Summary.

Grating photographs of three of the principal helium bands have been measured and analysed, with the following results :—

(1) Tables showing wave-lengths, intensities, wave-numbers and allocation to series are given, also diagrams exhibiting the structure of the bands.

(2) The chief features of their structure are shown to be accounted for by the quantum theory of band spectra, a brief *résumé* of which is given.

(3) In each of the three bands a new type of series is found which, although closely related to the others, has not yet received a theoretical explanation. Other departures from the theory are also noted.

(4) It is concluded that the spectrum is due to an unstable helium molecule, having a moment of inertia of about $1 \cdot 8 \times 10^{-40}$grm.-cm.^{2}

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On the Molecular Scattering of Light in Water and the Colour of the Sea.

By C. V. Raman, M.A., Hon. D.Sc., Palit Professor of Physics in the Calcutta University.

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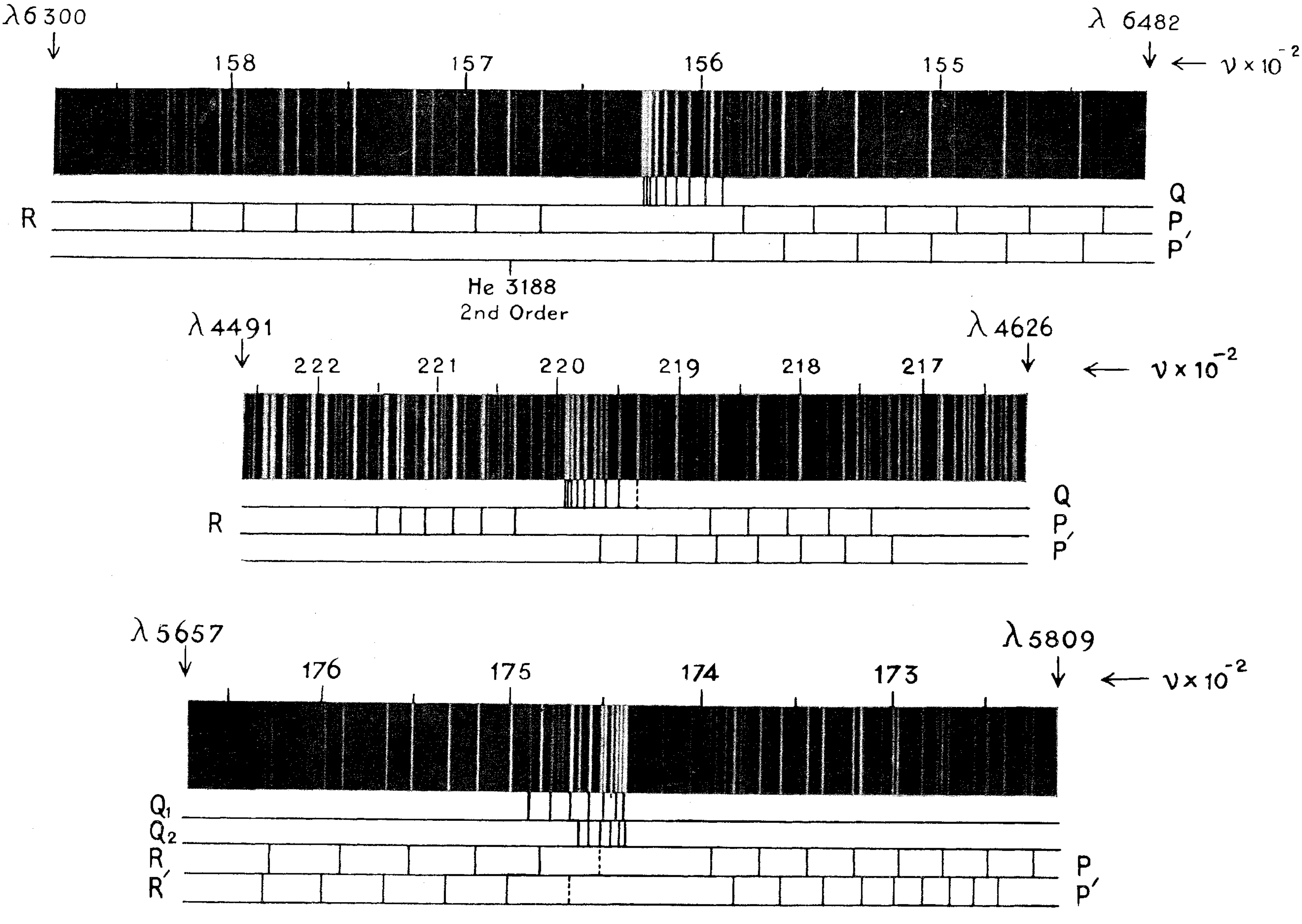
1. *Introduction.*

The theory that the light of the sky owes its origin and colour to diffraction by the molecules of the atmosphere is now established on a firm experimental basis by the brilliant work of Cabannes and of Lord Rayleigh on the scattering of light by dust-free gases, and by the measurements of the transparency of the higher levels of the atmosphere in the visual region of the spectrum, which have yielded results in close agreement with the calculated values. It is the purpose of the present paper to point out the part played by molecular diffraction in another of the great natural optical phenomena, that is, the colour exhibited by large masses of clear water when



Roy. Soc. Proc. A, vol. 101, pl. 1.

illumined by sunshine and viewed from above, the depth being so great as to provide a perfectly black background for observation. The subject at present is in a somewhat peculiar position, as even on the question of the reality of the phenomenon there appears to be a divergence of opinion. On the one hand, we have the following view expressed by so eminent an authority as the late Lord Rayleigh:* "We must bear in mind that the absorption, or proper, colour of water cannot manifest itself unless the light traverses a sufficient depth before reaching the eye. In the ocean the depth is, of course, adequate to develop the colour, but if the water is clear, there is often nothing to send the light back to the observer. Under these circumstances, the proper colour cannot be seen. The much-admired dark blue of the deep sea has nothing to do with the colour of water, but is simply the blue of the sky seen by reflection." On the other hand, observers familiar with the sea, such as J. Y. Buchanan, of the "Challenger" expedition, who have had very wide opportunities for study, have published detailed descriptions which support an entirely contrary view.† An admirable *précis* of the literature on the whole subject has been recently published by Prof. W. D. Bancroft.‡ From a perusal of this very convenient summary, and from the account given in Kayser and Runge's 'Handbuch,' it would appear that the general trend of opinion is that, so far as there is any real effect to be explained at all (that is, apart from reflected sky light) the colour of water is due to absorption, the return of the light from the depths of the liquid being due to suspended matter in it. During a recent ocean voyage, the present author has had an opportunity of making some observations which show that the view indicated above is entirely inadequate. It is proposed in this paper to urge an entirely different view, that in this phenomenon, as in the parallel case of the colour of the sky, *molecular diffraction* determines the observed luminosity and in great measure also its colour. As a necessary preliminary to the discussion, a theoretical calculation and experimental observations of the intensity of molecular scattering in water will be presented.

2. *Theory of Molecular Diffraction of Light in Liquids.*

In the theory of the molecular scattering of light by gases developed by the late Lord Rayleigh, a very simple relation is established between the refractivity of the medium and the energy scattered laterally by it. These quantities are calculated on the assumption that the scattered waves originating from the individual molecules are, except in the direction of the

* 'Scientific Papers,' vol. 5, p. 540.

† 'Nature,' July, 1910, p. 87.

‡ 'Franklin Inst. Journal,' 1919, and also reprinted in 'Chemical News,' 1919.

propagation of primary waves, in entirely arbitrary phase-relationships and that their energy-effects may therefore be treated statistically as additive. The justification for this view, namely, that the molecules are in irregular order and possess large thermal movements, has been further discussed by Sir Joseph Larmor* and the present writer.† Experiment shows that the Rayleigh law of scattering is in good agreement with observation, even when the gas is very dense or highly compressed. On the other hand, in the case of liquids, the spacing of the molecules is far closer and their freedom of movement much less, and we should no longer be justified in making the same assumptions. A gramme-molecule of steam occupies at 100° over 1600 times the volume which an equal mass of water would occupy, and it is clear, *prima facie*, that volume for volume, water would not scatter light 1600 times as strongly as pure steam, but only in a lesser degree. The question is, by how much less?

A method of approach to the problem of molecular scattering, which is somewhat different from Rayleigh's and which enables the case of liquids to be included, is the "theory of fluctuations" developed by Einstein and Smoluchowski, and used by the latter especially to elucidate the optical phenomena observed in the vicinity of the critical state.‡ In this theory, the medium is regarded as undergoing small local variations of density owing to the irregular movements of the molecules, and the result of these fluctuations of density is that a certain proportion of the incident light is scattered. The formula developed is quite general and it is shown that the intensity of the light diffused by a cubic centimetre of the fluid at right angles to the direction of the incident rays is

$$\frac{\pi^2}{18} \cdot \frac{\beta}{\lambda^4} \cdot \frac{RT}{N} \cdot (\mu^2-1)^2 (\mu^2+2)^2.$$

λ is the wave-length, β the compressibility of the substance, μ its refractive index, and R, T, N, have the usual significance attached to them in the kinetic theory.§ In the case of gases, β is simply the reciprocal of the pressure, and μ being nearly unity, the expression reduces identically to Rayleigh's formula. The result may be applied equally well to find the intensity of the light scattered in liquids. For air under standard conditions,

$$\beta = 0{\cdot}987 \times 10^{-6} \text{cm.}^2\text{dyne}^{-1},\ T = 273° \text{ and } \mu = 1{\cdot}000293.$$

For water at 30°, $\beta = 48{\cdot}9 \times 10^{-12}\text{cm.}^2\text{dyne}^{-1}$, $T = 303°$ and $\mu = 1{\cdot}337$. From

* 'Phil. Mag.,' January, 1919.

† 'Nature,' May 1, 1919.

‡ For references, see Perrin's 'Atoms,' Chapter V, authorised translation. Also Epstein, 'Ency. Math. Wiss.,' vol. 3, p. 520 ("Spezielle Beugungsprobleme").

§ R and N refer to a gramme-molecule and not to unit volume.

these data, it is readily found on calculation that, volume for volume, water at 30° should scatter light 159 times as strongly as dust-free air under standard conditions.

It should be remembered that in the theory on which the foregoing result is based, the scattering considered is merely that associated with the ordinary refractivity of the medium, considered along with the non-uniformity of optical density resulting from molecular movement. The light scattered in a direction perpendicular to the incident rays should be completely polarised. This result holds even when the regions in which the small density fluctuations occur are not of dimensions small compared with the wave-length.* It is a point worthy of notice that according to the formula, the scattering power of liquids is proportional to the absolute temperature, apart from the changes which would result also from the variation of compressibility and refractive index with temperature.

3. *Experimental Study of Molecular Diffraction by Water.*

To determine whether the intensity of light molecularly scattered in water, as indicated by the theory, is at least of the same order of quantities as in experiment, some observations have been made by the writer. On examination, the ordinary town-supply water as taken from the pipes showed a very strong scattering when a beam of light was sent through it. The track was practically white and showed innumerable motes floating about in the water. Repeated filtration through several thicknesses of Swedish filter paper made an improvement, the track of the beam being now of a bluish colour, and a still better result was obtained when an earthenware filter was used. Suspended matter was, however, still in evidence and the track was also much brighter when viewed nearly in the direction of the source than when seen transversely or in the opposite direction. A somewhat casual attempt was then made to clear the water by adding alkali and alum and thus throwing out a gelatinous precipitate of hydroxide. This made a further improvement, but small particles of the precipitate remained floating about, apparently because the depth of the water was insufficient, and the appearance of the track of the beam was not very prepossessing. The next attempt was made with ordinary distilled water which had been prepared without any special precautions and stored in the chemical laboratory. This gave immediately a much smaller intensity of light scattering than the tap-water had done after several attempts at filtration. For purposes of observation, the distilled water was put into a stoppered glass bottle with square sides and allowed to stand.

* Rayleigh, 'Scientific Papers,' vol. 5, p. 547.

Test-observations from day to day of the scattered beam with a double-image prism and a set of Wratten colour filters showed a progressive improvement. After about a fortnight's standing, the track of the light was hardly conspicuous unless a dark background was provided for it to be viewed against, and the defect of polarisation at the violet end of the spectrum was much less striking than it was when the observations were begun. Small motes were still to be seen glistening in the liquid, particularly when it was viewed nearly in the direction of the source, but the track of the beam viewed transversely was of a blue colour and it was judged that the greater part of the observed luminosity was probably due to the water itself.

For a quantitative estimate, the brightness of the beam in the water was compared directly with that of its track in saturated ether vapour. The latter was contained in a pear-shaped bulb with a long neck which was covered over with black paint and formed the "black cave" against which the light scattered by the vapour was observed. The bottle and the bulb were set side by side and a parallel beam of light passed through both. An Abney rotating sector was placed in front of the water-bottle and the opening of the sector varied till the tracks appeared to be of equal intensity in both vessels as judged visually. The opening of the sector gave the ratio of intensities, a correction being made for the loss of light by reflection in the passage of the direct and scattered pencils through the glass walls. It is not pretended that the determinations made in this way were anything more than approximate estimates; it was thought that more elaborate measures could well be reserved till thoroughly satisfactory samples of "mote-free" water could be obtained. The scattering of light in saturated ether-vapour has been measured by comparison with air by Rayleigh, and shown to be strictly in proportion to the square of its refractivity. Using this result, the observations showed that the scattering power of the sample of water used was 175 times that of dust-free air under standard conditions. This, though not agreeing exactly with the theoretical value is only slightly in excess, and the difference is not more than can reasonably be explained as due to residual suspended matter present in the sample of water used.

The light scattered by water in a direction transverse to the incident beam was found to be strongly, but not quite completely, polarised. It seems quite likely that the imperfect polarisation is really a characteristic of water, and not merely due to presence of residual suspended matter. More complete measurements of the defect of polarisation have, however, been held up till a thoroughly pure sample of water is obtained.

4. *Molecular Scattering and Transparency of Water.*

Since the energy of the light laterally scattered is derived from the primary beam, there must result a certain attenuation in the intensity of the latter in its passage through the liquid, the magnitude of which may be readily calculated from the coefficient of scattering. The expression for the intensity of the transmitted beam is $I = I_0 e^{-\alpha x}$, where x is the length of path traversed through the liquid and

$$\alpha = \frac{8\pi^3}{27} \cdot \frac{RT\beta}{N\lambda^4} \cdot (\mu^2-1)^2(\mu^2+2)^2.$$

As in the case of atmospheric scattering, we may expect that the coefficient of attenuation α will exactly indicate the observable transparency of the medium *in those parts of the spectrum for which it does not exercise any selective absorption.* From the data already given and the known values of R, T and N, α may readily be determined for any value of the wave-length.

From the observations of various experimenters, it is known that water exercises a selective absorption on the longer wave-length side in the visible spectrum. The most reliable measurements of any hitherto made appear to be those of Count Aufsess, quoted in Kayser's 'Handbuch.' This experimenter used double-distilled water, and convinced himself that it was free from suspended matter: it was found by him that the selective absorption in the visual region practically ceased for wave-lengths less than 558 $\mu\mu$. For the two wave-lengths 522 $\mu\mu$ and 494 $\mu\mu$, Aufsess gives us the coefficient of absorption 0·00002. For these two wave-lengths, the coefficient of attenuation α, calculated from the formula given above, is respectively 0·000022 and 0·000029. The agreement of observation and theory is significant, and it would be interesting if further accurate measurements for different wave-lengths up to the extreme violet end of the spectrum were available, so that the increase of the coefficient of attenuation inversely as the fourth-power of the wave-length could be tested. It would also be interesting to determine by careful experiment whether the intensity of the light scattered by water exactly follows the fourth-power law; if the selective absorption in the longer wave-lengths is accompanied by any selective scattering, deviations from the λ^{-4} law may be expected to appear in that region of the spectrum.

5. *Luminosity of Deep Water due to Molecular Scattering.*

Since, in round numbers, water diffuses light 160 times as strongly as an equal volume of air, a layer of the liquid 50 metres deep would scatter approximately as much light as 8 kilom. of homogeneous atmosphere, in other words, it should appear nearly as bright as the zenith sky. This rough calculation, however, omits to take into account two important factors, the diminution in the intensity of sunlight before it reaches the level of the water, and its further attenuation in the passage through the liquid, and also the loss in intensity of the scattered light before it re-emerges from the depths. It is the two last factors just mentioned which, together with the magnitude of the scattering itself, ultimately determine the total observed luminosity of an ocean of liquid of very great depth. Neglecting the effect of self-illumination within the liquid, and also the contribution which is made by diffuse skylight, which enters the water and is then subsequently re-scattered within the liquid—both of which may, in certain circumstances, rise to importance—the observable luminosity of a very deep layer of liquid may be readily calculated. For simplicity, we shall consider a case in which the altitude of the sun is sufficiently great to enable its rays within the water to be treated as approximately vertical in direction, and the intensity of the light scattered will also be assumed to be observed in an approximately vertical direction, *e.g.*, by an observer in an aeroplane flying at some height above the water. The coefficient of scattering in such a case will be twice as great as when the scattering is observed laterally. Denoting it by $2B/\lambda^4$, and the coefficient of absorption of light in water by γ, the total observed luminosity is given by the integral

$$\frac{2B}{\lambda^4}\int e^{-2\gamma x}\,dx,$$

x being the depth of any layer. For a sufficiently great depth, this reduces to $B/\gamma\lambda^4$. For the case of pure water, the values of γ are taken from the determinations of Count Aufsess for wave-lengths up to 522 $\mu\mu$, and, for shorter wave-lengths, we may take them to be the same as the value of coefficient of attenuation α given by theory. The value of B is in round numbers 160 times the coefficient of lateral scattering by dust-free air. From these data, and making an allowance for the diminution of the solar intensity in transmission through the atmosphere as on an average day, the total luminosity of deep water for different wave-lengths is expressed in Table I in terms of the kilometres of dust-free air at atmospheric pressure, which would, by lateral scattering of full sunlight, give an equal effect.

If we take the scattering by 8 kilom. of dust-free air as the standard and compare with it the figures shown in Table I, it is seen that in the light returned by the water practically all the red is cut out, the orange and yellow are quite feeble, but the green is greatly enhanced, and also the blue, indigo, and violet, but to a considerably less extent. The standard of comparison

Table I.—Luminosity of Deep Water.

λ in $\mu\mu$.	658	622	602	590	579	558	522	494	450	410
Equivalent kilometres of dust-free air.	0·4	0·5	0·7	1·4	2·5	3·0	50	40	24	15

(scattering by dust-free air) being itself of a blue colour, it is clear that the cutting out of the red and the enfeeblement of the orange and yellow would result in the colour of the light scattered by the water being a highly saturated blue. The enfeeblement of the orange and yellow would, however, considerably diminish the visual intensity, which, at a rough estimate, would probably not exceed two or three times that of the zenith sky.

It will be understood from the figures given in Table I that the blue colour of the light scattered by the water arises primarily from the operation of the Rayleigh λ^{-4} law, the absorption of the red and yellow regions of the spectrum in the water resulting merely in the colour being more *saturated* than it would otherwise be. If the figures entered in the columns of Table I had represented ratios of comparison with *white* light, the presence and predominance of the green would result in the perceived colour being a greenish blue, and not a deep blue colour. In other words, the blue colour of the scattered light is really due to diffraction, the selective absorption of the water only helping to make it a fuller hue.

6. *Colour of the Sea not due to Reflected Sky-light.*

There does not appear to be any way of escape from the consequences of the Einstein-Smoluchowski theory of molecular scattering worked out in the foregoing pages. Postulating an ocean of clear water, and of great depth, we have necessarily to accept the consequence that under the illumination of the sun's rays it would scatter light of a colour greatly transcending the light of the sky in the saturation of its blueness, and, also, unless the transparency of the water is much inferior to that of the pure liquid as observed in the laboratory, comparable with the light of the sky in its brightness. There is ample evidence regarding the great transparency of oceanic waters, at least under normal conditions, in calm weather. Writing of the mid-Pacific, J. Y. Buchanan states* that a metal plate only 4 inches by 4 inches, painted white and suspended at a depth of 25 fathoms (45 metres), was distinctly seen with sharply defined edges. The plate became indistinct at greater depths, but this was only on account of its smallness and want of steadiness, owing to

* 'Nature,' *loc. cit.*

the movement of the boat from which the observations were made. The plate was seen through the glass bottom of a floating tub, in order to eliminate the effect of ripples on the surface of the water. Buchanan adds that the colour of the column of the liquid, 25 fathoms in length, resting on the plate was a pale but pure ultramarine; that of the external and uninterrupted column surrounding it was of the same tone, but of many times greater intensity. He infers that the length of the uninterrupted column, which contributed to the luminous effect by diffusing sunlight upwards, must have been much greater than 25 fathoms. Buchanan's observations clearly indicate a high degree of transparency, and show that the colour of the sea really arises from a scattering of light upwards from within the water.

The statement by the late Lord Rayleigh, that the deep blue colour of the sea is merely due to reflected sky-light, has already been quoted in the introduction. We shall now proceed to examine the grounds urged in support of this view: "When the heavens are overcast the water looks grey and leaden, and even when the clouding is partial, the sea appears grey under the clouds, though elsewhere it may show colour. . . . One circumstance that may raise doubts is that the blue of the deep sea often looks purer and fuller than that of the sky. I think the explanation is that we are apt to make comparison with that part of the sky which lies near the horizon, whereas the best blue comes from near the zenith. In fact, when the water is smooth and the angle of observation such as to reflect the low sky, the apparent blue of the water is much deteriorated. Under these circumstances a rippling due to wind greatly enhances the colour by reflecting light from higher up. Seen from the deck of a steamer, those parts of the waves which slope towards the observer show the best colour for a like reason." The *facts* indicated in this quotation are, of course, quite correct; but the *explanations* given may well be questioned, and a closer examination shows that they require to be modified considerably.

Considering first the effect of clouds in the sky, careful observation shows that the presence of a cloud alters the appearance of the sea in two entirely distinct ways. In the first place, the water under the shadow of the cloud is screened from the direct rays of the sun, and the amount of light that can be diffused upwards from within the liquid is greatly diminished, and it must therefore necessarily appear darker. This feature is admirably shown in aeroplane photographs of water when the sky is clouded. In the second place, the presence of a cloud greatly increases the brightness of the part of the sky against which it is seen, and therefore also the brightness of its reflection in the surface of the water. In the case of an individual cloud, the apparent position of its reflected image on the surface of the water (which depends on the position of the observer) and the position of the shadow (which is independent of it) may be entirely different. When the clouds are more numerous and the sky gets more or less completely overcast, the two effects occur together over practically the whole area of the water, and the result is that the brightness of the surface-reflection is considerably enhanced, and the brightness of the light diffused out from within the water made quite small. The appearance of the sea is therefore naturally completely altered, but this in no way indicates that the blue colour of the sea, as ordinarily seen when the sun shines full into it, is merely reflected sky-light.

The difference in the colour of the sea, when it is entirely smooth and when its surface is slightly ruffled, or even merely rippled, is, indeed, remarkable; closely connected with this effect is the difference in colour between the fore and back parts of an undulation on the surface of the water. Careful observation shows that the explanation for this suggested by Rayleigh is not adequate, and that the effect, or at least the greater part of it, really arises in another way. It is obvious that the light molecularly diffused within the water before it can emerge into the air must in part be reflected internally at the surface of the liquid. If the surface of the liquid be viewed very obliquely, that is in a direction nearly parallel to it, the only part of the diffused light which can reach the observer's eye is that which is incident at nearly the critical angle on the boundary between the two media, and of this a considerable part would be reflected internally, and the portion that emerges would also be greatly attenuated by the increased angular divergence of the scattered pencils. In the same circumstances, the external surface would reflect the low-lying parts of the sky almost completely, the incidence being nearly grazing. The diffused light from inside the water would thus be overpowered by the sky-reflection. When, however, the surface of the water is even slightly disturbed, the conditions are completely altered. The scattered light can emerge freely into the air through the parts of the surface that slope towards the observer, and to a lesser extent through the parts that slope away from him, so far as they are visible at all, the latter portions showing the reflections of the sky more conspicuously. The differences in colour that arise in this way, and are actually observed, are much greater than can be explained merely by reference to the difference between the different parts of the sky.

Again, as has been pointed out by Tyndall and Buchanan, the colour of the sea is best seen when looking almost vertically down on its surface. The effects seen in this way can hardly be influenced by sky-reflection, as the brightness of the zenith sky is relatively small, and the reflecting power of water for normal incidence is only 2 per cent. Further, both of these writers describe observations made in circumstances in which the sky-reflection is eliminated altogether. One view that might perhaps be taken is that, while the colour of the sea is a real phenomenon which may be observed under suitable conditions, the appearance of the sea as a whole, as seen from the deck of a steamer, is largely determined by reflected sky-light. I think even this view would be a mistake. If it were true, the elimination of the reflection should result in the general appearance of the sea becoming impoverished. It will be shown later in the paper how this test can be applied, and the result is exactly the opposite. As a result of the discussion, we are thus led to the conclusion that the colour of the sea is a real phenomenon, that it is not due to reflected sky-light, and that the latter is merely a somewhat inconvenient disturbing factor in the observations.

7. *Colour of the Sea not due to Suspended Matter.*

It has been shown in the foregoing pages that pure water of the highest obtainable transparency is capable of exhibiting in its own body, as the result of molecular scattering, a blue colour of intensity amply sufficient to explain all that is observed in any actual case. There is a consensus of opinion among observers that the natural waters which show a deep blue are the most transparent of all. Nevertheless, in order to account for the observed return of the light from within the water, they have also agreed amongst themselves to supply a greater or less amount of suspended matter, according to the supposed requirements of theory! The position here is fairly analogous to that we find illustrated in regard to the theories of the colour of the sky. Ignoring the possibilities arising from the molecular structure of air itself (regarding which at least an early hint was given by Herschel), vesicles (!) of water were postulated. Subsequently dust-particles took their place, and were dispensed with only after it was recognised that the air itself was capable of explaining all that was observed; dust is now only a disturbing factor, the effect of which in favourable circumstances may be quite negligible. In the opinion of the writer, it would make for progress to adopt at once the position finally reached in the parallel case, and to recognise that the observed colour of the sea is primarily due to the water itself, and that suspended matter, if present at all in appreciable quantity, is to be regarded as a disturbing factor, of which the effect requires to be assessed in each individual case. As regards the deep blue or ultra-marine colours of the oceanic waters, at any rate, there is good reason for believing that the observed luminous effect is not due to suspended matter in any appreciable degree. In order that suspended matter might have a noteworthy optical effect, it should be present in a highly dispersed or colloidal form. Not only is this unlikely, in view of the actual marked transparency of these waters, which has already been remarked upon, but it would also be inconsistent with the coagulative property of the electrolytes present in the sea-water. As is well known, the colloidal matter brought down by the great rivers is thrown down when the fresh and salt waters mix, and practically none of it gets far out to sea. This is very prettily shown in sailing out from the mouth of a river or from the coast by the rapidly decreasing intensity of the Tyndall phenomenon shown by the sunbeams playing in the water. In the deep sea the Tyndall phenomenon can only be perceived if one looks down into the water in nearly the same direction as that in which the sun's rays enter the liquid. The tracks of the sunbeams can then be perceived going down into the water, and appearing by virtue of perspective to converge to a point at a considerable depth within it. This relative faintness of the Tyndall phenomenon in deep water is itself the best proof of the negligibility of any effect save that of molecular scattering. Reference may be made also to the observations of Tyndall,* who examined different specimens of sea-water, and found that, while the green seas showed suspended matter, the deep blue waters were very pure, and contained very little matter. Aitken,† speaking of the Mediterranean, mentions large white reflecting particles present in it; but, from the details mentioned in his paper, it is clear that he is referring to the greenish-blue regions near the coast, and not to deep-sea water.

As regards inland lakes, it is difficult to be very precise, as so much depends on the individual circumstances of each case, but it is more than likely that a detailed examination will show that, in the case of the very transparent deep blue waters, the influence of suspended matter is almost negligible. In this connection, it is useful to consider how suspended matter, if present, would influence the observed results. The quantity of suspended matter and the state of its dispersal are here both relevant. First, we shall consider the case of *very finely* dispersed matter, and note the changes that would occur as the quantity is increased. In Section 5, it has been shown that the total observed luminosity for any wave-length is proportional to the scattering coefficient, and varies inversely as the attenuation coefficient. In the region of the spectrum in which there is no selective absorption, both of these quantities would be increased in the same ratio, and hence the luminous effect would remain unaltered. In the region of selective absorption, the scattering would be increased without any

* Quoted *in extenso* in Bancroft's paper, *loc. cit.*

† Bancroft's paper, *loc. cit.*

appreciable increase in the coefficient of attenuation. Taking this into account, along with the figures given in Table I, we may draw the following inference: (*a*) a *very small* quantity of finely dispersed matter would not appreciably alter either the colour or intensity; (*b*) a larger quantity of such matter would cause some increase in intensity, accompanied by a decrease in the saturation of the hue.

Suspended matter not very finely dispersed would operate in a different way. The first effect of increasing size of the particles would be the breakdown of the λ^{-4} law as regards the intensity of the light scattered in any given direction. With a collection of particles of different sizes, the colour of the light scattered would be practically the same as the colour of the light incident on the particles in any given layer, and we should find the water exhibiting a greenish-blue or green colour according to the quantity of suspended matter. It must not be supposed that the presence of suspended matter necessarily increases the intensity of the light scattered upwards. This depends a good deal upon the nature and the size of the particles. If their diameter be not small compared with the wave-length, they would diffract light unsymmetrically, that is, scatter more strongly in the direction of the primary beam than in the opposite direction towards the source, and this would result in a diminution of the intensity of scattering in the latter direction. If, further, the particles are of a fairly uniform size, special polarisation effects would also be observed. It is, however, not necessary here to enter further into these details.

Finally, it should be remarked that in regard to the total quantity of light scattered upwards from the water, small changes in the quantity of suspended matter, if any, present in the water are of much less importance than variations of the transparency of the water arising from other causes, *e.g.*, the appearance of a very small quantity of organic matter in the water exercising a selective absorption in the blue region of the spectrum. This would greatly enfeeble the scattered light that emerges from the water, without much altering its colour.

8. *Polarisation and Colour Phenomena observed at Sea.*

According to the theory of molecular diffraction in liquids, the light scattered at right angles to the direction of the illuminating beam should be polarised. In attempting to test by observation at sea, other interesting effects are also noticed which will now be described.

As already remarked above, the reflection of sky-light at the surface of the water is an embarrassing feature in making observations of the colour of the sea. Its influence may, however, be eliminated in the following simple way:

Light reflected at the polarising angle from the surface of a liquid may be quenched by observation through a suitably oriented nicol. Hence, by observing a tolerably smooth patch of water through a nicol at the polarising angle, the surface reflection may be got rid of. The nicol may be mounted at the eye-end of a cardboard tube, so that it can be conveniently held at the proper angle with the surface of the water and rotated about its axis so as to get the correct position for extinction of the reflected light. During a recent voyage, the writer made some observations by this method in the deeper waters of the Mediterranean and Red Seas, and found that the colour of the sea, so far from being extinguished when the sky-reflection is cut off, is seen with wonderfully improved vividness and with saturated hues. Even when the water is ruffled or when it is viewed more obliquely than at the polarising angle, the nicol helps to weaken the sky-reflection. Further, as is well-known, the light of the sky is itself strongly polarised, and this fact may in favourable circumstances be used to practically eliminate sky-reflection from the whole surface of the sea. For this purpose, the time most suitable is when the sun has reached its maximum altitude, and the observer should stand with his back towards the sun and view the surface of the sea through a nicol. The part of the sky facing the observer has then its maximum polarisation, especially the low-lying parts, and the amount of polarisation is further enhanced when the light is reflected from the water at various angles of incidence. By turning the nicol about its axis, the best position for extinction should be found, and the whole surface of the sea will then be found to glow with a vivid blue light emerging from inside the water. Part of this improvement is also due to the fact that the nicol in great measure cuts off the atmospheric haze which covers the more distant parts of the sea.

The obvious way of testing the light from the sea for polarisation, that is, viewing it through a nicol and turning the latter about its axis, is interfered with by the fact that the intensity of the reflected light also varies at the same time and obscures the variation in the intensity of light diffused from inside the water. Even thus, however, it is possible to observe the polarisation of the scattered light, the surface of the water appearing *less* blue when seen through the nicol in one position than when viewed directly. Much the better way of detecting the polarisation of the diffused light, however, is to hold the nicol at the proper angle for extinguishing the surface-reflection from the water, and to vary the azimuth of observation relatively to the direction of the sun's rays entering the liquid. Striking changes in the colour and intensity of the light diffused by the water will then be noticed. The best time for making this observation is when the altitude of the sun is moderately large but not too great. Obviously, if the sun's rays are too nearly vertical, varying the azimuth of observation can make no difference. But when the sun's rays inside the water proceed at an angle to the surface, the variation of the azimuth of observation alters the relation between the direction of the primary beam and the scattered rays under test. When the observer has his back to the sun, he looks down practically along the track of the rays inside the water, and the scattered light reaching his eye is unpolarised inside the water and is not extinguished in any position of the nicol. The colour of the scattered light is then seen as a vivid but comparatively lighter blue. As the azimuth of the plane of observation is swung round, the intensity of the scattered light diminishes and its colour changes to a deeper blue, until finally when the observer nearly faces the sun,* the intensity of the scattered light is very small and it appears of a dark indigo colour. If the polarisation of the scattered light were complete and the direction of observation exactly transverse to that of the primary beams inside the water, the nicol would have completely quenched the light. This is, however, not actually the case, evidently because we have to deal not only with the scattering of the sun's direct rays inside the water, but also with multiply-scattered light, and also with the blue light of the sky which enters the water and is then re-scattered within it. It is evident that these contributions to the luminosity of the water would diminish the perfectness of the polarisation,† and would give a much darker blue than the primarily scattered rays.

The relatively deep colour of the secondarily scattered rays mentioned in the preceding paragraph is also prettily illustrated by observing the water on the shadowed side of the ship, where the sun's rays do not strike it directly. Such water shows a much darker and deeper colour than the contiguous parts exposed directly to the sun's rays. A similar explanation may be given of the deepening of the colour of the sea as the sun goes down. The lower the altitude of the sun, the more important is the contribution of sky-light re-scattered within the water to the observed luminous effect. The blue

* He cannot, of course, exactly face the sun, as the reflection of the sun's rays from the surface of the water would then interfere with the observations. It is advantageous to choose a time when the altitude of the sun is such that these reflections are also quenched by the observing nicol. It should also be mentioned that the partial polarisation of the sunlight, when it enters the water obliquely, and a similar effect which occurs when the diffused light emerges from the water, make it possible to detect an appreciable dependence on the azimuth of observation of the colour, even without the use of the observing nicol.

† Much in the same way as the polarisation of sky-light, even at 90° from the sun, is incomplete. It is also possible that the imperfectness of the polarisation of the molecularly-scattered light (due to asymmetry of the molecules or other cause) may contribute to this result. But on this point, the author reserves opinion.

colour of the sea, as observed with the aid of a nicol when the sky is completely overcast by clouds, also appears of a distinctly deeper tint than sunlit water. It is probable that this may, at least in part, be due to the importance of multiple scattering in such cases.

The difference between the colour of the parts of a wave sloping towards and away from the observer has already been mentioned and explained. A remarkable feature noticed in this connection is that when the surface of the sea is viewed through a nicol, the degree of contrast varies enormously as the nicol is rotated about its axis. The precise effect, of course, depends upon the relative intensity, colour, and polarisation of the light reflected from the surface of the water at different angles and of the light emerging from inside the water. Broadly speaking, the phenomenon observed is that in one position of the nicol the sea appears almost flat and undisturbed, and in another position ruffled and full of ripples. The visibility of the horizon, which depends on the contrast between sea and sky, also varies, in some cases very greatly, as the nicol is rotated.

9. *Colours of the Transmitted Light.*

Finally, a few remarks would not be out of place regarding the nature of the colours observed when an opaque body, *e.g.*, a white plate, is immersed at some depth under water. It should not be assumed that the colour which it exhibits really corresponds to that transmitted by an equivalent column of water of twice the depth. The observed effect is really the resultant of two distinct factors: (*a*) the light molecularly scattered upwards towards the observer by the column of water between the plate and the surface; and (*b*) the light scattered by the plate and reaching the observer after attenuation in passing through the column of water. The effect (*b*) itself is composite, for the light reaching the plate and scattered by it consists of two parts: (*c*) regularly transmitted light, and (*d*) lateral illumination of the plate, due to molecular scattering in the liquid. It is clear from this that the colour of the plate would appear much bluer than that of the transmitted light really is, and that observations of the latter by this method are quite futile.

10. *Summary and Conclusion.*

The paper puts forward a new theory of the colour of the sea, namely, that it is due to the molecular scattering of light in water. The following are the principal conclusions contained in the paper:—

(*a*) The intensity of molecular scattering in water can be calculated from the "theory of fluctuations" developed by Einstein and Smoluchowski, and is found to be in round numbers 160 times that in dust-free air. This agrees with the value observed experimentally.

(*b*) The coefficient of extinction of light in water calculated from theory also agrees with the observed value in the parts of the spectrum in which there is no selective absorption.

(*c*) A sufficiently deep layer of pure water exhibits by molecular scattering a deep blue colour more saturated than sky-light and of comparable intensity. The colour is primarily due to diffraction, the absorption only making it of a fuller hue.

(*d*) The theories hitherto advanced that the dark blue of the deep sea is reflected sky-light or that it is due to suspended matter are discussed and shown to be erroneous.

(*e*) A number of interesting effects, due to polarisation and multiple scattering observed at sea, are described and explained.

(*f*) It is pointed out that the colour of a white plate as seen when immersed at some depth under transparent water does not really correspond to the character of the transmitted light.

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The Design of Repeating Patterns.—Part I.

By Major P. A. MacMahon, F.R.S., and W. P. D. MacMahon, F.R.A.S.

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1. By a repeating pattern, or "repeat," as it is sometimes termed for brevity of expression, is to be understood a figure in two dimensions of such shape that a number of figures identical with it may be assembled so as to fill space of two dimensions without leaving any interstices. We include in the definition any number of separate figures, relatively fixed in position, which, as a whole, possess the repeat property.

The object of the present communication is, after some general notions concerning the subject, to establish a simple method for the design of repeats which leads naturally to a useful classification of these geometrical forms. In particular, in view of the circumstance that it is æsthetically desirable to construct forms which possess some kind of symmetry, a calculus for the design of symmetrical repeats is brought forward.*

* The subject studied herein has been broached in a little book by the first author, entitled 'New Mathematical Pastimes,' which is on the point of publication by the