1.426	37.05	145.0	56.7	0.84
15	1.287	0.03300	1.412	34.95	160.3	67.3	0.76
30	1.191	0.04175	1.379	29.35	196.1	74.0	0.63
45	1.110	0.05228	1.341	20.50	236.2	62.0	0.56
60	1.093	0.05689	1.282	18.15	191.9	55.3	0.51
90	1.026	-	1.148	16.30	114.8	53.3	0.49

TABLE XXI.

Gold.

(a)

Sol dialysed for 2 days.			
Age in days.	Cat. speed.	Sp.conductivity $\times 10^6$	F. V. $MgCl_2$
0	105.80	363.8	5.35
15	101.20	327.8	4.82
27	96.60	321.8	4.29
42	94.30	302.9	3.93
58	92.23	298.1	3.39

(b)

Sol dialysed for 22 days.			
Age in days.	Cat. speed.	Sp.conductivity $\times 10^6$	F. V. $MgCl_2$
0	49.97	193.0	3.57
13	46.00	156.0	2.86
23	43.70	156.0	2.50
33	41.86	147.0	1.96
40	41.40	144.8	1.57

TABLE XXII.

Vanadium pentoxide.

(a)

Sol dialysed for 2 days.			
Age in days.	Cat. speed.	F. V. $MgCl_2$	Sp.conductivity $\times 10^6$
0	38.60	0.575	167.7
7	37.30	0.500	155.4
14	36.00	0.400	142.0
21	35.10	0.300	133.2
28	33.80	0.260	124.5
39	33.00	0.150	101.3

(b)

Sol dialysed for 15 days.			
Age in days.	Cat. speed.	F. V. NaCl	Sp.conductivity $\times 10^6$
0	26.00	4.40	89.5
6	22.00	3.13	79.5
12	20.90	2.50	75.6
18	16.40	1.50	70.5
27	12.80	1.13	67.2

SECTION - V - Changes in sols dialysed for different periods on exposure to sun light (also artificial light in the case of arsenious sulphide).

TABLE XXIII.

(a) Prussian blue.

Exposure in hours.	Sol dialysed for 10 days.		Sol dialysed for 21 days.	
	Cat. speed.	Sp.conductivity $X10^{6}$	Cat. speed.	Sp.conductivity $X\ 10^{6}$
0	44.30	1845.0	42.70	154.50
1	43.90	1457.0	37.80	27.18
2	-	-	36.20	31.37
3	37.90	1388.0	-	-
5	-	-	34.10	33.04
10	-	-	33.60	41.27
29	-	-	27.60	127.10

(b) Prussian blue.

Period of dialysis -days.	Time after which sol coagulates on exposure.
0	1 to 1.5 minutes.
1	2.5 to 3.0 minutes.
7	18 minutes.
10	3 to 4 hours.
21	> 29 hours.

TABLE XXIV.

(a) Arsenious sulphide.

(Undialysed sol exposed to artificial light)

Period of exposure in minutes.	Total As.	Free As_2O_3 in terms of As.	Total S.	Cat. speed	Sp. conductivity X 10^5	F. KCl.	V. $MgCl_2$
0	1.306	0.0028	1.482	37.05	14.50	56.70	0.85
50	1.306	0.0214	1.473	31.05	15.38	58.67	0.80
100	1.306	0.0337	1.462	27.20	16.47	61.67	0.77
150	1.296	0.0416	1.456	23.60	18.22	57.33	0.73
200	1.290	0.0484	1.448	21.85	20.77	53.33	0.70
300	1.286	0.0536	1.431	19.50	25.33	39.33	0.63
500	1.284	0.0623	1.405	17.00	34.20	28.67	0.43
900	1.283	-	1.371	15.38	40.88.	19.33	0.03

(b) Arsenious sulphide.

(Undialysed sol exposed to sunlight).

Exposure in minutes.	Total As.	Free As_2O_3 in terms of As.	Total S.	Cat. speed.	Sp. conductivity X 10^5
0	1.529	0.0000	1.467	50.10	25.92
30	1.519	0.0024	1.458	51.25	28.15
70	1.514	0.0362	1.450	48.35	28.78
150	1.500	0.0564	1.425	43.80	35.98
300	1.452	0.0825	1.338	34.05	75.48
450	1.422	0.1075	1.326	32.05	112.80
1200	1.403	0.1781	1.312	29.85	192.00

TABLE XXIV. (Contd.).

(c) Arsenious sulphide.

(Sol dialysed for 35 days exposed to sunlight).

Exposure in minutes.	Total As.	Free As_2O_3 in terms of As.	Total S.	Cat. speed.	Sp. conductivity $X\ 10^5$
0	1.413	0.0437	1.390	36.20	42.59
60	1.374	0.1812	1.308	30.05	65.31
300	1.219	0.5563	1.120	17.40	143.40
600	1.132	0.4625	1.049	14.25	182.50
1200	1.074	0.6437	0.967	11.45	-

TABLE XXV.

Gold.

Exposure in hours	Sol dialysed for 2 days.			Sol dialysed for 22 days.		
	Cat. speed.	Sp. conductivity $X10^6$	F. V. $MgCl_2$	Cat. speed.	Sp. conductivity $X10^5$.	F. V. $MgCl_2$
0	104.88	363.1	5.35	49.91	193.0	3.57
10	90.03	355.9	4.82	42.32	184.3	3.22
20	85.17	348.8	3.57	39.36	176.9	2.43
35	70.38	343.3	3.29	36.34	167.0	1.87
60	53.59	293.1	3.00	33.58	134.0	1.43

TABLE XXVI.

Vanadium pentoxide.

	Sol dialysed for 2 days.			Sol dialysed for 15 days.		
Exposure in hours	Cat speed.	F. V. $MgCl_2$.	Sp.conductivity. X 10^6	Cat. speed.	F. V. $MgCl_2$.	Sp.conductivity X 10^6.
0	49.00	0.65	378.3	30.80	0.35	247.3
5	40.70	0.60	274.4	34.70	0.31	197.3
10	38.20	0.57	256.8	29.20	0.27	123.3
15	30.20	0.51	219.5	25.20	0.24	114.2
25	22.30	0.35	122.5	18.00	0.20	63.5

DISCUSSION.

Theories about origin of charge on colloidal particles.

Before proceeding to discuss the results given here it will not be out of place to give a brief summary of the various theories about the origin of charge on colloidal particles.

The question of the origin of charge on the colloid particles assumed significance as soon as the importance of the electrical charge for the stability of colloids was recognised. In the beginning as long as the concept of the electric double layer introduced by Helmholtz[13] for explaining capillary electrical phenomena, was capable of explaining many of the properties of the colloid particles, no serious attention was, however, paid to the question of the origin of charge. Helmholtz in his theory had assumed that the dielectric constant in the double layer was unity. Smoluchowski[14] however, showed that the dielectric constant in the double layer is not unity and introduced correction in the theory of Helmholtz for the same. The Helmholtz-Smoluchowski equation for the cataphoretic speed (U) of a spherical particle has the following form:-

$$U = \frac{\zeta D}{4\pi\eta} X \qquad (1)$$

where ζ = Potential of double layer,
D = Dielectric constant,
η = Viscosity,
and X = Applied potential gradient.

According to the above equation the cat. speed is independent of the shape and size of the particle. Debye and Hückel[15] have shown that for a spherical particle factor 4 in the above equation should be replaced by 6; according to them cat.speed would depend upon the shape of the particles. Regarding the shape of the particles one may as a first approximation assume that in any particular sol it may be the same, although the shape of the particles of different sols is not the same as cases of sols having spherical and non-spherical particles are known. Regarding the size of the particles it is well known that in the same sol particles of different aggregation exist; further even if all the particles in the beginning are of the same size, particles of different aggregation are produced as soon as an electrolyte is added to a sol. Mukherjee, Chaudhury and Bhabak[16] have observed an increase in cat.speed with time in presence of an electrolyte, at a concentration which produces an appreciable rate of coagulation, due to aggregation of the colloidal particles. The increase in the cat.speed noticed by them is wholly due to aggregation and not due to preferential adsorption of similarly charged ions of the added electrolyte in view of the fact that the concentration of the electrolyte is not changed during coagulation and that even with salts having polyvalent coagulating ions of very low concentrations where the concentrations of the similarly charged ions

ions are also very small, the cat.speed sometimes increases to a much greater extent than it does with uni-univalent salts.

Gouy[17] introduced the idea of the existence of a diffused double layer; Smoluchowski[14] also reached the same view a little later. According to Gouy there are the same species of positive and negative ions in the liquid contiguous to the surface of the colloidal particles as within the bulk of the liquid; but in the former case ions of one sign are in excess over that of the other. This picture thus dealt with the origin of the double layer which was not clear in the Helmholtz theory, but Gouy also does not deal with the origin of charge on the particles of a colloid or with the interchange of ions. The gradient of distribution of ions is determined by the gradient of the potential inside the double layer, the magnitude of the electric charges on the ions and the concentration of ions in the solution. In this theory changes in concentration of ions in the solution affect the thickness of the double layer i.e. its capacity. Stern[18] modified Gouy's theory in the light of experimental results since published, but he also stressed the importance of the variations of the capacity of the double layer.

The theory postulated by Mukherjee[19] gives a definite picture of the origin of the charge, the distribution of ions in double layer and of their interchanges

interchanges with ions in solution. According to this theory the origin of charge is the result of the presence on the surface of the particles of a colloid of a firmly adhering layer of ions which are osmotically inactive; this layer constitutes the primarily adsorbed layer and is built in the crystal lattice of the surface. The ions of the primarily adsorbed layer are considered to be adsorbed by the atoms in the surface as a result of chemical affinity. Thus the role played by constituent ions of the crystal lattice is accounted for. (The theory regarding the double layer at the boundary of crystalline particles was also worked out independently by Fajans and Beckenrath[20]). The adsorption of one kind of ions on the surface will impart a charge to the surface, in virtue of which ions of opposite sign will be drawn near the surface. In the liquid there remains an equivalent amount of ions of opposite sign. The electrical energy will be a minimum when these ions are held near the surface so that the distance between the oppositely charged ions has the minimum value possible under the conditions, and they will be held opposite to the ions chemically adsorbed. An ion so held will not be free to move if its kinetic energy is less than 'W' the energy required to separate the ion from the oppositely charged surface. The number of such bound ions i.e. the secondarily or electrically adsorbed ions determines

determines the diminution in the charge of the surface due to primarily adsorbed ions. When the concentration of ions of opposite charge in the intermicellary liquid is small, the number of ions held to the surface by electrical attraction will be small. If the chemically adsorbed ions have a valency equal to N_1 and if N_2 is the valency of oppositely charged ions in the liquid in contact with the surface, then

$$W = \frac{N_1 N_2 E^2}{D x} \quad .. \quad ... \quad (2)$$

where E = Electronic charge,

x = Distance between the centres of the ions at the position of minimum distance,

and D = Di-electric constant of water.

Further according to Mukherjee, depending on the concentration of the oppositely charged ions in the liquid near the surface, at any instant a certain number of the chemically adsorbed ions are covered by ions of opposite charge. The total amount of ions of opposite sign both bound and free is as mentioned above equivalent to the amount of ions chemically adsorbed. These free ions, which are osmotically active, form the second sheet of the double layer. As a result of their thermal motion the mean distance between the two layers will be greater than 'x'. The uncovered primarily adsorbed ions, which are responsible for the charge on the particles, exist on the surface of the particle as point charges widely separated from each other compared with molecular dimensions.

Mukherjee's theory gives a rational explanation of the fact that a reversal of the charge of a surface can be brought out only by polyvalent ions of opposite charge and is in agreement with the valency rule, the influence of the mobility of the oppositely charged ion and with the influence of concentration on the charge of the surface. Further it follows from this theory that variations in U_o (the cat.speed per unit potential gradient) would indicate directly variations in the surface density of the charges according to the equation

$$U_o = \frac{\rho}{4\pi\eta c} \quad \ldots \quad \ldots (3)$$

Where ρ = The net effective density of the charges of the firmly adhering primarily and secondarily adsorbed ions,

c = The capacity the double layer would have per unit area if the distribution of ions along the normal to the interface remained the same as it is for the double layer under consideration but the medium had a di-electric constant (D) equal to unity, and the other symbols have the same meaning as before; the capacity can be taken constant as a first approximation in most cases.

Mukherjee's theory can explain satisfactorily most of the observed facts.

Lange and Berger[21] assume that the formation of double layer is due to a difference in the thermodynamic potential of an ion in the lattice and in the solution. Recently Chaudhury and Sen Gupta[22] have stated that in order to explain the nature of charge of precipitates formed under different conditions it is necessary to elaborate Mukherjee's theory in the sense that

that in addition to residual chemical affinity of the surface, adsorption of ions also depends on their thermodynamic potentials as assumed by Lange and their crystalline or jelly-like structure.

The above paragraphs give a summary of the development of the physical view about the origin of charge on the colloidal particles. It is now proposed to give an outline of the chemical view about the same. The colloidal particle with its electrical double layer is often considered to be identical in its behaviour and properties with an electrolytic ion with its ion atmosphere, the existence of which has been postulated by the famous Debye-Hückel theory of strong electrolytes[23]. This view was taken as it was found that in many cases the surface of the particles showed in no way the chemical reactions of an elementary ion which gives rise to the charge but rather that of a definite compound of it. The composite colloid consists of a neutral part, which is also a larger part and practically non-dissociated and of ionogenic complex which is attached to it and the dissociation of which gives rise to the charge on the particle. The neutral part can have a number of relationships to the ionogenic complex and can influence its properties in a number of ways. Further several kinds of neutral parts can exist together. The ionogenic complex plays a very important part according to the chemical view. The inconsistancies to which

which these ideas of chemical school lead have been discussed by Mukherjee[24]. Rabinovitch and Kargin[25] have also discussed the defects in the chemical view point about the origin of charge on the colloid particles. From a direct examination of a number of sols by X-Ray diffraction methods Milligan and Weiser[26] have concluded that the common inorganic hydrosols consist in general of particles of simple oxides or hydrates, elements or salts and not of complexes as postulated by some investigators. If one takes into consideration all the properties of the lyophobic colloids, then it is clear that the chemical view point about the origin of charge can not be applied to them although it can be successfully applied in the case of proteins, soaps, starches etc. The changes in the charge on the particles of the lyophobic sols can best be understood from the physical point of view as will be seen from the following discussion of the results given before.

SECTION I - Changes during dialysis.

(a) Charge.

It would appear that in all the cases (Tables I(a), II, III(a), V(a) and VI(a) and (b) also Figs.1 to 3 and 5 and 6(a) and (b)) except As_2S_3 sol, the charge or the cat.speed with the progress of dialysis first increases, reaches a maximum and then decreases. In the case of As_2S_3 sol (Table IV(a) also Fig. 4) the cat.speed first decreases and reaches a minimum, then increases and

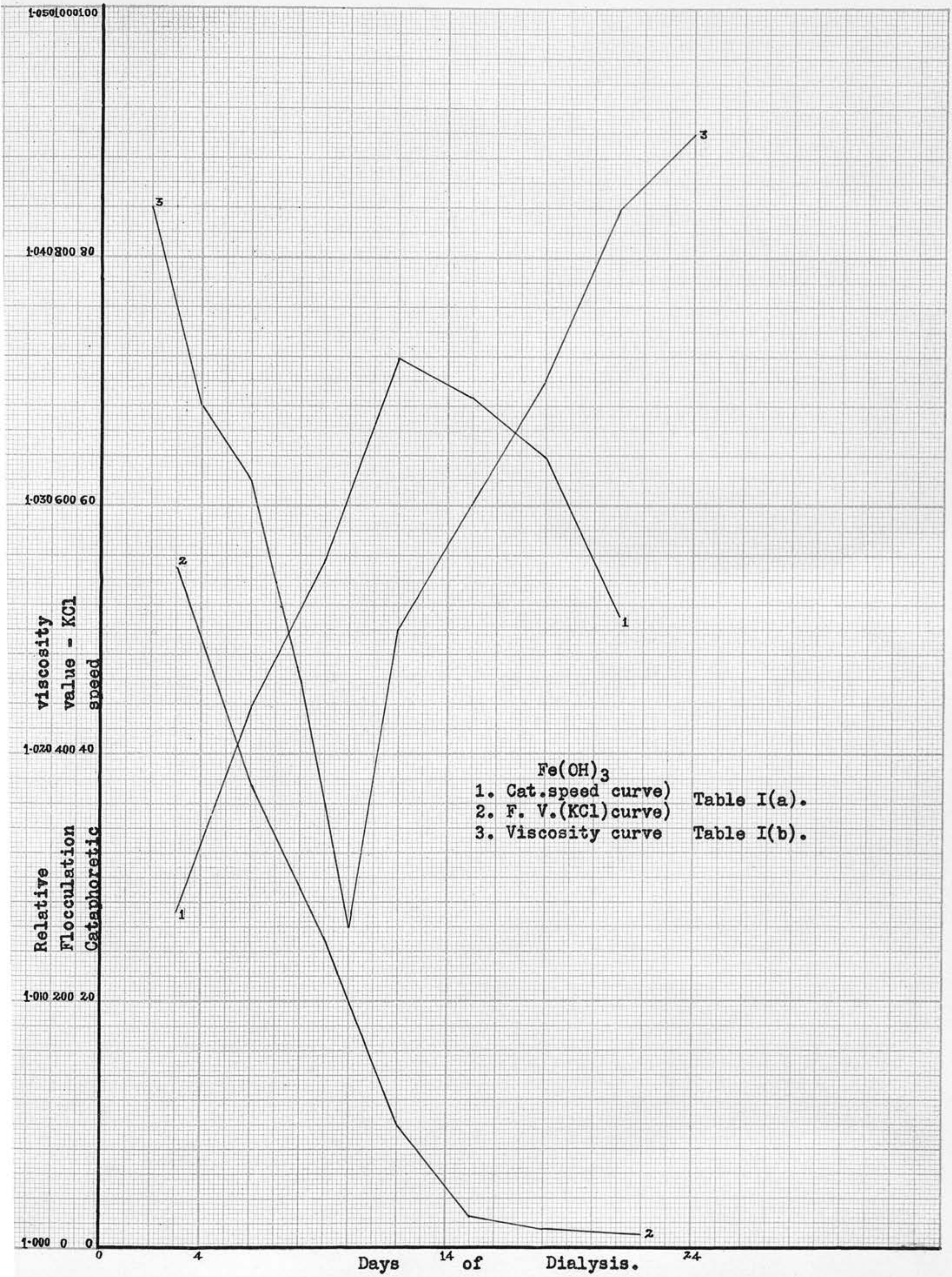

1·050 1000 100
1·040 800 80
1·030 600 60
1·020 400 40
1·010 200 20
1·000 0 0
Relative viscosity
Flocculation value - KCl
Cataphoretic speed
0
4
14
24
Days of Dialysis.
1
2
3
Fe(OH)$_3$
1. Cat.speed curve) Table I(a).
2. F. V.(KCl) curve)
3. Viscosity curve Table I(b).

FIG-1

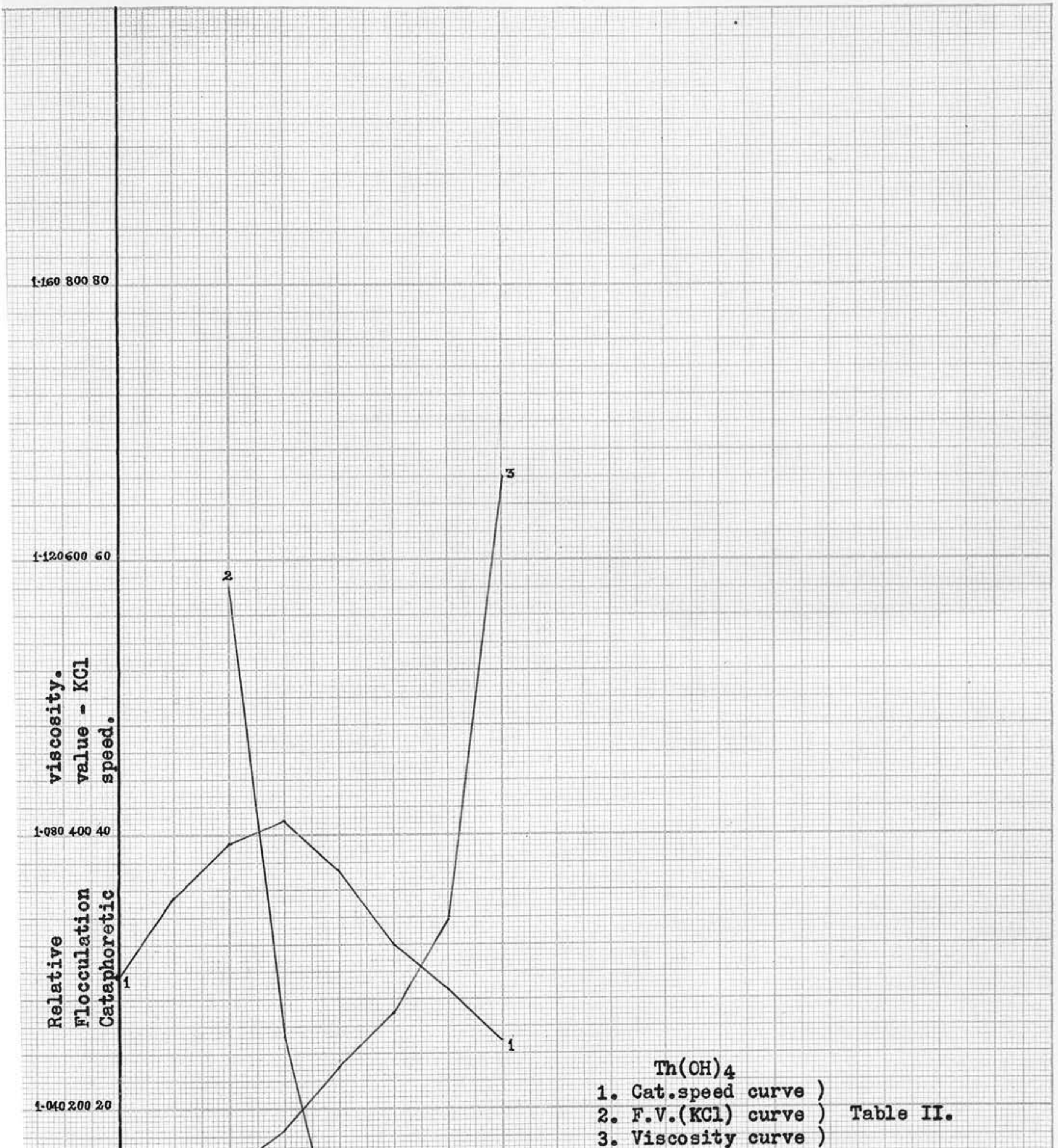

1·160 800 80
1·120 600 60
1·080 400 40
1·040 200 20
1·000 0 0
Relative viscosity.
Flocculation value - KCl
Cataphoretic speed.
0
4
14
24
Days of Dialysis.
1
1
2
2
3
3
Th(OH)4
1. Cat.speed curve)
2. F.V.(KCl) curve) Table II.
3. Viscosity curve)

FIG-2

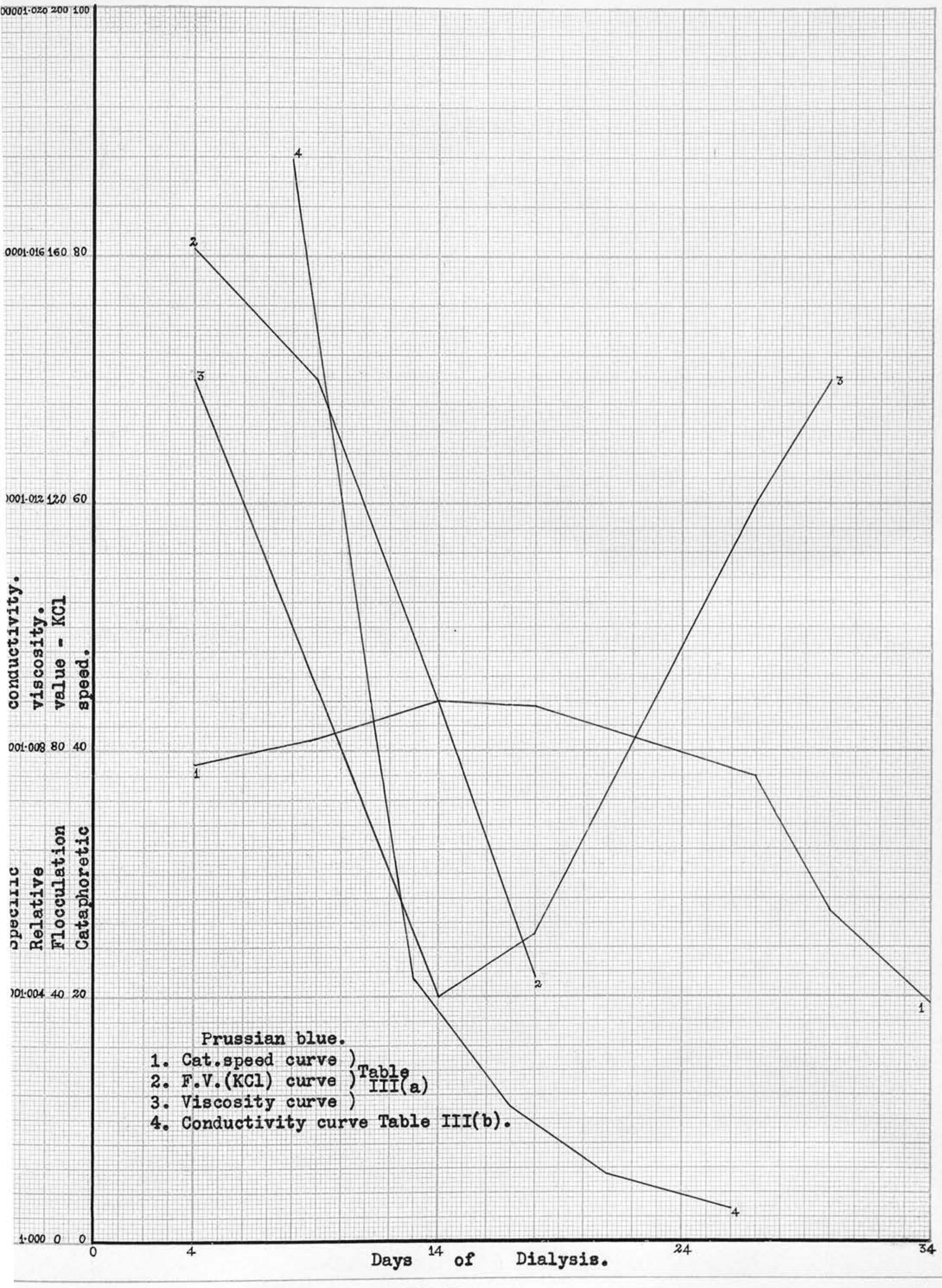

00001·020 200 100
0001·016 160 80
)001·012 120 60
001·008 80 40
)01·004 40 20
1·000 0 0
Specific conductivity.
Relative viscosity.
Flocculation value - KCl
Cataphoretic speed.
0
4
14
24
34
Days of Dialysis.
1
2
3
4
Prussian blue.
1. Cat.speed curve) Table III(a)
2. F.V.(KCl) curve)
3. Viscosity curve)
4. Conductivity curve Table III(b).

FIG-3

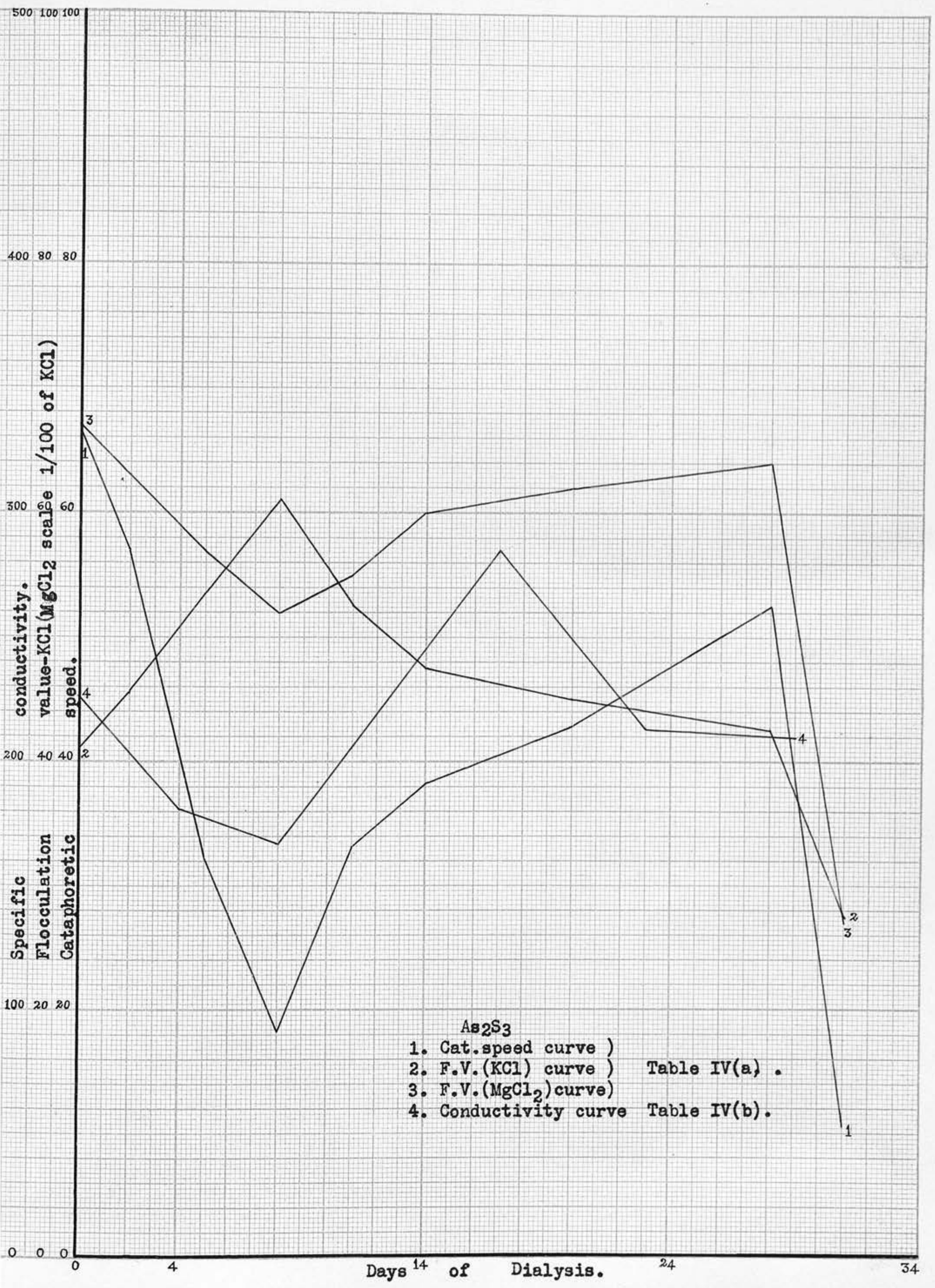

500 100 100
400 80 80
300 60 60
200 40 40
100 20 20
0 0 0
Specific conductivity.
Flocculation value-KCl(MgCl2 scale 1/100 of KCl)
Cataphoretic speed.
0
4
14
24
34
Days of Dialysis.
1
2
3
4
As2S3
1. Cat.speed curve)
2. F.V.(KCl) curve) Table IV(a).
3. F.V.(MgCl2)curve)
4. Conductivity curve Table IV(b).

FIG-4

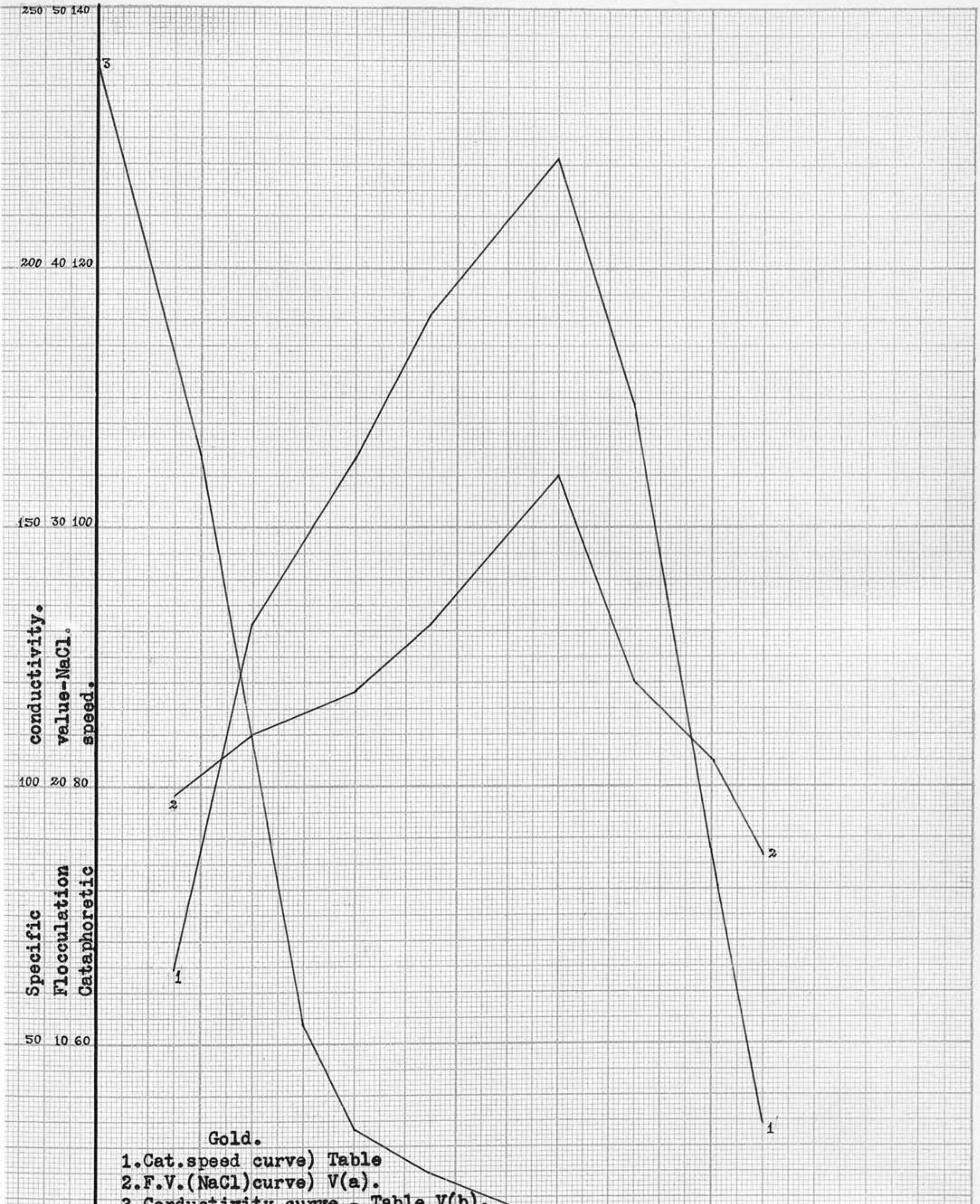

250 50 140
200 40 120
150 30 100
100 20 80
50 10 60
0 0 40
Specific conductivity.
Flocculation value-NaCl.
Cataphoretic speed.
3
2
1
0
4
14
24
34
Days of Dialysis.
Gold.
1.Cat.speed curve) Table
2.F.V.(NaCl)curve) V(a).
3.Conductivity curve - Table V(b).

FIG-5

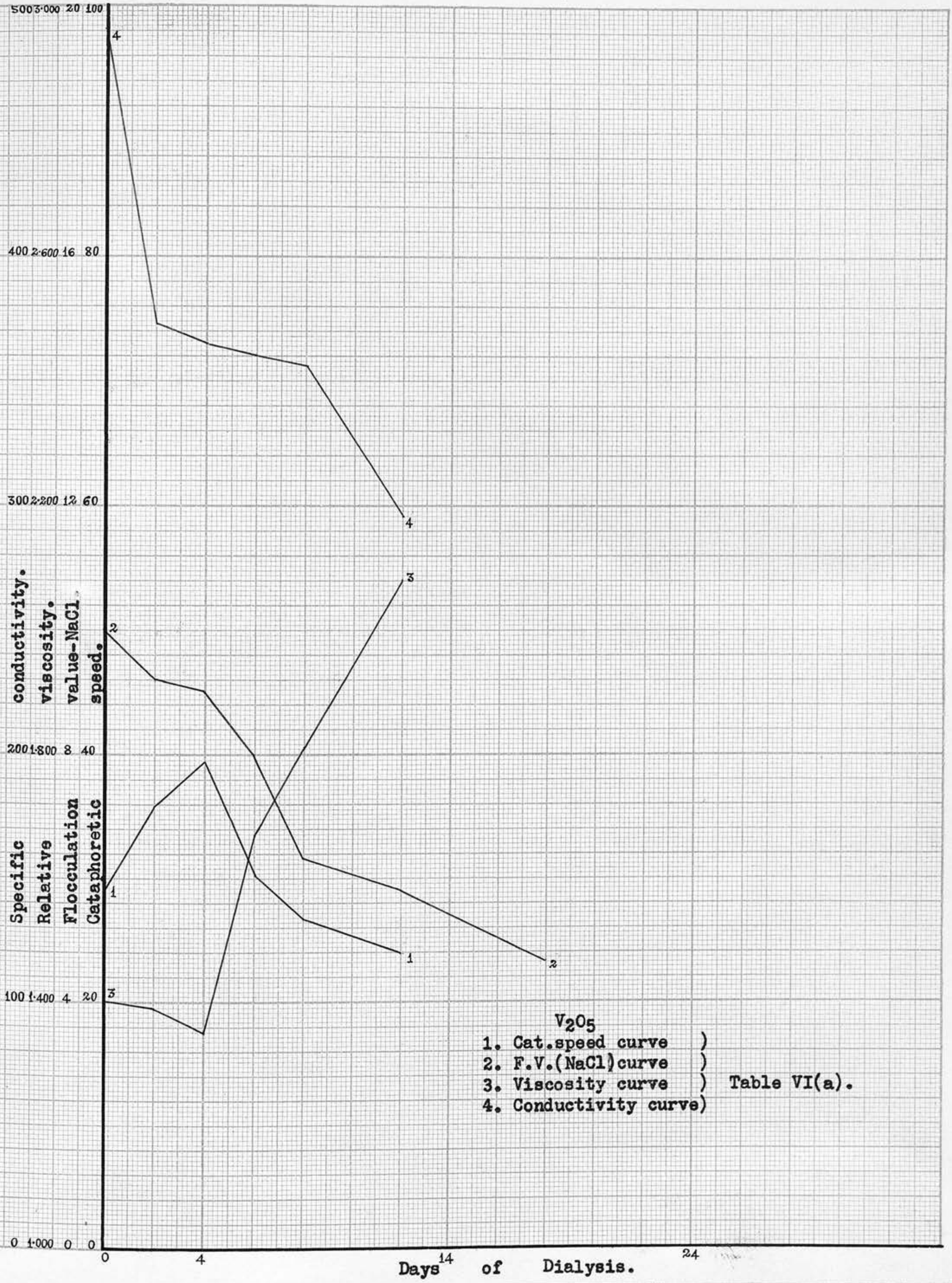

500 3·000 20 100
400 2·600 16 80
300 2·200 12 60
200 1·800 8 40
100 1·400 4 20
0 1·000 0 0
Specific conductivity.
Relative viscosity.
Flocculation value-NaCl
Cataphoretic speed.
0
4
14
24
Days of Dialysis.
1
2
3
4
V_2O_5
1. Cat.speed curve)
2. F.V.(NaCl)curve)
3. Viscosity curve) Table VI(a).
4. Conductivity curve)

FIG-6(a)

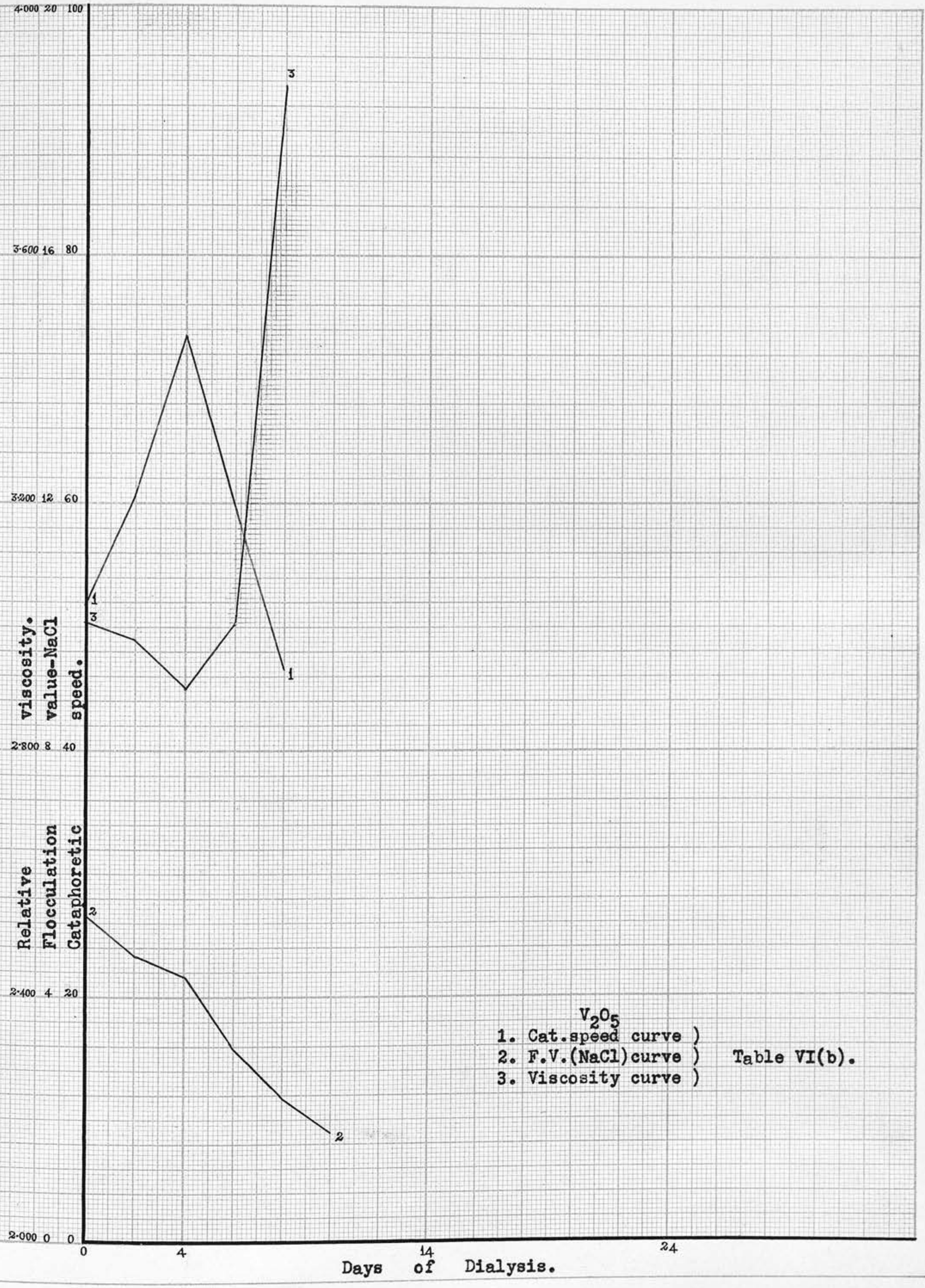

4·000 20 100
3·600 16 80
3·200 12 60
2·800 8 40
2·400 4 20
2·000 0 0
Relative viscosity.
Flocculation value-NaCl
Cataphoretic speed.
0
4
14
24
Days of Dialysis.
1
2
3
V_2O_5
1. Cat.speed curve)
2. F.V.(NaCl)curve) Table VI(b).
3. Viscosity curve)

FIG-6(b)

and reaches a maximum and again decreases thereafter.

Let us now see how we can account for the above changes in charge during dialysis. With the progress of dialysis the amount of the peptising electrolyte continuously decreases as the same passes out in the dialysate. The process of dialysis can thus be considered roughly as a reverse of the process of adding small increasing amounts of the peptising electrolytes to the colloid in so far as the effect of the peptising electrolyte is concerned. The following Table indicates the peptising or the primarily adsorbed ions in each case.

Sol.	Peptising ions.
Ferric hydroxide	$\mathrm{Fe^{\cdot\cdot\cdot}}$ and also $\mathrm{H^{\cdot}}$.
Thorium hydroxide	$\mathrm{Th^{\cdot\cdot\cdot\cdot}}$ and also $\mathrm{H^{\cdot}}$.
Prussian blue	$\mathrm{Fe(CN)_6{''''}}$ and also Oxalate $\begin{pmatrix}\mathrm{COO}\\ \mathrm{COO}\end{pmatrix}''$.
Arsenious sulphide	$\mathrm{HS'}$ and $\mathrm{S''}$.
Gold	$\mathrm{OH'}$
Vanadium pentoxide	Vanadate $\mathrm{(VO_3)'}$.

It will appear from the results given in Section III (See Figs. 7, 8 and 9 for illustration) that in all the cases wherever peptising electrolytes have been tried, on adding small increasing amounts of the same to the colloid the cat. speed first increases, reaches a maximum and then decreases. The shape of the cat.speed-dialysis curve (Figs. 1 to 3 and 5 & 6) and cat.speed -

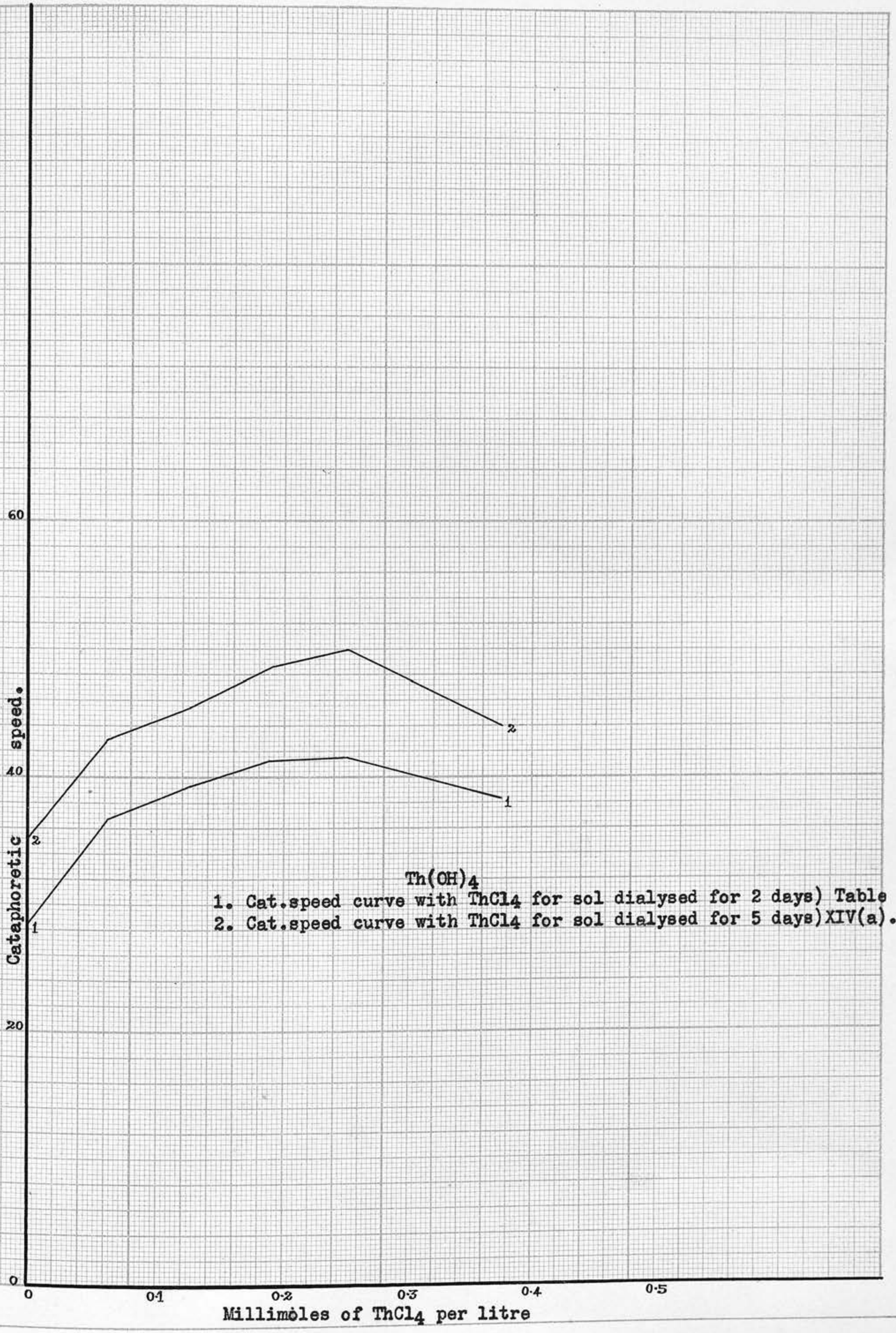
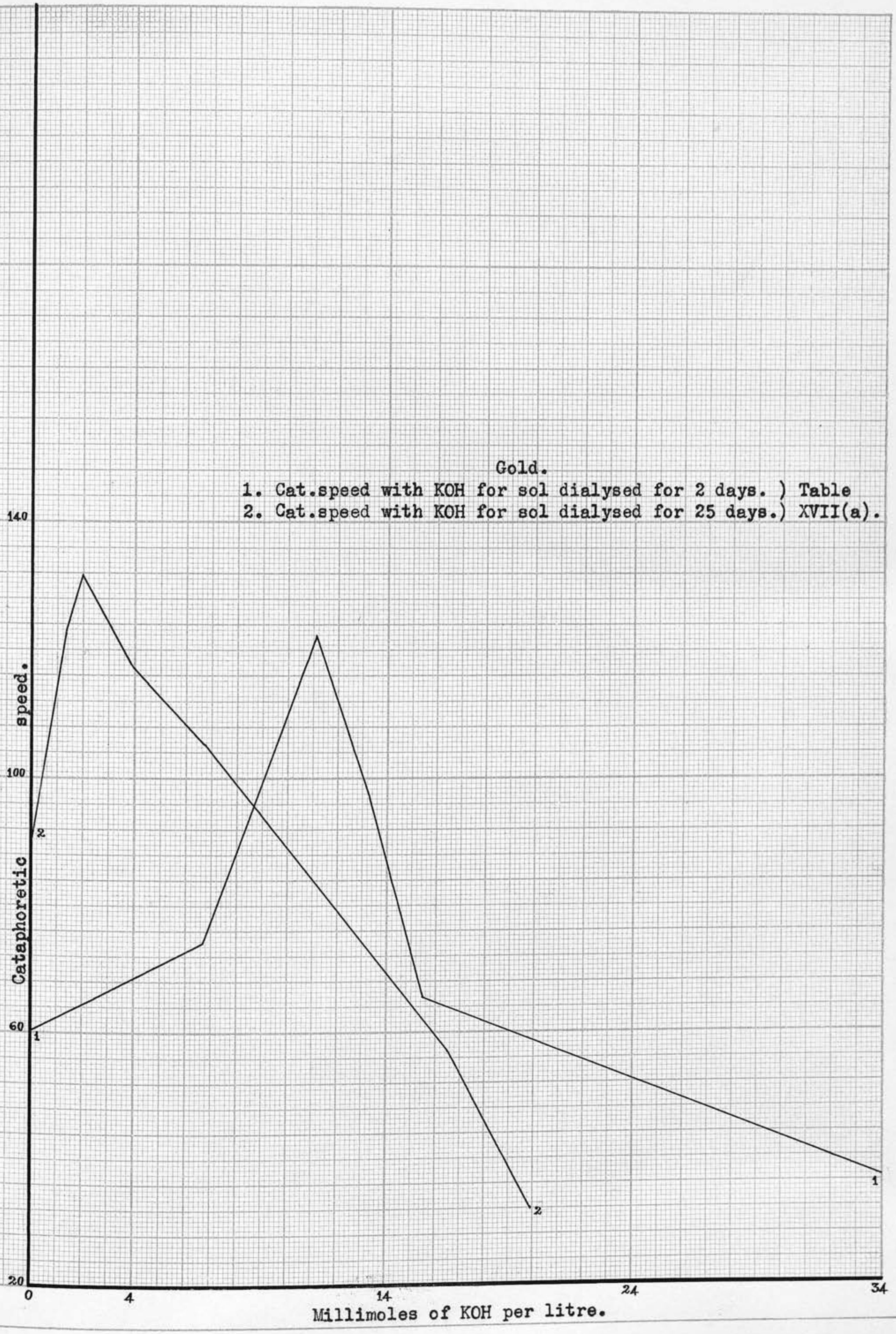
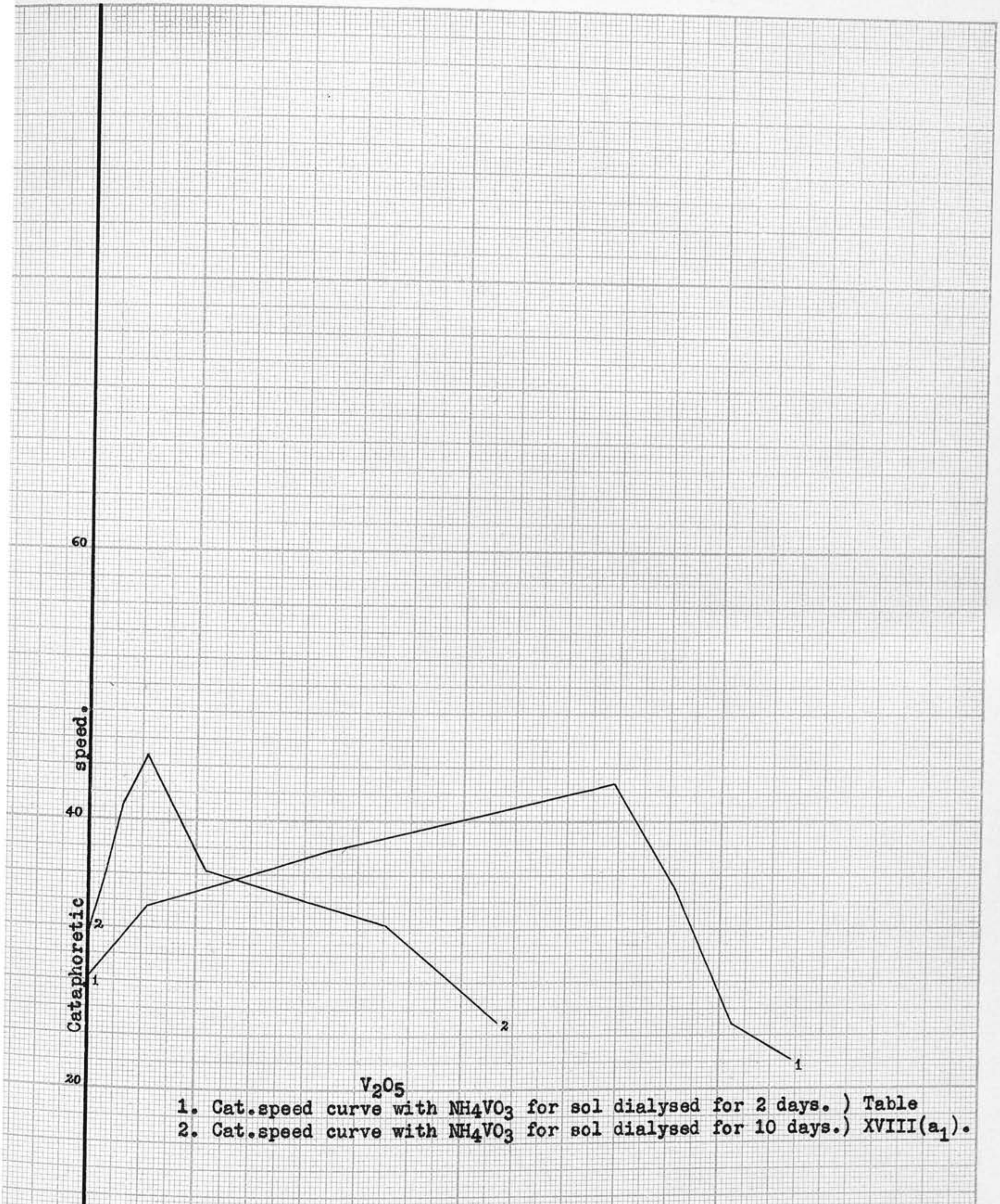

60
40
20
0
Cataphoretic speed.
0
0·1
0·2
0·3
0·4
0·5
Millimoles of ThCl4 per litre
1
2
1
2
Th(OH)4
1. Cat.speed curve with ThCl4 for sol dialysed for 2 days) Table
2. Cat.speed curve with ThCl4 for sol dialysed for 5 days) XIV(a).

FIG-7



Gold.
1. Cat.speed with KOH for sol dialysed for 2 days.) Table
2. Cat.speed with KOH for sol dialysed for 25 days.) XVII(a).

FIG-8



V_2O_5

1. Cat.speed curve with NH_4VO_3 for sol dialysed for 2 days.) Table
2. Cat.speed curve with NH_4VO_3 for sol dialysed for 10 days.) XVIII(a_1).

FIG-9

concentration (of the peptising agent) curve (Figs.7,8 and 9) is similar. Dialysis is therefore roughly the reverse of the process of adding small increasing amounts of the peptising electrolyte to the colloid so far as the changes in the amounts of the peptising electrolyte during dialysis are concerned. In order therefore to understand the changes in cat.speed during dialysis with reference to changes in the amount of the peptising electrolyte, we may consider the changes in the cat.speed in presence of the peptising electrolytes.

It is seen that on adding small increasing amounts of the peptising agent the cat.speed first increases, reaches a maximum and then decreases (Figs.7, 8 and 9). The increase in cat.speed is evidently due to preferential adsorption (the word preferential indicating that the ion is adsorbed in the inner sheet of the double layer i.e. on the surface of the particle, the other ion of the peptising electrolyte remaining away in the double layer) i.e. chemical adsorption of the similarly charged ion. The question arises how is the preferential adsorption of the similarly charged ion allowed to take place inspite of forces of repulsion. First of all the surface of any colloidal particle is not necessarily saturated and as such adsorption of similarly charged ions on the surface would be possible as a result of chemical affinity if any of the similarly charged ions have sufficient kinetic

kinetic energy to overcome the potential of the double layer. The preferential adsorption of the similarly charged ions will specially be more at a low density of electric charge or small cat. speed than at a higher density as there will be a greater opportunity for the forces of chemical affinity (which operate over shorter distances than electrostatic forces) to be effective in the former case than in the latter. Side by side with the concentration of the similarly charged ion, the concentration of the oppositely charged ion will also be increasing in the sol and there will be increasing tendency for its electrical adsorption on the particles, i.e. for the primarily adsorbed similarly charged ions to become covered. At small concentrations of the electrolyte the net effect will be a rise in the cat.speed due to preferential adsorption of the similarly charged ion unless the oppositely charged ion is strongly adsorbable or multivalent (see Section III), while at higher concentrations, the cat.speed will continuously decrease due to the preponderating influence of electrical adsorption. If the oppositely charged ion has strong adsorption, under favourable conditions after complete neutralisation of the charge, there might be a reversal of charge as stated by Mukherjee[19]. Dialysis being roughly the reverse of the above process, the changes in charge can therefore be explained on the following basis:-

As the concentration of the peptising electrolyte in the sol decreases during dialysis some of the electrically adsorbed ions (i.e. those which have been referred to as covered or bound ions before) will become free as their concentration in the sol diminishes and the charge will increase due to this effect. At the same time there will also be a chance for the desorption of the primarily adsorbed ions (the charge decreasing due to this effect), but this will occur only in the later stages of dialysis when the concentration of the peptising electrolyte is low as the primary adsorption due to chemical affinity is strong. The decrease in the cat. speed in the later stages of dialysis is due to desorption of the primarily adsorbed ions.

One might expect that for sols dialysed for short periods, there should not be any initial increase in the charge or cat. speed on adding small increasing amounts of the peptising electrolyte as the concentration of the same in the sol is appreciable. But as mentioned before the surface of the particle may not be saturated with the primarily adsorbed ions even then and therefore under favourable conditions, the initial rise in cat.speed on adding small increasing amounts of the peptising electrolyte to the short period dialysed sols would be noticed due to preferential adsorption of similarly charged ions. That such is the case will be seen by referring to results in Section III (also see Figs.7,8 and 9) as as the cat.speed has increased on adding small increasing amounts of electrolytes even to sols dialysed for short periods.

It will appear from Table VI(a) and (b) that the concentration of V_2O_5 has changed with the progress of dialysis. This is due to the fact that V_2O_5 has greater solubility in water than other colloidal substances investigated here. With the progress of dialysis as some V_2O_5 passes out in the dialysate, some of the colloidal particles dissolve to restore the equilibrium in the intermicellary liquid to a certain extent. But from the cat.speed changes during dialysis of this sol, it would appear that at no stage is the amount of dissolved V_2O_5 in the sol due to dissolution of colloidal particles equal to or greater than that originally present; if it was not so the changes in the cat.speed during dialysis would have been different from those in the case of other sols.

Arsenious sulphide (Table IV(a) and Fig.4) shows a behaviour regarding changes in cat.speed during dialysis which is in the early stages different from that shown by other colloidal solutions. The causes of this peculiar behaviour become clear if one considers the changes in its composition during dialysis. It will appear from Table IV(a) that although with the progress of dialysis the amount of total arsenic and sulphur continuously decreases, the amount of free arsenious acid in the sol which was nil to start with, increases

increases up to a period of 8 days dialysis, decreases thereafter for a short period after which it becomes constant. The production of free arsenious acid in the sol during dialysis suggests that arsenious sulphide hydrolyses giving rise to free arsenious acid and hydrogen sulphide. The arsenious acid will pass out to a certain extent in the dialysate and it is because of this that the total amount of arsenic in the sol continuously decreases during dialysis. Similarly a part of hydrogen sulphide may escape as gas as produced and a portion of that which remains dissolved in the sol may pass out in the dialysate; this accounts for a continuous decrease during dialysis of the total amount of sulphur in the sol. Some of the remaining 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 adsorb preferentially polythionate ions and pass into colloidal sulphur.

In view of the fact that the cat.speed has decreased during the first 8 days of dialysis when the amount of free arsenious acid in the sol has also increased, one might infer that arsenious acid has to do something with the abnormal behaviour of cat.speed in the beginning. To understand this effect, cat.speed was measured on adding small increasing amounts of As_2O_3 to the sol. From the results given in Table XVI of Section III it will appear that for sols dialysed for 5 and 25 days

days the cat.speed has first increased and then decreased, while for the sol dialysed for 31 days the cat.speed has not shown any initial rise; the initial rise is more for the sol dialysed for 5 days than that dialysed for 25 days. S.N. Mukherjee[27] observed that the cat.speed of As_2S_3 continuously decreases on the addition of As_2O_3, while Mukherjee and co-workers[28] noticed that the cat. speed of this sol increases in the presence of small amounts of As_2O_3. Our results support both the observations, the difference being due to differences in the composition of the sol during dialysis which has been mentioned above. The initial increase in the cat. speed is due to preferential adsorption of AsO_3''' ions due to chemical affinity, while the decrease is due to electrical adsorption of $H^{\cdot}$ ions. Sols dialysed for long periods show no initial rise in the cat.speed because there is already appreciable As_2O_3 in the sol due to hydrolysis and on further addition of the same electrical adsorption of $H^{\cdot}$ions is preponderating. The fact that cat.speed of the freshly prepared sol free from arsenious acid first increases and then decreases on the addition of small increasing amounts of the 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 As_2O_3 were produced due to hydrolysis. Leaving aside this particular point, it is clear that the decrease in the cat.speed up to 8 days is due to an an increase in the amount of arsenious acid in the sol. Between 8 and 14 days' dialysis the cat.speed has increased due to some bound H' ions electrically adsorbed becoming free due to decrease of As_2O_3 in the sol. The cat. speed changes up to dialysis of 14 days are thus mostly due to changes in the amount of As_2O_3 in the sol. 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 are due to changes in the amount of the peptising electrolyte (H_2S) in the sol as in the case of other sols.

The changes in the amount of As_2O_3 during dialysis suggest that up to 8 days the rate of its production by hydrolysis is greater than that of its passing out in dialysate and that between 8 and 14 days the former is smaller than the latter, while after 14 days both the rates are about the same.

The amount of total arsenic and sulphur in the sol are not according to the formulae As_2S_3. This is probably due to the fact that during the preparation of the sol, a portion of H_2S gets oxidised ultimately giving rise to colloidal sulphur as stated above; the arsenious sulphide sol thus contains some colloidal sulphur from the beginning. It is as a result of this that different investigators have given different formula to the colloidal arsenious sulphide.[8,29,30,31.]

With the progress of dialysis the size of the

the particles continuously increases as mentioned before. If other things remain constant, this should also mean a continuous increase in charge on the particle as observed by Mukherjee, Choudhury and Bhabak[16]. The initial increase in cat.speed might be also slightly due to this effect. It is however considered that the changes in the amounts of the peptising electrolytes are mainly responsible for changes in the cat.speed during dialysis.

From the foregoing it will be clear that with the progress of dialysis the cat.speed would first increase and then decrease for all the hydrophobic sols initially containing appreciable amounts of the peptising electrolyte except for As_2S_3 where the composition of the sol changes during dialysis due to hydrolysis of the same. Hitherto in explaining their results, it has been assumed by all the investigators that the charge decreases continuously with the progress of dialysis except for the alkaline gold sol[5] where actual measurements showed a first increase and then a decrease in the cat.speed during dialysis. A first increase and then a decrease in the cat.speed during dialysis is thus a general behaviour of hydrophobic sols having appreciable amounts of peptising electrolytes. Choudhury[32] has also observed a first increase and then a decrease in the cat.speed with the progress of dialysis of a copper ferrocyanide sol initially containing appreciable amounts of $K_4Fe(CN)_6$- the peptising electrolyte. If however, the sol initially contains an amount of the peptising agent equal to or less than that corresponding to the maximum in the cat.speed concentration curve (Fig. 7

(Figs. 7 to 9) of the colloid with that particular electrolyte, the cataphoretic speed on dialysis will continuously decrease; the maximum point in the cat.speed dialysis curves would probably correspond to the stage when all oppositely charged ions bound to the primarily adsorbed ions have become free and further dialysis means desorption of the primarily adsorbed ions themselves from the surface of the particle, their concentration in the intermicellary liquid being very low. This point is of significance in understanding changes in charge during dialysis of the sols as will be seen from discussion in Section II.

According to the chemical view the initial increase in charge during dialysis will have to be assumed as being due to the formation of new complex ions on the surface of the particles or due to increase in the dissociation of the ionogenic complex as a result of decrease in the electrolyte content of the intermicellary liquid. This process should however continue throughout dialysis and therefore the charge should not have decreased in the later stages of dialysis as it actually did. The subsequent decrease in charge might be due to membrane-hydrolysis of the complex, whereby alkali metal ions are replaced by hydrogen ions, giving a less ionised complex; such a view might apply in the case of gold sol[33] where the amount of electrolyte is very small from the beginning, but not in the case of the other sols where the

the amount of electrolyte is not negligible even at the stage of dialysis when the charge begins to decrease. The changes in the adsorption of the ions of the peptising electrolyte as a result of its removal in the dialysate can only give a rational explanation of changes in the charge as shown above during dialysis of sols including those of $Fe(OH)_3$, $Th(OH)_4$, alkaline Au and As_2S_3 which have been considered by Pauli as supporting the chemical view point.

(b) Stability.

The stability as determined by flocculation values with electrolytes has first increased and then decreased with the progress of dialysis in the case of colloidal gold (Fig.1) and continuously decreased in the cases of $Fe(OH)_3$, $Th(OH)_4$, Prussian blue and V_2O_5 sols (Figs. 2,3,5 and 6(a) and (b)); in the case of As_2S_3 sol (Fig.4) the stability has first increased and then decreased with reference to KCl, while it has first decreased and reached a minimum, then increased and reached a maximum and later again decreased with reference to $MgCl_2$. Considering the simultaneous changes in charge which have occurred in different cases, it is clear that stability and charge go hand in hand throughout during dialysis in the case of gold sol and As_sS_3 sol with reference to $MgCl_2$, thus supporting the accepted view that the greater the charge the greater the stability or the smaller the charge the smaller the stability.

In the case of $Fe(OH)_3$, $Th(OH)_4$, Prussian blue and V_2O_5 sol and As_2S_3 sol with reference to KCl, the cat.speed and stability go hand in hand only during certain stages and vary inversely for other stages. It is thus clear that it is erroneous to use stability data for getting an idea about changes in charge on colloidal particles as is being done usually by colloid chemists, for although charge and stability may go hand in hand in some cases, they do not do so in others.

We may now consider why in the initial stages of dialysis charge and stability do not go hand in hand in the case of $Fe(OH)_3$, $Th(OH)_4$, Prussian blue and V_2O_5 and As_2S_3 with reference to KCl.

(i) With the progress of dialysis the size of the particles continuously increases as judged from turbidity or colour changes. It is therefore likely that as a result of this, smaller amounts of electrolytes may be necessary to coagulate the sol dialysed for some days and having a greater cat.speed than that which is undialysed and has a smaller cat.speed. For what is observed in determining flocculation values is the appearance of turbidity or the change in colour and a smaller amount of electrolyte will be required to produce a given degree of turbidity or a standard colour in a given time in the case of a sol which initially contains particles of bigger size than the sol which contains particles of smaller size. It should be mentioned that this influence will also be at work in the case of colloidal gold during the period

period when the cat.speed has increased during dialysis, but its effect has not been noticed as the same is probably not preponderating; also the cat.speed and stability go hand in hand for As_2S_3 with reference to $MgCl_2$. Hence this factor is not wholly responsible for no direct relation between charge and stability in the initial stages of dialysis of the sols mentioned before.

(ii) It will be seen from the results in Section III that with electrolytes containing monovalent coagulating ions there is generally an initial rise in cat.speed on adding small amounts of an electrolyte due to preferential adsorption of the similarly charged ions either of the peptising electrolyte in the presence of the added electrolyte or of the added electrolyte itself. As a result of this effect a greater amount of electrolyte will be necessary for coagulation of a sol when initial rise in cat.speed occurs at small concentrations than for a sol when no such rise occurs. It will however appear from Section III that initial rise in cat.speed in the presence of small amounts of electrolytes having monovalent coagulating ions occurs for sols dialysed for short as well as long periods. Hence this effect alone also cannot explain no relation between charge and stability mentioned above.

(iii) One might perhaps consider that the fact that the particles of hydroxide sols and V_2O_5 sol mentioned above are hydrated is responsible for no relation between charge and stability of these sols in the initial stages of dialysis. Against this it should however be mentioned that

that particles of prussian blue are certainly not so much hydrated as those of the other sols but still there is no direct relation between charge and stability in the early stages of dialysis. This factor alone is also therefore not responsible for no relation between charge and stability mentioned above.

It is considered that the influence of all the factors mentioned above should be considered while discussing results of charge and stability in order to come to a correct conclusion about relation between the two.

In the case of stability of arsenious sulphide with reference to KCl, it will appear from Section III that the initial rise in cat.speed on the addition of KCl is appreciably more than that noticed with As_2O_3 for sols dialysed for short periods. It is therefore likely that the increase in stability with reference to KCl inspite of a smaller original charge on the particles is due to preferential adsorption of Cl' ions. The same factor however cannot explain no relation between charge and stability with reference to KCl for sols dialysed between 8 and 28 days for initial rise in cat.speed with KCl occurs even with sol dialysed for 25 days as will be seen from Section III.

(c) Conductivity.

The conductivity of a colloidal solution K_s is due to the conductivity of the electrolyte contained in the sol or of the intermicellary liquid (K_i) and of the colloidal particles

particles (K_c). Hence

$$K_s = K_i + K_c \quad .. \quad . (4).$$

In discussing the conductivity results of the colloidal solutions one must therefore consider the changes in the amount of the electrolytes in the sol besides the changes due to the conductivity of the colloidal particles themselves. The sp. conductivity of the sol will increase with an increase in the amount of electrolytes in it. The changes in the amount of electrolytes in a sol can be effected either by dialysis or dilution - the amount of electrolyte decreasing in both the cases - or desorption of ions from or adsorption of ions on the surface of particles, the latter effect however introducing only small changes in the conductivity. Of course the desorption of ions from or the adsorption of ions on the surface of particles will introduce a change in the conductivity of the colloidal particles themselves and in general the conductivity will increase with an increase of the charge on the particles. The variation in the conductivity of colloidal particles with changes in charge or cat.speed and other properties is governed by the following equation:-

$$K_c = \frac{4\pi\eta nr(r+\sigma)U_o^2}{N\sigma} \quad . \quad .. \quad (5)$$

where n = Number of particles per c.c.,

σ = Thickness of the double layer,

N = Avogadro's number

and other symbols have the same meaning as before.

'n' is specially important for the magnitude of K_c. The value of 'n' will increase greatly with decrease in the size of the particles and the indirect influence of the radius (r), through its great effect on 'n', outweighs the direct influence, in the opposite direction of 'r' on K_c. The value of 'δ' may not change appreciably under different conditions and so also the value of 'η' unless the sol sets to a gel. While discussing the conductivity results therefore we may only consider as important the variations due to the changes in the amount of electrolytes in the colloidal solutions and the number per c.c. and the cat.speed of the particles.

It will appear from the results given in Tables III(b), V(b) and VI(a) (also see Figs. 3, 5 and 6(a)) that in the case of prussian blue, gold and V_2O_5, the conductivity decreases with the progress of dialysis; the cat.speed as mentioned before has first increased and then decreased in all the cases. A decrease in conductivity during dialysis of the sols would be expected in view of decrease in the amount of electrolytes in the sols. The influence of changes in the cat.speed of the particles is apparently less marked and the influence of the changes in the amount of electrolytes outweighs it as in the initial stages of dialysis the K_s has decreased inspite of increase of cat.speed. As the size of the particles during dialysis gradually increases as mentioned before, the number of particles per unit volume will decrease and the conductivity will also decrease continuously due

due to this effect.

In the case of arsenious sulphide sol (Table IV(b) and Fig. 4) the conductivity has first decreased, then increased and again decreased somewhat on further dialysis of the sol. The electrolyte which is present in appreciable amounts in the sol during dialysis is As_2O_3, but if the conductivity was governed by it to a large extent, it should have first increased, then decreased and remained constant later as that has been the variation in the amount of As_2O_3 (Table IV(a)) during dialysis. Up to 17 days and after 23 days the cat.speed and conductivity have changed in the same manner (Table IV(b) and Fig. 4) and it would thus appear that the cat.speed has to a certain extent at least affected the conductivity. The causes of the increase in the conductivity during about the middle period of dialysis are not clear. As mentioned before considerable complications are introduced during dialysis due to decomposition of As_2S_3 and production of colloidal sulphur and polythionic acids. It is also difficult to say due to same reasons how exactly the number of colloidal particles in the sol will change during dialysis. It should be further noted that changes in cat.speed during dialysis of As_2S_3 sol are not so large as in the case of other sols,

On comparing the conductivity changes with the progress of dialysis for gold (Table V(b)) and V_2O_5 (Table VI(a)) it will appear that the conductivity has not decreased so much for V_2O_5 as for gold. This is due to the fact that as V_2O_5 is appreciably soluble, as mentioned

mentioned before, some of the colloidal particles dissolve as concentration of V_2O_5 in the intermicellary liquid decreases during dialysis thereby decreasing the conductivity to a smaller extent than what it should actually do if V_2O_5 particles did not dissolve at all.

(d) Viscosity.

It will appear from Table I(b) and Fig. 1 that in the case of $Fe(OH)_3$, the viscosity with the progress of dialysis first decreases, reaches a minimum and then increases, the minimum in viscosity and maximum in cat. speed however not occurring at the same stage of dialysis.

In the case of thorium hydroxide (Table II and Fig.2) the viscosity has continuously increased although the cat.speed has first increased and then decreased with the progress of dialysis.

The viscosity has first decreased and then increased with the progress of dialysis for prussian blue (Table III and Fig. 3) as in the case of $Fe(OH)_3$ but here the minimum in viscosity and maximum in charge have occurred at the same stage of dialysis.

In the case of V_2O_5 sol(Table VI(a) and (b) also see Fig. 6(a) and (b)) the viscosity has first decreased and then increased as in the case of $Fe(OH)_3$ and prussian blue, the minimum in viscosity and maximum in charge also occurring at the same stage of dialysis as in the case of the latter sol.

These changes in viscosity with the progress of dialysis of the sols can be due to one or all or some of of the following causes:-

(i) With the progress of dialysis the amounts of electrolytes in the sol continuously decrease. This should continuously decrease the viscosity of the sol with the progress of dialysis except in the case of electrolytes which show negative viscosity where the viscosity should increase when dialysis is carried out to the extreme. In the case of $Fe(OH)_3$, prussian blue and V_2O_5 the initial decrease in viscosity might be also somewhat due to this effect of decrease in electrolyte, although in the later stages of dialysis the effect is not allowed to be noticed for the first two sols due presumably to predominence of the influence of other factors; in the case of V_2O_5 in the later stages of dialysis also, the increase might be slightly due to decrease in the amount of ammonium chloride or vanadate as it is known that the ammonium cation shows the phenomenon of negative viscosity[34]. In the case of $Th(OH)_4$ the effect of decrease of electrolyte during dialysis is obscured by the other factors.

(ii) If the concentration of the colloid decreases during dialysis, the viscosity should show a decrease. As mentioned before the concentration of the sol does not decrease to any appreciable extent in the case of $Fe(OH)_3$, $Th(OH)_4$ and prussian blue and hence the effect of this factor is absent as far as these sols are concerned. In the case of V_2O_5 sol however, the concentration of the colloid continuously decreases during dialysis (Table VI(a) and (b)) and the initial decrease in viscosity can be be also due to this effect, the influence of this factor being not allowed to be noticed by other factors in the later stages of dialysis.

(iii) According to Dhar and co-workers[7], other things being identical, a decrease in the electric charge on colloidal particles causes an increase in hydration and necessarily in the viscosity of the sols. They have thus explained an increase in viscosity with the progress of dialysis as being due to a decrease in charge. It should however be mentioned that their conclusions about changes in charge during dialysis are based on stability determinations; as mentioned before however in all the cases the charge first increases and then decreases during dialysis and it is not safe to draw conclusions about changes in charge from stability results. From the results it is clear that the present results do not support completely Dhar's conclusions about relation between charge and viscosity.

According to v.Smoluchowski[6] however, the movement of electrically charged particles of a sol causes the development of an electric field, which hinders the flow of the sol resulting in an increase of its viscosity. Thus a sol with particles having a high electric charge should be more viscous than another sample of the same sol with particles having a low electric charge. The present results, it will be seen, do not completely support Smoluchowski's view probably because of the fact that the influence of other factors is also at work.

(iv) With an increase in hydration of the particles (this tendency is most pronounced towards the later stages of dialysis when the sol shows a tendency to set to gel) the viscosity will also increase, there being an increase in the effective volume of the particles. This effect is most pronounced for V_2O_5 sol in the later stages of dialysis as the sol sets to gel 'enbloc' on carrying the dialysis to extreme.

It should be mentioned that Dhar and Ahobalacharya[35] got a continuous increase in viscosity with the progress of dialysis of V_2O_5 sol, while according to the results given here, there is first a decrease and then an increase in viscosity. The difference in the results of V_2O_5 given here and of those of Dhar is probably due to a difference in the rate of purification of the sols in the two cases.

(v) Variation in the shape and structure of the particles which is sure to take place during dialysis will also affect the viscosity of the sol. There will be a tendency for the small spherical particles to change on extreme dialysis into other forms. For example the particles of V_2O_5 which if the sol is highly dispersed, may be almost spherical, will during dialysis become definitely rod shaped. This will introduce complications in the flow of the sol through the capillary viscometer and the results of even relative viscosity, leaving aside the absolute viscosity, are sure to be not quite accurate.

The structure of the particles will vary during dialysis as progressively large aggregates are formed with

with the progress of dialysis. Formation of net-like aggregates[36] will increase the effective volume of the particles and hence the viscosity of the sol. This effect is likely to be quite pronounced in the case of $Fe(OH)_3$, $Th(OH)_4$ and V_2O_5 sols.

In the end it may be mentioned that in explaining results of viscosity with the progress of dialysis of sols, one has to consider the influence of all the factors mentioned above instead of any one factor alone as done by some investigators.

SECTION II - Changes during dilution of sols dialysed for different periods.

(a) Charge.

It will appear from the results given in Tables VII, VIII(a) and IX(a) (Figs. 10 to 12) that in the case of $Fe(OH)_3$, $Th(OH)_4$ and prussian blue on diluting the sols, the cat.speed first increases, reaches a maximum and then decreases for samples dialysed for periods shorter than that corresponding to the maximum in the cat.speed-dialysis curve (Figs. 1 to 3), while for samples dialysed for periods equal to or longer than that period, the cat.speed continuously decreases on dilution.

In the case of As_2S_3 sol (Table X(a)) the changes in the cat.speed on dilution are irregular (See Fig.13).

In the case of colloidal gold (Table XI(a) the cat. speed continuously decreases for all the samples of the sol dialysed for different periods (see Fig.14).

In the case of V_2O_5 sol (Table XII(a) and (b)) the

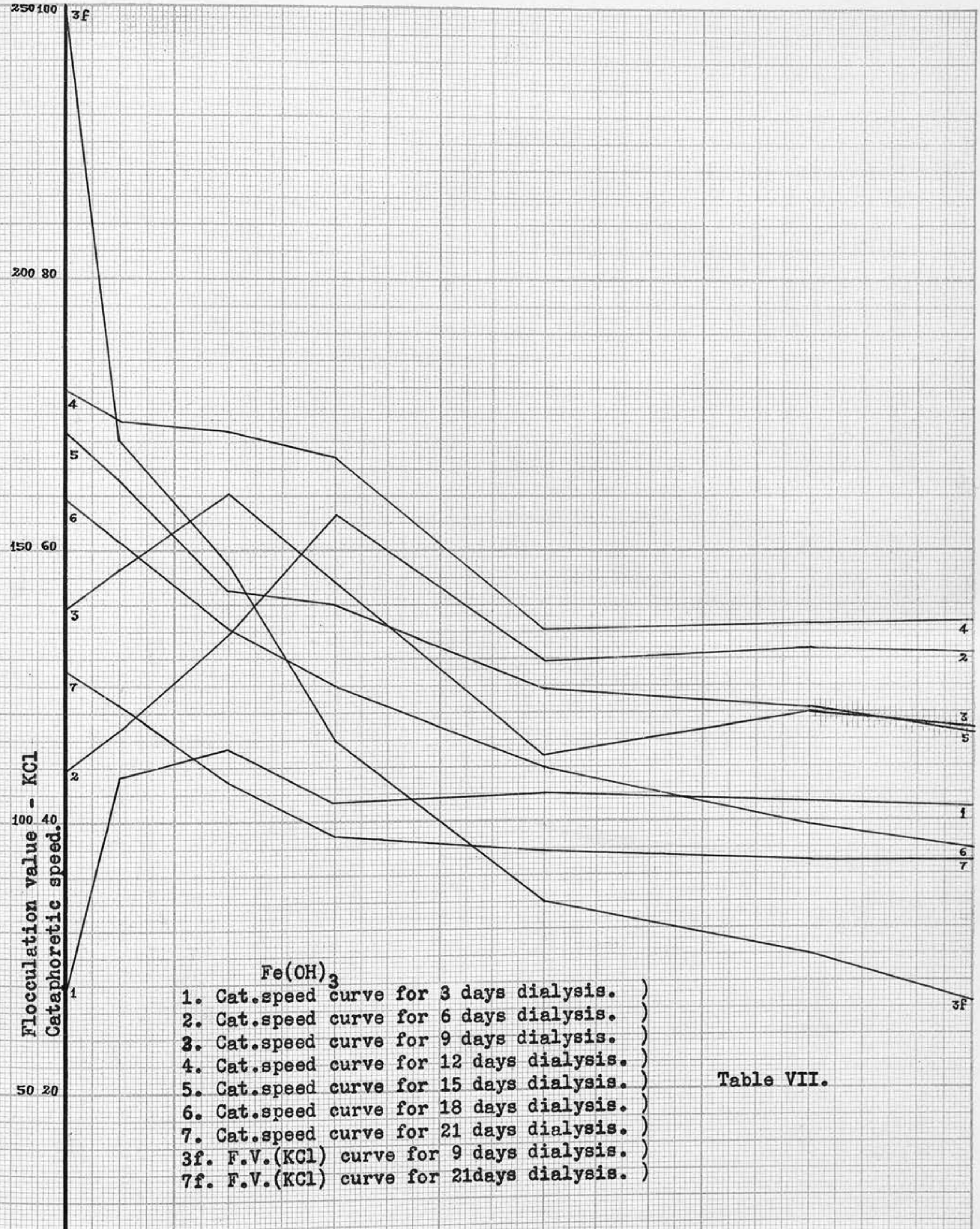

Flocculation value - KCl
Cataphoretic speed.
250 100
200 80
150 60
100 40
50 20
0 0
Dilution.
1
3
8
13
18
3f
4
5
6
3
7
2
1
7f
4
2
3
5
1
6
7
3f
7f
Fe(OH)$_3$
1. Cat.speed curve for 3 days dialysis.)
2. Cat.speed curve for 6 days dialysis.)
3. Cat.speed curve for 9 days dialysis.)
4. Cat.speed curve for 12 days dialysis.)
5. Cat.speed curve for 15 days dialysis.)
6. Cat.speed curve for 18 days dialysis.)
7. Cat.speed curve for 21 days dialysis.)
3f. F.V.(KCl) curve for 9 days dialysis.)
7f. F.V.(KCl) curve for 21days dialysis.)
Table VII.

FIG-10

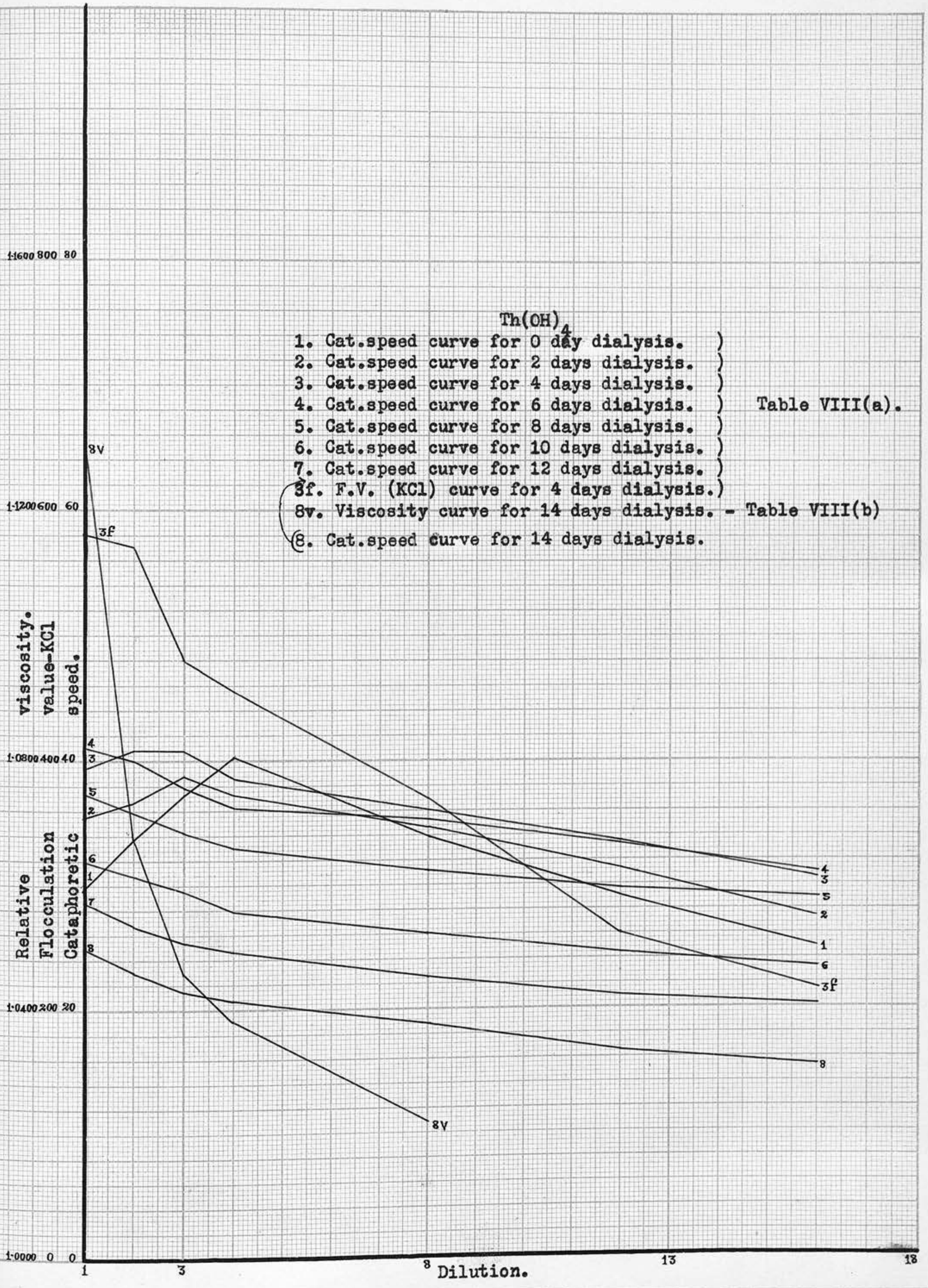

Th(OH)$_4$
1. Cat.speed curve for 0 day dialysis.)
2. Cat.speed curve for 2 days dialysis.)
3. Cat.speed curve for 4 days dialysis.)
4. Cat.speed curve for 6 days dialysis.) Table VIII(a).
5. Cat.speed curve for 8 days dialysis.)
6. Cat.speed curve for 10 days dialysis.)
7. Cat.speed curve for 12 days dialysis.)
3f. F.V. (KCl) curve for 4 days dialysis.)
8v. Viscosity curve for 14 days dialysis. - Table VIII(b)
8. Cat.speed curve for 14 days dialysis.
Relative viscosity.
Flocculation value-KCl
Cataphoretic speed.
1·1600 800 80
1·1200 600 60
1·0800 400 40
1·0400 200 20
1·0000 0 0
1
3
8
13
18
Dilution.
8V
3f
4
3
5
2
6
1
7
8
8V
4
3
5
2
1
6
3f
8

FIG-11

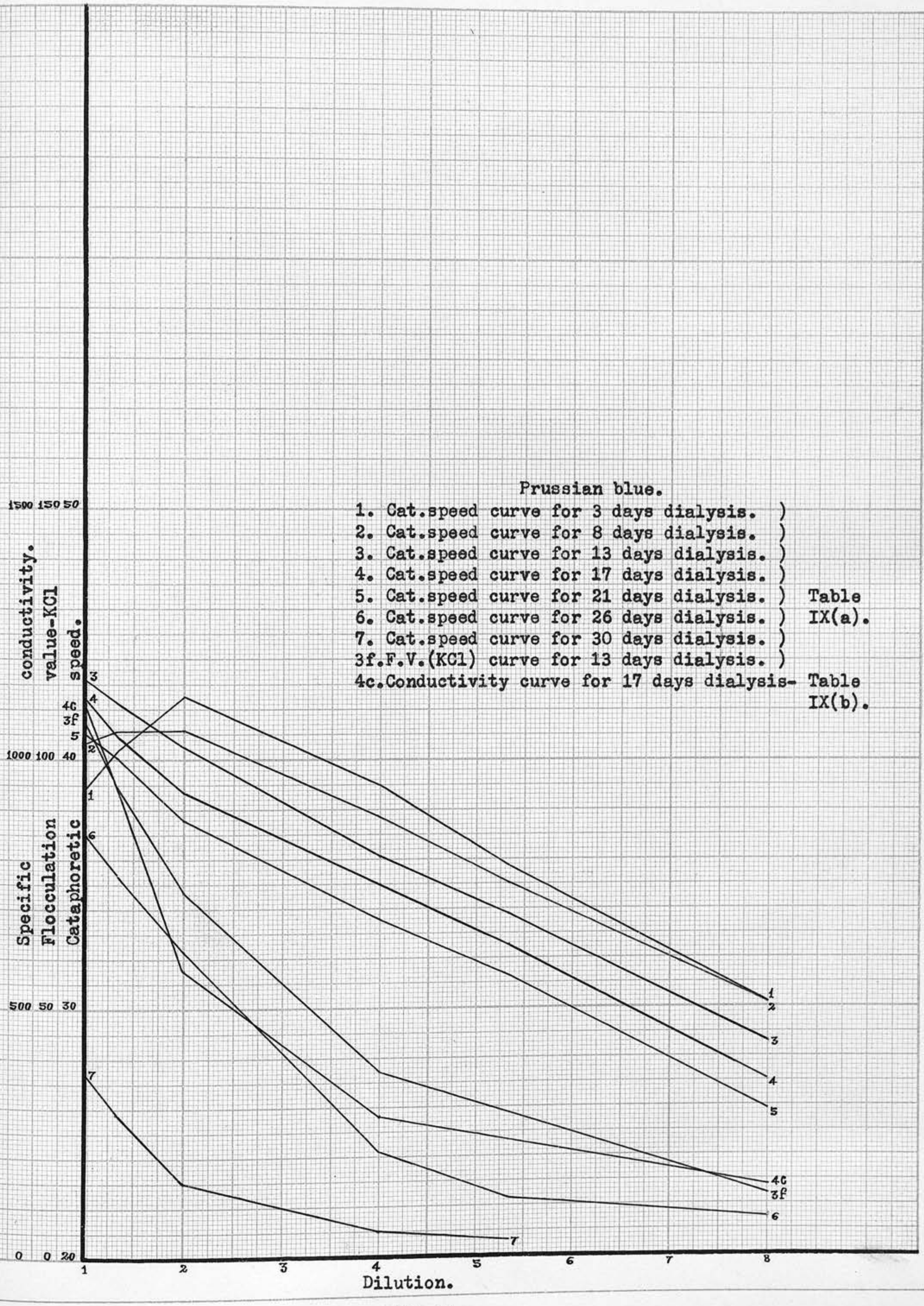

Prussian blue.
1. Cat.speed curve for 3 days dialysis.)
2. Cat.speed curve for 8 days dialysis.)
3. Cat.speed curve for 13 days dialysis.)
4. Cat.speed curve for 17 days dialysis.)
5. Cat.speed curve for 21 days dialysis.) Table
6. Cat.speed curve for 26 days dialysis.) IX(a).
7. Cat.speed curve for 30 days dialysis.)
3f.F.V.(KCl) curve for 13 days dialysis.)
4c.Conductivity curve for 17 days dialysis- Table IX(b).
Specific conductivity.
Flocculation value-KCl
Cataphoretic speed.
1500 150 50
1000 100 40
500 50 30
0 0 20
1
2
3
4
5
6
7
8
Dilution.
3
4c
4
3f
5
2
1
6
7
1
2
3
4
5
4c
3f
6
7

FIG-12

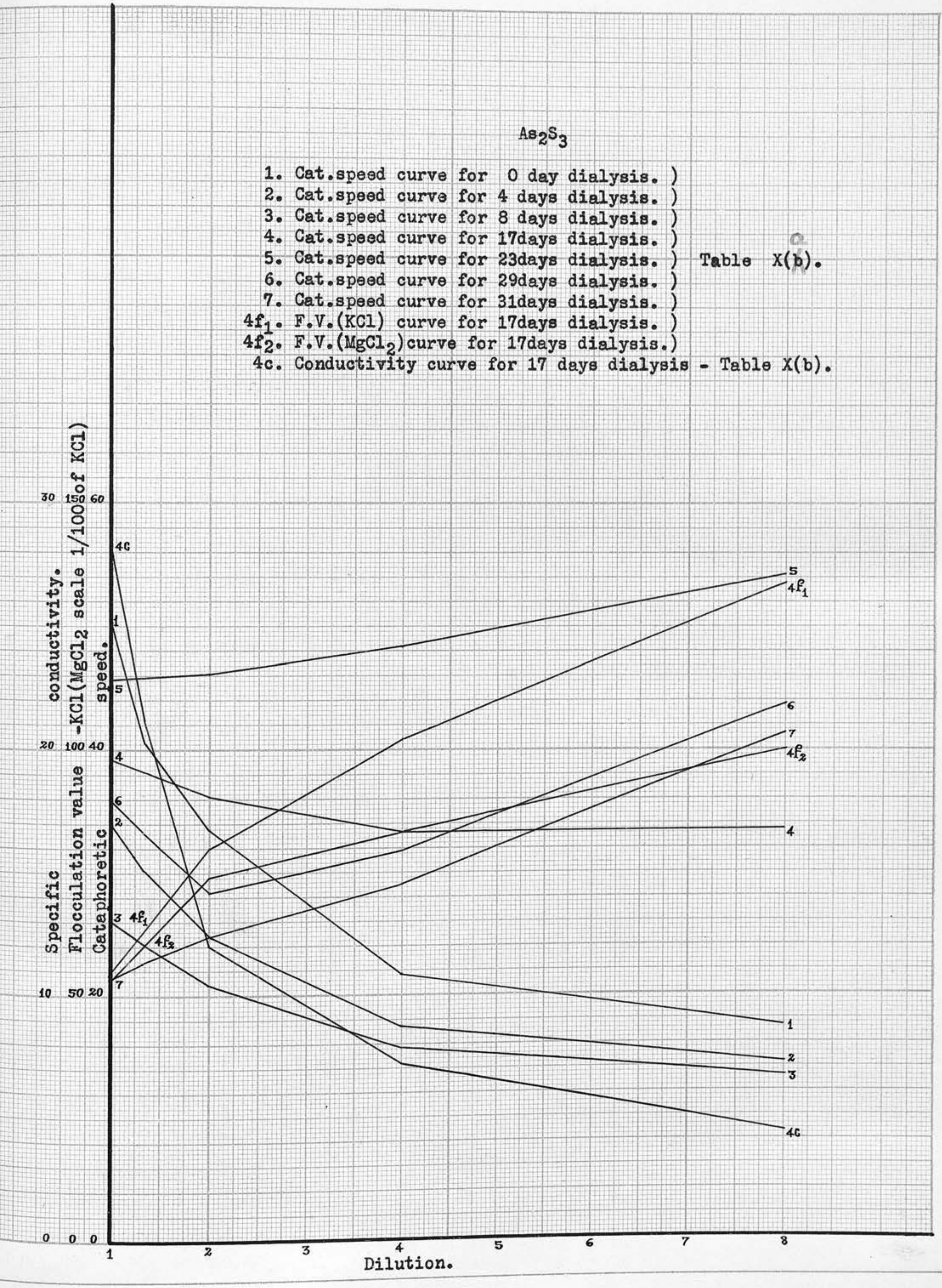

As_2S_3
1. Cat.speed curve for 0 day dialysis.)
2. Cat.speed curve for 4 days dialysis.)
3. Cat.speed curve for 8 days dialysis.)
4. Cat.speed curve for 17days dialysis.)
5. Cat.speed curve for 23days dialysis.) Table X(b).
6. Cat.speed curve for 29days dialysis.)
7. Cat.speed curve for 31days dialysis.)
$4f_1$. F.V.(KCl) curve for 17days dialysis.)
$4f_2$. F.V.($MgCl_2$)curve for 17days dialysis.)
4c. Conductivity curve for 17 days dialysis - Table X(b).
Specific conductivity.
Flocculation value -KCl($MgCl_2$ scale 1/100of KCl)
Cataphoretic speed.
30 150 60
20 100 40
10 50 20
0 0 0
1
2
3
4
5
6
7
8
Dilution.
4c
1
5
4
6
2
3
$4f_1$
$4f_2$
7
5
$4f_1$
6
7
$4f_2$
4
1
2
3
4c

FIG-13

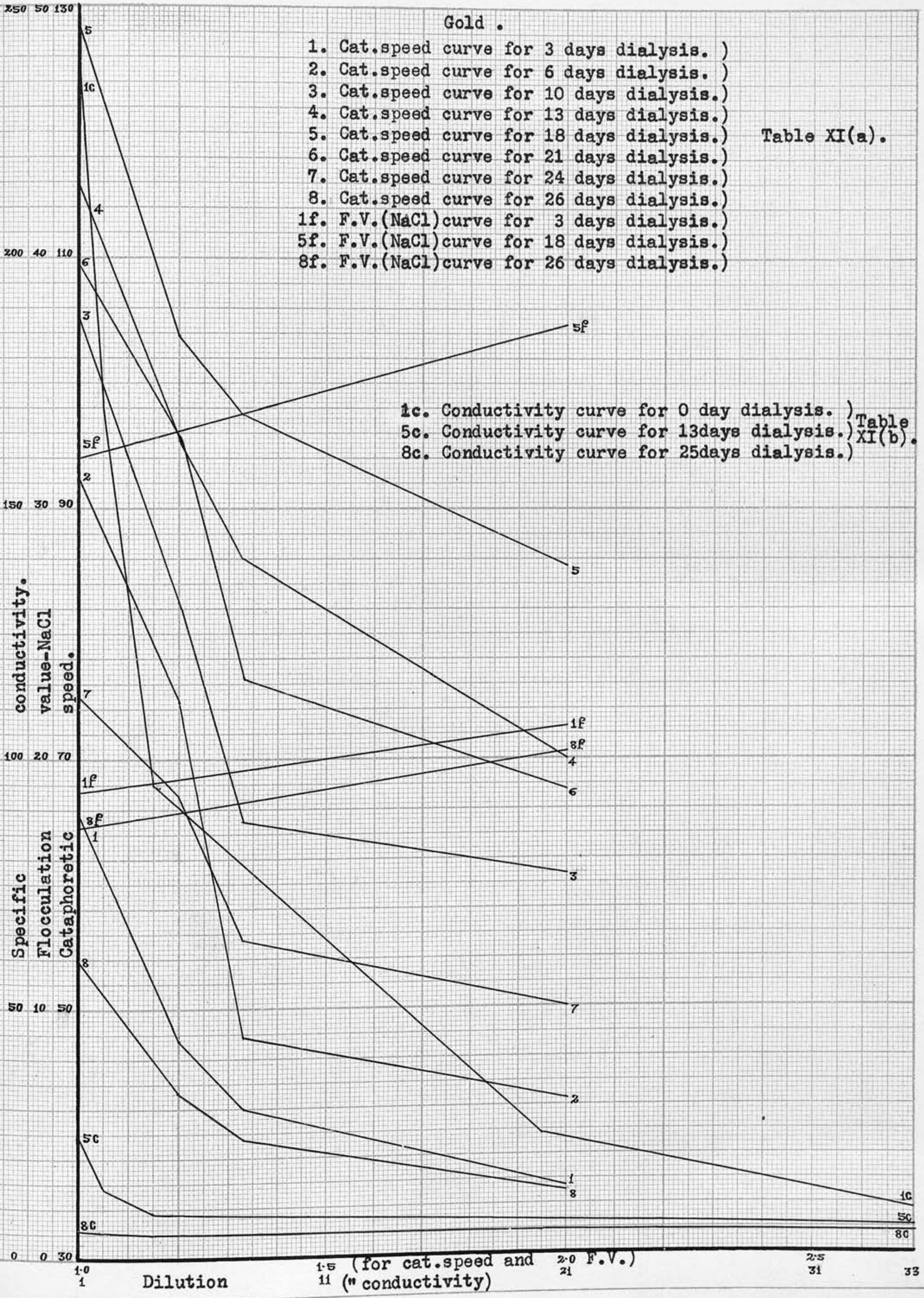

Gold .
1. Cat.speed curve for 3 days dialysis.)
2. Cat.speed curve for 6 days dialysis.)
3. Cat.speed curve for 10 days dialysis.)
4. Cat.speed curve for 13 days dialysis.)
5. Cat.speed curve for 18 days dialysis.)
6. Cat.speed curve for 21 days dialysis.)
7. Cat.speed curve for 24 days dialysis.)
8. Cat.speed curve for 26 days dialysis.)
1f. F.V.(NaCl)curve for 3 days dialysis.)
5f. F.V.(NaCl)curve for 18 days dialysis.)
8f. F.V.(NaCl)curve for 26 days dialysis.)
Table XI(a).
1c. Conductivity curve for 0 day dialysis.)
5c. Conductivity curve for 13days dialysis.)
8c. Conductivity curve for 25days dialysis.)
Table XI(b).
Specific conductivity.
Flocculation value-NaCl
Cataphoretic speed.
250 50 130
200 40 110
150 30 90
100 20 70
50 10 50
0 0 30
1·0
1
Dilution
1·5
11
(for cat.speed and
(" conductivity)
2·0
21
F.V.)
2·5
31
33
5
1c
4
6
3
5f
2
7
1f
8f
1
8
5c
8c
5f
5
1f
8f
4
6
3
7
2
1
8
1c
5c
8c

FIG-14

the cat.speed decreases on dilution for all the samples of the sol dialysed for different periods (see Fig. 15(a) and (b)) as in the case of gold sol.

We may now try to understand these changes in cat. speed on dilution in different cases. In the first instance the processes of dilution and dialysis are similar in so far the changes in the peptising electrolyte are concerned. In view of this one would expect that the cat. speed should first increase and then decrease on dilution for those samples of the sol which have been dialysed for period shorter than that corresponding to the maximum in the cat.speed dialysis curve of that colloid and which have therefore some of the primarily adsorbed ions covered by the electrical adsorbed oppositely charged ions, because in the beginning some of the primarily adsorbed ions which are covered with or to which are bound the oppositely charged ions due to electrical adsorption, will become uncovered and hence increase the cat.speed; at higher dilutions even the primarily adsorbed ions will be desorbed, their concentration in the intermicellary liquid being very low and the cat.speed will decrease due to this effect. Such a behaviour is shown by short period dialysed $Fe(OH)_3$, $Th(OH)_4$ and prussian blue sols (Figs. 10 to 12). For samples of sol dialysed for period equal to or more than that corresponding to the maximum in the cat.speed dialysis curve of that colloid, because probably all the covered primarily adsorbed ions have become uncovered due to removal of electrically adsorbed

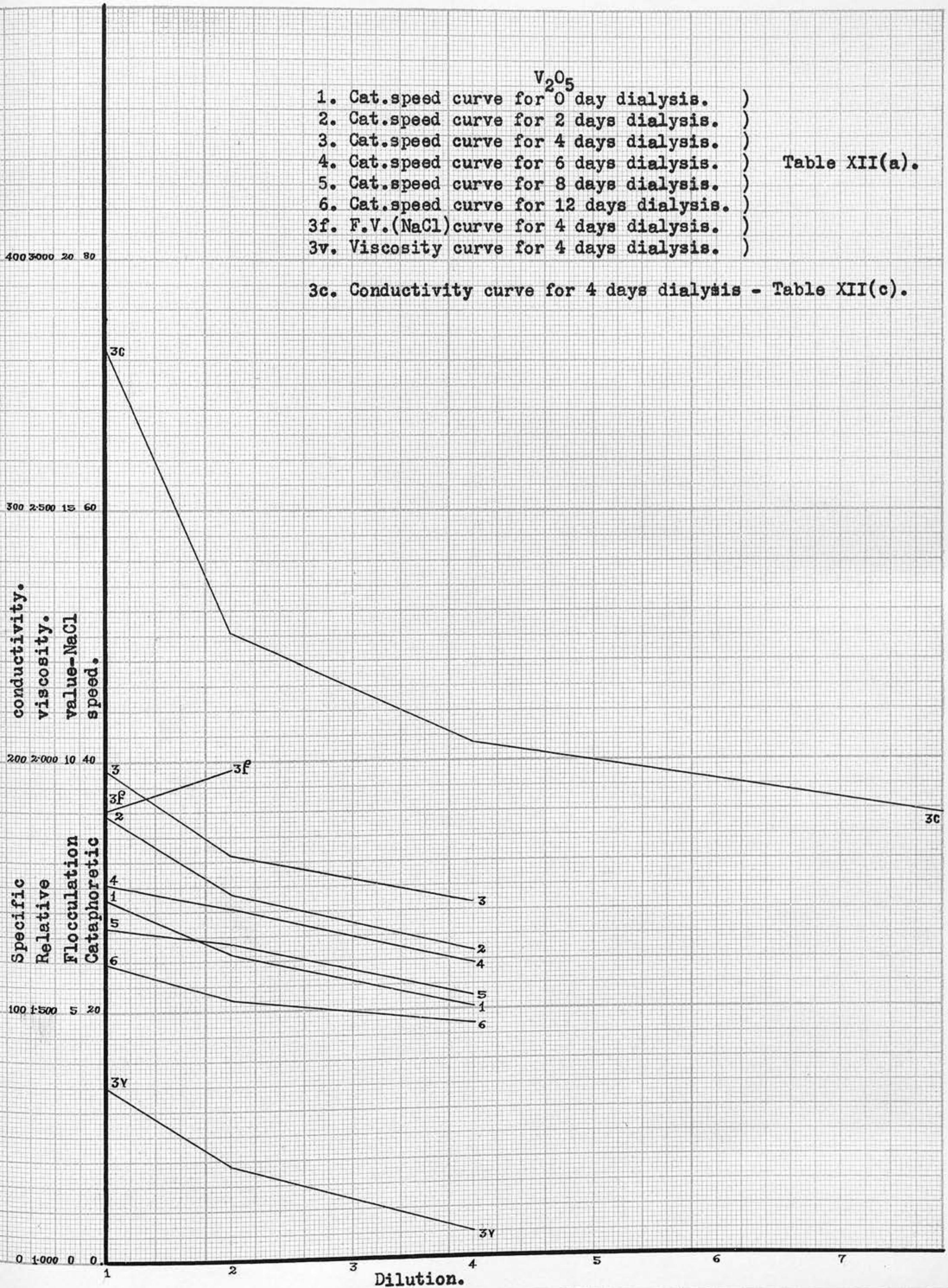

V_2O_5
1. Cat.speed curve for 0 day dialysis.)
2. Cat.speed curve for 2 days dialysis.)
3. Cat.speed curve for 4 days dialysis.)
4. Cat.speed curve for 6 days dialysis.) Table XII(a).
5. Cat.speed curve for 8 days dialysis.)
6. Cat.speed curve for 12 days dialysis.)
3f. F.V.(NaCl) curve for 4 days dialysis.)
3v. Viscosity curve for 4 days dialysis.)
3c. Conductivity curve for 4 days dialysis - Table XII(c).
Specific conductivity.
Relative viscosity.
Flocculation value-NaCl
Cataphoretic speed.
400 3000 20 80
300 2·500 15 60
200 2·000 10 40
100 1·500 5 20
0 1·000 0 0.
1
2
3
4
5
6
7
Dilution.
3c
3c
3
3
3f
3f
2
2
4
4
1
1
5
5
6
6
3v
3v

FIG-15 (a)

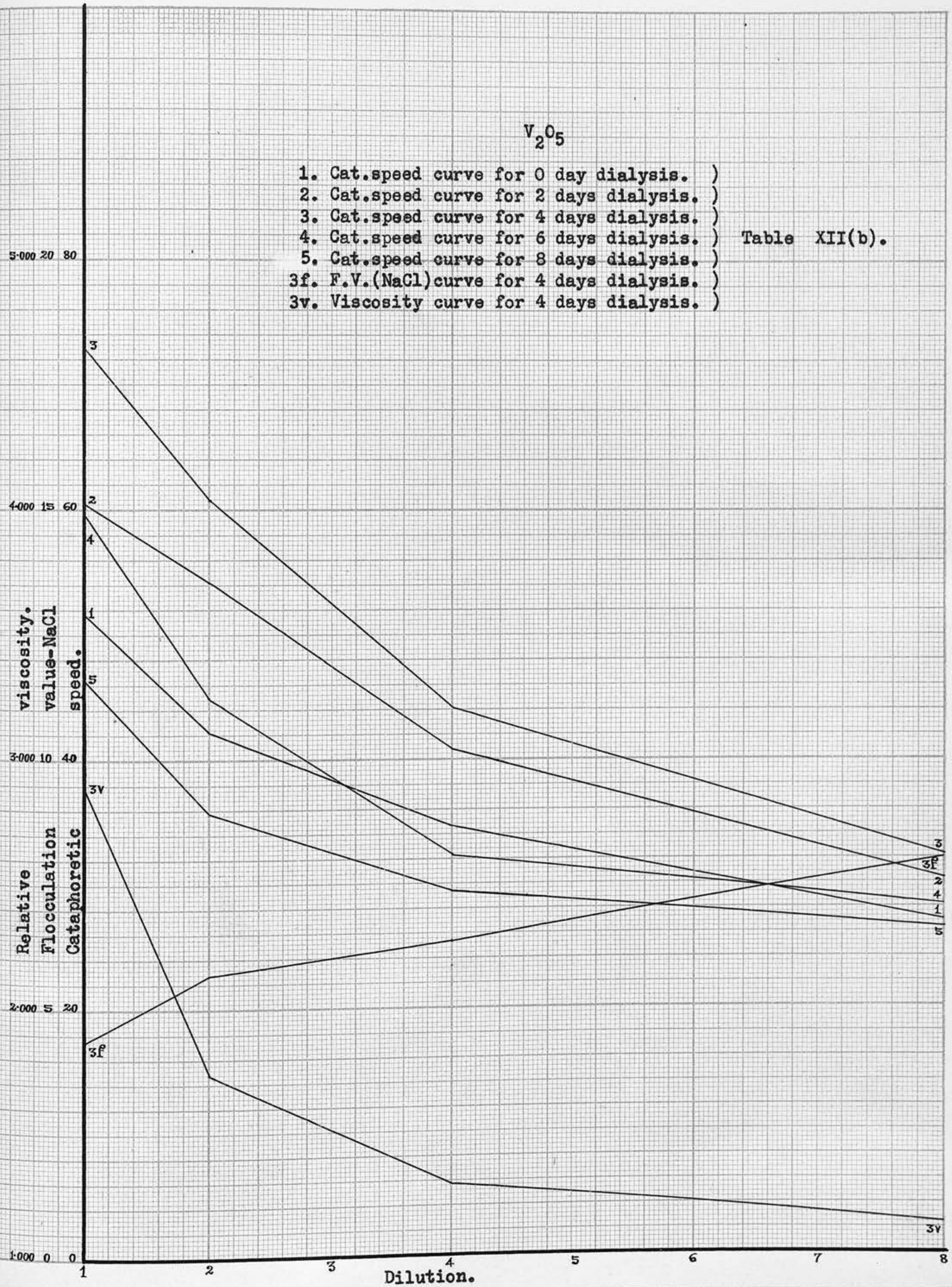

V_2O_5
1. Cat.speed curve for 0 day dialysis.)
2. Cat.speed curve for 2 days dialysis.)
3. Cat.speed curve for 4 days dialysis.)
4. Cat.speed curve for 6 days dialysis.) Table XII(b).
5. Cat.speed curve for 8 days dialysis.)
3f. F.V.(NaCl)curve for 4 days dialysis.)
3v. Viscosity curve for 4 days dialysis.)
Relative viscosity.
Flocculation value-NaCl
Cataphoretic speed.
5·000 20 80
4·000 15 60
3·000 10 40
2·000 5 20
1·000 0 0
1
2
3
4
5
6
7
8
Dilution.
3
2
4
1
5
3v
3f
3
3f
2
4
1
5
3v

FIG-15(b)

adsorbed ions during dialysis, any dilution should result in the desorption of the primarily adsorbed ions as during further dialysis and therefore the cat.speed should continuously decrease on dilution. As will be seen from the results (Figs. 10 to 12) long period dialysed $Fe(OH)_3$, $Th(OH)_4$ and prussian blue sols show such a behaviour as the cat.speed has continuously decreased during dilution. It may be mentioned that Mukherjee and coworkers[37] got different types of curves of cat.speed with dilution of $Fe(OH)_3$ sol. The difference in their results from those given here is probably due to a lack of systematic investigation in their case and different composition of the sols tried in different experiments.

In the case of gold sol (Table XI(a)) the initial rise in cat.speed on dilution (Fig.14) is not noticed for both short period as well as long period dialysed samples. The behaviour of this sol is thus partly different from that of $Fe(OH)_3$ or $Th(OH)_4$ and prussian blue. In the case of $Fe(OH)_3$, $Th(OH)_4$ and prussian blue, the primarily adsorbed layer consists of $Fe^{\cdot\cdot\cdot}$, $Th^{\cdot\cdot\cdot\cdot}$ and $Fe(CN)_6{}''''$ ions respectively (besides the other ions mentioned in the Table on page 48), which also constitute one of the part of the substance in colloidal condition; in the case of gold sol the colloidal particles are charged due to primarily adsorbed OH' ions and they may not be so firmly attached to the surface as in the case of the other sols peptised mostly by one of their constituent. In that case dilution of the sol dialysed for even short periods may from the beginning

beginning show predominence of desorption of the primarily adsorbed OH' ions (instead of removal of the electrically adsorbed oppositely charged ions as in the other cases), thereby decreasing the cat.speed. There might also be some other factors which are not clear, as being responsible for the peculiar behaviour of short period dialysed gold sol. Mukherjee and coworkers[38] also observed a continuous decrease in the cat.speed on dilution of gold sol dialysed for a long period.

In the case of V_2O_5 (Table X~~X~~II(a) and (b), see also Fig.15(a) and (b)) the cat.speed has continuously decreased on dilution of short period dialysed sols although the primarily adsorbed ions which charge the particles constitute a part of the substance in colloidal condition as in the case of $Fe(OH)_3$, $Th(OH)_4$ and prussian blue. This is probably due to the fact that as V_2O_5 is appreciably soluble in water, dilution will mean dissolution of some V_2O_5[25] from the surface of the colloidal particles, thus disturbing the distribution of ions in the double layer - the primarily adsorbed ions which are uncovered may be washed during dilution; this will result in a continuous decrease in cat. speed on dilution of even short period dialysed sols. For long period dialysed sols, there being no more covered primarily adsorbed ions, as mentioned above, dilution results in the desorption of the primarily adsorbed ions, thus decreasing the charge; in this case also the charge will decrease to a certain extent due to dissolution of some V_2O_5 from the surface of the particles on dilution as in in the case of short period dialysed sols.

In the case of As_2S_3 sol (Fig. 13) the variations in the cat.speed on dilution are many. This is first due to the fact that the composition of the sol changes during dialysis as mentioned in Section I. Further it is likely that As_2S_3 also hydrolyses on dilution and some As_2O_3 will be produced as a result of the same, thus affecting the cat. speed. In the case of As_2S_3 sol complications are thus definitely produced due to changes in the composition of the sol[38,39]. Peculiar changes in cat.speed on dilution of As_2S_3 observed by Mukherjee[40] are also probably due to a difference in the composition of the various samples tried by them.

It should be mentioned that dialysis and dilution are similar only so far the changes in the amount of the peptising electrolyte are concerned. During dialysis as mentioned before, the concentration of the colloid does not change appreciably except in those cases where the colloidal particles pass into solution due to their appreciable solubility (V_2O_5) or where the colloidal particles decompose (As_2S_3), while during dilution the concentration of the colloid also changes to the same extent as the peptising electrolyte. Further dilution may give rise to peptisation[41], while dialysis gives rise to aggregation of particles as mentioned before.

The rise in cat.speed on dilution noticed for some samples of the sols for As_2S_3 and short period dialysed $Fe(OH)_3$, $Th(OH)_4$ and prussian blue cannot satisfactorily

satisfactorily be explained on the basis of chemical view of the origin of charge on colloidal particles as different assumptions of formation of complex ions will have to be made for the same sol when charge has decreased and increased or vice versa on dilution.

(b) Stability:

It will appear from the results given in Tables VII, VIII(a) and IX(a) (Figs. 10 to 12), that in the case of $Fe(OH)_3$, $Th(OH)_4$ and prussian blue the stability on dilution decreases continuously for both short period and long period dialysed sols.

In the case of As_2S_3, gold and V_2O_5 (Tables X(a), XI(a), and XII(a) and (b) (Figs. 13 to 15)) the stability has increased on dilution for all samples of the sols whether dialysed for short or long periods. Mukherjee and Ganguly[42] in the case of As_2S_3, Kruyt and Van Arkel[43] in the case of gold and Dhar and Ahobalacharya[35] in the case of V_2O_5 also observed that the stability increases on dilution.

It would thus appear that charge and stability go hand in hand in some cases for certain range of dilutions, while in others for other ranges of dilution the stability has decreased inspite of increase of charge or increased inspite of decrease of charge. The increase of stability inspite of decrease of charge on dilution noticed in some of the cases might be due to the following:-

We know that the stability has been determined by determining the concentration of electrolyte necessary for

for producing a given change in a given time. Now distance between colloidal particles increases on dilution and therefore the chances of collision giving rise to flocculation on adhesion of particles decrease. Therefore to obtain the same change in a given time a greater amount of electrolyte would be necessary in the case of dilute sol than for a concentrated sol inspite of an increase in charge. This effect is likely to be more pronounced in the case of univalent coagulating ions than multivalent ones as observed by Kruyt and van der Spek[44] and Mukherjee and Sen[45]. But from the results of stability of As_2S_3 with reference to $MgCl_2$, it would appear that this effect is noticed even in the case of bivalent coagulating ion; Mukherjee and Sen also observed such a behaviour with HgS and Cus sols. Thus sometimes even if the coagulating ions are multivalent and hence strongly adsorbable, the influence of the increase in the distance between the particles preponderates, thus giving rise to abnormal behaviour to dilution rule. In the case of $Fe(OH)_3$, $Th(OH)_4$ and prussian blue dialysed for long periods it appears that the influence of the increased distance between the particles on dilution is not allowed to be noticed by the preponderating influence of concentration changes and charge; in the case of these three sols dialysed for short periods the influence of concentration changes on dilution appears to be so marked that the influence of changes in the charge and increase in distance between the particles is not allowed to be noticed.

It would be clear from these results that as mentioned

mentioned before it is not always safe to draw conclusions about changes in charge on colloidal particles from stability results.

(c) Conductivity.

It will appear from the results given in Tables IX(b), X(b), XI(b) and XII(c) that for prussian blue, arsenious sulphide, gold and vanadium pentoxide (Figs.12 to 15(a)) the conductivity has decreased on dilution. Mukherjee and coworkers[37] also observed a decrease in sp. conductivity of Fe_2O_3 sol on dilution.

On comparing the changes in cat.speed on dilution of these sols with those in conductivity, it would appear that in some cases both conductivity and cat.speed have decreased on dilution, while in others the conductivity has decreased when the cat.speed has increased. The changes in conductivity are thus governed only to a very small extent by the changes in the cat.speed or charge on the particles. Further even in those cases where the changes in the cat.speed and conductivity are in the same direction, the amount of change in conductivity is generally larger than that in the cat.speed.

The decrease in conductivity on dilution of the sols is mostly due to the decrease in the amount of electrolytes contained in the same as well as due to the decrease in the number of colloid particles in unit volume. In the case of gold sol there is a tendency for the conductivity to decrease only by a small extent on dilution of sols dialysed for long

long periods (Table XI(b)). This is due to the fact that the amount of electrolytes in the sol being from the beginning very small, almost all of them are removed on long dialysis and probably the decrease in conductivity on dilution of such sols might be to a large extent due to a decrease in the number of particles in unit volume. In the case of V_2O_5 (Table XII(c)) the conductivity on dilution of all samples does not decrease so much as the prussian blue and As_2S_3 sols or short period dialysed gold sols probably because, as mentioned before, some V_2O_5 dissolves from the surface of the particles on dilution.

(d) Viscosity.

It will appear from Table VIII(b) (also see Fig.11) that the viscosity continuously decreases on dilution for all samples of $Th(OH)_4$ dialysed for different periods. From Table VIII(a) and Fig. 11 it will however be seen that the cat.speed for short period dialysed sols first increases and then decreases while that for long period dialysed sols continuously decreases during dilution.

In the case of prussian blue sol (TableIX(c)) the viscosity with dilution continuously decreases with short period dialysed sols for which cat.speed has first increased and then decreased at the same time (TableIX(a) and Fig.12), while it has first decreased and then increased for long period dialysed sols for which cat.speed has continuously decreased.

The viscosity on dilution of V_2O_5 sol(Table XII(a) and (b), also see Fig. 15(a) and (b)) continuously decreases

decreases as the charge.

During dilution, the electrolyte in the sol decreases as during dialysis and the viscosity will be affected in the same manner as discussed in Section I.

The viscosity should continuously decrease in all the cases as a result of dilution. The increase in viscosity on dilution after the initial fall in the case of prussian blue sol dialysed for long periods cannot however be explained on these ideas.

The relation between charge and viscosity as stated by Dhar[7] and Smoluchowski[6] is not completely supported in all the cases, presumably because the effect of concentration changes on viscosity is most pronounced.

Regarding the effect on viscosity of changes in the hydration of the colloidal particles on dilution, it may be mentioned that as emphasised by Hatschek[46] the hydration factor is constant over a moderate range of concentration for typical hydrophillic sols. In the case of $Th(OH)_4$ (Table VIII(b)) the value of the hydration factor calculated according to the formula proposed by Hatschek is reduced to about 1/3 for dilution 4 and 1/22 for dilution 12 for 0 day dialysed sol and to about 1/10 for dilution 4 and 1/55 for dilution 12 for 14 days dialysed sol. Similarly in the case of dilute V_2O_5 sol (XII(a)) the value of hydration factor is reduced to about 1/5 for dilution 2 and 1/10 for dilution 4 for 0 day dialysed sol, to about 1/5 for dilution 2 and 1/6 for dilution 4 for 4 days dialysed sol and to about 3/4 for dilution 2 and 1/10 for dilution 4~~;~~ for 8 days dialysed sol in the case of of concentrated sol (XII (b)) the value of hydration factor is reduced to about 3/5, 1/8 and 3/50 for dilution 2, 4 and 8 respectively for 0 day dialysed sol, to about 1/5, 3/100 and 1/200 for dilution 2, 4 and 8 respectively for 4 days dialysed sol and to about 2/5, 1/7 and 1/14 for dilution, 2, 4 and 8 respectively for 8 days dialysed sol. From this it would appear that the particles of colloidal thorium hydroxide and vanadium pentoxide are not hydrated to the same extent as in a typical emulsoid sol although for the V_2O_5 sol particularly the viscosity is markedly higher than that of typical hydrophobic sols. If the analogy of true solutions is applied to colloidal solutions, hydration of the particles should decrease with an increase in the concentration of the colloid and other things remaining the same, the viscosity should decrease with an increase in the concentration of the colloid; the viscosity for both $Th(OH)_4$ and V_2O_5 has however increased with the concentration.

Dilution of the colloid may give rise to a decrease in the size of the colloidal particles, thus decreasing to a certain extent their active volume and the viscosity should decrease due to this effect.

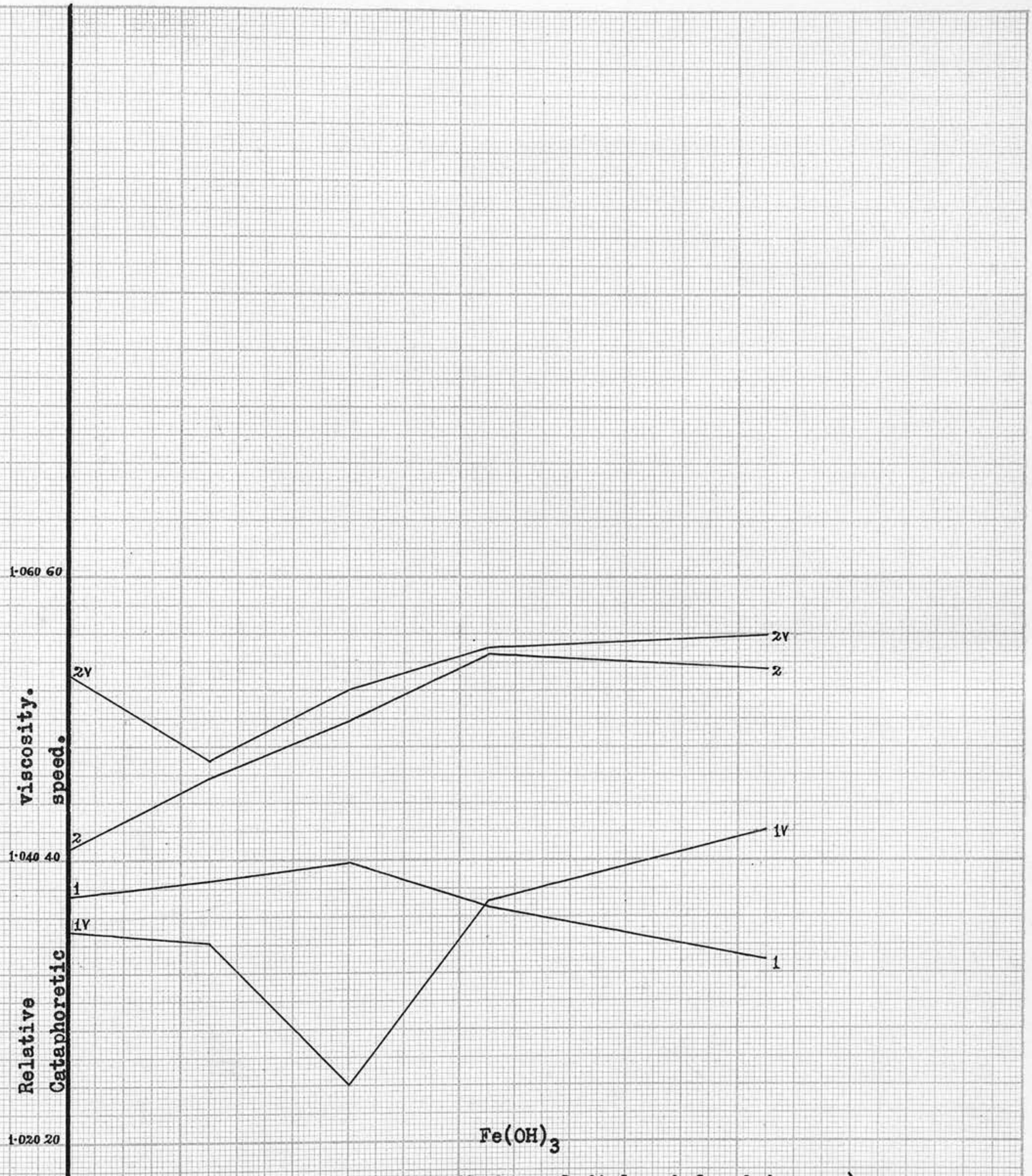
It is thus clear that the viscosity changes on dilution should also be considered from the point of view of the factors mentioned above as during dialysis, for the viscosity changes observed represent the net effect of the various factors.

SECTION III - Changes in sols dialysed for different periods in presence of small increasing concentrations of electrolytes.

(a) Charge:

It will appear from the results given in Tables XIII to XVIII that in general on adding small increasing amounts of the electrolytes containing univalent coagulating ions the charge first increases and then decreases (also see Figs. 7 to 9 and 16 and 17) except in the case of arsenious sulphide where in one case there is no initial rise in cat. speed with HCl and KCl (Table XVI(b)) and gold sol where in one case there is no initial rise in cat.speed with KCl and K_2SO_4 (Table XVII(b)). When small increasing amounts of electrolytes containing bivalent coagulating ions are added, the cat.speed however does not show any initial rise but continuously decreases (also see Fig. 18) except in the case of V_2O_5 (Table XVIII(a_2) also see Fig. 19) where the cat.speed has shown an intermediate rise.

As mentioned before the initial increase in cat. speed on adding small increasing amounts of electrolytes with univalent coagulating ions is due to preferential adsorption of the similarly charged ions as a result of chemical affinity, while the decrease at higher concentrations of the electrolytes is due to preferential adsorption of the oppositely charged ions (electrical adsorption). With electrolytes having bivalent coagulating ions the initial rise in cat.speed does not occur as the preferential



1. Cat.speed curve with HCl for sol dialysed for 6 days.)
2. Cat.speed curve with HCl for sol dialysed for 21 days.) Table
1v. Viscosity curve with HCl for sol dialysed for 6 days.) XIII(c).
2 v. Viscosity curve with HCl for sol dialysed for 21 days.)

FIG-16

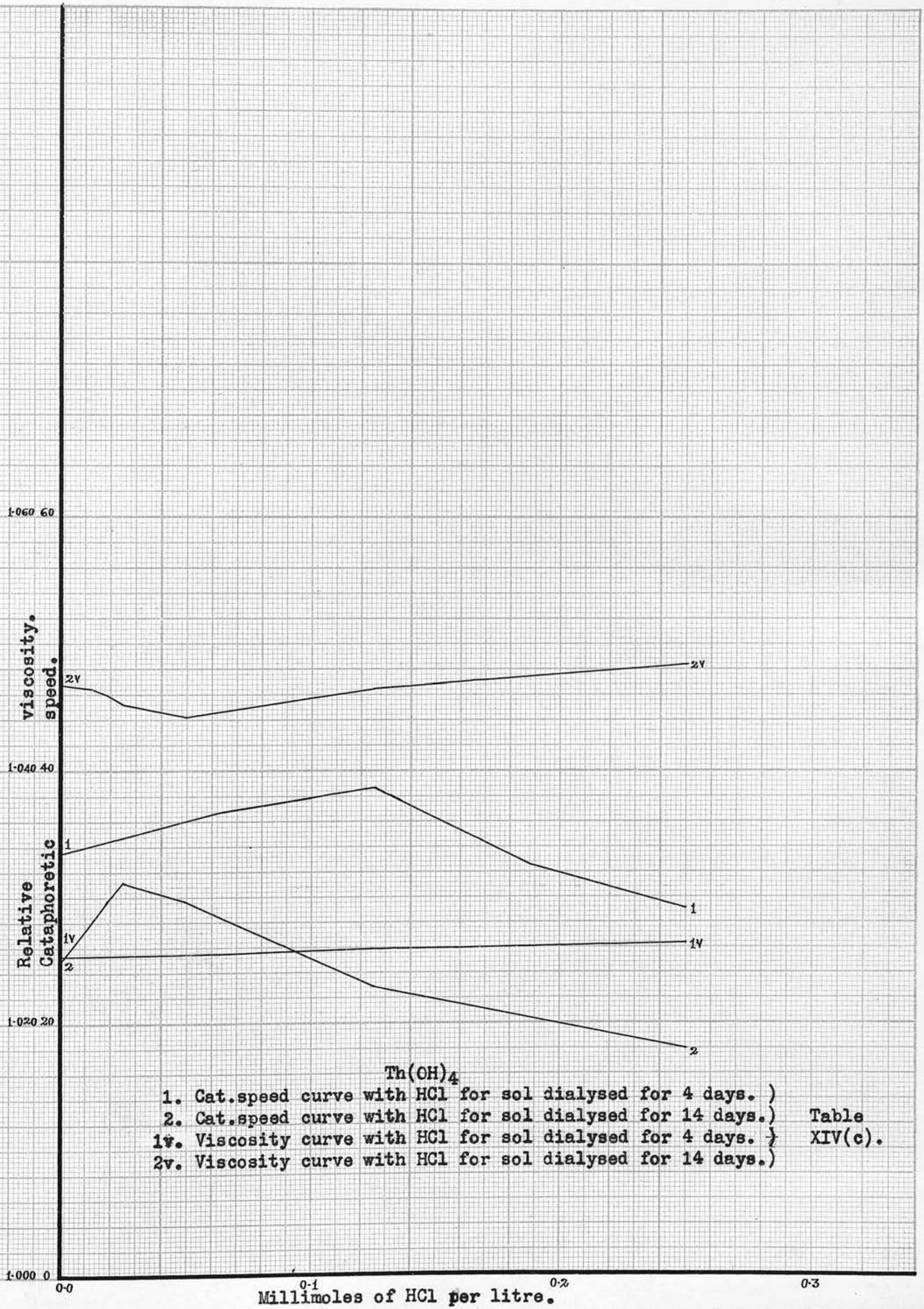

1·060 60
1·040 40
1·020 20
1·000 0
Relative viscosity.
Cataphoretic speed.
2v
1
1v
2
0·0
0·1
0·2
0·3
Millimoles of HCl per litre.
Th(OH)4
1. Cat.speed curve with HCl for sol dialysed for 4 days.)
2. Cat.speed curve with HCl for sol dialysed for 14 days.)
1v. Viscosity curve with HCl for sol dialysed for 4 days. }
2v. Viscosity curve with HCl for sol dialysed for 14 days.)
Table XIV(c).

FIG-17

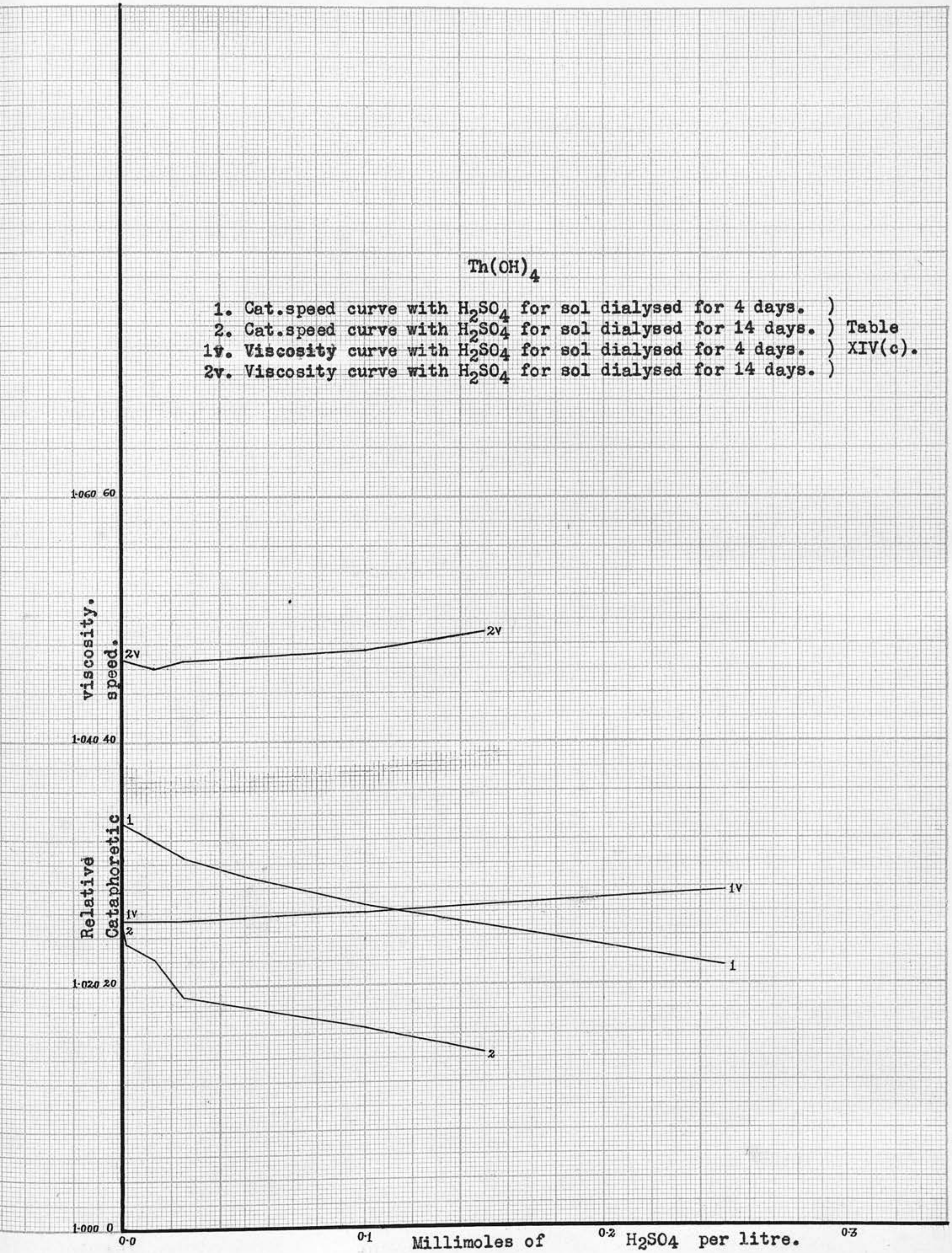

Th(OH)4
1. Cat.speed curve with H2SO4 for sol dialysed for 4 days.)
2. Cat.speed curve with H2SO4 for sol dialysed for 14 days.) Table
1v. Viscosity curve with H2SO4 for sol dialysed for 4 days.) XIV(c).
2v. Viscosity curve with H2SO4 for sol dialysed for 14 days.)
Relative viscosity.
Cataphoretic speed.
1·060 60
1·040 40
1·020 20
1·000 0
0·0
0·1
0·2
0·3
Millimoles of H2SO4 per litre.
2V
2V
1
1V
2
1V
1
2

FIG-18

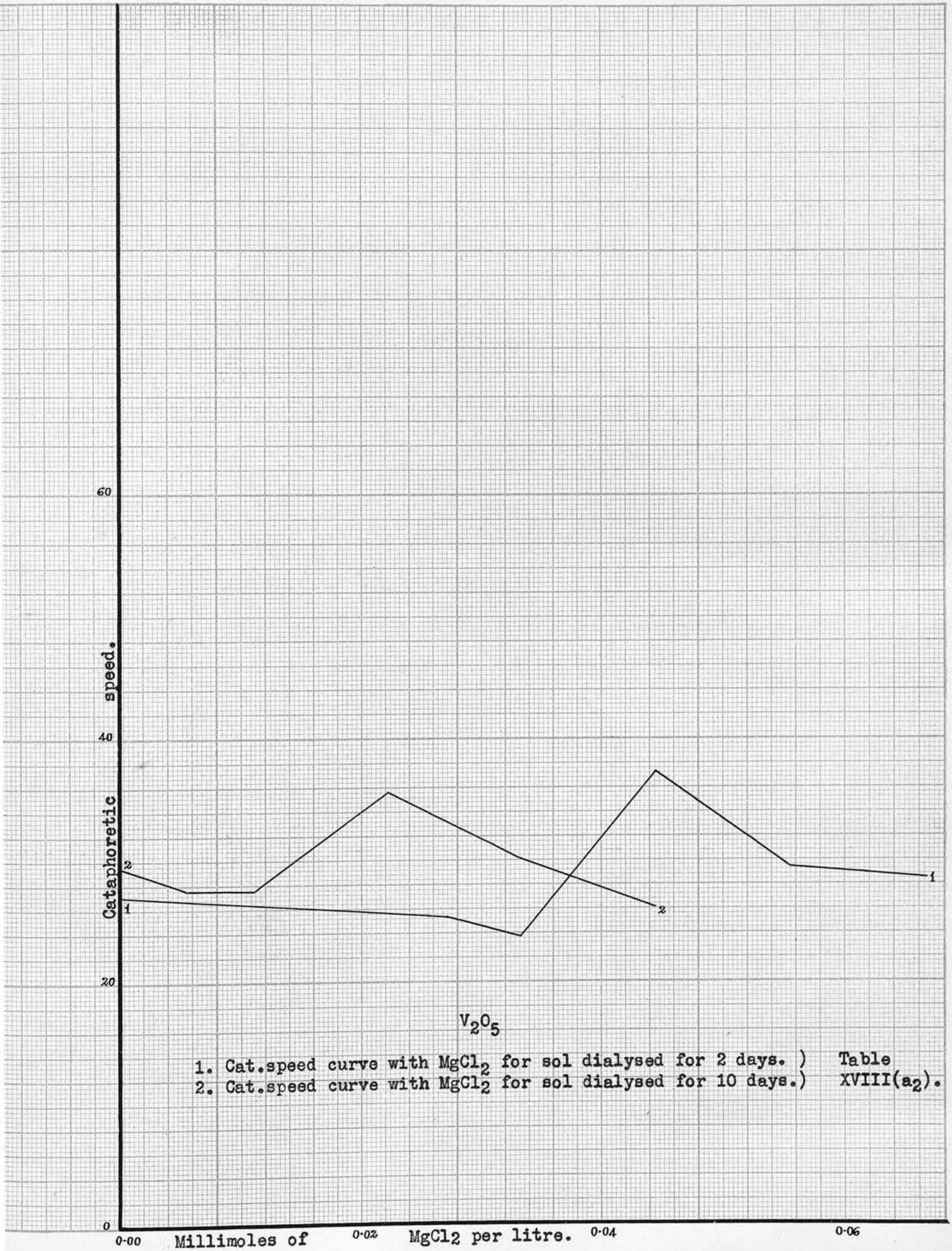

60
40
20
0
Cataphoretic speed.
0·00
0·02
0·04
0·06
Millimoles of MgCl2 per litre.
1
2
V_2O_5
1. Cat.speed curve with $MgCl_2$ for sol dialysed for 2 days.) Table
2. Cat.speed curve with $MgCl_2$ for sol dialysed for 10 days.) XVIII(a_2).

FIG-19

preferential adsorption of the similarly charged ions is not allowed to be noticed due to strong adsorption of the bivalent coagulating ions.

The absence of initial rise in one case in the cat. speed of As_2S_3 with HCl and KCl is due to the fact that that sample of the sol was dialysed for 31 days and as such there was considerable decomposition as mentioned before. In the case of gold sol the absence of initial rise in the cat.speed with KCl and K_2SO_4 is with sample dialysed for 23 days; the causes of this peculiar behaviour are not quite clear; it may be mentioned that at still smaller concentrations of the electrolytes than those tried, there might have been an initial rise in cat.speed. The absence of initial rise in cat.speed in the case of $Fe(OH)_3$ sol with KCl, NaCl and LiCl mentioned by Mukherjee, Chaudhury and Ghosh[9] is not understood. There is no reason why in the case of $Fe(OH)_3$ alone the electrical adsorption of the anions even in low concentrations should be so marked as not to allow the influence of the preferential adsorption of the similarly charged ions to be noticed as in other cases. It is likely that if still smaller amounts of the electrolytes mentioned above were used by them, the initial rise in cat.speed would have been noticed.

The intermediate rise in cat.speed with $BaCl_2$ and $MgCl_2$ and $MgSO_4$ in the case of V_2O_5 sol (Table XVIII(a_2) and see also Fig. 19) may be due to the following causes:-

As with other sols, here also, the cat.speed has first decreased in the presence of these electrolytes there-

thereby showing that the preferential adsorption of the similarly charged ions is not allowed to be noticed when there are strongly adsorbable bivalent coagulating ions. In the present case the peptising agent is the vanadic acid. This acid in the intermicellary liquid will also form insoluble salts when $BaCl_2$, $MgCl_2$ and $MgSO_4$ are added[25] to the sol. Thus on adding small increasing amounts of these electrolytes the acidity of the sol will increase due to the presence of HCl or H_2SO_4 formed as a result of double decomposition. From Table XVIII(b) it will be seen that the cat.speed of V_2O_5 shows an initial rise in the presence of HCl and H_2SO_4. One should therefore naturally expect that after the initial decrease in cat.speed on addition of $BaCl_2$, $MgCl_2$, $MgSO_4$, there should be an increase in the same within a certain range of concentration as the amount of HCl and H_2SO_4 in the sol increases. This increase in acidity will occur only as long as there is dissolved vanadic acid in the intermicellary liquid. The final decrease in cat.speed is again due to preferential adosorption of the oppositely charged ions.

From the results it would also be clear that generally the initial rise in cat.speed due to preferential adosorption of the similarly charged ions is greater for $Mg^{\cdot\cdot}$ ions than $K^{\cdot}$ ions in the case of positively charged sols and for Cl' ions than SO_4'' ions in the case of negatively charged sols. This is due to the fact that a bivalent similarly charged ion will be adsorbed more than a univalent similarly charged ion. $H^{\cdot}$ ions in the case of positively charged

charged sols and OH' ions in the case of negatively charged sols give a larger initial rise in the cat.speed than $K^{\cdot}$ and Cl' ions respectively because of their marked adsorption which has been so well recognised.

From the results given in all the Tables (b) in Section III of results it will appear that in all the cases a smaller equivalent amount of electrolyte is necessary for coagulation when the coagulating ions are bivalent than when they are univalent. This is to be expected in view of greater adsorbability of bivalent than univalent coagulating ions. Mukherjee, Chaudhury and Ghosh[9] have stated that although the cat.speed at which coagulation begins may vary widely, the coagulating concentration of an electrolyte for different preparations of the same colloid does not vary in an equal degree. The results given here however do not support their conclusion. In fact the conclusion of Mukherjee and coworkers is not correct in view of their own statements in so many of their papers that different coagulating and similarly charged ions have different adsorbability even if they have the same valency and that bivalent ions are more strongly adsorbable than univalent ions.

It will appear from the Tables (b) of Section III that the same sol does not coagulate at the same value of cat.speed with all the electrolytes. The range within which coagulation occurs for different sols with various electrolytes tried here varies from about 5 in the case of $Th(OH)_4$ and prussian blue to about 20 in the case of As_2S_3 sol. Further in a large number of cases in the case of of V_2O_5 sol (Table XVIII(b)) the coagulation begins at a value of cat.speed which is higher than the initial cat. speed of the sol.

The widespread opinion, first put forward by Hardy[47] that coagulation begins only when colloidal particles are completely discharged and the iso-electric point has been reached, has been found to be erroneous by Powis[48]. According to Powis coagulation begins as soon as the electro-kinetic potential or the electric charge falls below a certain value. The value of the electro-kinetic~~al~~ potential at which coagulation first begins has been termed by Freundlich the "first critical potential" and is said to have the same characteristic value for any particular sol when coagulated with salts having coagulating ions of different valencies. The experiments of Burton[49], Kruyt, Roodvoets and van der Willigen[50] and Kruyt and van der Willigen[51] have shown that their results support Powis' theory of critical potential. From the results given here however it would appear that there is no definite characteristic critical potential for each sol with different electrolytes.

Mukherjee and coworkers[9] have expressed doubts about the existence of critical potential characteristic of coagulation of a colloid by electrolytes. They have mentioned that the phenomenon of coagulation should be interpreted in terms of several factors including the electric charge or potential, the redistribution of ions resulting from aggregation, the entertainment of ions of opposite sign during the process of aggregation, changes in the ionic

ionic composition of the surface and of the solution, and perhaps of the cohesive forces responsible for a stable aggregation. From the present results it is also clear that one can not be dogmatic about the existence of critical potential for a colloid of the same substance for different electrolytes, or for the same electrolyte with diferent preparations of the same colloidal substance. One has certainly to consider the effect of different factors during coagulation as mentioned by Mukherjee.

According to the chemical view of the origin of charge an increase in the charge with increasing electrolytic concentration is to be interpreted as an indication of the formation of complex ions by the interaction between groups on the surface and ions of the same charge in the solution. But the various changes in the presence of electrolytes noticed in these experiments can not be satisfactorily explained by the chemical view.

(b) Viscosity.

It will be seen from Table XIII(c) that on adding small increasing amounts of HCl (also see Fig.16) and KCl to $Fe(OH)_3$ sol the viscosity first decreases and then increases. The cat.speed in these cases has first increased and then decreased, but the maximum in the cat.speed and the minimum in the viscosity have not occurred at the same concentration of the electrolyte except for short period dialysed sol with HCl.

For $Th(OH)_4$ sol with HCl (Table XIV(c)) viscosity continuously increases for short period dialysed sol, while

while it first decreases and then increases for long period dialysed sol (Fig. 17); the cat.speed in both the cases has first increased and then decreased. The minimum in viscosity and the maximum in charge with HCl for long period dialysed sol has not occurred at the same concentration of the electrolyte.

When H_2SO_4 is added to $Th(OH)_4$ sol (Table XIV(c) and Fig.18) the viscosity continuously increases for short period dialysed sol and first decreases and then increases for long period dialysed sol. The cat.speed in both the cases has continuously decreased.

The electroviscous effect of Smoluchowski[6] can not explain changes in viscosity for in that case the viscosity should have increased when charge increased and also decreased with the charge. The view of Dhar[7] is also not supported because in that case the maximum in cat.speed and the minimum in viscosity should have occurred at the same concentration in all the cases; further it is found that with H_2SO_4 for long period dialysed sol the viscosity has first decreased and then increased although the charge has continuously decreased.

The viscosity should have continuously increased as a result of increase in the concentration of the electrolyte in the sol except with KCl where there is an initial decrease in viscosity[34].

The structure of the particles continuously changes on addition of more and more of the electrolyte, the resulting increase in the effective volume also increasing the viscosity

viscosity to a certain extent.

The effect of the electrolytes on the hydration will to a certain extent be to decrease it and the viscosity should decrease as a result of it.

From the results it is clear that neither the view of Smoluchowski nor of Dhar can individually explain the changes in charge and viscosity under different conditions. One has also to consider the other factors mentioned above. It is also unsafe to draw conclusions about changes in charge of colloidal particles from viscosity measurements just as in the case of flocculation values; for although in some cases they may afford a correct criterion they are likely to lead to erroneous conclusions in other cases.

SECTION IV. - Changes in sols dialysed for different periods on ageing.

(a) Charge.

It will appear from Tables XIX to XXII (Fig.20 to 23) that the cat.speed gradually decreases on ageing for prussian blue, arsenious sulphide, gold and V_2O_5 sols, similar changes being noticed for both short and long period dialysed sols. The decrease in cat.speed on ageing is comparatively more marked with As_2S_3 than other sols. Freundlich[52] has stated that many sols show immediately after their preparation various comparatively rapid changes in their properties, while after sometime a less changeable stationary state is reached. From the present results it would appear that gradual changes on ageing continue even for periods of two months or more.

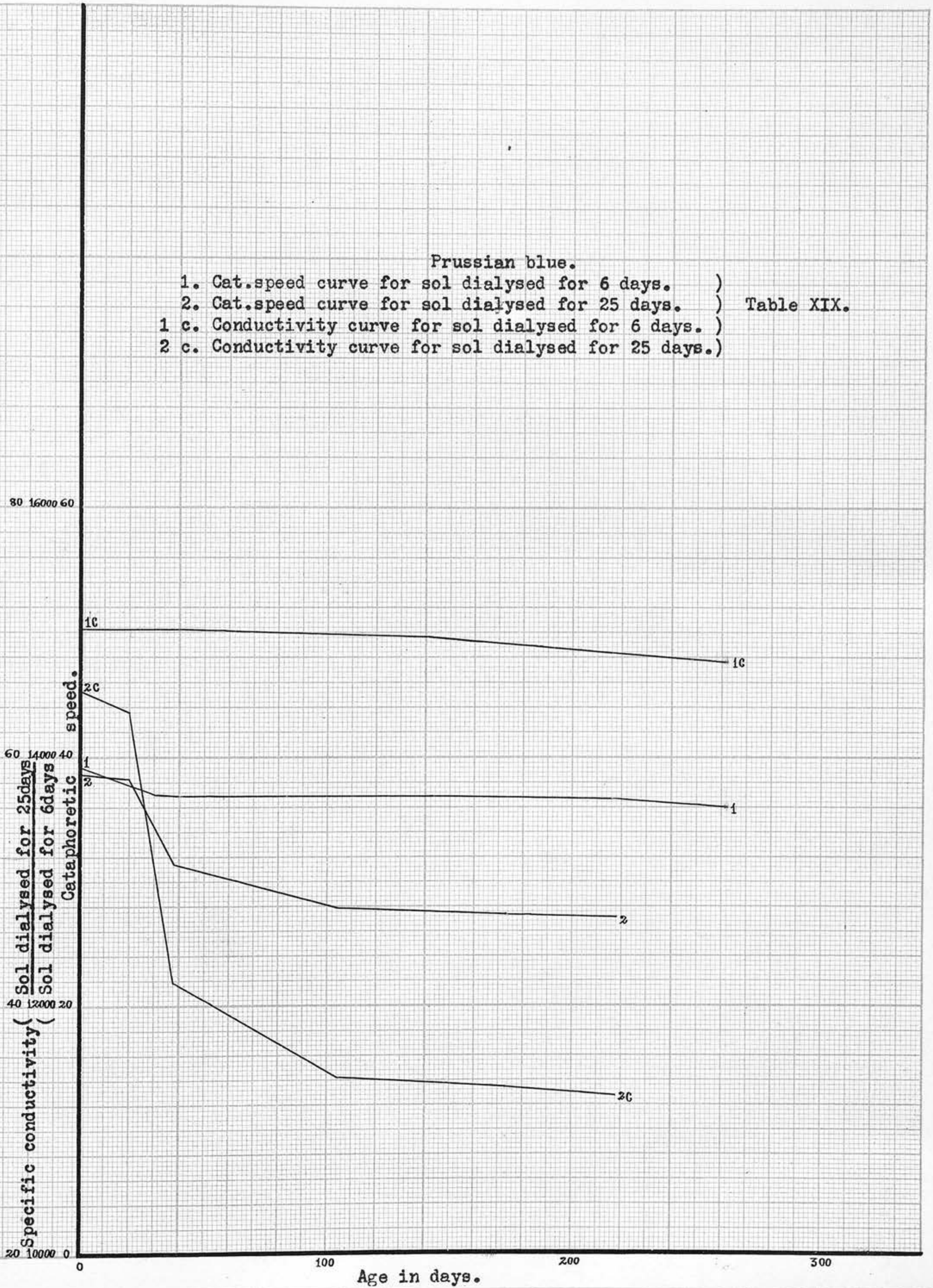

Prussian blue.
1. Cat.speed curve for sol dialysed for 6 days.)
2. Cat.speed curve for sol dialysed for 25 days.) Table XIX.
1 c. Conductivity curve for sol dialysed for 6 days.)
2 c. Conductivity curve for sol dialysed for 25 days.)
80 16000 60
60 14000 40
40 12000 20
20 10000 0
Specific conductivity (Sol dialysed for 25days / (Sol dialysed for 6days
Cataphoretic speed.
1C
2C
1
2
0
100
200
300
Age in days.

FIG 20

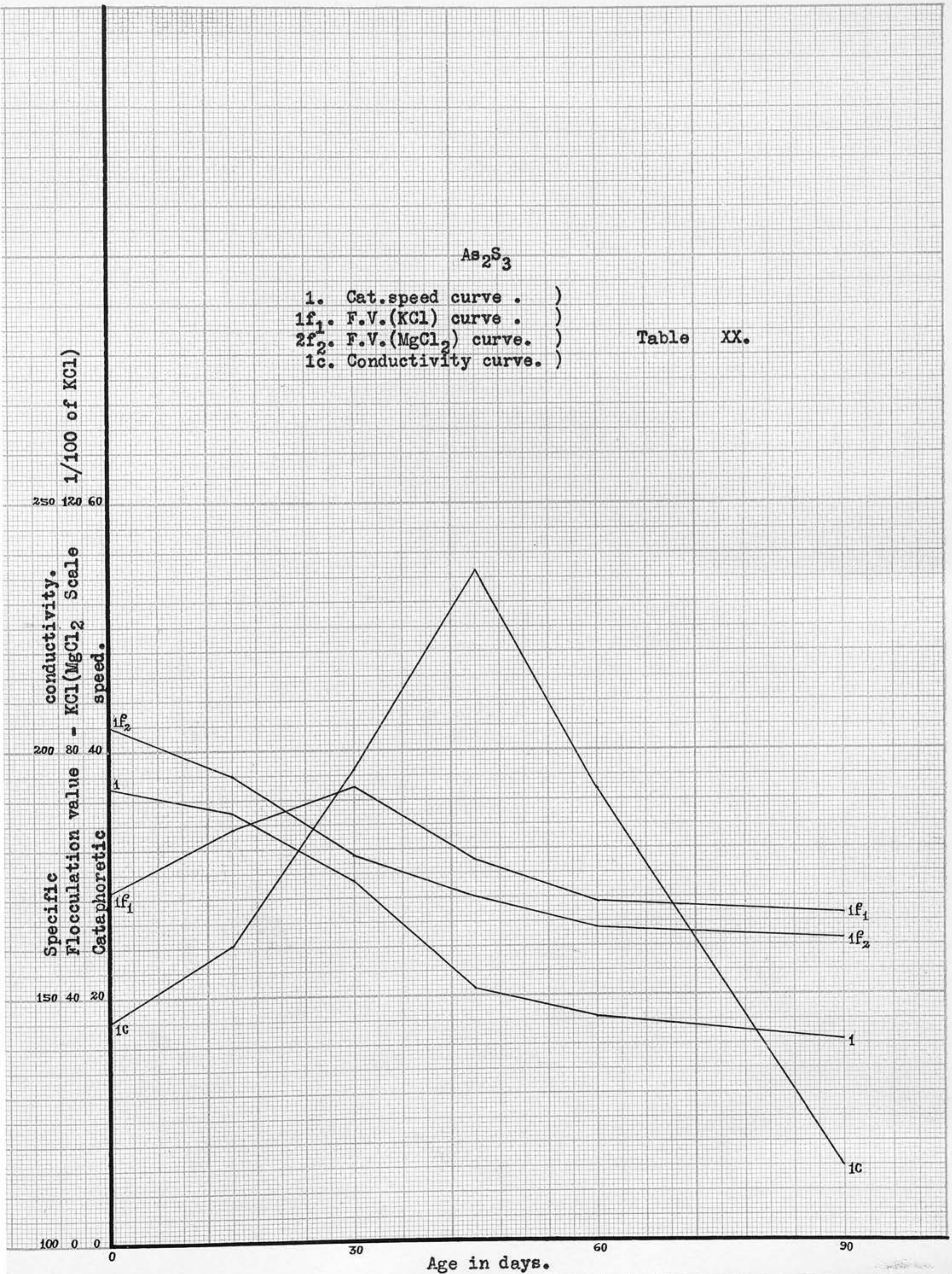

As_2S_3
1. Cat.speed curve.)
$1f_1$. F.V.(KCl) curve.)
$2f_2$. F.V.($MgCl_2$) curve.)
1c. Conductivity curve.)
Table XX.
Specific conductivity. 1/100 of KCl)
Flocculation value - KCl($MgCl_2$ Scale
Cataphoretic speed.
250 120 60
200 80 40
150 40 20
100 0 0
0
30
60
90
Age in days.
$1f_2$
1
$1f_1$
1C
$1f_1$
$1f_2$
1
1C

FIG-21

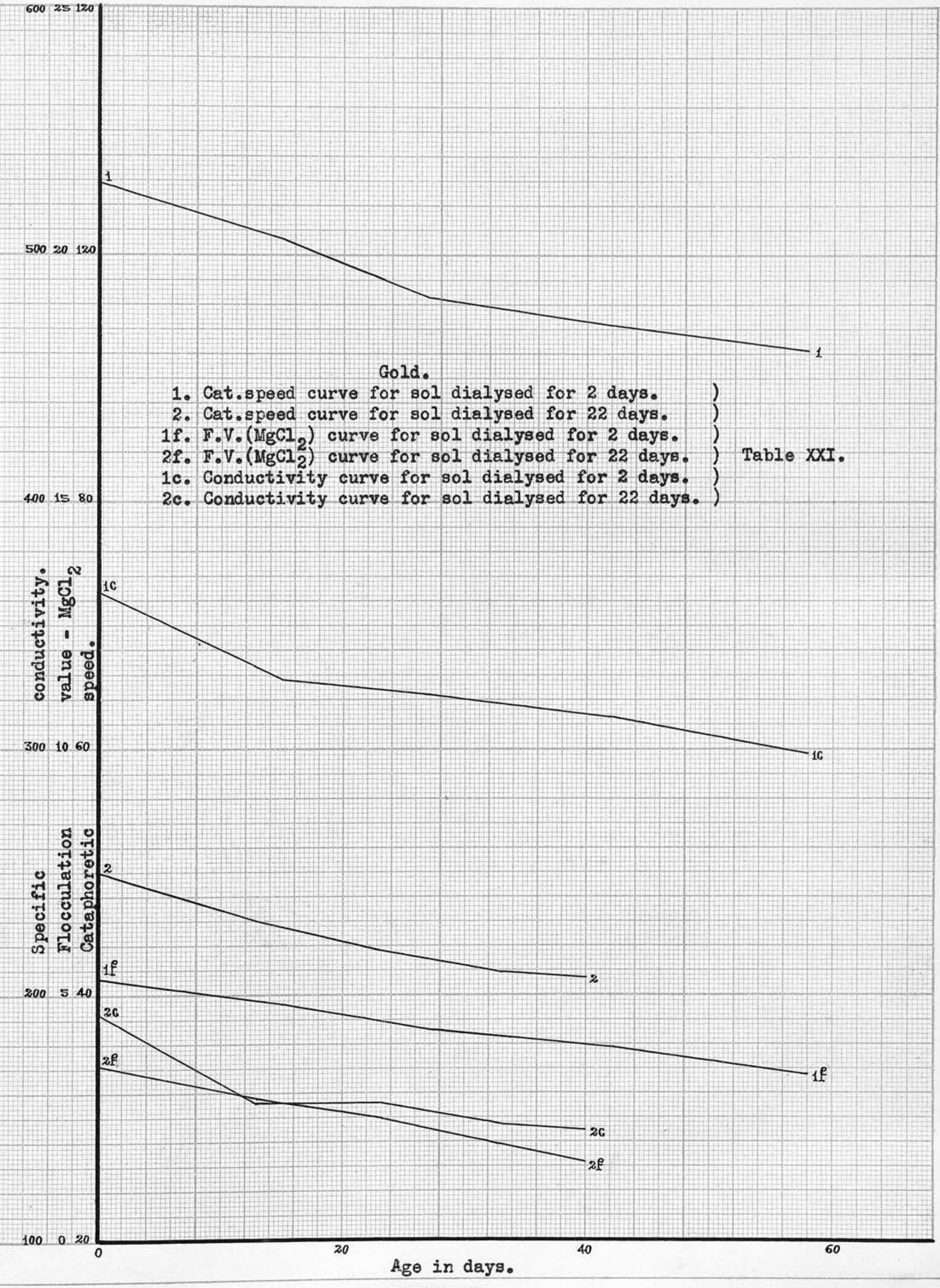

Gold.
1. Cat.speed curve for sol dialysed for 2 days.)
2. Cat.speed curve for sol dialysed for 22 days.)
1f. F.V.($MgCl_2$) curve for sol dialysed for 2 days.)
2f. F.V.($MgCl_2$) curve for sol dialysed for 22 days.) Table XXI.
1c. Conductivity curve for sol dialysed for 2 days.)
2c. Conductivity curve for sol dialysed for 22 days.)
Specific conductivity.
Flocculation value - $MgCl_2$
Cataphoretic speed.
600 25 120
500 20 120
400 15 80
300 10 60
200 5 40
100 0 20
0
20
40
60
Age in days.
1
1
1C
1C
2
2
1f
1f
2C
2C
2f
2f

FIG-22

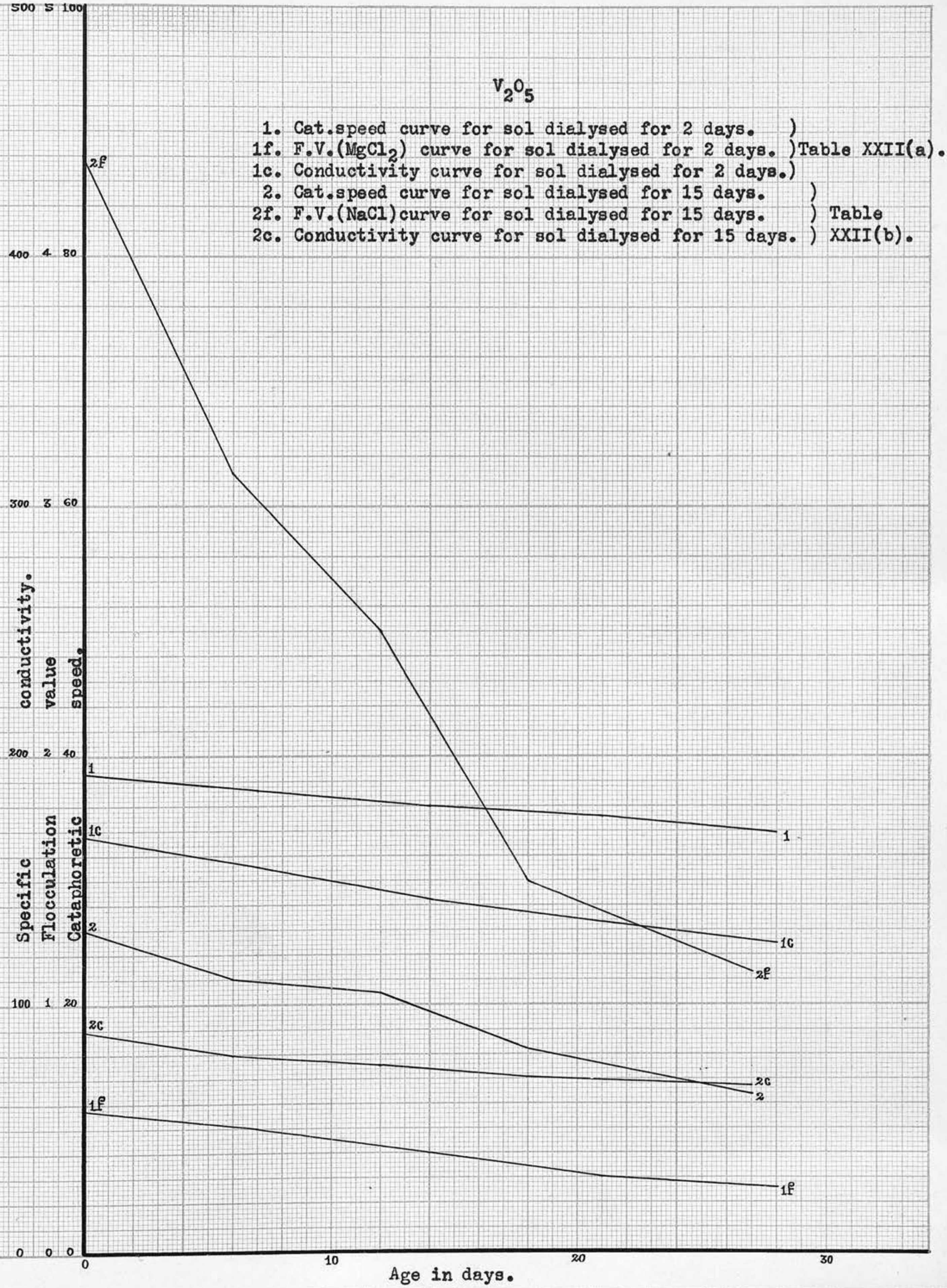

V_2O_5
1. Cat.speed curve for sol dialysed for 2 days.)
1f. F.V.($MgCl_2$) curve for sol dialysed for 2 days.)Table XXII(a).
1c. Conductivity curve for sol dialysed for 2 days.)
2. Cat.speed curve for sol dialysed for 15 days.)
2f. F.V.(NaCl)curve for sol dialysed for 15 days.) Table
2c. Conductivity curve for sol dialysed for 15 days.) XXII(b).
Specific conductivity.
Flocculation value
Cataphoretic speed.
500 5 100
400 4 80
300 3 60
200 2 40
100 1 20
0 0 0
0
10
20
30
Age in days.
2f
1
1c
2
2c
1f

FIG-23

On ageing there is generally a tendency for aggregation of the particles. The amount of electrolyte in the sol having remained constant during ageing, this aggregation should under certain circumstances show an increase in cat. speed (Mukherjee, Choudhury and Bhabak[16]). In the present instance a rise in the cat.speed on ageing has however not been noticed. This is probably due to the fact that the colloidal particles on standing have adsorbed oppositely charged ions, thus decreasing the charge; the aggregation of particles has resulted in a redistribution of ions in the double layer in such a manner that the net effect has been a decrease in the surface density of charge.

In the case of As_2S_3 (Table XX) on ageing the composition of sol has changed as a result of hydrolysis as during dialysis. The continuous decrease in the amount of total sulphur and total arsenic is due to the fact that in all the cases before estimations were made, the deposit formed in the sol was removed by filtration. The continuous increase in the amount of free arsenious acid on ageing will incline one to the view that it might have to do largely with continuous decrease in cat.speed as during dialysis. The larger increase in cat.speed in the case of As_2S_3 than the other sols is also probably due to changes in composition as a result of hydrolysis which are absent in other sols.

(b) Stability.

It will appear from Table XX (also see Fig.21) that in the case of As_2S_3 sol the stability with reference to to KCl has first increased and then decreased, while that with reference to $MgCl_2$ has continuously decreased. Freundlich and Schucht[53] also observed an appreciable decrease with time in the stability of As_2S_3 with reference to $Al_2(SO_4)_3$. Thus the stability and charge go hand in hand in the case of multivalent coagulating ions as during dialysis. The causes of stability and charge not going hand in hand with reference to KCl might be somewhat similar to those mentioned in Section I.

In the case of gold (Table XXI, Fig. 22) and V_2O_5 (Table XXII, Fig. 23) sols the stability on ageing has decreased as the cat.speed, thus showing direct relation between charge and stability.

The decrease in stability besides being as a result of decrease in cat.speed, can also be due to aggregation on ageing as during dialysis.

According to Dhar and Chakravarti[54] hydrophobic sols decrease in stability on ageing and the present results are in line with their observation except in the case of stability of As_2S_3 with reference to KCl up to a certain period.

(c) <u>Conductivity</u>.

The specific conductivity on ageing of prussian blue, gold and V_2O_5 (Tables XIX, XXI and XXII, Figs. 20,22 and 23 respectively)has also generally gradually decreased as the cat.speed. On ageing the number of colloid particles per unit volume will decrease as a result of aggregation and the conductivity would decrease due to this effect. Similarly the adsorption of ions on the surface of particles

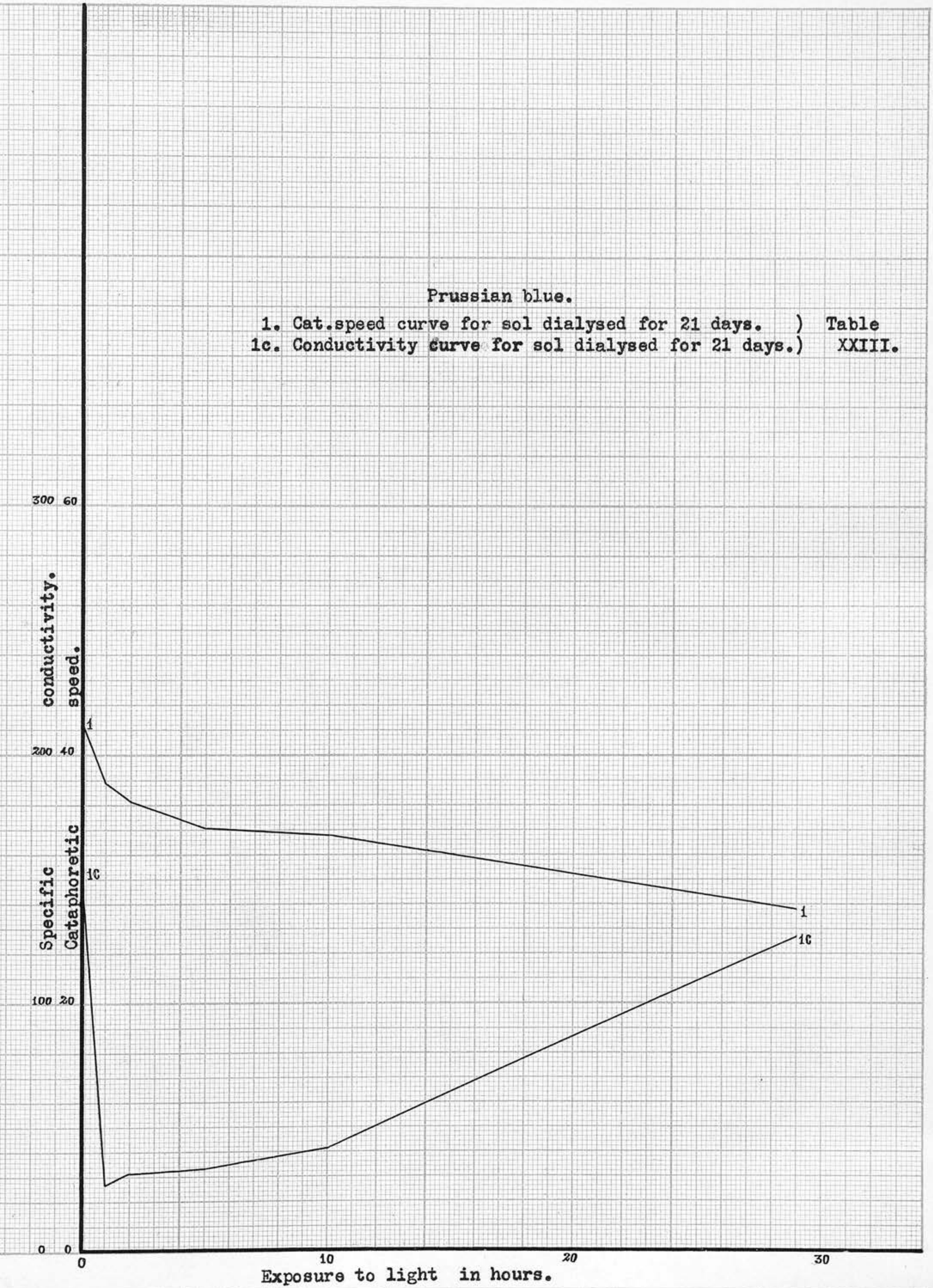
particles will also decrease slightly the amount of electrolyte in the intermicellary liquid and hence the conductivity. The decrease in the cat.speed will also slightly contribute to the decrease in conductivity. The influence of the first factor viz. the aggregation will probably be more predominant than that of the other two i.e. adsorption of ions on the surface and decrease of cat.speed.

In the case of As_2S_3 (Table XX, Fig.21) the conductivity has first increased and then decreased. If the conductivity changes are wholly due to changes in the amount of As_2O_3 in the sol, the conductivity should have continuously increased with an increase in the amount of As_2O_3. Similarly the changes in charge and aggregation also can not satisfactorily explain all the changes in conductivity. As mentioned before the changes in composition of the sol on ageing introduce considerable complications and make the As_2S_3 sol show some peculiar behaviours when compared with the other sols.

SECTION V. - Changes in sols dialysed for different periods on exposure to sunlight (also artificial light in the case of arsenious sulphide sol).

(a) Charge.

It will appear from the results given in Tables XXIII, XXV and XXVI (Figs. -24, 26 and 27 respectively) for prussian blue, gold and V_2O_5 sols respectively that on exposing both the short period and long period dialysed sol the cat.speed gradually decreases. As mentioned by



Prussian blue.

1. Cat.speed curve for sol dialysed for 21 days.) Table
1c. Conductivity curve for sol dialysed for 21 days.) XXIII.

FIG-24

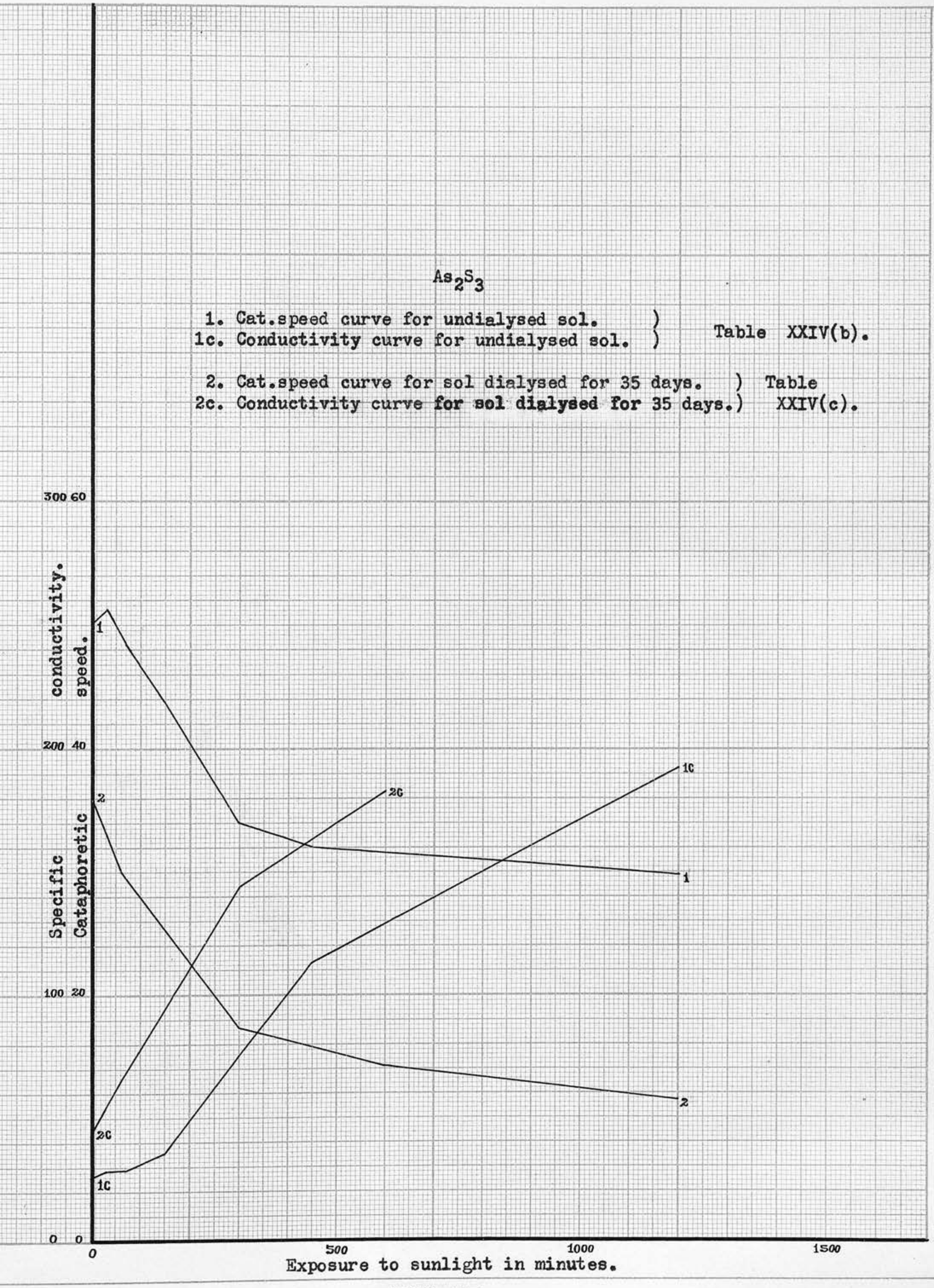

As_2S_3
1. Cat.speed curve for undialysed sol.)
1c. Conductivity curve for undialysed sol.) Table XXIV(b).
2. Cat.speed curve for sol dialysed for 35 days.) Table
2c. Conductivity curve for sol dialysed for 35 days.) XXIV(c).
Specific conductivity.
Cataphoretic speed.
300 60
200 40
100 20
0 0
0
500
1000
1500
Exposure to sunlight in minutes.
1
1C
2
2C
1
1C
2
2C

FIG-25

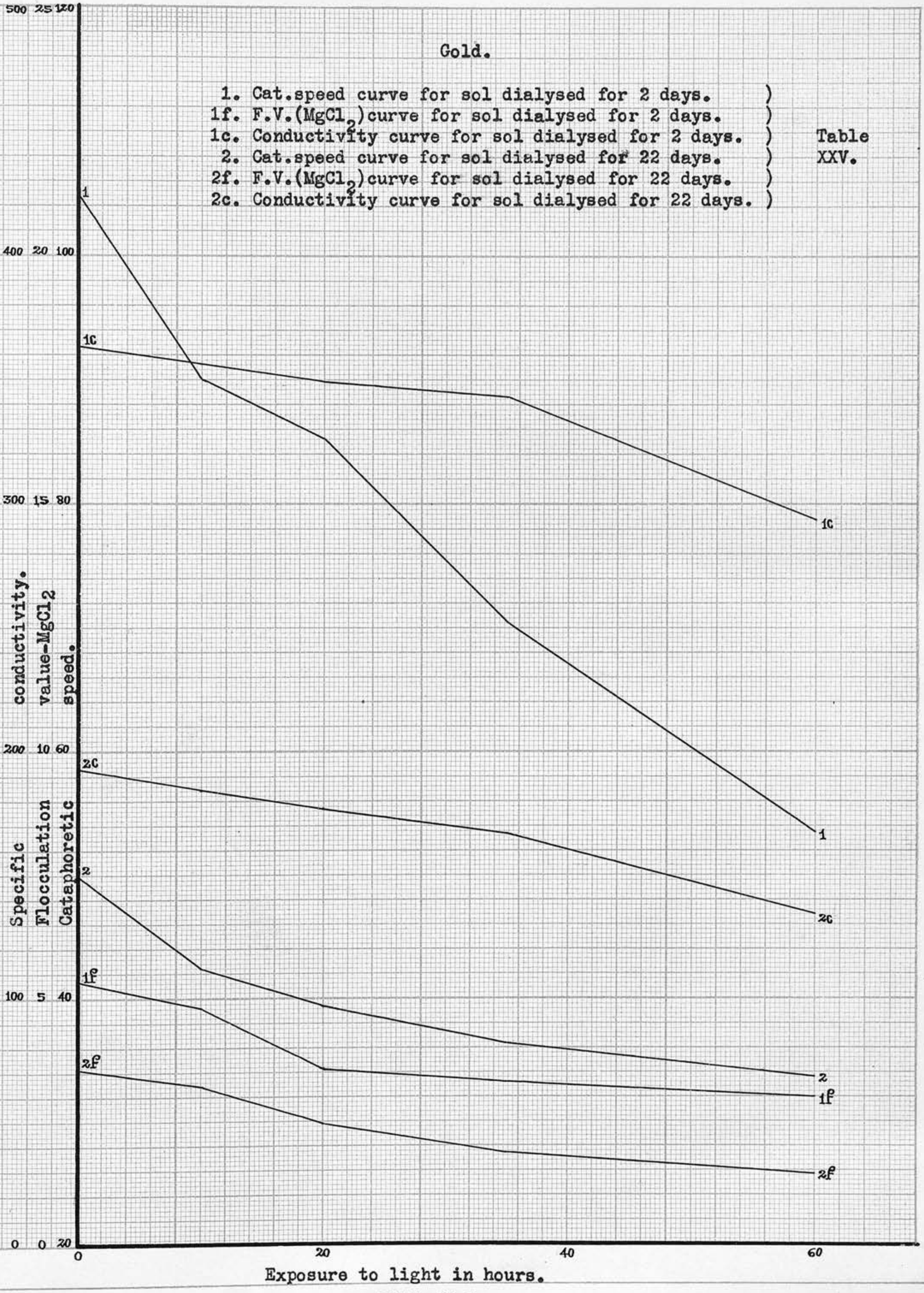

Gold.
1. Cat.speed curve for sol dialysed for 2 days.)
1f. F.V.($MgCl_2$)curve for sol dialysed for 2 days.)
1c. Conductivity curve for sol dialysed for 2 days.) Table XXV.
2. Cat.speed curve for sol dialysed for 22 days.)
2f. F.V.($MgCl_2$)curve for sol dialysed for 22 days.)
2c. Conductivity curve for sol dialysed for 22 days.)
Specific conductivity.
Flocculation value-$MgCl_2$
Cataphoretic speed.
500 25 120
400 20 100
300 15 80
200 10 60
100 5 40
0 0 20
0
20
40
60
Exposure to light in hours.
1
1C
2C
2
1f
2f

FIG-26

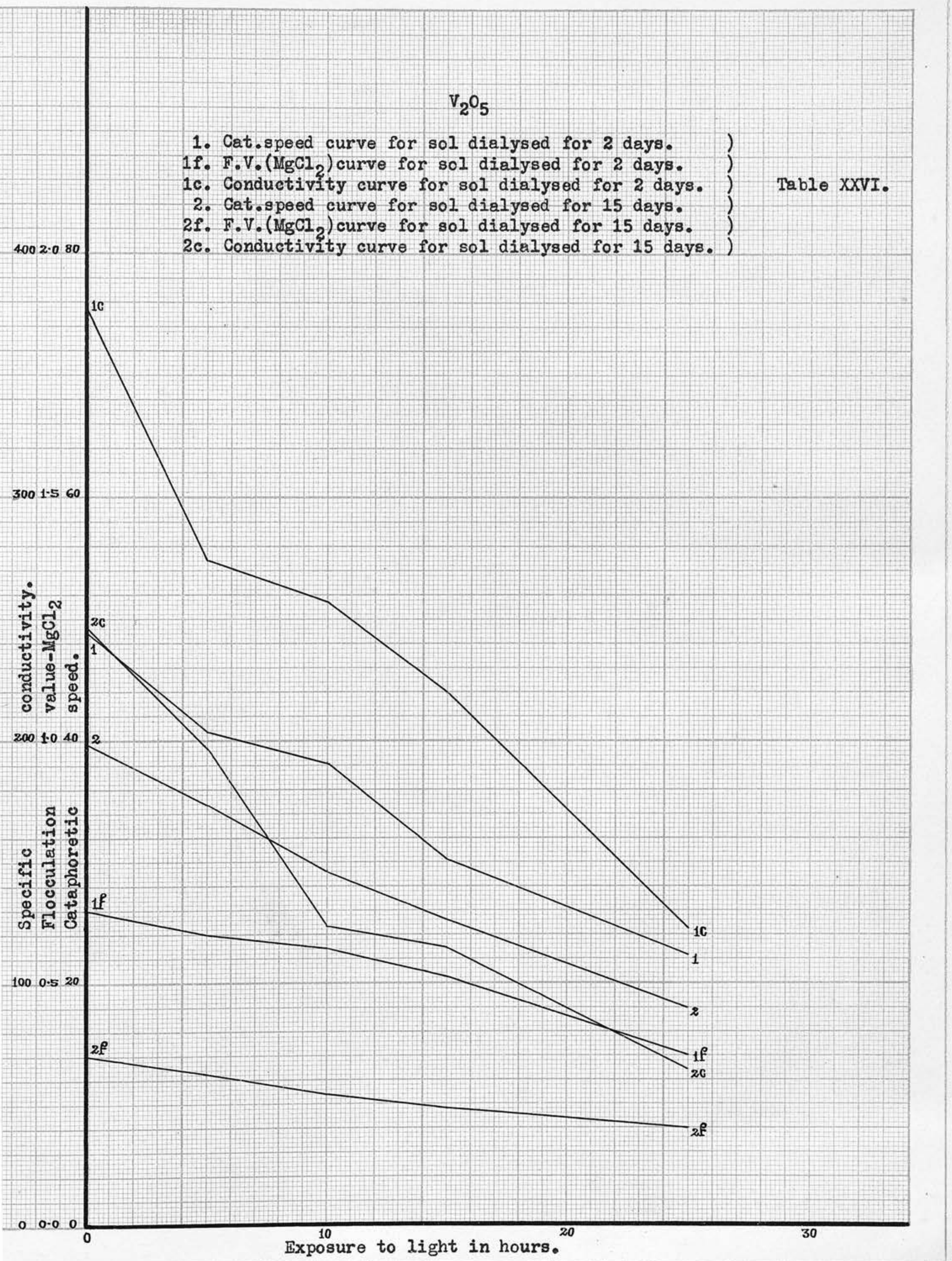

V_2O_5
1. Cat.speed curve for sol dialysed for 2 days.)
1f. F.V.($MgCl_2$)curve for sol dialysed for 2 days.)
1c. Conductivity curve for sol dialysed for 2 days.)
2. Cat.speed curve for sol dialysed for 15 days.)
2f. F.V.($MgCl_2$)curve for sol dialysed for 15 days.)
2c. Conductivity curve for sol dialysed for 15 days.)
Table XXVI.
Specific conductivity.
Flocculation value-$MgCl_2$
Cataphoretic speed.
400 2·0 80
300 1·5 60
200 1·0 40
100 0·5 20
0 0·0 0
0
10
20
30
Exposure to light in hours.
1c
2c
1
2
1f
2f
1c
1
2
1f
2c
2f

FIG-27

by Freundlich[55] two kinds of processes must be distinguished regarding action of light on hydrophobic sols; first a simple coagulation in which the particles associate under the influence of light and settle on account of gravity, and second a photophoresis in which the particles move under the influence of light in a certain direction. The process of photophoresis will also give rise to agglomeration of the colloid particles, but while in it agglomeration is localised at points in the sol, in coagulation agglomeration takes place in the whole body of the sol.

The decrease in cat.speed in the above cases is probably due to preferential adsorption of the oppositely charged ions on the surface of the particles from the intermicellary liquid. Even if agglomeration has taken place, it has not been able to show increase in the cat.speed due to marked effect of the preferential adsorption of the oppositely charged ions. In the case of gold sol Nordenson[56] observed that on irradiation of the sol, the number and size of particles undergo a considerable change; he actually found that the degree of dispersion of the particles considerably increases. In the present case if we take it that exposure to sun light might have also increased the degree of dispersion, the cat.speed may decrease due to this effect. As will be seen however from conductivity and stability results, increase in the degree of dispersion of gold particles does not appear to have taken place.

Undialysed As_2S_3 sol when exposed to artificial light (Table XXIV(a)) shows a gradual decrease in cat.speed.

The same is the case with long period dialysed sol exposed to sun light (Table XXIV(c)), but in the case of undialysed sol (Table XXIV(b)) the cat.speed has slightly increased on exposure to sunlight for short periods (Fig.25). Freundlich and Nathansohn[57] have stated that As_2S_3 sol hydrolyses on exposure to light giving rise to As_2O_3 and H_2S; the latter is oxidised giving rise to colloidal sulphur ultimately. In the present case also it will be seen from the tables that the amount of As_2O_3 in the sol continuously increases on exposure to sun light. The decrease in the amount of total As and total S in the sol is due to removal of precipitates from the sol before estimation was made. The decrease in the cat.speed in all the cases is due to increase in the amount of As_2O_3 in the sol as during dialysis and ageing. The initial rise in the cat.speed on exposure to sun light of undialysed sol (Table XXIV(b), Fig. 25) is due to the fact that that sol was in the beginning free from As_2O_3; as mentioned in Section I the cat.speed of undialysed As_2S_3 sol first increases and then decreases on adding small increasing amounts of As_2O_3; the other sols did contain in the beginning some As_2O_3 and hence a further increase in As_2O_3 would only result in a decrease in the cat.speed.

(b) Stability.

It will appear from Table XXIV(a) that the stability of As_2S_3 sol with reference to $MgCl_2$ continuously decreases on exposure as the cat.speed , thus showing direct relation between charge and stability. In the case of the stability with reference to KCl, there is however an initial increase

increase in the same as during ageing.

In the case of colloidal gold (Table XXV, Fig.26) and V_2O_5 (Table XXVI, Fig.27), the stability decreases on exposure as the cat.speed. A decrease in stability on exposure to light of gold sol would show an absence of increase in the degree of dispersion of the colloidal particles, for if dispersion had increased the stability should have increased.

In the case of prussian blue sol, time after which exposure to sun light can coagulate completely sols dialysed for different periods without addition of any electrolytes was also determined (Table XXIII(b)). It will be seen that as the purity of the sol increases i.e. the amount of the electrolytes in the sol decreases, the time after which the sols can coagulate on exposure also increases, sol dialysed for 21 days not coagulating even up to an exposure of 29 hours. These observations show that on exposure agglomeration of particles does result and the sols coagulate even with the electrolyte already present. In the case of pure sol coagulation does not result inspite of agglomeration because the amount of the electrolyte in the sol is negligible. According to Miss Shila Roy and Dhar[58] the prussian blue sol becomes more stable on exposure to light as a result of agglomeration. It is not clear how stability can increase as a result of agglomeration because ordinarily one would expect that the greater the size of the particles the smaller the stability of the sol as a smaller amount of electrolyte would be required to reach a given degree of turbidity when

when the particles are big than when they are relatively small.

(c) Conductivity.

The changes in the sp. conductivity of the prussian blue sol dialysed for 10 days on exposure to light (Table XXIII) are in the same direction as the cat.speed; the decrease in conductivity is mostly due to a decrease in the number of colloid particles per unit volume and to a smaller extent due to removal of ions from the intermicellary liquid to the surface of the particles. In the case of sol dialysed for 21 days (Fig.24) the conductivity has decreased with the cat.speed only during the first one hour of exposure and increased thereafter. The initial decrease in conductivity is due to the same causes as in the case of 10 days dialysed sol. The subsequent increase in the conductivity is perhaps due to desorption of the ions adsorbed on the surface of the particles; it is also likely that the changes in the nature of intermicellary electrolytes as a result of action of light on oxalic acid might be having some influence on the conductivity.

In the case of As_2S_3 sol (Tables XXIV(a), (b) and (c), also see Fig.25) the conductivity has increased regularly on exposure in all the cases. It will appear that the amount of As_2O_3 in the sol also increases on exposure and it is considered that the increase in sp.conductivity is due to increase in the amount of As_2O_3.

In the case of gold (Table XXV, Fig. 26) and V_2O_5 (Table XXVI, Fig. 27) the conductivity decreases on exposure

exposure with the cat.speed. The decrease is due primarily to the decrease in the number of particles per unit volume on exposure on account of aggregation and to a small extent due to removal of ions from the intermicellary liquid on account of their adsorption on the particles.

SUMMARY & CONCLUSIONS.

Simultaneous measurements of various properties of colloidal solutions of $Fe(OH)_3$, $Th(OH)_4$, prussian blue, As_2S_3, gold and V_2O_5 dialysed for different periods have been presented.

SECTION I.

It is found that with the progress of dialysis the cataphoretic speed (cat.speed) first increases,reaches a maximum and then decreases for all the sols except As_2S_3 in which case the cat.speed first decreases, reaches a minimum then increases and reaches a maximum after which it again decreases.

It is observed that As_2S_3 hydrolyses during dialysis. The amount of total S and As in the sol continuously decreases with the progress of dialysis, while that of As_2O_3 first increases, then decreases and remains constant afterwards.

The stability as determined by flocculation values (F.V.) with electrolytes continuously decreases with the progress of dialysis with the electrolytes tried in the case of $Fe(OH)_3$, $Th(OH)_4$, prussian blue and V_2O_5 and goes hand in hand with the cat.speed in the case of gold and As_2S_3

As_2S_3 with reference to $MgCl_2$. The stability of As_2S_3 with reference to KCl first increases and then decreases with the progress of dialysis.

With the progress of dialysis the conductivity decreases in the case of prussian blue, gold and V_2O_5 and first decreases, then increases and again decreases somewhat on further dialysis in the case of As_2S_3.

With the progress of dialysis the viscosity first decreases and reaches a minimum and then increases in the case of $Fe(OH)_3$, prussian blue and V_2O_5 and continuously increases in the case of $Th(OH)_4$. The stage of dialysis at which the minimum in viscosity and the maximum in cat. speed occur is the same for prussian blue and V_2O_5.

SECTION II.

The cat.speed first increases and then decreases on dilution of short period dialysed $Fe(OH)_3$, $Th(OH)_4$ and prussian blue and continuously decreases on dilution of the same sols dialysed for long periods. In the case of gold and V_2O_5 the cat.speed decreases on dilution of both short period and long period dialysed sols, while the variations in the cat.speed of As_2S_3 on dilution are irregular.

The stability decreases on dilution of both short period and long period dialysed $Fe(OH)_3$, $Th(OH)_4$ and prussian blue, while it increases on dilution of As_2S_3, gold and V_2O_5.

The conductivity decreases on dilution of prussian blue, As_2S_3, gold and V_2O_5.

The viscosity on dilution continuously decreases for both short period and long period dialysed $Th(OH)_4$ and

and V_2O_5; it continuously decreases, and first decreases and then increases for short period and long period dialysed prussian blue respectively.

SECTION III.

On adding small increasing amounts of electrolytes having univalent coagulating ions the cat.speed first increases and then decreases for both short period and long period dialysed sols except in one case with As_2S_3 with HCl and KCl and gold sol with KCl and K_2SO_4 where there is no initial rise in cat.speed.

When the added electrolytes contain bivalent coagulating ions there is no initial rise in cat.speed with all the sols dialysed for short and long periods, although in the case of V_2O_5 there is an intermediate rise in cat. speed in the presence of $BaCl_2$, $MgCl_2$ and $MgSO_4$.

Coagulation does not seem to occur for any sol dialysed for different periods at the same value of the cat. speed with different electrolytes. The difference between the cat.speeds at which coagulation takes place for different sols with the electrolytes tried varies from about 5 in the case of $Th(OH)_4$ and prussian blue to about 20 in the case of As_2S_3. In many cases with V_2O_5, the sol coagulates on adding electrolytes at a cat.speed which is higher than the initial cat.speed.

On adding small increasing amounts of HCl and KCl to $Fe(OH)_3$ the viscosity first decreases and then increases for both short period and long period dialysed sols. For $Th(OH)_4$ the viscosity continuously increases on adding small increasing amounts of HCl and H_2SO_4 to short period dialysed sol, while it first decreases and then increases in the case of long period dialysed sol.

SECTION IV.

The cat.speed gradually decreases on ageing of both short period and long period dialysed sols of prussian blue, As_2S_3, gold and V_2O_5.

As_2S_3 hydrolyses and the amount of As_2O_3 in the sol continuously increases on ageing.

The stability of As_2S_3 on ageing first increases and then decreases with reference to KCl and continuously decreases with reference to $MgCl_2$. In the case of gold and V_2O_5 sols the stability decreases on ageing.

The conductivity on ageing of prussian blue, gold and V_2O_5 generally gradually decreases, while that of As_2S_3 first increases and then decreases.

SECTION V.

The cat.speed on exposure to sunlight of prussian blue, gold and V_2O_5 dialysed for short and long periods generally gradually decreases. In the case of As_2S_3 sol, the cat.speed gradually decreases on exposure to artificial light and sunlight the undialysed and long period dialysed samples respectively, but it first increases and then decreases when undialysed sol is exposed to sunlight.

As_2S_3 hydrolyses and the amount of As_2O_3 in the sol continuously increases on exposure to light.

The changes in the stability of As_2S_3 sol with reference to KCl and $MgCl_2$ on exposure to light are the same as as during ageing. In the case of gold and V_2O_5 the stability decreases on exposure to light.

In the case of prussian blue it is observed that impure samples coagulate without adding any electrolyte when exposed to light. The time after which coagulation can occur in this manner however increases with the purity of the sol.

The conductivity of prussian blue on exposure decreases for sample dialyed for 10 days and first decreases and then increases for sample dialyed for 21 days. In the case of As_2S_3 conductivity continuously increases on exposure. The conductivity decreases on exposure in the case of gold and V_2O_5 dialysed for short as well as long periods.

Various views about origin of charge on the colloidal particles have been summarised briefly.

The results of changes in cat.speed of all the sols during dialysis, dilution, ageing and exposure are discussed from the point of view of changes in the adsorption of the ions present in the intermicellary liquid. The physical point of view about origin of charge on the colloidal particles is completely supported by the results given here. The chemical view point of Pauli about origin of charge is found to be inadequate to explain various observed changes in cat. speed. In discussing the cat.speed results it is shown that the process of dialysis can be taken roughly as the reverse of the process of adding small increasing amounts of the peptising electrolyte to the colloid so far as the changes in the amount of the peptising electrolyte during dialysis are

are concerned. It is also shown that the cat.speed results become quite intelligible if the processes of dialysis and dilution are considered similar so far as the changes in the amount of the peptising electrolyte in the sol during dialysis and dilution are concerned.

While discussing thê results of stability and viscosity under different conditions it is shown that is is unsafe to draw conclusions about changes in charge on colloidal particles from stability and viscosity data, for although in some cases they may give correct indication about changes in charge, in others they do not do so. Various points which may affect stability and viscosity besides the cat.speed have been also discussed.

The changes in conductivity under different conditions are found to be largely governed by changes in the amount of electrolytes in the sol and in the number of particles per unit volume, the influence of the changes of cat.speed and viscosity being relatively small.

It is found that there is no definite value of cat. speed at which any particular sol coagulates with different electrolytes; the idea of critical potential put forward by Powis is thus not supported. Various factors which should be considered in discussing coagulation results have been mentioned.

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