positive column of a vacuum tube. The high current densities which obtain when powerful condensed discharges are employed, and which give rise to a high concentration of charged particles, would seem to be of importance chiefly in permitting the violation of the principle of selection, owing to the intense local electric fields, the existence of which is demonstrated by the broadening of the lines in accordance with the Stark effect. It has long been known that when an inductance coil is introduced into the circuit of a condensed discharge the effect is to cause a disappearance of the spark lines and to reduce the spectrum to the arc type. The inductance must reduce the rate at which the charge on the electrodes can increase, and, hence, also the maximum potential attained. Further investigation will be required to elucidate fully all the changes in the band spectrum which occur under the different conditions.

We wish to express our thanks to the Department of Scientific and Industrial Research for a grant made to one of us (J. G. P.) during the course of this investigation.

The Scattering of Light by Liquid Boundaries and its Relation to Surface Tension.—Part III.

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(Received, June 3rd, 1925.)

[Plate 6.]

1. *Relative Scattering-power of Water and other Liquid Surfaces.*

In Part II, the phenomena of the scattering of light by the surface of transparent liquids were described in detail. No reference was, however, made to the case of water, which stands in a special category owing to the exceptional properties of this liquid. Of all known transparent fluids at ordinary temperatures water has the highest surface-tension. Its refractive index is also low, and hence its surface-opalescence may be expected to be very feeble. Fortunately, however, the internal scattering in dust-free water is also very small, being in fact much less than that for any other known liquid, and hence, provided water is obtained dust-free and with an uncontaminated surface, there should be no difficulty in observing its surface-opalescence. This was actually found to be the case. By using water subjected to repeated slow distillation *in vacuo* in carefully cleaned pyrex glass bulbs, it can be obtained quite pure and dust-free. The surface-opalescence may then be observed, and in agreement with anticipation is found to be very feeble ; it exhibits features of polarisation and intensity distribution in different directions very similar to those shown by other liquids.

For inter-comparison of the surface-scattering power of different liquids, the following simple arrangement was adopted. A beam of sunlight from a large heliostat was used and reflected vertically upwards by a second mirror inclined at 45°. The beam passed through two lenses of equal focal length, which were placed as near together as possible and formed images of the sun upon the surfaces of the liquids contained in bulbs, placed one above each of the lenses. By varying the apertures of the lenses, the brightness of the opalescent areas on the two liquid surfaces could be varied till they were estimated to be of equal brightness, as seen by the eye placed below the surfaces at approximately the same angle. The angle of observation chosen was in each case slightly greater than the critical angle, so that the surface-scattering had maximum brightness. By taking the mean of a sufficient number of readings, fairly dependable measures could be obtained of the ratio of surface-brightness, at least in the case of liquids, for which the internal scattering was not so large as to interfere with the judgment of the eye.

A check on the reliability of the measures is obtained by comparing liquid A with liquid B and liquid C, separately, and then comparing liquid B directly against liquid C, and so on. The accuracy of the method could no doubt be greatly improved by using photographic photometry and correcting for the known intensity of the internal scattering, which appears as a superposed effect. Nevertheless, it is felt that visual measures which could be made much more rapidly are not without value and represent the truth with fair accuracy, considering the very difficult nature of the investigation.

The table gives the relative surface-brightnesses of some thirty different liquids in terms of clean water as a standard, together with the surface-tensions and refractive indices (μ_F at 30° C) as given in Landolt's tables. The last column gives the internal (volume) scattering for purposes of comparison from data obtained in the author's laboratory by Mr. K. S. Krishnan.

The measurements show that, generally speaking, the intensity of the surface opalescence increases when the surface-tension is diminished or the refractive index is increased. There are, however, a few anomalous cases, the significance of which remains to be further investigated.

Substance.	Surface Tension.	Refractive index. μ_F	Intensity of surface scattering water = 1.	Intensity of internal scattering water = 1.
Water	72	1·336	1	1
Paraffins and unsaturated hydrocarbons.				
Pentane	—	1·353	11·3	5·70
i-pentane	—	1·352	8·9	5·30
Hexane	16·34	1·374	8·5	5·00
Heptane	—	1·387	8·8	5·00
Octane	20	1·396	7·8	4·80
β-iso-amylene	—	1·381	10·8	7·70
Chlorides.				
Ethylene chloride	30·10	1·445	3·8	7·20
Chloroform	25·32	1·446	6·3	6·30
Carbon-tetra chloride	24·60	1·462	12·6	5·10
Silicon- tetra chloride	15·80	1·420	7·4	—
Fatty acids.				
Formic acid....	35·75	1·372	4·6	6·10
Acetic acid	23·50	1·373	4·9	5·95
Propionic acid	26·6	1·387	5·8	6·20
Butyric	26·7	1·397	6·3	5·95
Oxides.				
Ethyl ether	15·27	1·352	7·4	5·00
Alcohols.				
Methyl alcohol	23·00	1·329	4·0	—
Ethyl alcohol	22·00	1·363	5·2	2·90
i-propyl	21·34	1·380	7·2	3·00
Butyl alcohol	24·40	1·400	7·4	3·25
i-butyl alcohol	22·80	1·397	9·3	3·70
Tri-methylcarbinol....	—	1·388	6·6	3·45
Allyl alcohol	23·15	1·419	7·8	6·10
Benzyl alcohol	39·70	1·547	10·0	12·35
Esters.				
Ethyl formate	22·00	1·359	5·2	5·00
Propyl formate	22·20	1·379	7·4	4·70
Propyl acetate	22·00	1·385	5·6	4·75
Aldehyde and ketone.				
Acetaldehyde	—	1·329	4·9	4·45
Methyl ethyl ketone	—	1·378	5·3	4·00

2. *Influence of Greasy Contamination on Water.*

As is well known from the investigations of Rayleigh, Langmuir, Adams, and others, the surface-tension of water is greatly diminished when even a very minute quantity of oily matter contaminates its surface. It appeared therefore of great interest to determine how the surface-opalescence of water is altered in such cases. It would obviously be extremely tedious and difficult to carry out experiments on the effect of greasing and re-cleansing water-surfaces *in vacuo.* Fortunately, however, it is actually possible to make observations with water-surfaces in the open. Distilled water is poured into a carefully cleaned glass dish painted dead black outside, and the surface of the liquid is cleaned by blowing off the superficial layer. Sunlight is focussed upon the clean surface of the water at about 45°, and the eye is placed so as to view the surface in a direction nearly adjacent to the reflected rays. A screen with an aperture suitably placed is found very convenient, as it cuts off the regularly reflected light and all stray illumination, the illuminated water-surface being seen through the aperture. The internal scattering in the water is considerably enhanced by the presence of motes caught by the water from the air. Nevertheless, the superficial opalescence by water clean enough to show vigorous camphor movements is readily observed with this arrangement as a greyish-white cap terminating the bluish-white internal track. Unless the air of the room is particularly free from dust, occasional dust-particles sail into view, are caught by the water surface and dragged down.

The effect of greasing the surface is readily observed ; with a very minute quantity of oleic acid, so small that camphor movements are only slightly affected, nothing noticeable happens ; but when the quantity is just sufficient to stop camphor movements, the surface-opalescence brightens up appreciably, and is then more easily distinguished from the internal scattering. The increase of intensity, though quite clear and definite, is not very large, say about 100 per cent. Figs. 7 and 8 in Plate 6 show the phenomenon, the former being obtained with clear water and the latter when the surface is greased in just sufficient quantity to stop camphor movements. Some dust tracks appear in the photographs, otherwise, however, the brightening of the surface-cap is evident enough on a comparison of the two pictures. (See Plate 6.)

Examined through a microscope, the greased surface showed no trace of structure, the opalescence being perfectly uniform and continuous. When, however, the oleic acid used is in excess of the minimum required to stop camphor movements, a remarkable change takes place. The opalescence of the surface brightens up enormously, perhaps a thousand-fold. At this stage, shown in fig. 9 in Plate 6, the illuminated area on the surface is no longer continuous, as seen in a microscope, but is seen to contain an enormous number of micro-globules of oil. A micro-photograph of the surface at this stage is shown in fig. 6 in Plate 6.

The light scattered by the film often exhibits colour which is different in different directions.

The observations of surface-opalescence thus seem clearly to confirm the existence* at one stage, as contemplated by Hardy, Langmuir and Adams, of a continuous film of the oleic acid of extreme tenuity, whose surface-tension is lower than that of water and whose light-scattering power is correspondingly larger. At a later stage, however, when the oleic acid is in excess, it forms micro-globules which appear to rest on a continuous film of the acid. Sometimes both stages can co-exist at different parts of the surface, as shown by observations of the scattering. A trace of palmitic acid in the molten condition allowed to spread on water shows similar effects.

We shall, in a later paper of this series, go more fully into the question of the ellipticity of the light reflected from clean and contaminated surfaces of liquids at the Brewsterian angle, and consider its relation to the present investigation. Meanwhile, a few observations on the effect of greasy contamination on the polarisation of the light *scattered* by liquid surfaces may be noted here. As mentioned in Part II, when light is incident from above at the polarising angle on the clean surface of a liquid, the light scattered upwards is most conspicuous in the plane of incidence, and is then almost completely polarised in all directions of observation in which it can be distinguished from the internal scattering. This is also found to be true for a clean surface of water. A contaminated surface of water covered by a continuous film shows an increased scattering, which in this case seems distinctly less perfectly polarised for directions of observation nearly normal to the surface than for observation inclined to or nearly parallel to the surface. The globular film shows this effect even more prominently.

3. *Surface-Opalescence of Liquid Carbon Dioxide: Critical State Phenomena.*

As is well known, the surface-tension of a liquid diminishes continually and tends to zero as the critical temperature is approached. Carbon dioxide is a convenient illustration for which data are available from the measurements of

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* In opposition to the view of Taylor ('Annales de Physique,' 1924, page 134), who studied the disintegration of oil-films on water by a less powerful method of investigation.

Verschaffelt. This substance when liquified by pressure has a surface-tension of 9·21 dynes/cm. at — 24·3°, which falls to 2·90 dynes at 8·90°, to 1·82 dynes at 15·2°, and to 1 dyne at 20·9°. On plotting these values as a smooth graph and extrapolating to zero at the critical temperature 31·40°, it is seen that at 30° C. the surface tension is of the order of one-tenth dyne. At this temperature the liquid has still a density about twice as large as that of the saturated vapour above it, its refractive index being 1·145, while that of the vapour is 1·074. At 20° C. the refractive indices of the liquid and vapour respectively are 1·18 and 1·04.

It is clear from these figures that even at 20° C. we should expect liquid carbon dioxide to show a surface-opalescence some fifty or a hundred times more intense than that of clean water, and that as the temperature is raised to 30° we should expect it to increase even further. These anticipations have been tested by observation. A sealed bulb a little over 1 cm. in diameter containing pure liquid carbon dioxide prepared for a quantitative study of its internal light-scattering* was available and was used for the purpose. Its temperature was regulated and maintained constant by immersion in a water-bath. On illuminating the liquid normally by a thin pencil, the surface opalescence could be easily seen at all temperatures, and at 20° C. was certainly several times brighter than the surface-brightness of hexane under equal illumination. It brightened up notably as the temperature approached 30° C. With further increase of the temperature up to the critical point, the surface-opalescence increases in a most remarkable way and becomes an exceedingly conspicuous phenomenon.† Figs. 1, 2 and 3, Plate 6, are photographs of the track of the light within the CO_2 at temperatures of 30°, 30·35°, and 30·6° respectively. The internal scattering in the liquid and vapour and the surface-opalescence separating them are clearly seen in the photographs.

In a later paper of the series we shall offer quantitative measurements and comparison with theory of these changes in intensity. A few observations on the state of polarisation and distribution of intensity of the scattered light in different directions may be now noted. As we have already described the general character of the phenomena for ordinary liquids in some detail in Part II of the series, it is only necessary to indicate the features observed with

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[*] 'Roy. Soc. Proc.,' A, vol. 104, p. 359 (1923).

[†] Careful measurements recently made show that above 30·6°, the intensity of the surface-opalescence *diminishes* rapidly, the boundary between liquid and vapour becoming visibly ill-defined and ceasing to reflect light before the critical temperature is actually attained.

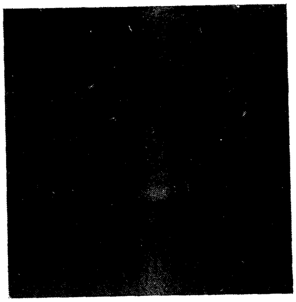
liquid carbon dioxide which are special for this case. The refractive index of the liquid does not differ so very much from that of the vapour above it. Consequently, the polarising angle for incidence on the liquid on either side does not differ very much from 45°, while the critical angle is much larger and approaches 90° as the temperature is gradually raised. On this account alone, we should expect the general distribution of the intensity of the scattered light as found for ordinary liquids to be somewhat modified in the case of carbon dioxide. This is actually the case. With liquid CO_2, particularly as the critical temperature is approached, the difference in the brightness as seen from above and below the surface is not so very marked as for ordinary liquids, and the directions of maximum brightness are more nearly parallel to the surface.

The most remarkable difference is noticed in the case in which the light is incident on the surface from above at the polarising angle. In the case of ordinary liquids, the light scattered upwards is, as nearly as can be observed, completely polarised for all directions of observation in the plane of incidence. In the case of CO_2, however, the polarisation of the scattered light is only complete in the immediate vicinity of the regularly reflected rays and rapidly becomes imperfect as we move away from this direction on either side. The cause of this remarkable difference in behaviour must be either the small surface-tension or the small difference of refractive index of the liquid and vapour, and its complete explanation is a matter of much interest which will be taken up later on.

4. *Interfacial Scattering of Light and Critical Solution Phenomena.*

Observations have also been made by the authors of the intensity and state of polarisation of the light scattered in different directions and at different temperatures by the interface between the two layers of a mixture of carbon disulphide and methyl alcohol. Using sunlight, and suitable colour-filters, the surface-scattering can be observed over a far wider range of directions and temperatures than those found possible by Mandelstamm. The phenomena observed, and the effect of raising the temperature to the critical solution point at which the two liquids become completely soluble in each other, are very similar to those observed in the case of liquid CO_2 and its vapour as the critical temperature is approached, the layer of higher refractive index corresponding to the liquid, and the layer of lower refractive index to the vapour. Figs. 4 and 5 in Plate 6 illustrate the enormous increase in the surface-scattering which occurs as the temperature of the mixture is raised from 28° to 40° C.

Raman and Ramdas. *Roy. Soc. Proc., A, vol.* 109, *Pl.* 6.



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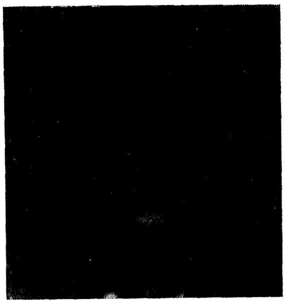

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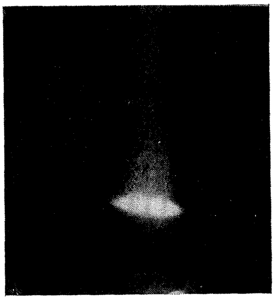

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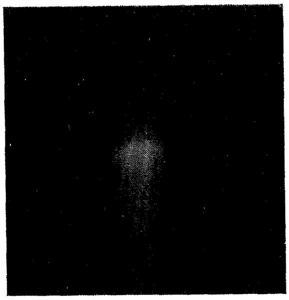

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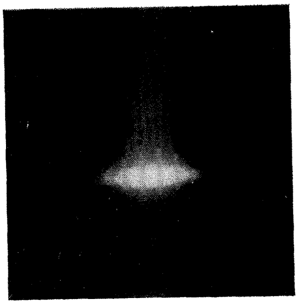

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(*Facing p.* 279.)

Quantitative measurements of this change will be presented in a later paper of the series. We shall also describe studies of the scattering of light by liquid interfaces in other binary mixtures.

Summary.

(1) Observations on the surface-scattering of light by clean water and comparisons of its brightness with those of some 28 other liquids are presented.

(2) The effect of oil-films on the surface-opalescence of water has been studied and described.

(3) The surface-opalescence of liquid carbon dioxide, its variation with temperature as the critical point is approached and the special polarisation phenomena observed in this case have been described.

(4) Similar observations have also been made of the interfacial scattering by the boundaries between the two components of a binary mixture of carbon disulphide and methyl alcohol, and the effect of raising the temperature to the critical solution point.

(5) Further quantitative studies regarding (3) and (4), observations with other binary mixtures, and theoretical discussions will be presented in the succeeding papers of this series.

DESCRIPTION OF PLATE 6.

Figs. 1, 2, and 3 illustrate the scattering by the surface of liquid carbon dioxide at 30°, 30·35° and 30·6° respectively.

Figs. 4 and 5 show the scattering by the interface of carbon disulphide and methyl alcohol at 28° and 40° respectively.

Fig. 6 is a microphotograph of the intense opalescent spot on a water surface contaminated with oleic acid when the film consists of microscopic droplets.

Figs. 7, 8 and 9 illustrate respectively the scattering by a pure water surface, a water surface covered by a film of oleic acid just sufficiently thick to stop camphor movements, and a water surface covered by a film with microscopic droplets.

Fig. 6 is a greatly enlarged picture of the effect seen in fig. 9. The few streaks in figs. 7 and 8 are due to the presence of a few dust particles on the surface, but the increased intensity of the spot in fig. 8 is clear enough.