REFRACTIVE INDICES AND DISPERSIONS OF GASES AND VAPOURS.

Substituted Methanes and Ethane, Cyclopropane, Ethylene Oxide and Benzene.

By K. L. Ramaswamy.

(From the Departments of General Chemistry and Physics, Indian Institute of Science, Bangalore.)

Received December 3, 1936.

(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

In a previous paper,[1] the dielectric coefficients of the above-mentioned gases and vapours at different temperatures have been given. Results of refractive indices and dispersions of the same samples of materials form the subject of this communication.

Many of the substances investigated are liquids at the ordinary temperatures and therefore have very low vapour pressures. Consequently measurements had to be carried out at extremely small pressures to avoid spurious results due to effects of adsorption. But then the difficulties in determining the values of compressibilities were considerable. In order to arrive at fairly reliable results several additional precautions were taken. The pressures were read with greater accuracy using a micrometer eye-piece. Repeated measurements with the mercury meniscus rising and falling were made and the zero reading in each case was checked at the end of a count.

The apparatus, method of measurement, and the general procedure adopted were in essence similar to those described in the earlier papers.[2] Slight modifications, however, were made for introducing and purifying the vapours, particularly those of high boiling liquids. In some experiments, the original tubes with ground ends were replaced by a new set of identical tubes having extensions which could be sealed on to the main apparatus. This had an additional advantage in that, the effects of adsorption and in some cases of decomposition at the wax joints were completely removed. After each measurement, the apparatus was evacuated with a hyvac cenco pump, warmed slightly and washed several times with dry air. The apparatus was then left in the evacuated condition for two to three days and the

[1] K. L. Ramaswamy, *Proc. Ind. Acad. Sci.*, A, 1936, 4, 108.

[2] H. E. Watson and K. L. Ramaswamy, *Proc. Roy. Soc.*, A, 1936, 156, 144-57; *Proc. Ind. Acad. Sci.*, A, 1935, 2, 360.

traces of desorbed gases removed. Before conducting a new series with another substance, the tubes were once or twice washed with the vapour of the material and thoroughly evacuated and dried.

Compressibility.

In spite of all the precautions taken the values of compressibility could not be determined with great accuracy for vapours of substances which are liquids at the ordinary temperature. A few measurements carried out at the beginning of the series using pressures near to the saturation pressures, indicated that in many cases the compressibility was not a linear function of pressure but indicated a rapid rise up to a certain limit, then decreased and thereafter remained more or less steady. The curves obtained resembled those of adsorption at a surface. Probably the effects of adsorption were considerable even at such pressures. It was, however, not possible to say whether it was solely due to changing compressibility or due to combined effects of changing compressibility and adsorption.

Later on the measurements were repeated at lower pressures far removed from the saturation pressures at the prevailing temperatures and as before the values of dn/dp (dn is the number of bands for a difference of pressure dp) were plotted against the mean pressures. The points lay more or less on a straight line from which the factor and the compressibility could be calculated as mentioned in the earlier papers.[2] The whole numbers of bands were then determined for all the wave-lengths. From each set of figures under each wave-length, the compressibility was determined as in the case of the counts for the green line of mercury. The mean of the five values was then taken, the pressures recorrected and the values finally were recalculated.

In the case of substances which are gases at the ordinary temperatures, the usual procedure was adopted employing high pressures and no difficulty was experienced in getting accurate values for compressibility.

Preparation and Purification.

The details regarding the methods of preparation and purification of the materials have already been dealt with in the earlier publication.[1]

Results.

Table I gives the values of refractive indices for the five wave-lengths employed, the calculated values of C and ν_0^2 in the Sellmeir dispersion formula, and the extrapolated value of $n - 1$ obtained by dividing C by ν_0^2. For the sake of uniformity, the constants C and ν_0^2 have been calculated from the values for the mercury green and violet lines. Just below the values of $n - 1 \times 10^6$ are given the differences between the observed and the calculated values for the three other wave-lengths. All the figures represent what they

TABLE I.

Values of $n-1^{760\ \mathrm{mm.}}_{25^\circ\cdot0\,\mathrm{C.}} \times 10^6$ *and Differences (calc.—obs.)* $\times 10^8$.

Wave-length	6440·24	5462·25	5087·23	4801·25	4359·56	$C \times 10^{-27}$	$\nu_0^2 \times 10^{-27}$	$C/\nu_0^2 \times 10^6$
CH_3F ..	403·46 −4	405·97	407·36 +1	408·66 +2	411·24	5·44004	13701·44	397·04
CH_3Cl ..	700·60 −9	706·15	709·25 +1	712·12 +4	717·88	7·42118	10810·70	686·47
CH_3Br ..	863·60 −4	872·08	876·74 +5	881·12 +8	889·91	7·47438	8872·10	842·46
CH_3I ..	1167·57 −55	1183·03	1191·66 +28	1199·88 +42	1216·93	7·29266	6465·74	1127·89
CH_3NH_2 ..	620·64 −20	626·10	629·08 +15	631·98 +16	637·91	5·80732	9576·73	606·40
CH_3CN ..	690·43 −47	695·52	698·49 +10	701·54 −9	707·10	7·29297	10786·98	676·09
CH_3OH ..	512·09 −18	515·79	517·77 +16	520·01 −9	523·85	5·75665	11462·19	502·23
$(CH_3)_2O$ ..	807·33 +4	813·79	817·29 +4	820·66 −3	827·14	8·65830	10940·83	791·38
$(CH_2)_2CO$ ..	987·04 −25	995·57	1000·30 +12	1004·96 −1	1013·89	9·46150	9804·95	946·15
C_2H_5Cl ..	995·68 −13	1003·69	1008·16 +2	1012·38 −1	1020·64	10·37832	10641·51	975·27

TABLE I—(*Contd.*).

Wave-length	6440·24	5462·25	5087·23	4801·25	4359·56	$C \times 10^{-27}$	$\nu_0^2 \times 10^{-27}$	$C/\nu_0^2 \times 10^6$
CH_2Cl_2 ..	1050·94 −5	1059·80	1064·75 −3	1069·32 −1	1078·37	10·56828	10273·30	1028·71
$CHCl_3$ ..	1314·85 −69	1325·02	1331·01 0	1336·48 +12	1347·63	13·56179	10536·50	1287·12
CCl_4 ..	1619·67 −119	1632·37	1640·27 −24	1647·41 −22	1661·31	16·09145	10159·07	1583·95
C_3H_6(*Cyclo*) ..	871·95 +4	879·24	883·24 0	887·06 −8	894·35	8·93666	10465·41	853·92
$(CH_2)_2O$ ..	682·18 −12	687·27	690·04 +10	692·79 +3	698·09	7·61438	11380·52	669·07
C_6H_6 ..	1606·49 −228	1627·80	1640·56 +39	1653·49 −19	1677·91	9·35987	6051·36	1546·74

would be had the gas or vapour been ideal. Since all the measurements were carried out in the neighbourhood of 25°·0 C., all the values have been calculated to 25°·0 C. and 760 mm. pressure. In the case of substances which are liquids at the ordinary temperature and pressure, the values at 760 mm. and 25°·0 C. appear meaningless since they do not exist as vapour under those conditions. As mentioned in an earlier paper,[1] they must be taken to represent what they would be if measured at 25°·0 C. and 760 mm. pressure.

In Table II, the values of compressibility have been repeated for the sake of convenience. For some substances the values mentioned here differ somewhat from those given in the earlier paper[1] and have either been obtained from later measurements or altered slightly to fit the dispersion fractions.

TABLE II.

Percentage compressibility corrections.

CH_3F	1·07	CH_3OH	4·7
CH_3Cl	1·75	$(CH_3)_2CO$	15·6
CH_3Br	2·51	CH_3CN	29·2
CH_3I	4·69	$(CH_3)_2O$	1·88
C_2H_5Cl	3·25	CH_3NH_2	2·93
CH_2Cl_2	6·5	$(CH_2)_3$	1·61
$CHCl_3$	9·6	$(CH_2)_2O$	2·81
CCl_4	14·1	C_6H_6	26·2

The figures in Table I show that in the case of several substances, the differences between the calculated and the observed values are quite appreciable particularly for the cadmium red line. Considering the enormous experimental difficulties, it is difficult to say whether they are due to errors in measurement or are real owing to the proximity of adsorption bands in the near infra-red. It is intended to investigate this question in greater detail at a later date.

Most of the substances mentioned in this paper have been investigated—though not in a systematic way—by Mascart, Prytz, Lorenz and Cuthbertson in the past and more recently by Lowery, Max Weiss, and others.

It appears, therefore, of interest to compare the results given in this paper with those of others, particularly in view of the fact that the methods employed by some differs essentially from the one adopted in these investigations. Table III gives a summary of most of the available data published so far.

For easy comparison all the values have been calculated to 25°·0 C. and a pressure of 760 millimetres for the wave-length 5894 Å. The author's figures for this wave-length have been obtained from the dispersion data given in Table I and are all corrected for compressibility. Results by others do not appear to have been corrected for compressibility in most cases. The wave-length 5894 Å has been particularly selected since it has been frequently employed in the past. All the values of $n-1\times10^6$ (where n represents the refractive index) in Table III are given to the nearest whole number.

A glance at the results in Table III shows that the results by different authors are in some cases extremely divergent. The discrepancies cannot always be attributed to impurities in the materials employed. Particularly in the case of vapours of high boiling substances, the question of adsorption has not been taken into account by earlier workers. This subject has been dealt with by Max Weiss in great detail in an important communication published nearly two years ago. It is not possible to go into the details of all the values given above. A few remarks, however, are necessary.

Cuthbertson has examined *methyl fluoride* but does not mention the details of measurement. The value does not appear to have been corrected for compressibility. Assuming that he has worked in the neighbourhood of 25°·0 C. and a pressure of 760 mm., and applying the correction for compressibility, the value comes out to be about 407, very near the observed value by the author.

Mascart's figures, are in general, higher than those given by others. Since he does not mention the sources of materials and the methods of purification, it is not possible to discuss about the results.

Prytz and Lorenz seem to have made the measurements with great care and their results are fairly in good agreement with the recent determinations. The value by Prytz for *benzene*, however, appears too low and it is possible that his specimen of the vapour contained air, which is very difficult to remove.

Wasastjerna has obtained in the case of *benzene* a value which is very close to that given by Mascart but is far higher than those given by both Max Weiss and the author. Max Weiss in a recent communication has discussed

TABLE III.

Values of $n-1^{760\ mm.}_{25^\circ.0\ C.} \times 10^6$* *for* $\lambda = 5894$ Å.

	Author	C.	M.	P.	W.	L.	Lo.	Ma.	T.&K.	H.&G.
CH_3F ..	405	411	..	..	..	..	..	..	..	..
CH_3Cl ..	703	..	797	..	..	..	711	..	..	..
CH_3Br ..	868	..	883	..	..	..	..	..	..	..
CH_3I ..	1175	..	1166	1159	..	..	..	..	..	..
CH_3NH_2	623	..	..	..	..	..	..	..	..	..
CH_3CN..	693	..	711	..	..	..	..	..	..	..
CH_3OH ..	514	..	571	..	..	506	..	..	..	..
$(CH_2)_3O$	811	..	816	..	..	..	810	..	..	..
$(CH_2)_3CO$	991	..	1008	991	..	..	1001	..	..	..
C_2H_5Cl ..	1000	..	1080	..	..	..	..	992	..	..
CH_2Cl_2 ..	1055	..	..	..	..	..	1012	..	..	..
$CHCl_3$ ..	1320	..	1341	..	..	1321	1317 1321 (H.)	..	..	..
CCl_4 ..	1625	..	1630	..	..	..	1628	..	..	1630
$(CH_2)_3$ ..	876	..	..	..	..	..	..	..	895	..
$(CH_2)_2O$.	685	..	..	..	..	..	..	..	..	..
C_6H_6 ..	1616	..	1670	1562	1667	..	..	1620	..	..

* *Note*:

C. .. C. Cuthbertson, *Phil. Trans. Roy. Soc.*, 1905, **204**, 323.
M. .. Mascart, *C. R.*, 1878, **86**, 321, 1182.
P. .. K. Prytz, *Wied. Ann*, 1880, **11**, 104.
W. .. Wasastjerna, *Soc. Scient. Fenn.*, 1924, **2**, No. 13, 24.
L. .. L. Lorenz, *Wied. Ann.*, 1880, **11**, 70.
Lo. .. H. Lowery, *Proc. Phys. Soc.*, 1927, **39**, 421-23; *ibid.*, 1927, **40**, 23-28; *Proc. Roy. Soc.*, A, 1931, **133**, 188-206.
L. & H. .. H. Lowery and T. S. Hartley, *Proc. Phys. Soc.*, 1931, **43**, 559-61.
Ma. .. Max Weiss, *Ann. Der. Physik*, 1934, **20**, 557.
T & K. .. Max Trautz and Karl Winkler, *Jour. pract. ch.*, 1922, **104**, 37.
H. & G. .. P. Hölemann and H. Goldschmidt, *Zs. anorg. chem.*, (B), 1934, **24**, 199-209.

the results of Wasastjerna and has concluded that the high values must have arisen from the effects of adsorption.

The results of Lowery are very close to the author's except in the case of *methylene chloride*. It was not possible to verify the results since the material was not available and therefore the data for this substance are given with reserve. Max Weiss has made a careful detailed investigation on *ethyl chloride* and *benzene* and has given the molar refractivities for $\lambda = 5461$ Å. He obtained a value of 3·8 per cent. for the compressibility of *ethyl chloride* at 20°·0 C. from refractometric studies. This value is comparable with the figure of 3·25 per cent. obtained by the author at 25°·0 C. employing the same method. For *benzene* he could not arrive at any value and he mentions that the results were viciated by the effects of adsorption. The figures 992 and 1620 for *ethyl chloride* and *benzene* respectively have been obtained from his results for 5461 Å assuming the dispersion obtained by the author and it may be mentioned that the values are in close agreement particularly for *benzene*.

Trautz and Winkler have measured the refractive index of *cyclopropane* for the helium yellow line but have not given the details of measurement. The same value has been reproduced after conversion to 25°·0 C., since the change in refractive index for 5894 Å would not be very much different from that for 5877 Å. Assuming as in the case of *methyl fluoride*, that the measurements have been made in the neighbourhood of 25°·0 C. and 760 mm. pressure, the value corrected for the compressibility comes to 879, which is fairly in agreement with the observed value of 876.

Carbon tetrachloride has been examined by several investigators and it is very satisfactory to note that the values by all are in satisfactory agreement. The most recent value is the one given by Hölemann and Goldschmidt, who have made the measurements at 180°C., at which temperature both the adsorption and the compressibility would be very small.

In Table IV, the results of electronic, distortion and atomic polarisation represented respectively by P_E, $P_E + P_A$, and P_A are given. The values of P_E have been calculated from the figures in the last column of Table I. The values of $P_E + P_A$ have been reproduced from the earlier paper.[1]

It has been already remarked in the previous paper,[1] that some substances gave either small or negative values for $P_A + P_E$. The negative values have no meaning or significance and might have arisen from errors in measurement of dielectric coefficients. The measurements of the latter were made only at two temperatures and the compressibilities obtained from refractometric studies were employed in correcting the values. In the case of gases

TABLE IV.

Values of $P_A + P_E$, P_E and P_A.

	$P_A + P_E$	P_E	P_A	$100\ P_A/P_E$
CH_3F ..	7·09	6·48	0·61	9·4
CH_3Cl ..	8·66	11·20	−2·54	..
CH_3Br ..	13·36	13·74	−0·38	..
CH_3I ..	18·65	18·39	0·26	1·4
C_2H_5Cl ..	15·21	15·90	−0·69	..
CH_2Cl_2 ..	18·74	16·78	1·96	11·7
$CHCl_3$ ..	24·92	20·99	3·93	18·7
CCl_4 ..	28·14	25·83	2·31	8·9
CH_3NH_2 ..	13·65	9·89	3·76	38·0
$(CH_2)_3$ ..	14·28	13·93	0·35	2·5
$(CH_3)_2O$ ..	15·03	12·91	2·12	16·4
C_6H_6 ..	27·43	25·22	2·21	8·8
CH_3OH ..	8·14	8·19	−0·05	..
$(CH_3)_2CO$ ..	6·0	15·43	−9·43	..
CH_3CN ..	−11·9	11·03	−22·93	..
$(CH_3)_2O$ ..	9·95	10·91	−0·96	..

the errors would be small and by taking a large number of readings, more accurate values of $P_A + P_E$ could be obtained. In the case of vapours of high boiling liquids, particularly when they are highly polar, the extrapolation of the dielectric polarisation to $1/T = 0$ from measurements at only two temperatures introduces considerable error. So far as the moment is concerned, it can be obtained with a fair degree of accuracy. It is intended, therefore, to repeat the measurements for some substances at different

intervals of temperature and thereby obtain more accurate values for the distortion polarisations.

However, it is interesting to mention that the atomic polarisation of *methyl fluoride* is comparatively small when compared with the values for other fluorides mentioned in the previous papers.[2] Another significant result is that of *methyl amine* for which the atomic polarisation is 38 per cent. of its electronic polarisation. Even for *chloroform* and *dimethyl ether* the values of atomic polarisations are fairly large.

Refractivity and Dispersion in Liquid and Vapour States.

The theories of the optical behaviour of liquids are, in general, based on the assumption that the well-known Lorentz formula $n^2 - 1/n^2 + 2 \cdot M/D =$ constant holds good for changes of temperature and pressure and for different states of aggregation. From the work of Fajans[3] and others it is evident that this relation is at best only an approximation. Taking the case of benzene Wasastjerna obtained values of refractivities 27·20 and 26·18 for the vapour and liquid for the sodium D line. Though this high value of 27·20 for the vapour has been attributed by Max Weiss to effects of adsorption, there is little doubt as to the indication that the vapour value should be higher than that of the liquid.

Investigations on light scattering have definitely shown that all known molecules are optically anisotropic, which means that the molecules are polarisable to different extents in different directions. From this point of view the refractivity of a liquid would be an average effect of the contributions of molecules variously orientated relatively to one another and to the field of incident radiation. From these and other considerations Raman and Krishnan[4] deduced an equation to explain the variation of refractivity from liquid to vapour.

It was therefore considered of interest to determine the refractivities of the liquids whose vapours also have been examined under known conditions and compare them with those for the vapours.

The refractive indices of the liquids were measured for two wave-lengths with the help of a Pulfrich refractometer using mercury arc as a source of light. The temperature was controlled by circulating water at constant temperature. All measurements were made at or nearly at the prevailing room temperature. The value of density at the temperature at which the refractive index and dispersion were measured, was obtained by interpolation

[3] Fajans, *Zeit. Physikal. Chem.*, B, 1934, **24**, 108.

[4] C. V. Raman and K. S. Krishnan, *Proc. Roy. Soc.*, A, 1928, **117**, 589; *ibid.*, 1930, **126**, 155.

from the values of density at different temperatures determined with the help of a specially constructed pyknometer.[2]

Table V contains the results of refractivities of the liquids and their corresponding vapours, the differences in refractivities in the two states and the dispersions expressed as the differences in $R_V - R_G$, where R_V and R_G represent the molar refractions for the mercury violet and green lines. The refractivities of the liquids have been calculated from the values of refractive indices and densities already given in the previous paper.[1]

TABLE V.

Refractivity and dispersion of liquids and vapours.

	$\lambda = 4359 \cdot 56$Å			$\lambda = 5462 \cdot 25$Å			Dispersion $R_V - R_G$	
	$R_{vap.}$	$R_{liq.}$	$R_{vap.}$-$R_{liq.}$	$R_{vap.}$	$R_{liq.}$	$R_{vap.}$-$R_{liq.}$	Liquid	Vapour
C_6H_6 ..	27·36	27·22	0·14	26·54	26·44	0·10	0·78	0·82
CCl_4 ..	27·09	27·05	0·04	26·62	26·57	0·05	0·48	0·47
$CHCl_3$ ..	21·98	21·86	0·12	21·60	21·49	0·11	0·37	0·38
CH_2Cl_2 ..	17·59	16·47	1·12	17·28	16·20	1·08	0·27	0·31
CH_3CN ..	11·53	11·37	0·16	11·34	11·20	0·14	0·17	0·19
CH_3I ..	19·85	..	..	19·29	19·45	—0·16	..	0·56
CH_3OH ..	8·54	8·39	0·15	8·41	8·26	0·15	0·13	0·13
$(CH_3)_2CO$	16·54	16·50	0·04	16·24	16·22	0·02	0·28	0·30

The tabulated values show that while the refractivities for the liquid and vapour states do not differ notably, the observed differences are always positive, indicating that in general, the value for the vapour state is slightly more than that for the liquid.

Regarding dispersion, it may be mentioned that the measurements are not so accurate as to ensure that the changes given in the table are real. Nevertheless the indications are that the dispersion in the vapours are slightly greater than in the corresponding liquids. Friberg[5] in a recent paper

[5] Friberg, *Z. Physikal. Chem.*, B, 1934, **26**, 195.

has come to the conclusion from his experiments that the dispersions in the liquid and vapour states are identical. Further investigations are necessary before this issue can be definitely decided.

Summary.

1. Refractive indices and dispersions have been measured for 16 gases and vapours using a Zeiss Interferometer of the Rayleigh type. Five wave-lengths 6440, 5462, 5087, 4801 and 4360 have been employed for the purpose.

2. Accurate values of compressibilities for the gases and approximate values for the vapours have been obtained by studying the variation of refractive index with pressure.

3. The electronic polarisation obtained in this paper have been compared with the dielectric polarisations given in the earlier paper[1] and from the two the atomic polarisations have been calculated.

4. The values of refractive index for the gases and vapours by the author have been compared with existing data by others and discussed.

5. Refractivities in the liquid state for substances which are liquids at the ordinary temperature and pressure were measured for two wave-lengths using a Pulfrich Refractometer and a mercury arc. These values have been compared with those obtained for the corresponding vapours.

6. The results show that in general the refractivities of the vapours are slightly higher than those of the liquids.

7. The dispersions in the liquid and vapour states have been compared. The indications are that the values in the vapours are slightly higher than in the corresponding liquids.

In conclusion, I wish to express my best thanks to Sir C. V. Raman, KT., F.R.S., N.L., for his kind interest in the work.