

A remarkable feature of these formulæ is their *invariance* with respect to such details of molecular structure as number and magnitude of dispersion charges, their position, and the mutual orientation of their principal directions.

Formulæ of the same invariant character are derived for scattering, depolarization and extinction of light in gaseous mixtures. In particular, the depolarization of air calculated in terms of that of its principal constituents, oxygen and nitrogen, is in good agreement with observation, making use of the present Lord Rayleigh's data. An important application of these formulae lies in the re-determination of Avogadro's constant from observations on the extinction of solar radiation by the earth's atmosphere, correcting for molecular anisotropy and the probable variation in the proportions of its constituent gases above the stratosphere.

An invariant formula analogous to (95), based on Smoluchowski's theory of fluctuations of density, has been obtained for the scattering of light by dust-free liquids, and is in satisfactory agreement with Martin's observations. This phase of the subject the writer hopes to deal with in a future paper.

---

*The Molecular Scattering of Light in Carbon Dioxide at High Pressures.*

By C. V. RAMAN, M.A., D.Sc., Palit Professor of Physics in the Calcutta University, and K. R. RAMANATHAN, M.A., Assistant Lecturer, University College, Rangoon.

(Communicated by Dr. G. T. Walker, F.R.S.—Received June 7, 1923.)

1. *Introduction.*

The investigation described in this paper was undertaken in order to test theories of light-scattering by quantitative observations on carbon dioxide, under pressures ranging from 1 to 100 atmospheres, and temperatures from 0° C. to 50° C. The work includes a study of the following cases :—(1) the scattering of light by the unsaturated vapour ; (2) by the saturated vapour in thermal equilibrium with the liquid ; (3) by the liquid under the pressure of its own vapour ; (4) by the liquid under impressed pressure higher than the vapour tension ; (5) by the substance in the vicinity of the critical state ; and (6) by the substance in the gaseous state above the critical temperature.\*

\* The cases in which the fluid is superheated or supercooled and is in metastable equilibrium are not dealt with here.

Carbon-dioxide was chosen as a suitable substance for a comprehensive study of this kind for several reasons. The fact that it can be obtained commercially in cylinders in a practically pure condition greatly simplifies the experimental technique, and any pressure within the limits mentioned can be obtained without the use of special compressors. Then, again, the necessary pressure-volume data for the vapour and the gas are available from the work of Amagat\* and for the liquid from that of Jenkin,† and the variation of its refractive index with density has also been fully studied by various investigators, notably by Phillips.‡ The existence of these data makes a theoretical calculation of the light-scattering possible. Further, carbon dioxide at atmospheric pressure shows a marked imperfection in the polarisation of the transversely scattered light, the ratio of the weak to the strong component of polarisation in the visual region of the spectrum being 10·6 per cent. Hence, it is a very convenient substance for studying the effect of variations of temperature and pressure on the state of polarisation of the scattered light.

Another reason why we felt impelled to take up a careful study of the scattering of light in carbon dioxide was that certain results obtained by Lord Rayleigh with this gas§ were, as has already been pointed out by us,|| anomalous and stood in need of explanation. Rayleigh determined the intensity of the light scattered by carbon dioxide vapour contained in a steel cross-tube provided with glass windows and kept in communication with a steel cylinder containing liquid CO<sub>2</sub> at 21° C. He found the scattering to be 102 times stronger than that of CO<sub>2</sub> at atmospheric pressure and inferred that the scattering power was proportional to the density within the limits of experimental error. According to the Einstein-Smoluchowski formula, however, the scattering power should have been much larger, about 800 times that of CO<sub>2</sub> at atmospheric pressure.

With regard to this discrepancy, it should be mentioned that Rayleigh's assumption that the density of the gas in his observation tube was equal to that of the saturated vapour at 21° C., is open to question. It is mentioned in his paper that the observation tube was leaky, and that a gauge in the communication tube from the supply cylinder indicated only 50 atmospheres, while according to the measurements of Andrews the saturation

\* Amagat, 'Ann. Chem. Phys.,' (6), vol. 29, p. 52 (1893).

† Jenkin, 'Proc. Roy. Soc.,' A, vol. 98, p. 170.

‡ Phillips, 'Proc. Roy. Soc.,' A, vol. 97, p. 225.

§ Lord Rayleigh, 'Proc. Roy. Soc.,' A, vol. 95, p. 155.

|| 'Molecular Diffraction of Light' (Calcutta University Press), p. 61 (1922); also Phil. Mag., Jan., p. 113 (1923).

pressure at 21° C. is 60 atmospheres. From the diagram given in Rayleigh's paper, it is noticed that after passing the pressure gauge the gas had to filter through a steel tube tightly packed with cotton-wool, which must have greatly impeded the inflow of the gas into the observation tube to replace that lost by leakage, and hence the density of the gas whose scattering power was measured was in all probability considerably less than that of the saturated vapour. If we assume that the pressure in the observation tube was somewhat less than that shown by the gauge and was, say, 45 atmospheres, the scattering power, if it were proportional to the density, would only have been about 60 times that of CO<sub>2</sub> at atmospheric pressure at the same temperature, while according to the Einstein-Smoluchowski theory of scattering, it would be about 125 times. The experimental result, rightly interpreted, thus tends to support the Einstein law of scattering, and not the Rayleigh law. The matter, however, appeared sufficiently important to justify a careful re-examination, with apparatus so designed that no uncertainty as to the actual density of the vapour arises.

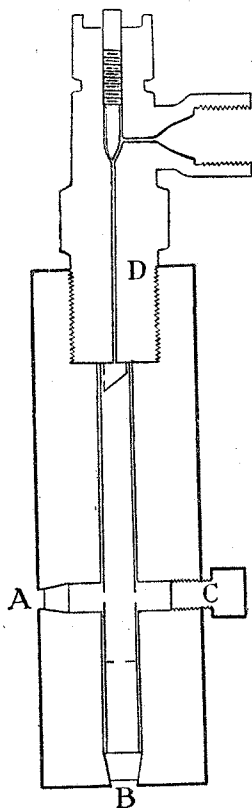
## 2. *Experimental Arrangements.*

In the present investigation, two distinct series of observations were made. In the first set, the scattering medium was CO<sub>2</sub> (vapour or liquid as the case may be) enclosed in sealed glass bulbs, thus avoiding all uncertainty regarding the density of the fluid used. A spherical bulb a little over 1 cm. in diameter was blown at one end of a stout walled capillary tube with rather a wide bore. The tube was carefully dried and exhausted, and dry CO<sub>2</sub> was introduced into it while immersed in liquid air. When the requisite quantity of carbon dioxide snow had condensed, the tube was sealed off leaving about 5 cm. attached to the bulb as a stem. Separate bulbs were prepared for the liquid and the vapour containing respectively an excess of the liquid and of the vapour: To prevent the bulbs bursting when the temperature is raised, sufficient volume for expansion is allowed in the stems attached to them. On removal from the liquid air, the carbon dioxide liquefies under the pressure.

The bulb and attached stem are completely blackened over with paint except for two tiny windows, one on either side of the bulb, for entry and exit of a narrow but powerful pencil of sunlight, and an aperture at the base of the bulb for observation of the scattered light. The stem with its bore forms a black cave against which the track of the beam through the CO<sub>2</sub> liquid or vapour, as the case may be, can be conspicuously observed. The bulb is completely immersed inside a water-bath with plate-glass slides, the rear-

walls being blackened so as to provide a dark field for observation. The temperature of the bath is regulated by adding either lumps of ice or hot water as desired. The brightness of the track of light is compared with that in another sealed tube containing a suitable dust-free liquid, like ether or benzene, or in a slab of optical glass, which serves as a standard and is also immersed in the bath, the same pencil of light passing through both. A rotating sector photometer with double disc placed in front of the cell enables the visual intensities of the two tracks to be equalised and their ratio thus to be determined.

Sealed bulbs, while convenient in many ways, are rather unsatisfactory optically when feeble light-scattering has to be measured, owing to the unavoidable reflections from the walls of the small-sized bulbs, which alone can sustain the high pressures. They are, therefore, not suitable for unsaturated vapours. It is also not possible with bulbs to work at pressures higher than the vapour-tension at the given temperature. Further, owing to the convergence of the light by the spherical walls, errors are also introduced in the photometry. In order to avoid these difficulties, in the second series of experiments, the simple form of apparatus shown was developed by the authors. This can safely withstand very high pressures and is suitable for the study of light-scattering in gases and liquids.



The observation tube consisted of a massive solid steel cylinder, 20 cm. long and 6.5 cm. in diameter, in which were drilled two cylindrical conical-ended holes, A and B, one axial and the other diametral. Two thick glass windows were ground in at A and B, the former to admit the primary beam of light and the latter for the observation of the scattered track. After the glass windows had been ground in, a tube with apertures for the entry of the primary beam and observation of the scattered light was put in place within the steel cylinder. This tube and the steel cylinder were enamelled black, a pin-valve was fitted to the end D, and the opening at C was closed up. To secure a good black background, a plate of black glass was fitted at an

angle of  $45^\circ$  inside the cylinder as shown. The observation tube could be connected to a pressure gauge and to the supply cylinder containing  $\text{CO}_2$ . Stopcocks placed on either side of the pressure gauge served to cut off its connection either with the observation tube or the supply cylinder as desired.

That the readings of pressure given by the gauge were reliable was tested in the following manner. The observation cylinder was *partly* filled with liquid and kept in communication with the gauge, the connection with the supply cylinder being cut off. The readings of the gauge were taken corresponding to different temperatures of the observation cylinder and were found to agree with the saturation pressures at those temperatures given by Amagat. The supply cylinder (which had been tested to stand 200 atmospheres) was placed in a vessel containing water, and by adjustment of the temperature of the water, pressures up to 100 atmospheres could be reached. The observation tube was placed in a rectangular glass vessel containing water, and its temperature could be kept constant at any desired value between  $5^\circ\text{C}$ . and  $50^\circ\text{C}$ . The observation cylinder and connecting tubes were evacuated before admission of carbon dioxide. The evacuation and re-admission of  $\text{CO}_2$  were repeated until the track appeared a good blue with no evidence of dust particles.

For measurements of the scattering in saturated vapour, a shallow layer of liquid was allowed to condense at the bottom of the observation cylinder and the pin-valve at D closed. After a sufficient time had elapsed for the attainment of equilibrium, the intensity of the scattered light was compared with that in a standard substance as usual. For observations in the liquid in equilibrium with the vapour, the liquid was allowed to fill up more than three-fourths of the observation cylinder. The measurements of the scattering power in these two cases gave results in conformity with those obtained with the sealed bulbs.

### 3. *Experimental Results : Intensity of Scattering.*

(a) *Unsaturated Vapour.*—For experiments on unsaturated vapour, the steel observation tube was cut off from the supply cylinder, and by blowing off gas through an auxiliary outlet, any desired pressure below that of saturation could be got. The following table gives the intensity of scattering at different pressures at  $30^\circ\text{C}$ . in terms of the scattering of  $\text{CO}_2$  at  $0^\circ\text{C}$ . and 76 cm. pressure.

Table I.

Pressure in atmospheres.	Density Density at N.T.P.	Reciprocal of compres- sibility in atmospheres.	Density scattering (Einstein formula).	Density scattering corrected for anisotropy.	Observed scattering.
15	14.5	13.5	17.2	21.3	22
20	20.0	18.7	23.4	29.0	33
30	32.1	23.0	49	59	54
40	47	29.4	65.2	77	83
50	64.5	31.5	123	144	140
55	75.7	30.2	180	207	197
60	89.7	27.9	276	315	307
65	109	22.9	514	576	665
68	127	19.1	847	940	1078

It will be noted from columns 2 and 6 that the observed scattering is much larger than in proportion to the density. The values in column 4 are calculated according to Einstein-Smoluchowski formula. When the molecules are anisotropic there is an extra scattering, the "orientation scattering," whose magnitude depends on the properties of the molecule and on the state of aggregation of the fluid. Its value has been worked out in a recent paper,\* and the total intensity at a distance  $d$  of the light transversely scattered by a unit volume of the fluid in any condition is given by

$$\frac{I_0}{d^2} \left[ \frac{\pi^2 RT\beta}{18 N \lambda^4} (\mu^2 - 1)^2 (\mu^2 + 2)^2 + \frac{\pi^2}{2n_0 \lambda^4} (\mu^2 - 1)^2 \frac{r_1(9 + 4\gamma)}{6 - 7r_1} \right],$$

where  $n_0$  is the number of molecules per unit volume in the fluid,  $r_1$  is the ratio of the weak component to the strong in the light transversely scattered by the substance in the state of vapour at very low pressures, and  $\gamma$  denotes  $\frac{RT\beta}{N} n_0 \left( \frac{\mu^2 + 2}{3} \right)^2$ . The other symbols have their usual meanings. The total scattering given by this formula is given in column 5 for comparison with the observed intensity of scattering given in column 6. The agreement is good except in the vicinity of the critical temperature, where uncertainties in temperature and impurities in the substance have a very great effect.

\* K. R. Ramanathan, 'Proc. Ind. Assoc. for the Cultivation of Science,' vol. viii, pp. 1-22 (1923).

Table II.

(b) Saturated Vapour.—

Temperature.	Density Density at N.T.P.	Reciprocal of compressibility.	Density scattering (Einstein formula).	Density scattering corrected for anisotropy.	Observed scattering.	Remarks.
0°	48	20.6	92	106		
5°	57	21.5	120	140	102	Bulb.
10°	68	21.9	180	205	195	"
15°	80	21.0	300	340	347	"
20°	96	19.7	560	620	567	"
24°	112	16.0	920	1000	1010	"
					1050	"
25°	121	15.0	970	1067	1190	Cylinder.
26°	126	13.7	1210	1330	1920	Bulb.
					1860	"
28°	140	10.0	2010	2190	3630	Cylinder.
					3490	Bulb.
30°	169	5.9 (?)	5100	5500	8000	Cylinder.
						Bulb.

Table III.

(c) Liquid in Equilibrium with Vapour.—

Temperature.	Density. Density at N.T.P.	Reciprocal of compressibility in atmospheres.	Density scattering (Einstein formula).	Density scattering corrected for anisotropy.	Observed scattering.	Remarks.
5°	448	700	380	494	360	Bulb.
10°	432	530	480	600	463	"
					500	Cylinder.
15°	411	372	618	760	630	Bulb.
					730	Cylinder.
20°	387	220	905	1086	980	Bulb.
					1000	Cylinder.
23°	369	146	1240	1450	1280	"
25°	355	110	1540	1786	1880	Bulb.
27°	340	65	2340	2620	2950	"
29°	317	25	5080	5590	6200	"
30°	302	15	7500	8350	11000	"
31°	271	4	28700	31000	35000	"

The compressibilities at temperatures higher than 20° were obtained in the following way. The reciprocals of the compressibility at the saturation points at temperatures below 20° C. (taken from Jenkin's paper) were plotted against the temperature, and taking the reciprocal of the compressibility at the critical point to be zero, a smooth curve was drawn through these points.

Table IV.

*(d) Liquid CO<sub>2</sub> at Higher Pressures.—*

Temperature.	Pressure in atmospheres.	Density. Density at N.T.P.	Reciprocal of compressibility in atmospheres.	Density scattering (Einstein formula).	Density scattering corrected for anisotropy.	Observed scattering.	Remarks.
15°	51	416	387	618	760	663	
	68	430	567	458	575	522	
	76	436	674	374	482	470	
	82	440	773	354	464	428	
25°	Saturation.	355	110	1540	1786	2100	
	68	373	195	976	1122	1650	
	74	383	243	827	968	1200	
	83	397	309	678	834	778	
	92	407	486	483	599	600	
30·5°	Saturation	289	10	10400	11300	22500	
	72·5	314	35	3600	3900	5480	These calculated values refer to 30° C.
	76·5	343	83	1880	2106	2610	
	84·0	366	155	1185	1351	1097	
	86·5	372	179	1063	1220	940	

*(e) Scattering above the Critical Temperature.—*

Table V.—(i) Scattering at 35° at different pressures.

Pressures in atmospheres.	Density Density at N.T.P.	Reciprocal of compressibility in atmospheres.	Density scattering (Einstein formula).	Density scattering corrected for anisotropy.	Observed scattering.
61	85	33·5	220	253	290
67	104	27·6	401	453	680
72	125	21·2	780	866	1170
77·5	177	13·3	2580	2830	3200
81	275	13·8	5170	5220	4230
87	330	72·1	2010	2250	1750
91					1430

Table VI.—(ii) Scattering at constant density (0·320 gm./cc.) at different temperatures above the critical temperature.

Temperature.	Density Density at N.T.P.	Reciprocal of compressibility in atmospheres.	Density scattering (Einstein formula).	Density scattering corrected for anisotropy.	Observed scattering.
32°	165	8·4	3420	3730	4550
35°	165	14·1	2060	2266	2730
40°	165	19	1550	1705	1620
50°	165	22	1380	1520	1410



## 4. Polarisation of the Scattered Light: Theory and Experimental Results.

In previous papers,\* the authors have discussed the influence of the physical condition of the substance on the imperfection of polarisation of the transversely scattered light. An exact investigation of the problem has been worked out† on the assumption of anisotropic molecules with three principal axes. It leads to the formula

$$r = \frac{2f}{f + \gamma g},$$

where  $r$  is the ratio of the weak component to the strong in the transversely scattered light, and  $\gamma$  has the meaning already indicated in the previous section. When the substance is in the gaseous state at low pressure and Boyle's law holds good,  $\gamma = 1$  and  $r$  assumes the value  $2f/(f+g)$  which has been already denoted by  $r_1$ .

Also

$$g - \frac{4}{3}f = \frac{9}{16\pi^2 n_0^2} \left( \frac{\mu^2 - 1}{\mu^2 + 2} \right)^2.$$

The formula indicates that when the scattering is very large, *e.g.* in the neighbourhood of the critical point, it is almost completely polarised; while in other cases, *e.g.* when the substance is in the liquid state much below the critical temperature, the polarisation is markedly less perfect than in the scattering by the vapour at low pressures. While these indications of theory are in qualitative agreement with facts, it is found that in the case of many liquids, there are considerable differences between theory and observation in the quantitative data, indicating that the assumption of a random orientation of the molecules made in the theory is not generally valid. This makes it all the more important that as many different substances as possible should be examined.

The problem of determining accurately the state of polarisation of light scattered by a fluid under high pressures is not without serious experimental difficulties. The principal source of error is the unavoidable strain and consequent ælotropy of the glass walls or the glass window through which the scattered light is observed. If the strain were perfectly symmetrical about the direction of observation no error would arise, but this condition is not easy to secure, especially when a conical glass window has to be pressed home into a metal recess provided for it to make it perfectly leak-tight. Small sealed bulbs are also not quite suitable in this type of work, owing to the very

\* C. V. Raman and K. Seshagiri Rao, 'Phil. Mag.', vol. 45, p. 625. K. R. Ramanathan, *loc. cit.*

† K. R. Ramanathan, *loc. cit.*

imperfect background which they furnish for observing the fainter component of polarisation. In view, however, of the fact that even an approximate determination of the state of polarisation under different conditions would be of interest, attempts were made to measure the effect with the apparatus used by the authors. The vapour or liquid inside the chamber was illuminated by a narrow horizontal beam of sunlight and on examination with a double-image prism set so as to transmit vertical and horizontal vibration, it was found that even near the critical point both images were bright, but that across the weaker one there was an intense black band running obliquely. The glass window was obviously under strain, but by isolating the portion of the glass wall transmitting the central portion of the black band alone by means of a narrow slit (nearly 1 mm. wide) placed in contact with the window, measurements of polarisation were made as usual with a double-image prism and nicol.

The following tables contain a summary of the results.

5. Imperfection of Polarisation.

Table VII.

(i) *Unsaturated Vapour at 30° C.*

Pressure in atmospheres.	Ratio : $\frac{\text{Weak component}}{\text{Strong component}}$	
	Observed.	Calculated.
	Per cent.	Per cent.
30	9	8
40	8	6
50	6	4.9
60	4.5	3.1
65	4	2

(ii) *Saturated Vapour.*

Temperature.	Ratio : $\frac{\text{Weak component}}{\text{Strong component}}$	
	Observed.	Calculated.
15°	5.8	2.6
20°	4	2.1
25°	3	1.2
30°	1.5	0.3

iii) *Liquid in Equilibrium with Vapour.*

Temperature.	Ratio : $\frac{\text{Weak component}}{\text{Strong component}}$	
	Observed.	Calculated.
10°	14	10.5
15°	10	7
20°	8	6
25°	5	3.8
28°	3	1.4

(iv) *Liquid under Higher Pressures.*

Temperature.	Pressure in atmospheres.	Ratio : $\frac{\text{Weak component}}{\text{Strong component}}$	
		Observed.	Calculated.
20°	92	13	14
	80	10	9
25°	90	9	8

The observed values are uniformly a little too high. This is probably due to the fact that the slit used has a finite width, and transmits light to a small distance on either side of the centre of the black band. The actual course of values, however, follows the indications of theory.

6. *Summary and Conclusion.*

The paper describes a simple form of apparatus which enables the intensity and state of polarisation of the light scattered by gases and liquids at high pressures to be measured. Results obtained with carbon dioxide are given, the noteworthy features being the following :—

(1) The scattering in carbon dioxide in the condition of unsaturated vapour below the critical temperature is not proportional to the density, but increases much more rapidly as the saturation pressure is approached, and the polarisation of the transversely scattered light becomes sensibly more and more *perfect*.

(2) The scattering in the saturated vapour and in the liquid phase in equilibrium with it has also been studied. When the liquid is further com-

pressed by application of pressure in excess of the vapour tension, its light-scattering power shows a striking diminution, and the polarisation becomes markedly more *imperfect*.

(3) Above the critical temperature, the scattering power at first increases with rise of pressure, reaches a maximum, and diminishes again.

(4) Except very close to the critical temperature, the experimental results agree well with the Einstein-Smoluchowski theory of scattering when the effect of molecular ælotropy is taken into account.

We have, in conclusion, to express our cordial thanks to Messrs. The Lightfoot Refrigeration Company, of Calcutta, who gave us much assistance in fitting up the high-pressure apparatus and in other ways.

---

### *The Carbon Arc Spectrum in the Extreme Ultra-Violet.—II.*

By F. SIMEON, B.Sc., F.Inst.P., Physicist in the Research Laboratory of Adam Hilger, Ltd.

(Communicated by Prof. A. W. Porter, F.R.S. Received July 31, 1923.)

#### 1. *Introduction.*

In a recent paper\* I have given measurements of some lines in the carbon arc spectrum in the Lyman region which had not previously been photographed. Further work has enabled me to photograph many more lines in this spectrum, and to record shorter wave-lengths in an arc spectrum than any previous worker with this source.

#### 2. *Experimental.*

The apparatus used was precisely similar to that described in the previous paper, except in respect of the grating. Several fresh gratings have been tried, including some ruled at Johns Hopkins University and others ruled on the Blythwood engine at the National Physical Laboratory. It was with one of the latter alone that it was possible to record any lines of shorter wave-length than those given in the previous paper, and with this grating the measure-

\* 'Roy. Soc. Proc.,' A, vol. 102, pp. 484-496 (1922).