

# DISPERSION OF DEPOLARISATION OF LIGHT-SCATTERING IN COLLOIDS.

Part IV. Iodine, Graphite, Stearic Acid, Vanadium Pentoxide, Arsenic Trisulphide and Ferric Hydroxide Sols.

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## 1. Introduction.

IN several previous communications the author (1937) has pointed out that in order to determine the size, shape and structure of colloidal particles, it is important to make comparative studies of the dispersion of depolarisation of the transversely scattered light with the incident light in different states of polarisation, namely, unpolarised, vertically polarised and horizontally polarised. Measurements of the depolarisation factors  $\rho_u$ ,  $\rho_v$  and  $\rho_h$  and also the extinction coefficients have been made in a large number of metallic sols, such as gold, silver, platinum, copper, selenium and tellurium. In all the cases studied a marked dependence of the degree of depolarisation on wave-length has been observed. The dispersion of depolarisation is found to be closely connected with the absorption curve. In the region of the characteristic absorption the depolarisation factors and hence the optical anisotropy show an enormous increase. This is connected with other well-known phenomena exhibited by colloidal solutions, namely, magnetic, electric and flow birefringence and their dispersion with wave-length. In the present paper the results obtained from a study of the absorption and the scattering of light in iodine, stearic acid, graphite, vanadium pentoxide, arsenic trisulphide and ferric hydroxide sols are given.

The state of polarisation of the Tyndall light in sols of arsenic trisulphide, vanadium pentoxide and ferric hydroxide was investigated by Lange (1928) by means of a spectrophotometer of the König-Martin type. From a measurement of the depolarisation factor with unpolarised

light alone he concluded that the particles in colloidal arsenic trisulphide were spherical in shape, whereas in iron oxide and vanadium pentoxide sols the particles were non-spherical in shape. He measured also the dispersion of the depolarisation factor  $\rho_u$  over a wave-length range from 4500 to 6500 A.U. In ferric hydroxide and vanadium pentoxide sols  $\rho_u$  was found to increase with diminution in wave-length. In arsenic trisulphide the dispersion was in the opposite direction. Very recently Mr. Subbaramaiya (1935) has measured the depolarisation factors  $\rho_u$ ,  $\rho_v$  and  $\rho_h$  for an arsenic trisulphide sol using incident white light. His measurements indicate that the particles in arsenic trisulphide sol possess a small but definite optical anisotropy. His method of preparation of the sol is slightly different from that employed by Lange.

## 2. Preparation of the Sols.

*Iodine sol.*—Since the unprotected hydrosols of iodine were extremely unstable, changing almost instantly into a dark precipitate, a stable sol was prepared by using gelatine as the protecting agent. To 100 c.c. of a 0.4 per cent. gelatine solution were added a few drops of iodic acid solution followed by the addition of a few drops of hydroiodic acid. A sol was formed at once by the interaction of these two acids.

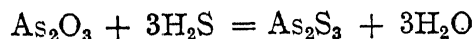
*Stearic acid.*—About 2 g. of (Kahlbaum's) stearic acid were dissolved in a few c.c. of ethyl alcohol. The resulting solution was boiled with double-distilled water for more than 24 hours so as to remove the alcohol. As the water was removed by evaporation fresh water was poured and the boiling continued till the last trace of alcohol was removed. The sol which resulted was kept in a Jena glass bottle. The sol was diluted to the desired extent before it was used for measurements.

*Graphite sol or aquadag.*—'Aquadag' is the technical term for the colloidal dispersion of graphite in water. The dag portion of the name is compounded from the first letters of deflocculated Acheson's graphite. Acheson's graphite is a synthetic product formed by heating amorphous carbon in the electric furnace in the presence of oxides, such as, silica, alumina and ferric oxide which are capable of yielding carbides as intermediate products. To prepare the hydrosol, the disintegrated graphite is treated with an aqueous solution of tannin containing 3–6 per cent. of the weight of graphite employed. The results are most satisfactory if a pasty mixture of graphite, tannin and water is first prepared and masticated, say for a month, before dilution with water preferably containing a small amount

of ammonia. The sol is quite stable and has an intense black colour. A small quantity of the aquadag from a sample sent by E. G. Acheson, Ltd. (London), was dissolved in 100 c.c. of double-distilled water and the solution was centrifuged in an ultra-centrifuge and the fraction containing the finest particles was separated and was used for the present investigation.

*Vanadium pentoxide sol.*—Colloidal vanadium pentoxide is one of the first sols in which magnetic double refraction and flow birefringence were observed. These solutions are therefore of special interest. To prepare the sol, about 1.5 g. of ammonium vanadate was triturated with 15 c.c. of 8 per cent. hydrochloric acid. The vanadium pentoxide obtained was washed out with distilled water. When the washing water began to be strongly coloured the sedimented oxide was left to stand together with about 100 c.c. of water, in which it gradually dissolved. A stable sol was obtained.

*Arsenic trisulphide sol.*—Numerous sulphide hydrosols may be prepared by condensation or peptization. In the condensation method we start with a suitable dilute solution of the initial material, and treat this with sulphuretted hydrogen or with a dilute solution of an alkaline sulphide; the electrolytes which may result from the reaction are removed by dialysis. Arsenic trisulphide is chosen as a typical sulphide sol, for in this case the experimental conditions are particularly clean cut, since according to the equation



no electrolytes are formed which need be dialysed away. The sol was prepared as follows. About 0.01 g. of anhydrous arsenious acid was dissolved in 100 c.c. of pure double-distilled water and a small stream of hydrogen sulphide gas was passed through the solution till the solution was turned yellow. Then hydrogen was bubbled through the system till the smell of hydrogen sulphide was completely removed. The suspension appeared yellow with a greenish tinge in reflected light, whereas it appeared orange in transmitted light.

*Ferric hydroxide sol.*—In the preparation of the hydrosols of the metallic hydroxides condensation methods are most important. A freshly precipitated hydroxide may be brought into colloidal solution by washing out with water or with a solution of a peptizing electrolyte. This method is employed here for the preparation of the ferric hydroxide sol. Ferric hydroxide was precipitated from a solution of ferric chloride with ammonia solution. The washed precipitate was peptized with a dilute ferric chloride solution. The sol was reddish brown in colour.

### 3. Absorption and Depolarisation Measurements.

The methods of measuring the extinction coefficients and the depolarisation factors  $\rho_u$ ,  $\rho_v$  and  $\rho_h$  from  $\lambda$  2500 to 7000 A.U. have already been described in detail in the earlier parts of this series. The extinction coefficients for the six sols are given in Tables I and III. Curves of absorption are plotted with extinction coefficient as ordinate and wave-length as abscissa. They are reproduced in Figs. 1 and 3. Values of  $\rho_u$ ,  $\rho_v$  and  $\rho_h$  after applying the necessary corrections for the finite angle of convergence of the incident beam, are given in Tables II and IV. The values of  $\rho_u$  are also plotted against wave-length. The curves are reproduced in Figs. 2 and 4.

TABLE I.  
*Extinction Coefficients.*

Wave-length $\lambda$ in A.U.	Iodine	Aquadag	Stearic acid
2250	>1.8	0.13	0.6
2500	>1.8	0.135	0.53
2750	0.57	0.14	0.46
3000	0.23	0.15	0.41
3250	0.12	0.145	0.35
3500	0.09	0.135	0.3
3750	0.13	0.13	0.25
4000	0.34	0.125	0.2
4250	0.68	0.12	0.175
4500	0.97	0.12	0.155
5000	0.68	0.12	0.14
5500	0.26	0.115	0.13
6000	0.16	0.11	0.12
6500	0.1	0.105	0.11
7000	0.05	0.1	0.1

TABLE II.  
Dispersion of Depolarisation  $\rho_u$ .

Wave-length $\lambda$ in A.U.	Iodine			Aquadag			Stearic Acid		
	$\rho_u$ %	$\rho_v$ %	$\rho_h$ %	$\rho_u$ %	$\rho_v$ %	$\rho_h$ %	$\rho_u$ %	$\rho_v$ %	$\rho_h$ %
2967	..	..	..	34.7	4.5	17.2	17	2.8	18.9
3650	4	..	..	32	4.5	18.9	14.8	2.5	20.8
4046	3	..	..	29.5	4.7	19.8	12.5	2.2	21.8
4358	1.5	..	..	27.1	4.7	20.8	8.8	1.7	22.8
4750	7.95	1.6	23.8	26.5	4.9	21.7	8.2	1.5	23.5
5000	6	0.5	9.5	26	5.0	22.4	7.5	1.4	24
5500	3.3	0.45	14	24.8	5.1	24.8	6.4	1.3	26
6000	2	0.2	10.5	23.8	5.3	27.1	5.3	1.2	29.8
6500	1.5	..	..	23.8	5.3	30.7	4.5	1.0	36
7000	1.2	..	..	..	..	..	..	..	..

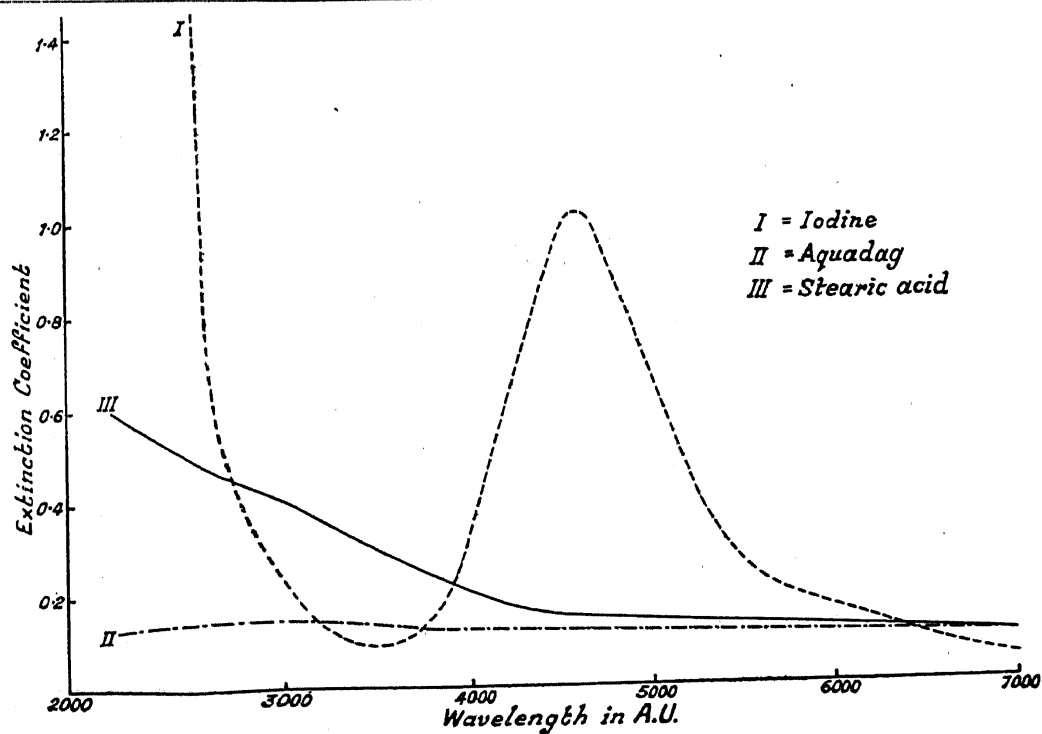


FIG. 1.  
Extinction coefficients.

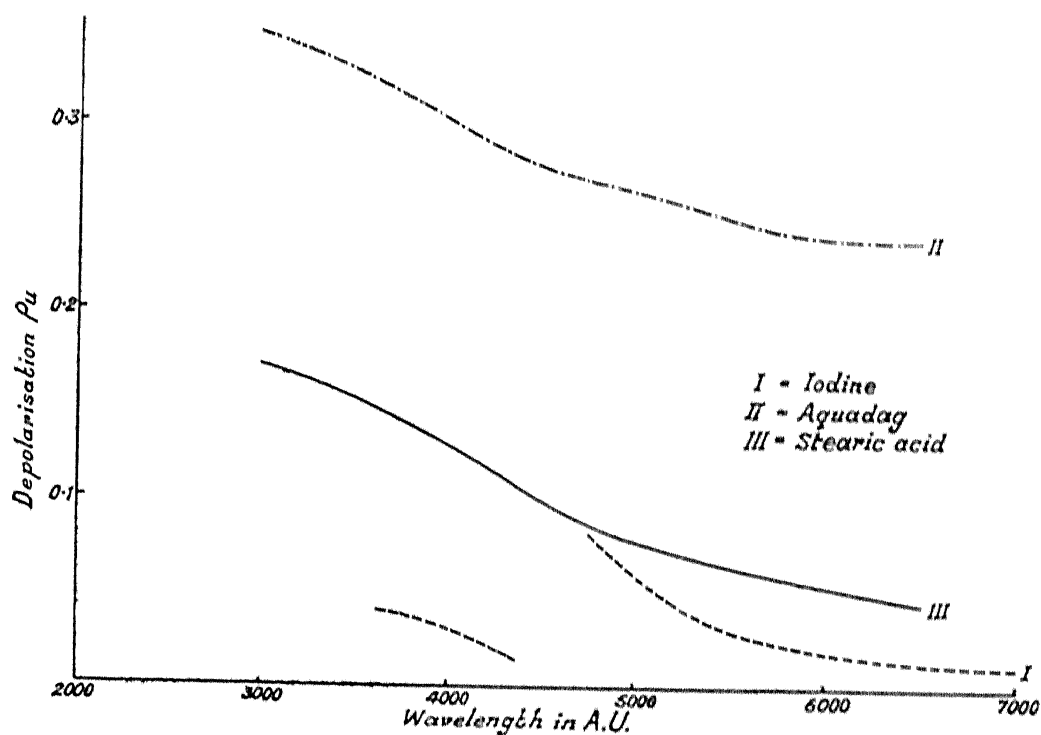


FIG. 2.  
Dispersion of depolarisation factor  $\rho_u$ .

TABLE III.  
*Extinction Coefficient.*

Wave-length $\lambda$ in A.U.	Vanadium pentoxide	Arsenic trisulphide	Ferrie hydroxide
3750	>3	>3	>3
4000	>3	1.8	2
4250	3	0.9	1.15
4500	1.50	0.54	0.78
5000	0.78	0.18	0.48
5500	0.34	0.11	0.34
6000	0.10	0.08	0.28
6500	0.05	0.06	0.26
7000	0.02	0.05	0.25

TABLE IV.  
Dispersion of Depolarisation.

Wave-length $\lambda$ in A.U.	Vanadium pentoxide			Arsenic trisulphide			Ferric hydroxide		
	$\rho_u$ %	$\rho_v$ %	$\rho_h$ %	$\rho_u$ %	$\rho_v$ %	$\rho_h$ %	$\rho_u$ %	$\rho_v$ %	$\rho_h$ %
3650	..	..	..	17	..	..	9.5	..	..
4046	..	..	..	18.8	1.0	4.0	9.5	..	..
4358	..	..	..	24.9	1.3	4.0	9.2	..	..
4750	26	9.9	60	33.5	1.9	4.6	9.0	..	..
5000	20	9	70	39	2.2	5.3	8.6	2.5	42
5500	18	7.7	80	43.6	2.9	6.9	7.7	2.0	57
6000	8.8	3.4	90	45.5	3.1	8.2	6.5	1.9	66
6500	7.75	3	..	45.5	3.1	8.2	6.2	1.9	66

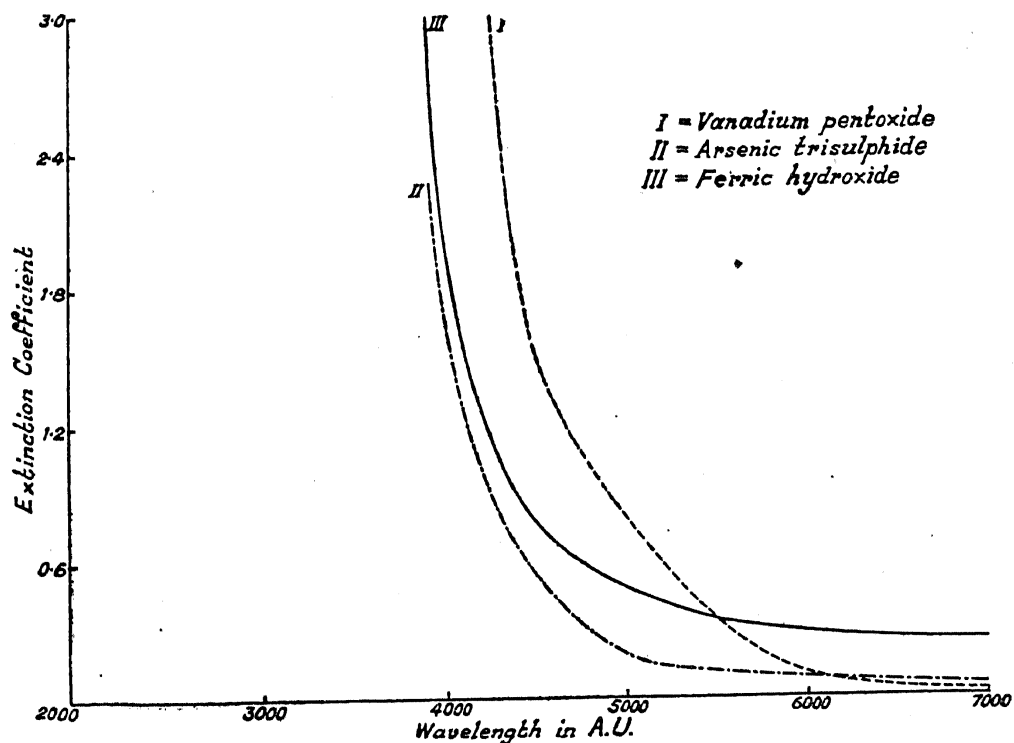


FIG. 3.  
Extinction coefficients.

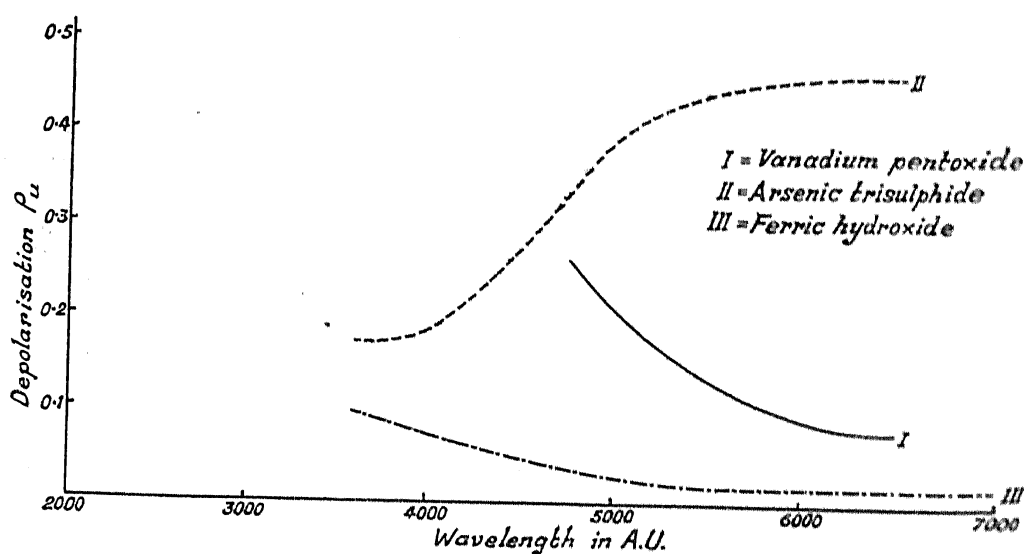


FIG. 4.  
Dispersion of depolarisation factor  $\rho_u$ .

#### 4. Discussion of Results.

A comparative study of the absorption coefficients, the depolarisation factors and also their dispersion with wave-length shows that the six sols investigated here can be classified under four different groups. The iodine sol which possesses a specific absorption at 4500 A.U. belongs to the first type. As in the case of gold and silver sols, so also in the case of iodine sol the depolarisation values attain their maximum value in the region of specific absorption. Stearic acid, vanadium pentoxide and ferric hydroxide sols come under the second type. These sols do not possess any region of specific absorption in the visible and the near ultra-violet regions of the spectrum. The extinction coefficient of these sols increases as one proceeds towards the ultra-violet. These sols belong to the same type as the sols of platinum, copper, selenium and tellurium. The observed dispersion of depolarisation in these cases is a size effect. The behaviour of graphite sol is slightly different from that of the sols of the second type, for in this sol  $\rho_v$  and  $\rho_h$  both diminish with decrease of wave-length. The behaviour of arsenic trisulphide is unique because as one proceeds from the red end of the spectrum towards the ultra-violet region, the absorption coefficient increases continuously, whereas the depolarisation factors including  $\rho_u$  decrease continuously.

*Iodine sol.*—Just as the copper sol (see Part III of this series in these *Proceedings*), iodine sol also gives comparatively small depolarisation. The observed depolarisation factor  $\rho_u$  shows a maximum at about 4500 A.U.



In this region the absorption curve also shows a maximum (see Figs. 1 and 2 and Tables I and II). The low values of  $\rho_v$  and  $\rho_h$  indicate that the particles are spherical in shape. Although a definite fall in the value of  $\rho_h$  from its limiting value of 100 per cent. suggests that the size of the particles is not small compared with the wave-length of light, the particles are only of ultra-microscopic dimensions, as is evidenced from the low value of  $\rho_u$ . These results are in agreement with the conclusions arrived at by the previous investigators from a microscopic examination of the protected iodine sol (Weiser, 1933). The microscopic examination shows that the particles are almost exclusively minute globules in rapid Brownian movement. The largest particles possess a very uniform diameter of approximately  $200\mu$ . The particles are unmistakably spherical in shape. It is also suggested that the sol is an emulsion of liquid iodine in a saturated aqueous solution of the element. Further information that such is the case is furnished by microscopic observation of the sol formation process.

*Graphite sol (aquadag).*—As has already been indicated this is the only one case where  $\rho_u$  increases and  $\rho_v$  decreases with wave-length. The particles of this sol are fairly anisotropic and ultra-microscopic in size. It has been shown from other investigations that the particles are in the form of thin plates. This may probably explain the observed anomalous variation of  $\rho_v$  with wave-length.

*Stearic acid sol.*—In the case of the stearic acid sol a number of phenomena are known which point to a non-spherical elongated form for the particles. The finite value of  $\rho_v$  and  $\rho_h$  indicate that the micellæ are non-spherical in shape. The size of these micellæ is of the order of the wave-length of light (see Tables I and II and Figs. 1 and 2).

*Vanadium pentoxide sol.*—The comparatively high values of  $\rho_u$ ,  $\rho_v$  and  $\rho_h$  obtained with this sol indicate that the particles are highly anisotropic. Owing to the strong absorption in the violet and the ultra-violet regions depolarisation factors could not be measured in these regions. The dispersion of depolarisation  $\rho_v$  with wave-length is rather considerable. This may be due to the fact that the particles are highly anisotropic. The way in which  $\rho_v$  varies with wave-length would seem to suggest that the particles are in the form of rods. In this sol also the size of the particles is not small compared with the wave-length of light.

*Arsenic trisulphide sol.*—From a comparative study of the values of  $\rho_u$ ,  $\rho_v$  and  $\rho_h$  for this sol one is led to conclude that the particles are more or less spherical in shape and amicroscopic in size. The small but definite

value of  $\rho_v$ , however, indicates that the particles do possess a small anisotropy. This is because the difference between the refractive index of the micellæ and the intermicellar liquid in the case of this sol is great and consequently even a trace of anisotropy will be magnified in the depolarisation factors. At present it is difficult to understand why in this case alone the depolarisation factors increase *pari passu* with wave-length, whereas the absorption is stronger in the ultra-violet region than in the red region. The same phenomena has been observed by Lange (1928). X-ray studies of this sol, however, suggest that the particles are amorphous.

*Ferric hydroxide sol.*—As in the case of vanadium pentoxide sol, in this case also the depolarisation factors indicate that the sol contains anisotropic ultramicroscopic particles.

#### 5. Other Experimental Evidence.

The double refraction occurring in many sols is closely connected with the non-spherical shape of colloidal particles. Rod-shaped double refraction is usually positive. Vanadium pentoxide (Diesselhorst and Freundlich, 1915) and stearic acid sols give positive flow birefringence. According to Diesselhorst and Freundlich arsenic trisulphide does not exhibit any detectable flow birefringence, showing thereby that the particles are of spherical shape. The double refraction produced by mechanical flow in iodine and graphite sols have not yet been investigated.

The magnetic double refraction is very pronounced in vanadium pentoxide sol (Bjornstahl, 1924). The effect is very small in the long-wave range of the spectrum but increases very quickly when approaching the short wave range. The depolarisation factors show a similar dispersion. Ferric hydroxide sol also exhibits a very high magnetic double refraction.

When vanadium pentoxide and stearic acid sols are examined under a Cardioid ultra-microscope, pronounced scintillations are observed. This is because these sols contain particles which are highly asymmetric in shape (*i.e.*, in the form of rods).

In conclusion the author wishes to record his indebtedness to Prof. Sir C. V. Raman, Kt., F.R.S., N.L., for his kind interest in the work.

#### 6. Summary.

Measurements of the depolarisation factors  $\rho_u$ ,  $\rho_v$  and  $\rho_h$  and the extinction coefficients of iodine, graphite, stearic acid, vanadium pentoxide, arsenic trisulphide and ferric hydroxide sols are made for different wavelengths from 2500 A.U. to 7000 A.U. All these sols except the iodine sol

do not possess any region of specific absorption. As in the case of gold and silver sols so also in the case of the iodine sol the depolarisation values attain their maximum value in the region of the characteristic absorption, *i.e.*, at 4500 A.U. In stearic acid, vanadium pentoxide and ferric hydroxide sols the depolarisation factors exhibit normal dispersion. The observed dispersion in these cases is a size effect. The behaviour of the graphite sol is slightly different from that of the sols mentioned above, for in this case,  $\rho_v$  and  $\rho_h$  both diminish with decrease of wave-length. Unlike all the other sols up till now studied, the depolarisation factors in the arsenic trisulphide sol increase *pari passu* with wave-length. The depolarisation measurements indicate that the particles in the sols of iodine and arsenic trisulphide are spherical in shape, while, those in vanadium pentoxide, stearic acid, ferric hydroxide and graphite sols are non-spherical in shape.

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