

That of sulphur, redetermined, is

$$\frac{4.808 \times 10^{27}}{4600 \times 10^{27} - n^2}$$

That of mercury, recalculated from old observations re-examined, is about

$$\frac{7.82 \times 10^{27}}{4360 \times 10^{27} - n^2} \text{ to } \frac{8.37 \times 10^{27}}{4740 \times 10^{27} - n^2}$$

On Drude's electronic theory, the numbers of "dispersion electrons" in hydrogen, oxygen, nitrogen, sulphur, and phosphorus are in the ratios of 1, 2, 3, 3, and $4\frac{1}{2}$ respectively.

With regard to the work recorded in this and the two connected papers, we have to express our great obligations to Prof. Trouton and Prof. Porter, of University College, London; also to the Royal Society for the assistance of a grant.

On the Refraction and Dispersion of Sulphur Dioxide and Hydrogen Sulphide, and their Relation to those of their Constituents.

By CLIVE CUTHBERTSON, Fellow of University College, London, and
MAUDE CUTHBERTSON.

(Communicated by Prof. F. T. Trouton, F.R.S. Received September 24,—
Read November 25, 1909.)

Sulphur Dioxide.

The refractive index of sulphur dioxide for a single wave-length has been measured several times, and in a recent paper* it was shown that nearly all the values, when corrected for density, approximated to $\mu - 1 = 0.000661$ for sodium light.

The dispersion has only been measured once, by Ketteler,† who found the numbers given in the second column below—

| $\lambda \times 10^8.$ | $(\mu - 1) 10^6.$ | $(\mu - 1) 10^6,$ corrected for density. |
|------------------------|-------------------|---|
| 6707 | 681.54 | 656.7 |
| 5889 | 686.01 | 661.0 |
| 5350 | 690.71 | 665.5 |

* C. Cuthbertson and E. P. Metcalfe, 'Roy. Soc. Proc.', vol. 80, p. 406, 1908.

† Ketteler, 'Theoretische Optik.', p. 478, 1885.

When corrected for density, these become the numbers given in the third column.

If we adopt Cauchy's formula, $\mu - 1 = a(1 + b/\lambda^2)$, and calculate $b \times 10^{11}$ between the first and second and the second and third wave-lengths, we obtain 10.15 and 11.5 respectively. If we adopt an equation of the form $\mu - 1 = C/(n_0^2 - n^2)$, the values of n_0^2 , calculated from the same data, are respectively 9335×10^{27} and 8388×10^{27} , which do not agree very well.

In view of this uncertainty we have redetermined the dispersion. The gas was taken from a syphon, which gives practically pure sulphur dioxide.

We assume for $\lambda = 5461$ the value $\mu - 1 = 0.00066397$, which corresponds with 0.000661 for sodium light. Our observations, then, work out as follows:—

| $\lambda \times 10^8$. | $(\mu - 1) 10^6$. | $n_0^2 \times 10^{-27}$. |
|-------------------------|--------------------|---------------------------|
| 6700 | 656.40 | 8856.2 |
| 6500 | 657.10 | 8996.0 |
| 5800 | 661.26 | 8971.3 |
| 5461 | 663.97 | 8934.3 |
| 5000 | 668.63 | 8885.3 |
| | Mean | 8929.0 |

Using Cauchy's formula, the value of b , calculated from the refractivities for $\lambda = 6700$ and $\lambda = 5800$ is 9.87×10^{-11} , and between 5800—5000 it is 10.83×10^{-11} . But using the formula of Sellmeier's type, we obtain

$$\begin{array}{l} \text{From the values for 6700 and 5800, } \mu_{\infty} - 1 = 0.00064225 \\ \text{,, ,, 5800 ,, 5000, } \mu_{\infty} - 1 = 0.00064083 \\ \text{Mean } 0.00064154 \end{array}$$

and, using the mean of these, the values of n_0^2 , calculated from the wave-lengths in the first column, are given in the third column. Hence, finally, for SO_2 ,

$$\mu - 1 = \frac{5.728 \times 10^{27}}{8929 \times 10^{27} - n^2}.$$

Hydrogen Sulphide.

The previous measurements of the refractive index of H_2S recorded by Dufet are—

| Light. | μ . | Observer. |
|-------------|----------|-----------|
| White | 1.000636 | Arago |
| ,, | 1.000641 | Dulong |
| D | 1.000619 | Mascart |

The discrepancy between Mascart's value and those of Arago and Dulong is considerable, and renders a new determination desirable. So far as we are aware, no one has hitherto measured the dispersion of this gas.

The gas we used was prepared by two methods: (1) by heating $MgCl_2$ and CaS_2 with water over a water bath, and (2) by the action of dilute sulphuric acid on pure Al_2S_3 . In both cases the gas was dried by passing it over a long tube filled with P_2O_5 .

The gas was allowed to flow through the refractometer tube, gradually displacing the air, and the interference bands were counted until the operation was complete. Taking, for air, $\lambda = 5461$, $\mu - 1 = 0.0002936$, the observed value for H_2S at the temperature and pressure of the room, reduced to 0° and 760 mm. by the formula $\nu - 1 = (\mu - 1) \frac{760 \times T}{P \times 273}$, where $\nu - 1$ is the value under standard conditions, was found to be 0.00064993 from five experiments, the extreme variations of which were one part in 300.

But our object is not to measure the refractive index of the gas as it would be at 0° and 760 mm., but as it would be if it contained the same number of molecules per unit volume as hydrogen at 0° and 760 mm. Taking the following figures from Leduc:—*

| Element. | Molecular weight. | Weight of 1 litre. | | Coefficient of expansion. | Mean temperature of experiment. |
|----------------|-------------------|--------------------|------------|---------------------------|---------------------------------|
| | | Experiment. | Theoretic. | | |
| Hydrogen | 2.0152 | 0.06948 | — | 1.003663 | |
| Sulphur..... | 32.0558 | | | | |
| H_2S | 34.071 | 1.1895 | 1.1747 | 1.003885 | $16^\circ C.$ |

We find that the experimental value of the refractivity should be multiplied by

$$\frac{1.1747 \times [1 + 0.003663 \times 16]}{1.1895 \times [1 + 0.003885 \times 16]} = 0.99092,$$

and therefore becomes 0.00064403, which we take as the value for $\lambda = 5460.7$.

* Leduc, 'Ann. de Ch. et de Phys.,' vol. 15, p. 1, 1898.

Dispersion of Hydrogen Sulphide.

Our results for dispersion are as follows:—

| | $\lambda \times 10^8.$ | $(\mu-1) 10^6.$ | $n_0^2 \times 10^{-27}.$ |
|-----|------------------------|-----------------|--------------------------|
| (1) | 6563 | 636.22 | 7797 |
| (2) | 5790 | 641.17 | 7823 |
| (3) | 5461 | 644.03 | 7819 |
| (4) | 4861 | 650.98 | 7793 |
| | | Mean..... | 7808 |

Using Cauchy's formula, the value of b , calculated from (1) and (2), is 11.67×10^{-11} ; from (2) and (3) it is 12.4×10^{-11} , but, with a formula of Sellmeier's type

From (1) and (3) we obtain $\mu_\infty - 1 = 0.00061941$

„ (2) „ (4) „ $\mu_\infty - 1 = 0.00061893$

Mean 0.00061917

and the values of n_0^2 calculated from each wave-length are given in the third column above.

Whence we have the formula

$$\mu - 1 = \frac{4.834 \times 10^{27}}{7808 \times 10^{27} - n^2}.$$

Remarks.

Refractivity has so often been adduced as a typically additive quality of compounds that there is some danger lest it should be forgotten that the statement is only partially true, to a first approximation, in solids and liquids, and when the refractive constants are determined from compounds. In gases it is obviously untrue. Out of 16 gaseous compounds of which the refractivities of all the components have been experimentally measured in the free state, not one obeys the additive rule.* In all the nitrogen compounds the refractivity of the compound exceeds the sum of the refractivities of the constituents by amounts varying from 5 per cent. to 19 per cent. In sulphur compounds it is deficient by as much as 18 per cent. (SO_2), 30 per cent. (SeF_6), and 45 per cent. (TeF_6).

The law remains to be found: and it seemed probable that the study of H_2S and SO_2 would throw light upon it. In each case one atom of sulphur is combined with two atoms of a well-known element; but in one case the

* See a paper in 'Science Progress' for October, 1908, by C. Cuthbertson.

sulphur is electro-negative and in the other electro-positive. The difference promises to be instructive.

In the previous paper it has been shown that the refraction and dispersion of the three elements concerned may be expressed as follows:—

| Element. | $\mu - 1.$ |
|-------------|--|
| H_2 | $\frac{1.692 \times 10^{27}}{12409 \times 10^{27} - n^2},$ |
| O_2 | $\frac{3.397 \times 10^{27}}{12804 \times 10^{27} - n^2},$ |
| S_2 | $\frac{4.808 \times 10^{27}}{4600 \times 10^{27} - n^2}.$ |

If the additive rule were followed, the refractivity of SO_2 would be expressed, to a first approximation, in a single equation by*

$$\mu - 1 = \frac{788 \times 5840 \times 10^{21}}{5840 \times 10^{27} - n^2},$$

whereas experiment gives

$$\frac{641.54 \times 8929 \times 10^{21}}{8929 \times 10^{27} - n^2} = \frac{5.728 \times 10^{27}}{8929 \times 10^{27} - n^2}.$$

Thus the refractivity is 18 per cent. less than the additive law would give, while the square of the free frequency (assuming there is only one) is 53 per cent. greater.

Similarly, the additive equation for H_2S would be

$$\mu - 1 = \frac{659 \times 5268 \times 10^{21}}{5310 \times 10^{27} - n^2},$$

whereas experiment gives

$$\frac{619 \times 7808 \times 10^{21}}{7808 \times 10^{27} - n^2} = \frac{4.833 \times 10^{27}}{7808 \times 10^{27} - n^2}.$$

In this case the refractivity has fallen only 6 per cent., while the square of the free frequency has increased 48 per cent.

These are the broad facts requiring interpretation and explanation. If we accept the theory on which dispersion formulæ of the type developed by

* The value of $\mu - 1$ is proportional to the aggregate polarisations induced in the molecules per unit volume by the electric field. In a mixture of gases these must be additive, as the molecules are outside each others' range, as shown, for example, by the agreement of μ^2 with the dielectric constant. The formula for the compounds, as calculated in this additive manner, is that given in the text. The discrepancy, waiving the adequacy of the present type of formula, is obviously assignable (as *supra*) to the fact that the free periods of a compound molecule are different from those of its constituents, or, on the electron theory, to a change in the number of electrons influencing dispersion.

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Lorentz and Drude are based, the numerator of the fraction which denotes the refractivity for infinite wave-lengths is proportional to the number of "dispersion electrons" in the atom. For S_2 the numerator of the dispersion formula is found experimentally to be 4.808×10^{27} , and for O_2 it is 3.397×10^{27} . Hence, if the number of dispersion electrons in SO_2 is equal to the sum of the dispersion electrons in S and O_2 , the numerator of the dispersion formula for SO_2 should be

$$\left(\frac{1}{2} \times 4.808 + 3.397\right) \times 10^{27} = (5.801) \times 10^{27}.$$

Experiment gives $(5.728) \times 10^{27}$; an agreement within the limits of experimental error.

In the case of H_2S , however, the same rule does not hold. Here the numerator of the dispersion formula should be

$$\left(\frac{1}{2} \times 4.808 + 1.692\right) \times 10^{27} = (4.096) \times 10^{27},$$

whereas experiment gives $(4.833) \times 10^{27}$. The difference is approximately half the number 1.692, which is proportional to the number of electrons in two atoms of hydrogen; and if this be taken as two, then we may suppose that in H_2S there is one more dispersion electron than in H_2 and S.

The existence of such a difference is not wholly unexpected. Drude* has shown that in solids and liquids the number of "dispersion electrons" in the compound generally differs from the sum of the valencies exerted, but in his experiments the discrepancy generally lay in the reverse direction, the number of dispersion electrons being usually less than the valencies, except in halogen compounds, where it is greater if the valency of the halogen be taken as one.

* Drude, 'Ann.,' vol. 14, p. 706, 1904.
