

THE RECIPROCITY THEOREM IN COLLOID OPTICS AND ITS GENERALISATION.

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1. *The Case of Transverse Scattering.*

It is well known that the light transversely scattered by any colloidal solution is, in general, only partially polarised. The imperfectness of polarisation arises from two causes, (1) the scattering particles being of finite size not small compared with the wave-length of light and (2) the scattering particles being anisometric in shape and/or anisotropic in structure. In order to separate these two effects, the depolarisation of the Tyndall scattering should be measured with the incident light (1) unpolarised, (2) polarised with vibrations perpendicular to the plane containing the incident and scattered beams and (3) polarised with vibrations parallel to this plane. The values, both relative and absolute, of the three quantities ρ_u , ρ_v and ρ_h thus measured, are determined by the size, shape and structure of the colloidal particles and their distribution in space. The value of ρ_v mainly depends on the lack of spherical symmetry in shape or structure of the particles, while the value of ρ_h is specially sensitive to the size of the particles and to their grouping in space. The author¹ has shown that there is a very general relation connecting the three quantities ρ_u , ρ_v and ρ_h namely

$$\rho_u = (1 + 1/\rho_h)/(1 + 1/\rho_v) \quad (1)$$

which is valid for any colloidal solution irrespective of the size, shape, structure and distribution of the particles contained in them and also for light of any wave-length.² This relation can be derived theoretically by considering an unpolarised beam of light passing horizontally through the solution; this may be regarded as made up of two beams of equal intensity and unrelated in phase, one with vibrations vertical and the other with vibrations horizontal. The light scattered transversely in the horizontal direction by an element of volume of the solution can therefore be supposed to

¹ R. S. Krishnan, *Proc. Ind. Acad. Sci.*, (A), 1935, 1, 717 and 782.

² ———, *ibid.*, 1935, 1, 915 ; 1935, 2, 221 ; 1936, 3, 211 ; 1937, 5, 94, 305, 407, 498, 551 and 577 ; *Curr. Sci.*, 1937, 6, 90.

be made up of four components V_v , H_v , V_h and H_h , the first two arising from the vertical component and the last two arising from the horizontal component of the incident beam. The depolarisation factors ρ_u , ρ_v and ρ_h are then given by

$$\rho_u = (H_v + H_h)/(V_v + V_h); \rho_v = \frac{H_v}{V_v}; \rho_h = \frac{V_h}{H_h}. \quad (2)$$

According to the theories of Rayleigh and Mie, the two quantities H_v and V_h both vanish when the particles are spherical in shape and isotropic in structure. Hence, when they are present they have a common origin, namely, the anisotropy of structure and/or the non-spherical shape of the particles. Further, H_v and V_h are obviously related to each other in a reciprocal fashion, the direction of electric oscillation in the incident and the scattered radiations in them being interchanged. Hence we may write

$$H_v = V_h. \quad (3)$$

Relation (1) follows directly on combining (2) and (3).

The principle of the experimental method employed to test relation (3) consists in splitting the incident unpolarised light by means of a double-image prism into two beams of equal intensity, but polarised in the vertical and horizontal planes respectively. The light scattered transversely in the horizontal direction is also viewed through another double-image prism which is so orientated that the images given by it are separated in a vertical plane. Four images of the tracks corresponding to the components V_v , H_v , V_h and H_h will then be visible at the same time and their intensities may be compared. Typical photographs are reproduced in Plate II. In all the cases studied, it is found that the two middle components, *i.e.*, H_v and V_h , are always exactly identical in intensity and colour, establishing thereby the validity of relation (3) and therefore also of relation (1). The colour and intensity of the two outermost components differ greatly from each other and from those of the middle two components, and these differences furnish indications regarding the size and shape of the scattering particles.

For the most general case of the scattering by particles of arbitrary size, shape or structure the equality of the components H_v and V_h can be derived from theoretical considerations by applying the "*Principle of Reciprocity*" as indicated below.

Let a beam of plane polarised light of intensity I with vibrations vertical be incident along the X-axis of a system of co-ordinates X, Y, Z on the colloidal particles placed at O. Let the X-Y plane be the horizontal plane, the transverse observation being made along the Y-axis. This will give rise to a vertical component V_v and a horizontal component H_v in the light

scattered along OY [full lines in Fig. 1 (a)]. In the same way a horizontal electric vector of intensity I incident on the particle along the X-axis gives

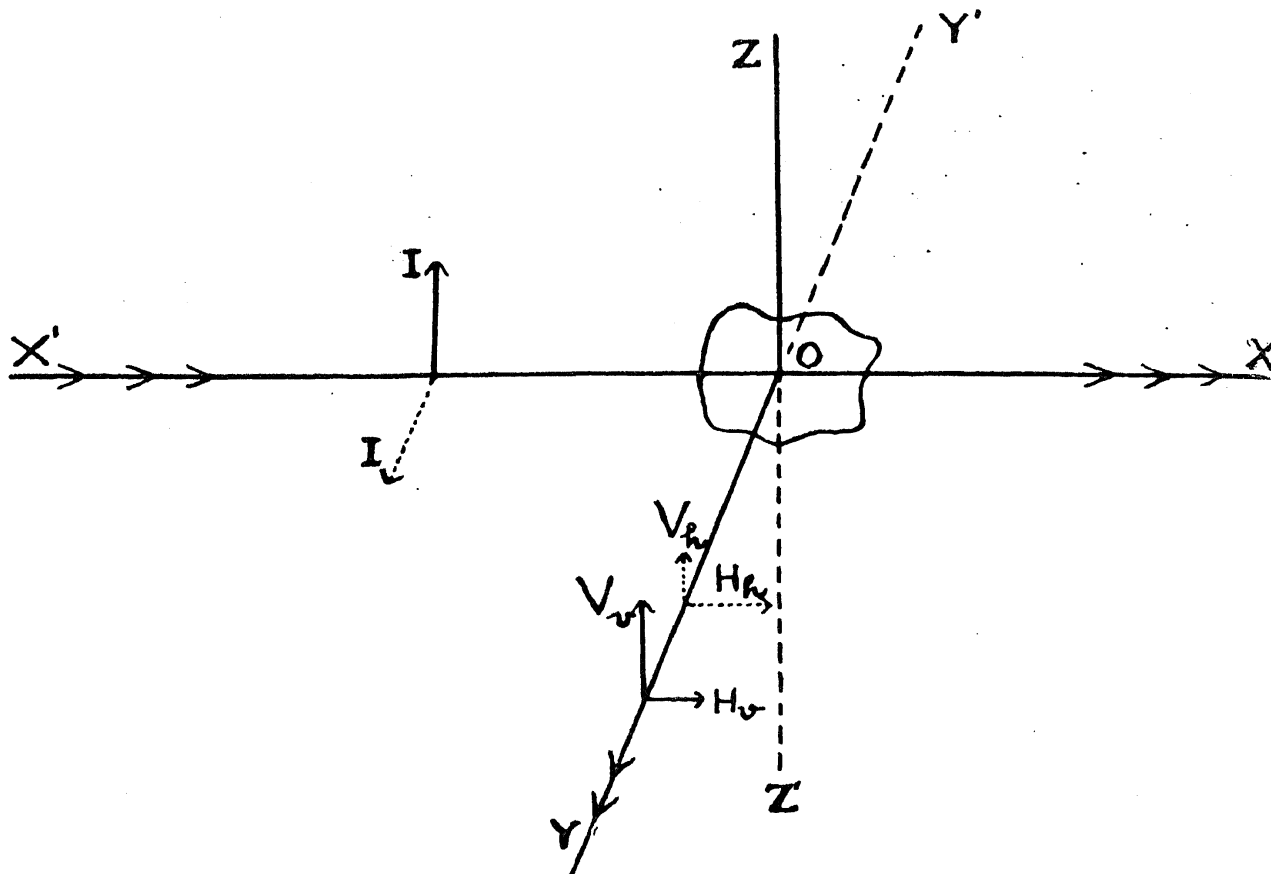


FIG. 1 (a)

rise to a vertical component V_h and a horizontal component H_h in the light scattered along the Y-axis [dotted lines in Fig. 1 (a)]. The depolarisation factors ρ_u , ρ_v and ρ_h of the solution are given by

$$\rho_u = \frac{\Sigma H_v + \Sigma H_h}{\Sigma V_v + \Sigma V_h}; \quad \rho_v = \frac{\Sigma H_v}{\Sigma V_v}; \quad \rho_h = \frac{\Sigma V_h}{\Sigma H_h}. \quad (4)$$

Σ indicates that the summation should be extended for all the particles in a volume element of the colloidal solution.

Imagine the direction of observation and the direction of the incident beam interchanged keeping the particle under observation fixed in position and orientation [see Fig. 1 (b)]. We may now find the state of polarisation in the scattered light by applying the "Theorem of Reciprocity" stated by the late Lord Rayleigh³ in the following words:—"A force of any type acting alone produces a displacement of a second type equal to the displacement of the

³ Lord Rayleigh, I., *Theory of Sound*, 1926, 1, 93.

first type due to the action of an equal force of the second type." The vertical electric force I in the incident beam along the X -axis produces a vertical displacement V_v in the scattered beam along the Y -axis [Fig. 1 (a)]. Hence, by the reciprocity principle, a vertical force in the incident beam along the Y -axis [Fig. 1 (b)] must produce a vertical displacement V_v in the scattered beam along the X -axis. Then again if a horizontal force I in the incident beam along the X -axis produces a vertical displacement V_h in the scattered beam along the Y -axis [see Fig. 1 (a)], we infer from the reciprocity principle that a vertical force I in a beam incident along the Y -axis must produce a horizontal displacement V_h in the scattered beam along the X -axis [see Fig. 1 (b)]. Similarly, it follows that a horizontal force I in the incident beam

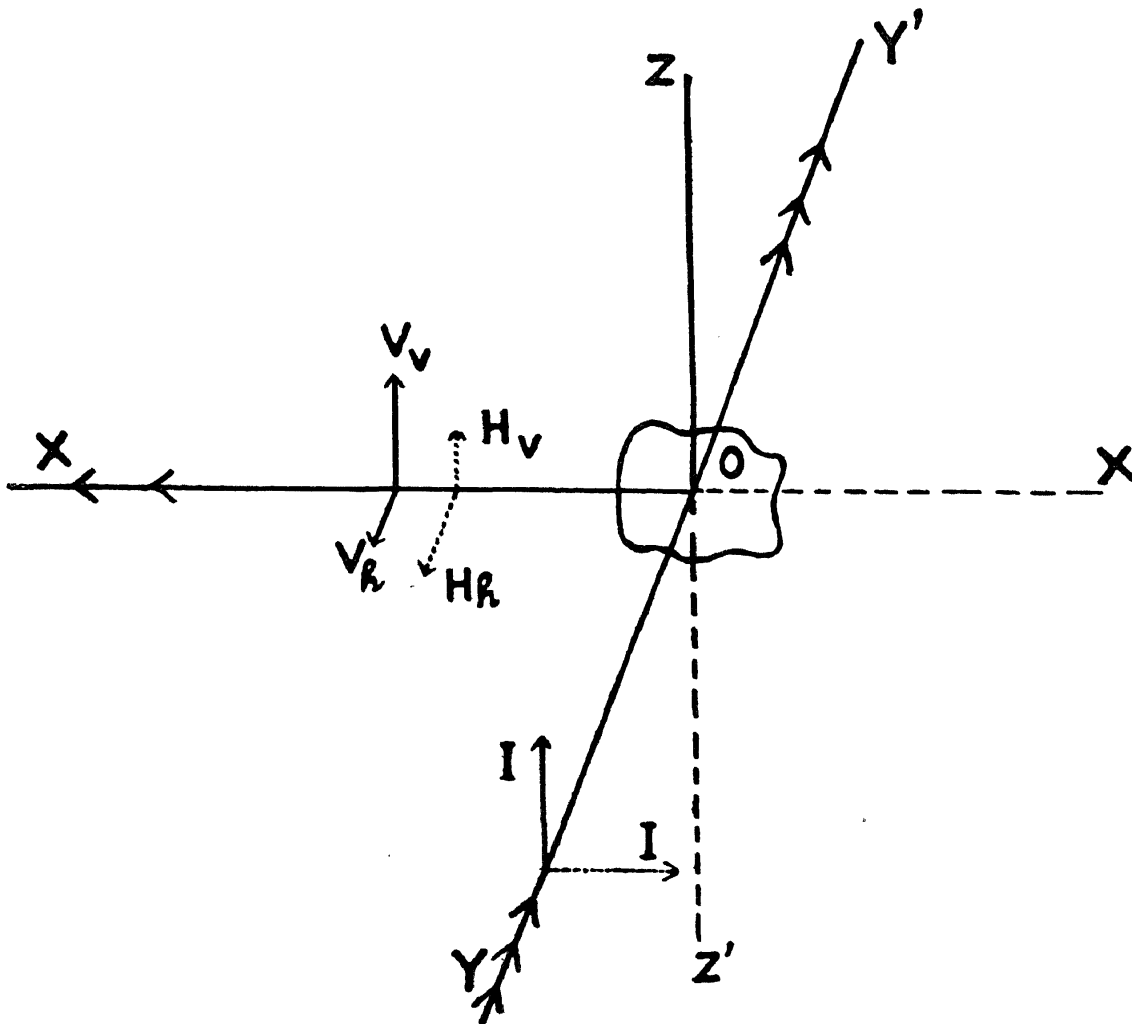


FIG. 1 (b).

along the Y -axis would give rise to a vertical displacement H_v and a horizontal displacement H_h in the scattered beam along the X -axis. In the case represented in Fig. 1 (b) the depolarisation factors ρ_u' , ρ_v' and ρ_h' would then be given by

$$\rho_u' = \frac{\sum V_h + \sum H_h}{\sum V_v + \sum H_v}; \quad \rho_v' = \frac{\sum V_h}{\sum V_v}; \quad \rho_h' = \frac{\sum H_v}{\sum H_h}. \quad (5)$$

But, now, we may remark that

$$\rho_u = \rho_u' ; \rho_v = \rho_v' \text{ and } \rho_h = \rho_h' \quad (6)$$

provided the particles in the colloidal solution considered in the aggregate have no preferred orientation in the horizontal plane XY. For, in such a case, the depolarisation factors should not depend on the actual direction of observation and the actual direction of the incident beam, so long as these two directions lie in the same horizontal plane and are at right angles to each other. On comparing (4) and (5), we see that if relations (6) are to subsist, we must have

$$\Sigma H_v = \Sigma V_h \quad (7)$$

It is important to notice that H_v and V_h for an individual particle of arbitrary size and shape orientated in a specific way, are not equal to each other. Actually, from the expressions given by Rayleigh⁴ for the case of small ellipsoidal particles, it is seen that H_v and V_h are not equal for one such particle for a fixed orientation in space. But if an averaging be carried out over all orientations of the particle in the horizontal plane which are similarly situated with respect to a vertical axis, it is easily verified from the expressions given by Rayleigh that the two quantities mentioned above become identical. Thus it is clear that the reciprocity relations embodied in (1) and (3) are valid, not for a single colloidal non-spherical particle, but only for a solution containing a large number of particles which have no preferred orientation in the plane of observation. By combining (4) and (7) we get relation (1) which will hold good for the transverse scattering of light by a colloidal solution irrespective of the size, shape, structure and distribution of particles provided, however, they have no preferred orientation in the plane containing the incident and the scattered beams.

2. *The Case of Oblique Scattering.*

We may now proceed to generalise the reciprocal theorem (1) for oblique directions of scattering. In the most general case of large anisometric and anisotropic particles, the quantities \bar{V}_v , \bar{H}_v , \bar{V}_h and \bar{H}_h are finite and their values depend on the angle of scattering γ . Hence the depolarisation factors ρ_u , ρ_v and ρ_h of the light scattered in a direction OR in the horizontal plane by an element of volume of the colloidal solution, will markedly be functions of γ . But if the particles in that volume element have no preferred orientation in the plane of observation, the depolarisation factors measured in any particular direction in the same plane will only depend on the angle of scattering γ and not on the actual direction of observation and that of the incident beam. Hence, applying the same reasoning as in the preceding

⁴ Lord Rayleigh, I., *Phil. Mag.*, 1918, 35, 373.

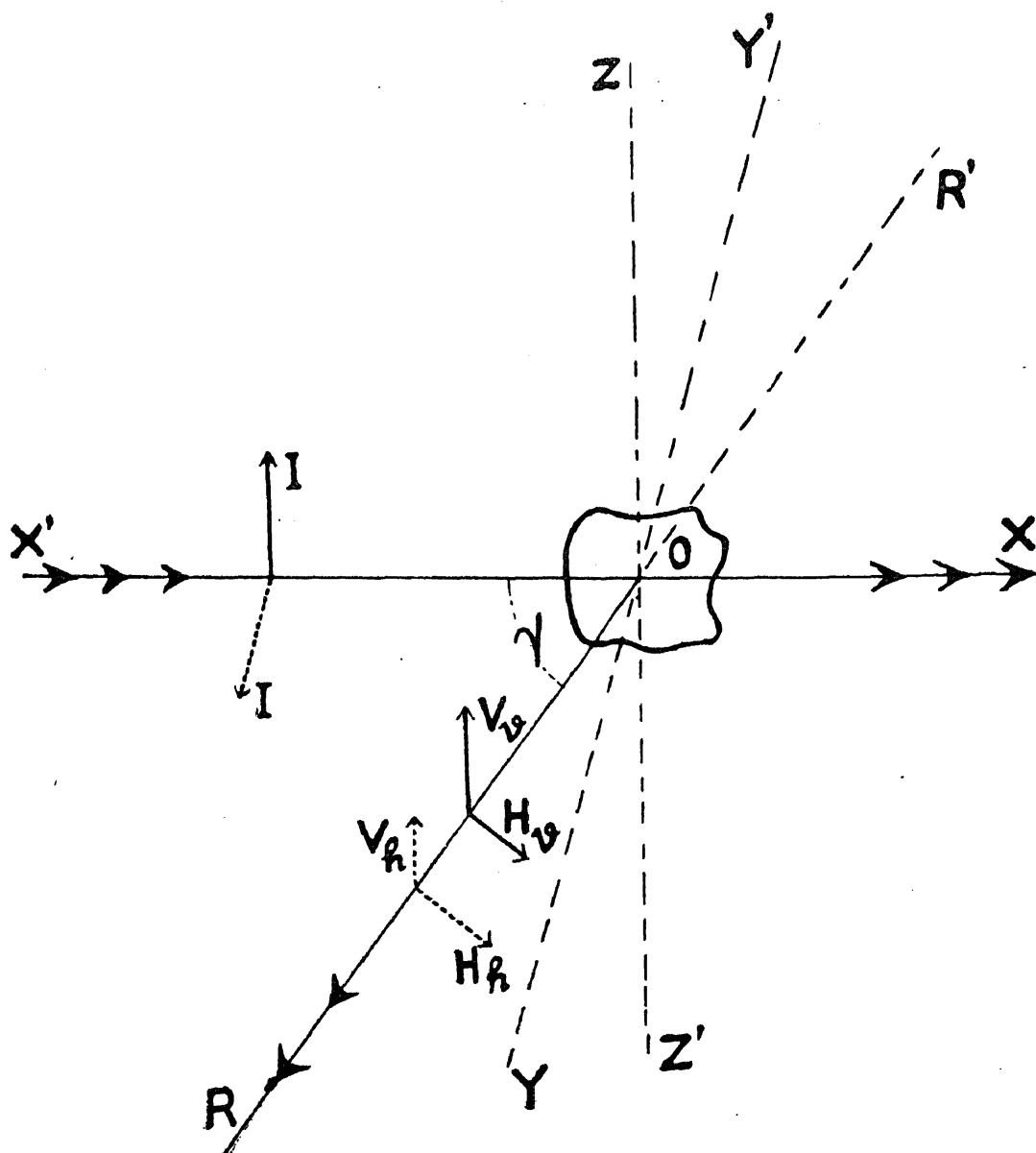


FIG. 2 (a).

section, we see that relations (4), (5), (6) and (7), and consequently the reciprocity relation (1) should hold good for any direction of observation OR in the horizontal plane [see Figs. 2 (a) and 2 (b)], although the actual values of the quantities involved are different for different directions. In general, the evaluation of the four quantities \bar{V}_v , \bar{H}_v , \bar{V}_h and \bar{H}_h and hence ρ_u , ρ_v and ρ_h for any value of γ is difficult. But from symmetry considerations it can be seen that if the particles are randomly orientated in space, \bar{V}_v will be equal to \bar{H}_h for $\gamma = 0^\circ$ and 180° . Hence ρ_v and ρ_h will be equal and ρ_u will attain the value of unity for these values of γ . In certain simple cases, the directional dependence of the three quantities ρ_u , ρ_v and ρ_h can be calculated from the theories of Rayleigh⁵ and Mie.⁶

⁵ Lord Rayleigh, I., *loc. cit.*; *Scientific Papers*, 5, 547.

⁶ G. Mie, *Ann. d. Phys.*, 1908, 25, 377.

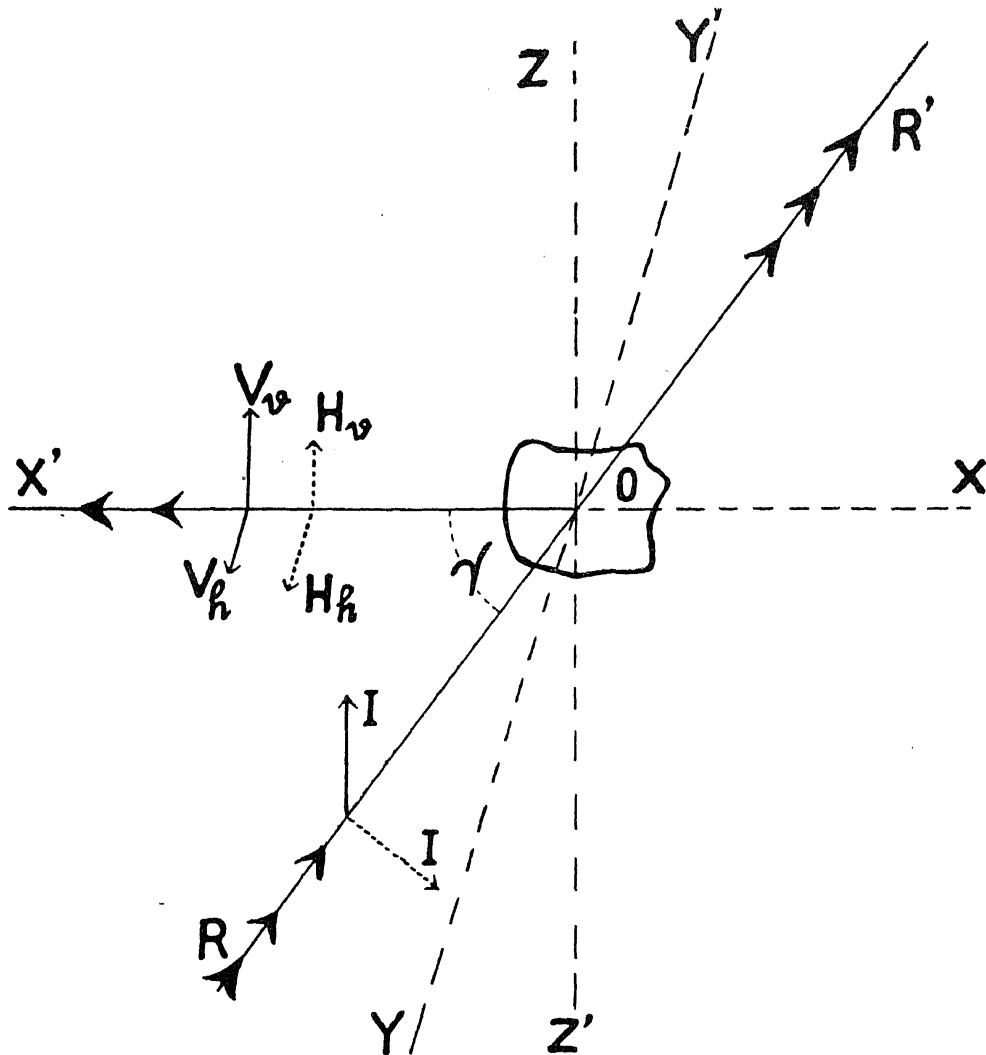


FIG. 2 (b).

CASE 1. *Small spherical particles.*—For particles of size small compared with the wave-length of light, the components H_v and V_h are both equal to zero not only for the transverse direction but also for any direction in the horizontal plane. Hence, it follows that ρ_v and ρ_h are both equal to zero for all values of γ . The component V_v will be independent of the angle of scattering. The intensity of the component H_h depends on the direction of observation. For any oblique direction its value is given by

$$H_h = V_v \cos^2 \gamma. \quad (8)$$

Hence $\rho_u = \cos^2 \gamma$ and is zero at 90° and is 1 at 0° and 180° . Its variation is represented graphically in curve (1) in Fig. 3. The curve is symmetrical about the minimum point.

CASE 2. *Large spherical particles.*—In this case also Mie's theory indicates that the two components H_v and V_h both vanish for all values of

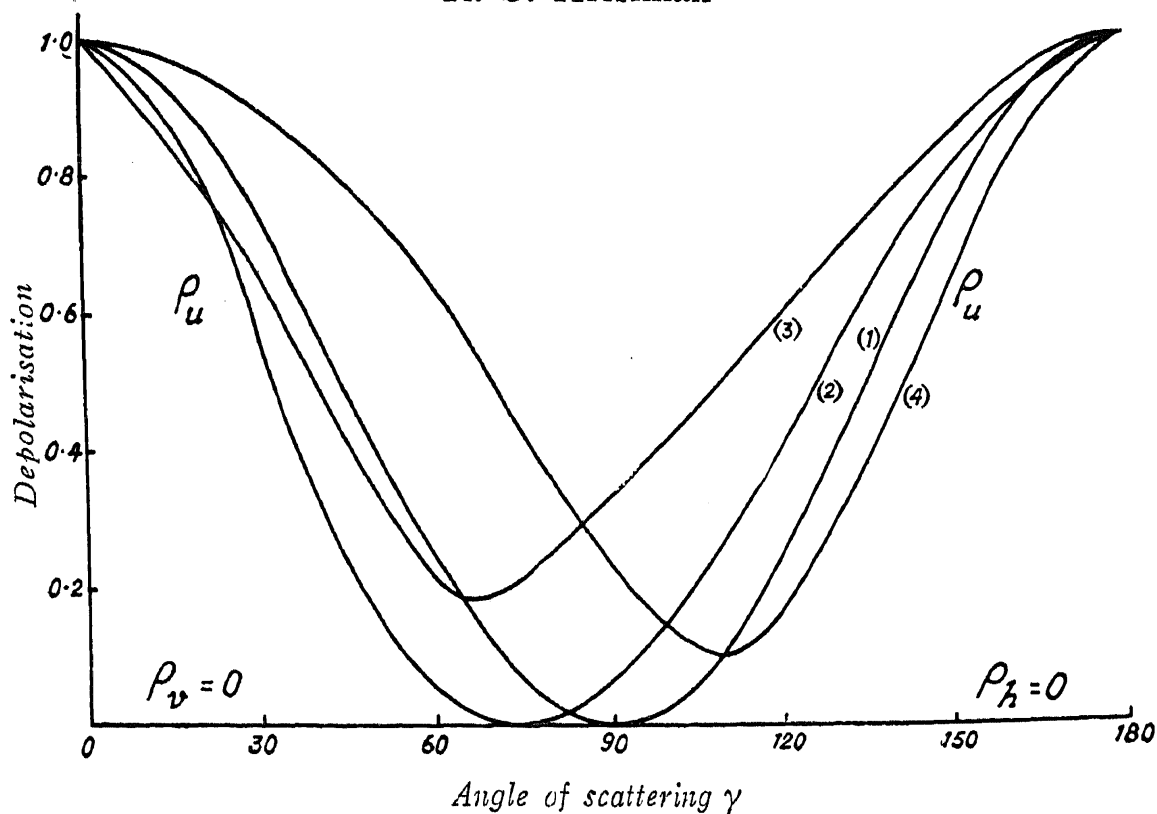


FIG. 3.

Depolarisation as a function of angle of scattering for spherical particles.

1. Particles of radius $r < 10$ A.U.
2. Dielectric particles of radius $r = 100 \mu \mu$
3. " " " $r = 120 \mu \mu$
4. Gold spheres of radius $r = 160 \mu \mu$

γ and hence ρ_v and ρ_h continue to be equal to zero. The components V_v and H_h have finite values for all values of γ , and in consequence when the incident light is unpolarised, the laterally scattered light is partially polarised. The values of ρ_u for spherical particles of moderately small size calculated from Mie's theory, are plotted against the angle of scattering γ in curves (2), (3) and (4) in Fig. 3, from which it will be seen that ρ_u has the value of unity for $\gamma = 0^\circ$ and 180° , and intermediately shows a pronounced minimum. As the size of the particle increases, the minimum is displaced towards the direction of decreasing γ in the case of dielectric spheres, and towards the direction of increasing γ in the case of metallic particles. Further, with increasing particle size the minimum value of ρ_u increases progressively. When the size of the particles exceed a certain value, the curve for ρ_u becomes violently oscillatory. In all these cases ρ_v and ρ_h are zero for all values of γ , and their graphs therefore coincide with the X-axis.

CASE 3. *Small ellipsoidal particles.*—In the case of ellipsoidal particles of size small compared with the wave-length of light and randomly orientated in space, Rayleigh's theory indicates that \bar{V}_v , \bar{H}_v , \bar{V}_h and \bar{H}_h have finite values and that the two quantities \bar{H}_v and \bar{V}_h are equal for all values of γ . The intensities of the components \bar{V}_v , \bar{H}_v and \bar{V}_h do not depend on γ , while

that of \bar{H}_h is given by

$$\bar{H}_h = \bar{V}_v \cos^2 \gamma + \bar{H}_v \sin^2 \gamma. \quad (9)$$

For this, the values of ρ_u , ρ_v and ρ_h may be readily calculated (see Fig. 4).

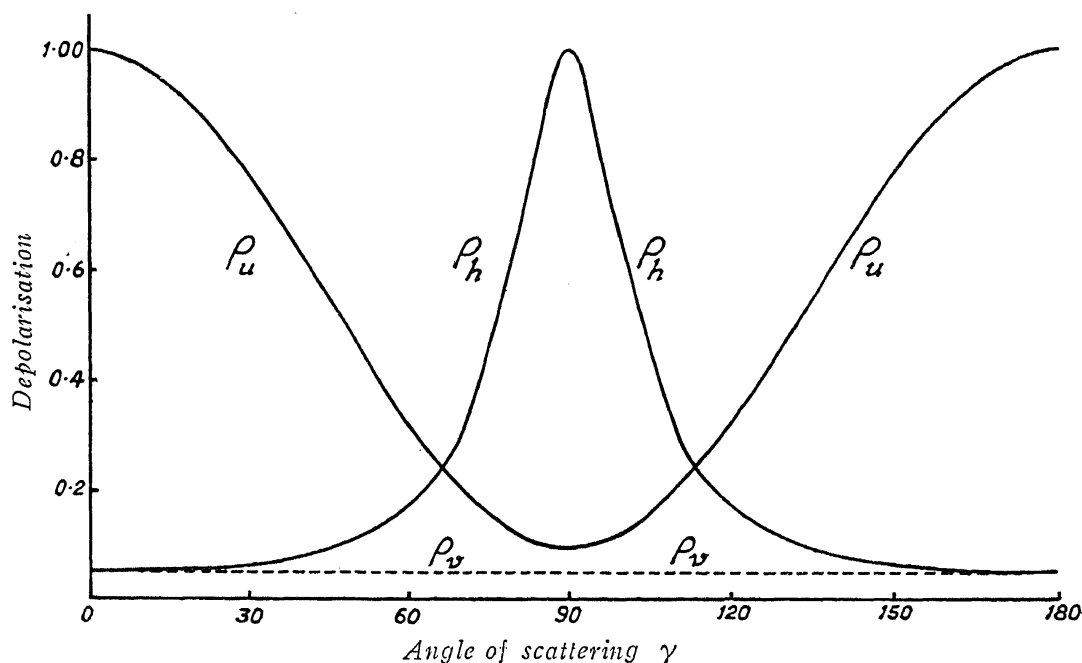


FIG. 4.

Depolarisation as a function of angle of scattering for small ellipsoidal particles.

ρ_v is independent of γ and its graph is therefore a straight line parallel to the axis of X. ρ_u and ρ_h , on the other hand, are markedly functions of γ . The curve of ρ_u shows a minimum equal to $2\rho_v/(1 + \rho_v)$ at $\gamma = 90^\circ$, while ρ_h reaches the maximum value of unity at the same angle. For $\gamma = 0^\circ$ and 180° , ρ_v and ρ_h become equal, while ρ_u attains its limiting value of unity.

3. Experimental Verification.

The experimental set up for the measurement of the depolarisation factors at various angles of scattering is shown in Fig. 5. The apparatus consisted of a rigid tripod stand to which was fixed a circular disc which was graduated in degrees. A movable arm T was attached to the fixed support, which could be rotated in a horizontal plane about an axis passing through the centre of the graduated disc. Inside the movable arm were fixed a double-image prism D and a square ended nicol N capable of independent rotation, with their axes coinciding with the axis of the tube. The double-image prism was orientated so as to have the vertical and horizontal components of the scattered light separated in a vertical plane.

The light emerging out of the illuminated aperture A (2 mm. square) was passed through a long focus lens of very small aperture. At the focus

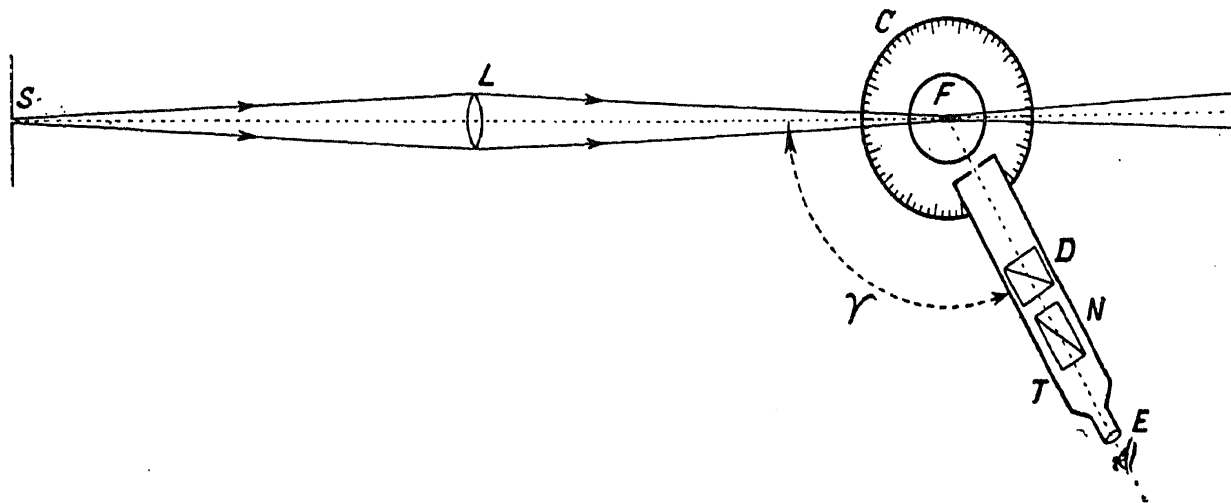


FIG. 5.

the light passed through a transparent fused silica flask placed right at the centre of the disc C . The flask was coated all over the outside with black paint except for a narrow strip $0.75''$ wide running along half the circumference of the flask. The scattered light was viewed through a vertical slit attached to the end of the movable arm T , which was nearer to the flask.

Before taking depolarisation measurements, relation (7) was tested out in the following way. A second double-image prism was introduced in the path of the incident beam at a suitable distance from the flask containing the colloidal solution. It was orientated in such a manner that the upper beam was polarised with vibrations vertical. The nicol was removed from the movable arm T and the scattered light was observed through the double-image prism D . Four images of the tracks were seen corresponding to the components \bar{V}_v , \bar{H}_v , \bar{V}_h and \bar{H}_h . The movable arm was set at various inclinations with respect to the incident beam and the relative intensities of the four components in the case of graphite sol and arsenic trisulphide sol were examined visually. For various settings of the arm T , it was found that the two middle components \bar{H}_v and \bar{V}_h were always equal in intensity and colour, establishing thereby the validity of the reciprocity theorem irrespective of the direction of observation in the horizontal plane. It was also found that the intensities of the four components were considerably greater in forward directions than in the backward directions. The effect was very striking in the case of graphite sol in which the particles were coarser than those in the arsenic trisulphide sol.

The depolarisation factors ρ_u , ρ_v and ρ_h were then measured in the usual way. Measurements were made with white light in the case of the graphite sol whereas in the case of the arsenic trisulphide sol, an orange filter was inserted in the path of the incident beam. The values of ρ_u , ρ_v and ρ_h are given in Tables I and II. The depolarisation factors are plotted against the angle of observation and the curves are reproduced in Figs. 6–9.

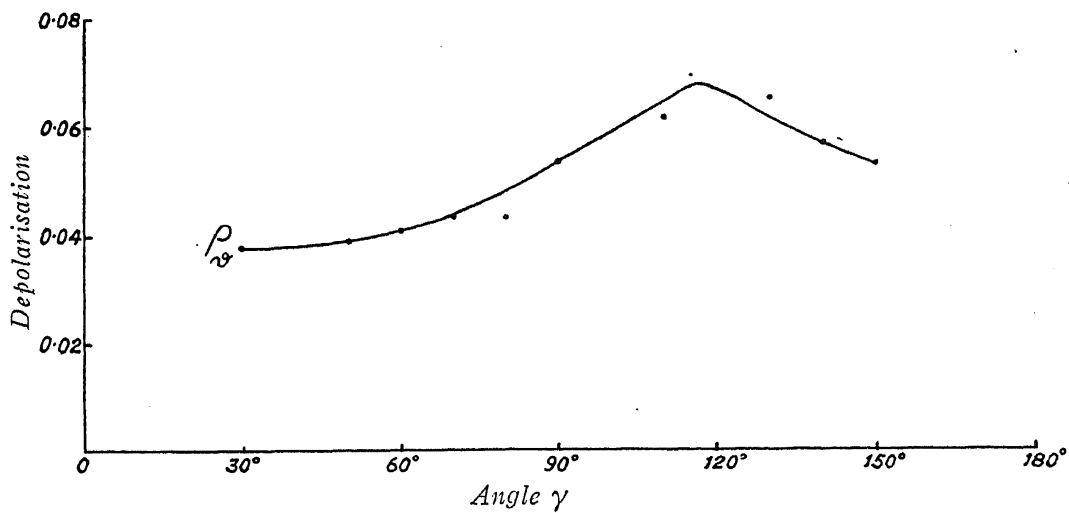


FIG. 6.

Depolarisation (ρ_v) as a function of angle of scattering for graphite sol.

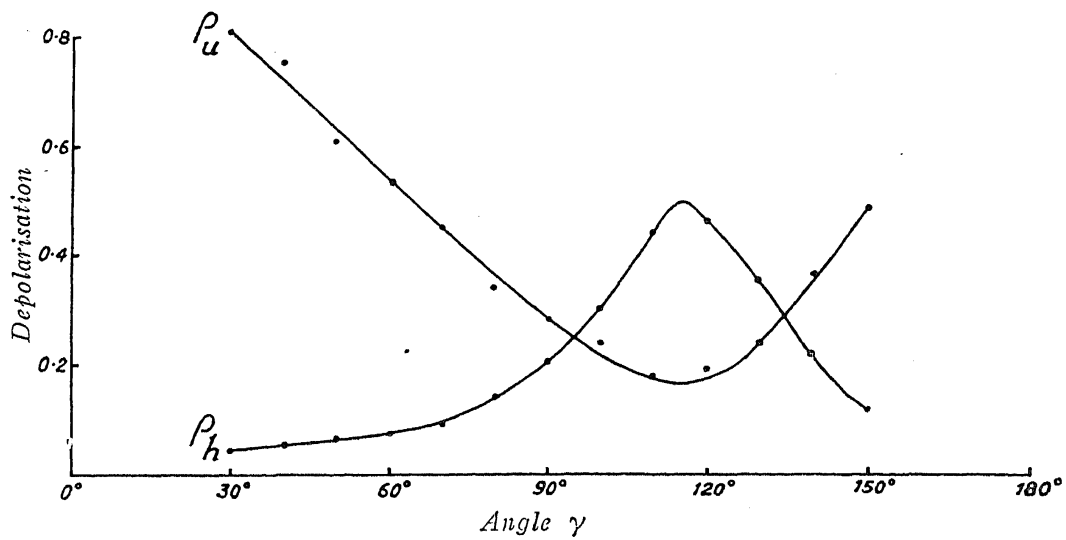


FIG. 7.

Depolarisation (ρ_u and ρ_h) as a function of angle of scattering for graphite sol

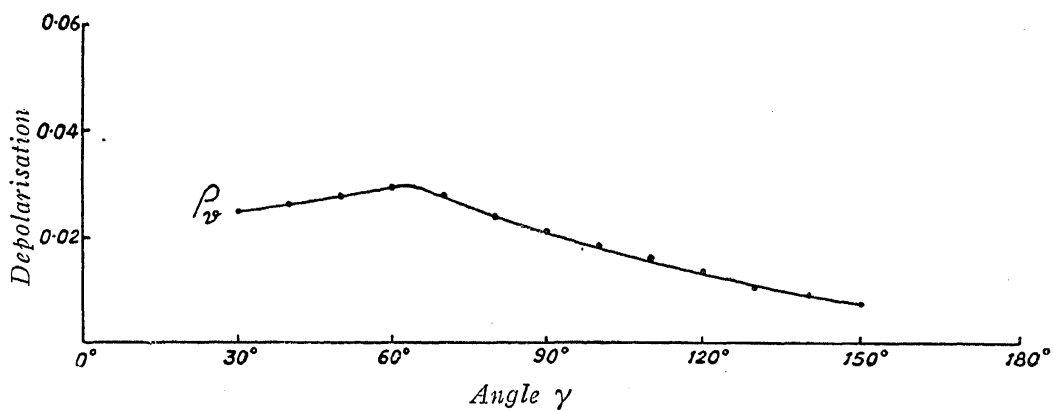


FIG. 8.

Depolarisation (ρ_v) as a function of angle of scattering for arsenic trisulphide sol.

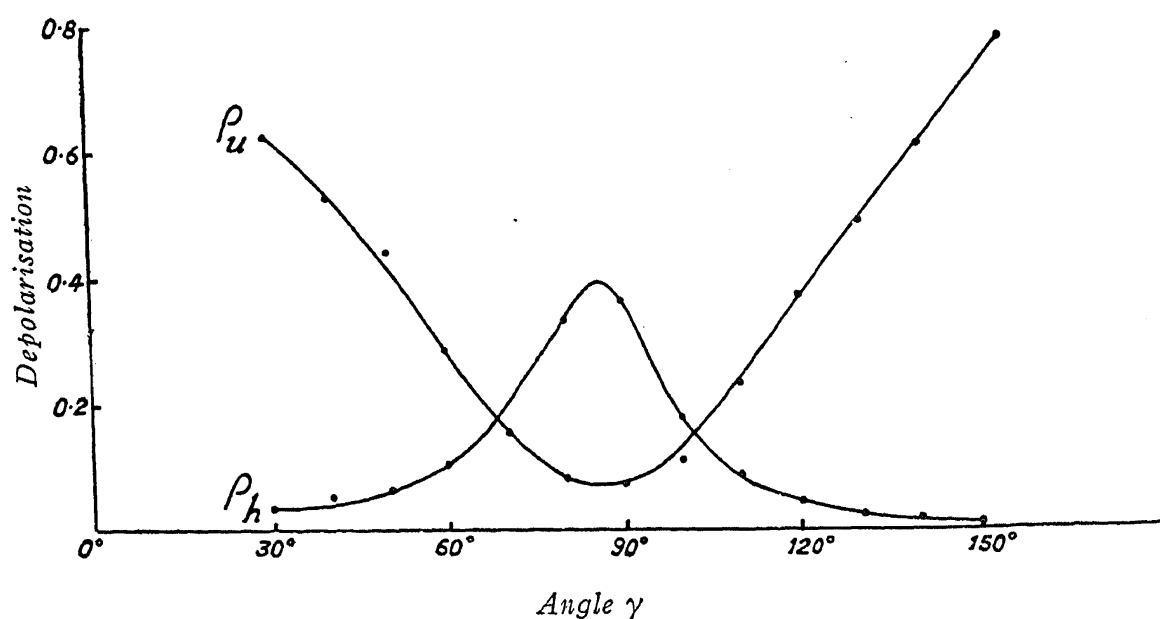


FIG. 9.

Depolarisation (ρ_u and ρ_h) as a function of angle of scattering for arsenic trisulphide sol.

TABLE I.

Depolarisation factors of graphite sol with white light.

γ	30° %	40° %	50° %	60° %	70° %	80° %	90° %	100° %	110° %	120° %	130° %	140° %	150° %
ρ_v ..	3.78	3.78	3.95	4.14	4.33	4.33	5.33	5.99	6.2	6.7	6.57	5.76	5.33
ρ_h ..	4.91	5.43	6.7	7.82	9.6	14.2	20.8	30.1	44.65	46.8	35.73	20	12
ρ_u (obs.)	81	75	61	53.8	45.5	34.3	28	24	18.2	19.8	24.3	33.8	49
ρ_u (cal.)	79.6	67.7	60.5	54.8	39.7	33.4	29.3	24.4	18.9	19.66	23.4	32.6	47.7

TABLE II.

Depolarisation factors of arsenic trisulphide sol with orange filter.

γ	30° %	40° %	50° %	60° %	70° %	80° %	90° %	100° %	110° %	120° %	130° %	140° %	150° %
ρ_v ..	2.4	2.64	2.8	2.95	2.8	2.4	2.16	1.85	1.62	1.4	1.1	0.93	0.77
ρ_h ..	4.14	5.33	6.93	10.7	19.4	33.3	36.1	18	8.77	4.33	2.5	1.72	1.1
ρ_u (obs.)	62.7	53	44.2	28.9	15.9	8.63	7.95	11.5	23.3	36.9	49.0	61.0	81
ρ_u (cal.)	58.9	50.8	42	29.0	16.8	9.6	7.97	11.9	20.	34.8	45.1	58.5	70.0

4. Discussion of Results.

The last row in Tables I and II gives the values of ρ_u calculated from the observed values of ρ_v and ρ_h according to relation (1). The fairly satisfactory agreement between the observed and calculated values of ρ_u indicates that the reciprocity theorem is true not only for the transverse horizontal direction but also for any angle of scattering in the horizontal plane. It is instructive to compare the experimental curves of ρ_u , ρ_v and ρ_h given in Figs. 6-9 with the theoretical curves drawn in Figs. 3 and 4 for large spherical particles and for small ellipsoidal particles respectively. The experimental graphs exhibit characteristics which in some respects combine the features exhibited by the theoretical curves in Figs. 3 and 4 and in other respects are intermediate between them. We shall now comment on these features in detail.

Variations of ρ_u .—The value of ρ_u for the two sols examined falls to a finite minimum value at an angle intermediate between 0° and 180° , but this minimum instead of being at 90° , is shifted to an angle $\gamma > 90^\circ$ for graphite sol to an angle $\gamma < 90^\circ$ for arsenic trisulphide sol; this indicates that graphite particles simulate metallic particles in their behaviour, whereas arsenic trisulphide particles behave like dielectrics. For the two limiting values of γ (*i.e.*, 0° and 180°), the observed value of ρ_u tends to unity, as it is to be expected theoretically for all particles orientated at random irrespective of their size and shape.

Variations of ρ_h .—The value of ρ_h both for graphite sol and for arsenic trisulphide sol shows a maximum for a value of γ intermediate between 0° and 180° . But this maximum instead of being at 90° as in Fig. 4, is shifted towards smaller or larger values of γ in the same way as the minimum of ρ_u . The curve for ρ_h is in fact markedly unsymmetrical in shape. The theoretical values of this maximum is unity for small ellipsoidal particles and zero for large spherical particles. The observed value for the sols studied is intermediate between these extremes, from which it may be inferred that the particles are neither spherically symmetrical nor small in size.

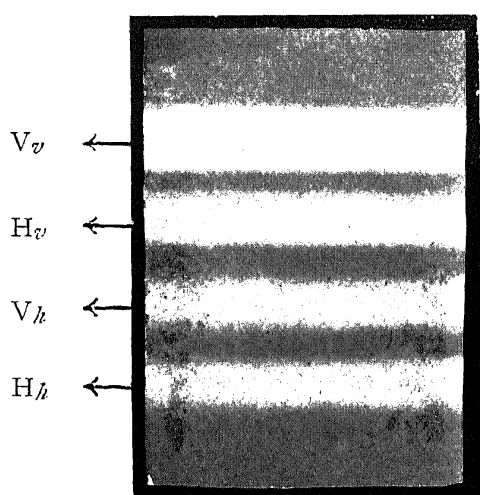
Variations of ρ_v .—Instead of ρ_v being zero as indicated in Fig. 3, or finite and constant in value for all angles of γ as in Fig. 4, the observed ρ_v curves show a maximum for an angle intermediate between 0° and 180° . The curves are distinctly unsymmetrical in shape about the maximum, but both the maximum and the asymmetry are rather less pronounced than in the corresponding curve for ρ_h . In graphite sol the maximum value of ρ_v falls approximately in the same region as the maximum of ρ_h and the

minimum of ρ_u . On the other hand, in arsenic trisulphide sol such a coincidence does not occur; ρ_v is maximum at 60° , whereas ρ_h is maximum at 85° . The experimental curves indicate that both for the values of $\gamma = 0^\circ$ and 180° , the values of ρ_v and ρ_h tend to be equal to each other, as is required by theory. But this common value is not the same when $\gamma = 0^\circ$ and $\gamma = 180^\circ$. For the two cases studied, it would appear that ρ_v at 0° is $>$ or $<$ ρ_v at 180° according as the maximum of the curve of ρ_v is shifted towards 0° or towards 180° .

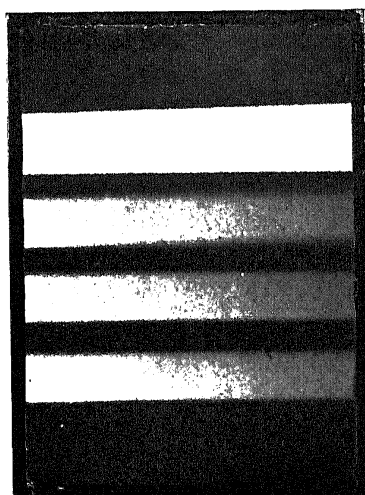
In conclusion, the author wishes to express his grateful thanks to Professor Sir C. V. Raman under whose inspiring guidance the present investigation has been carried out.

5. Summary.

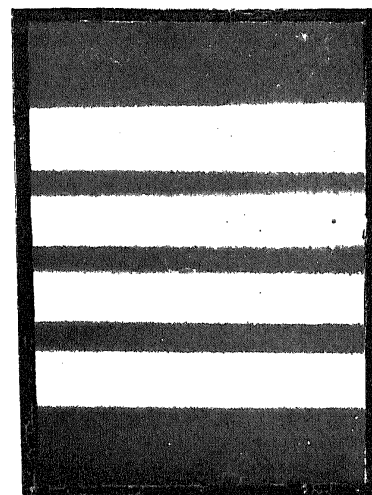
The reciprocity relation $\rho_u = (1 + 1/\rho_h)/(1 + 1/\rho_v)$ connecting the three depolarisation factors ρ_u , ρ_v and ρ_h for the case of the transverse scattering is deduced theoretically. It is pointed out that this relation is valid, not for a single colloidal non-spherical particle with fixed orientation in space, but only for a solution containing a large number of particles which have no preferred orientation in the plane containing the incident and scattered beams. The same considerations are extended to the case of oblique directions of scattering and it is shown that the relation continues to be valid under the same conditions, ρ_u , ρ_v and ρ_h being now functions of the angle γ of scattering and, of course, of the wave-length of the light used. These inferences have been tested out experimentally by the usual double double-image prism method and found valid. Direct measurements of the depolarisation factors ρ_u , ρ_v and ρ_h for oblique scattering for graphite and arsenic trisulphide sols are also found to satisfy the reciprocity relation. Curves representing ρ_u , ρ_v and ρ_h as a function of γ , the angle of scattering, have been plotted and compared with the theoretical curves for the two cases of (a) large spherical particles and (b) small ellipsoidal particles. The experimental graphs exhibit characteristics which, in some respects, combine the features exhibited by the theoretical curves and in other respects are intermediate between them. The values of ρ_v and ρ_h for the two sols examined show a maximum and the value of ρ_u shows a minimum for a value of γ intermediate between 0° and 180° . The curves for ρ_u , ρ_v and ρ_h are markedly unsymmetrical in shape; but both the maximum and the asymmetry of the curve for ρ_v are rather less pronounced than the corresponding curves for ρ_h and ρ_u .



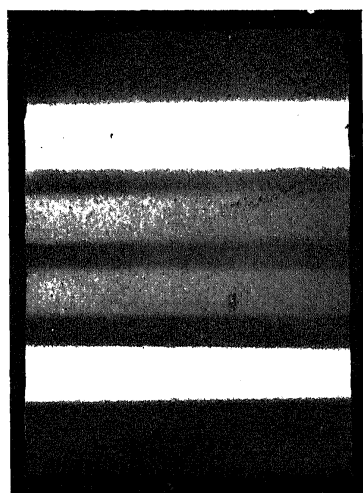
1. Benzene.



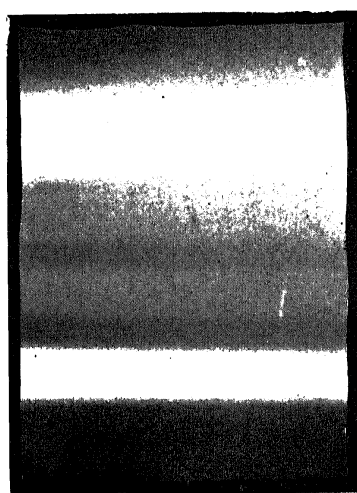
2. Red gold sol.



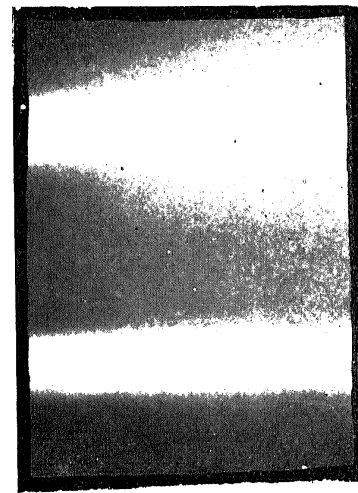
3. Bredig's silver sol.



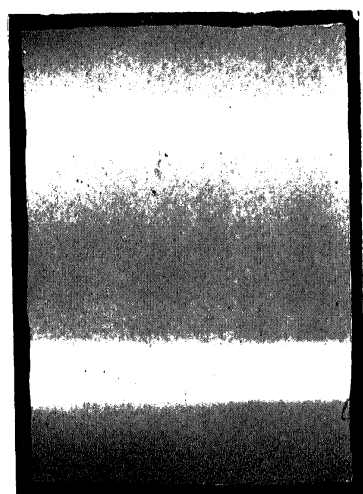
4. Graphite sol.



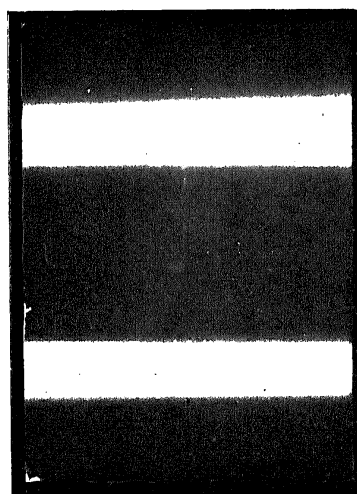
5. Stearic acid sol.



6. Dilute milk.



7. Sulphur suspensions.



8. Dilute toluene emulsion.



9. Concentrated toluene emulsion.