Notes on some Recent Determinations of Molecular Refraction and Dispersion

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hydrocarbon vapours. Then, by altering the break so as to produce frequent discharges of lower potential, the stratifications gradually change in shape and become all pink; again, altering the break, so as to send less rapid discharges at a much higher potential, once more we get the coloured stratifications. When in this state, if we introduce a water resistance into the circuit, so as to damp down the potential, exactly the same thing happens. *The blue disk is caused by mercury*; its spectrum is that of mercury only, without even a trace of the bright red line of hydrogen. Experiments not yet finished make it very probable that the pink discs are due to hydrogen, and that the grey discs indicate carbon. The tube contains nothing but hydrogen, mercury, and a minute trace of carbon; but with all the resources at my command I have not been able to get hydrogen quite free from impurity. Indeed I do not think absolutely pure hydrogen has ever yet been obtained in a vacuum-tube. I have so far succeeded as to completely eliminate the mercury, and almost completely to remove the trace of carbon.

IX. *Notes on some Recent Determinations of Molecular Refraction and Dispersion.* By J. H. GLADSTONE, D.Sc., F.R.S.*

AMONG the various indices of refraction which have been published by different observers of late years, there are some which have led me to further studies bearing on the general relation of this branch of Physics to Chemical theory. The following notes relate to the new metallic carbonyls, the metals indium and gallium, sulphur, and to liquefied oxygen, nitrous oxide, and ethylene.

I. METALLIC CARBONYLS.

Messrs. Ludwig Mond and Nasini† determined the molecular refraction of nickel tetracarbonyl for the red ray of

* Read February 10, 1893.

† *Lincei, Rendiconti*, vii. 411.

hydrogen (H_a) as 57·7, and the specific dispersion between the lines γ and α of hydrogen as 0·03475, which will give a molecular dispersion between those limits of 5·93. This indicates a very great refraction and an enormous dispersion.

Through the kindness of Mr. Mond I have been able to determine the refraction of two specimens of iron pentacarbonyl for several lines of the spectrum, with the following result. The second and third lines in the Table relate to the same specimen, the latter representing measurements taken in a very acute-angled prism, and under the most favourable circumstances for seeing the more refractive rays; nevertheless the spectrum was cut off so suddenly about the bundle of rays at G that I cannot be sure of the exact measurement, but think it differs little from the line γ of hydrogen.

Specimen.	Temp. C.	Sp. Gr.	μ_A .	μ_B .	μ_C .	μ_D .	μ_E .	μ_F .	μ_G .
I. ...	22°	1·460	1·5026	1·5076	1·5096	1·5180	1·5289		
II. ...	15·5	1·4705	1·5063	1·5117	1·5146	1·5224	1·5329		
II. ...	13·4	1·474	1·5071	...	...	1·5230	...	1·5446	1·5650

From these observations we obtain the following molecular refraction, $\frac{\mu-1}{d} P = R$.

Specimen.	R_A .	R_B .	R_C .	R_D .	R_E .	R_F .	R_G .
I.	67·47	68·14	68·41	69·54	71·00		
II.	67·48	68·20	68·59	69·63	71·03		
II.	67·43	...	...	69·54	...	72·42	75·13

It is evident that in the iron compound also the refraction and dispersion are very great. The molecular refraction for the line α of hydrogen may be assumed at 68·5, and the

molecular dispersion between the lines γ and α of hydrogen at 6.6. If we reckon for the lines A and H, we may assume H would be about 78.0, which would give a molecular dispersion between these limits of about 10.5.

In discussing their observations, Messrs. Mond and Nasini, assuming that CO has a molecular refraction of 8.4, reckoned the atomic refraction of nickel at 24.1, instead of 9.9, which I had assigned to this element in solutions of its salts, and which subsequently has been fairly corroborated by Nasini's own experiments. This difference they attributed to a difference of valency in the metal. By parity of reasoning the atomic refraction of iron for the line C would be 26.5, or 25.5 for the line A, instead of 11.6 previously determined for bivalent iron from solutions of its salts.

But this involves the assumption that CO in these carbonyls has the same value as we should expect to find in an organic substance. It also assumes that the nickel has 8 valencies, while the iron has 10, in the above-named compounds, and that iron has presumably $\frac{7}{2}$ in diferrohepta-carbonyl; and that potassium in its compounds with CO has still other valencies. There is also another difficulty; for if we determine the atomic dispersion of nickel and iron on the same principle, it will be found to be 4.8 and 5.2 respectively for the interval between the lines γ and α^* ; these numbers are about one fifth of the atomic refraction of the two metals given above, viz., 24.1 and 26.5. But the ratio between the atomic dispersion ($\gamma - \alpha$) and the refraction of the most dispersive elements hitherto calculated, sulphur and phosphorus, is only about one tenth.

It seems more probable that the metals really retain their ordinary valency, and that the excessive refraction and dispersion is to be sought rather in the peculiar arrangement of the CO. In such compounds we may imagine the CO playing a part similar to that of the CH_2 in ordinary organic compounds, which may be increased or diminished in number without altering the general type of the substance. In fact I accept on optical grounds as well as chemical, the ring-formulæ indicated in Mond's lecture at the Royal Institution.

* Proc. R. S. xlii. p. 401.

In that case the molecular refraction due to each CO would be, from the nickel compound about 11·9, and from the iron compound about 11·3.

Although the atomic dispersion of nickel or of iron has not yet been definitely measured, it cannot greatly exceed 0·5 for $\gamma - \alpha$. It is evident therefore from the figures for the dispersion, viz., $\text{Ni}(\text{CO})_4 = 5\cdot9$, $\text{Fe}(\text{CO})_5 = 6\cdot6$, that the molecular dispersion of each CO must be about the same in these two compounds, viz. 1·3, or thereabouts.

II. INDIUM AND GALLIUM.

In 1885 I calculated the atomic refraction of indium and gallium from determinations of the refraction of certain alums made by M. Charles Soret. Very shortly afterwards he published another paper giving fresh and additional values for alums containing these metals*.

For indium the available data are derived from rubidium and cæsium indium alums, and for gallium from no fewer than five compounds, viz., potassium, rubidium, cæsium, thallium, and ammonium gallium alums. Calculated from these data, I find as mean values for the atomic refraction of these two metals the following :—

Metal.	Atomic Weight.	Specific Refraction.	R_A .
Indium	113·4	0·121	13·7
Gallium.....	69·9	0·166	11·6

* *Archives Sc. Ph. & N. Genève*, xiv. p. 96.

These no doubt are nearer the truth than the higher figures previously given, though they must still be looked upon as only approximate. In regard to the atomic dispersion of these metals, the new observations quite confirm the previous remark that the order is "iron far the highest, chromium, indium, gallium, and aluminium lowest."

III. SULPHUR.

In the following Table is given the atomic refraction of sulphur, either uncombined, or in very simple combination:—

Condition.	A.	C, or "red."	D, or "white."	F.	G or γ .	H.
Solid		15.7	16.0			
Liquid	15.98		16.47			
Gaseous		16.1				
In solution	15.5	15.7	16.0	16.7	17.3	
From CS ₂	15.8	16.05	16.3	17.05	17.7	18.4
" Cl ₂ S		15.8	16.0			
" Cl ₂ S ₂		15.9	16.1			
" Br ₂ S ₂		16.35				

Sulphur in the solid condition is deduced from the observations of Descloiseaux and other physicists; but as the crystals of sulphur give three different indices of refraction for the same ray, the arithmetical mean of these three indices has been simply taken as the basis of calculation.

Sulphur in a liquid condition is from the observations of myself and the late Pelham Dale. It agrees, as far as D is concerned, with a determination by Becquerel. $R_D = 16.86$.

Sulphur in the gaseous condition was determined by Le Roux in 1861. The specific refraction was calculated out by me shortly afterwards, and recently by Nasini and Costa*. I give their number for the atomic refraction in the Table.

The sulphur in solution is from five determinations of this element dissolved in carbon bisulphide which I made some years ago with another object, and which have never been published. The solutions contained from about 22 to 27

* *Universita Inst. Ch. Roma*, 1891.

per cent. of sulphur. Two determinations of somewhat weaker solutions were lately published by Nasini and Costa, and were practically identical with mine. The refraction of 17.3 for the line γ is deduced from their figures alone.

The four last lines give the values of sulphur reckoned from its simplest compounds.

In the case of bisulphide of carbon the figures in the Table are derived from my own most recent observations, which agree closely with those of other observers. The deduction made for the atom of carbon is 5.0 for the line A, 5.26 for the line H, and proportional numbers for the intermediate lines.

In the case of bichloride of sulphur the calculations have been made from the observations of Costa; and in that of chloride of sulphur from those of Haagen, Becquerel, and Costa, which fairly agree. The refraction due to an atom of chlorine is assumed to be 9.95 for the line C, and 10.05 for the line D. Costa, in treating of these substances, has adopted a slightly smaller value for chlorine.

In the case of the bromine compound the sulphur is calculated from Becquerel's observations, taking the value for bromine at 15.35.

The figures for sulphur derived from these various sources are very similar. I doubt, however, whether the sulphur dissolved in bisulphide of carbon and the sulphur which forms part of that compound do exert exactly the same influence upon the rays of light. If we were to reckon the value of carbon in bisulphide of carbon by deducting the value found for sulphur in solution, we should get for A, $36.6 - 31.0 = 5.6$, a higher figure than we ever find for carbon in a saturated compound. The difference would be still greater if reckoned by Lorenz's formula.

The accordance of the dispersion as exhibited throughout the Table is worthy of notice.

From the elaborate paper of Nasini and Costa, already referred to, it would appear that in some organic compounds, such as the xanthates, sulphur has at least the value of 16.0; but in the large majority of cases it has a distinctly lower value. In its oxygen compounds it is known to be far less refractive and dispersive.

IV. LIQUEFIED OXYGEN, NITROUS OXIDE, AND ETHYLENE.

In the recent paper of Professors Liveing and Dewar (Phil. Mag., Aug. 1892) they give determinations of the specific refraction of liquefied oxygen, nitrous oxide, and ethylene. It is, of course, possible to compare these interesting results with what theory would have led us to expect. The authors have themselves done so in the case of liquid oxygen at its boiling-point of -182° C. They remark that the refraction-equivalent, 3.182, which they found, differs but little from that deduced from gaseous oxygen at the ordinary temperature, viz. 3.0316, and "corresponds closely with the refraction-equivalent deduced by Landolt from the refractive indices of a number of organic compounds," which was 3.0. It actually comes between the two values, 2.8 and 3.4, which were assigned by Brühl to oxygen in its different states of combination with carbon, and to which an intermediate value has since been added.

Liveing and Dewar were able to determine the refraction of liquefied nitrous oxide for six different wave-lengths, the extremes being the red ray of lithium and G. These gave for $\frac{\mu-1}{d}$ 0.2595 and 0.2691 respectively, and for the molecular refraction of the red ray 11.418, and of G 11.840. The molecular dispersion between G and the lithium-line is therefore 0.422, which would indicate about 0.63 between H and A. Now it is difficult to say what the rational composition of nitrous oxide is, and therefore what its theoretical refraction and dispersion should be. Nitrogen in ammonia and its congeners is reckoned at 5.1, in nitriles at 4.1; oxygen double-bonded is reckoned at 3.4, with two separate bonds at 2.8. We therefore, according to our theoretical views, might reckon nitrous oxide at 13.6, 13.0, 11.6, or 11.0. The probability is therefore clearly in favour of the lower figure for nitrogen. As the dispersion-equivalent of nitrogen in ammonia is as high as 0.38, this would also seem to exclude the idea of the nitrogen in nitrous oxide being in the same condition as in ammonia. This will probably be considered the most likely alternative also on chemical grounds.

On calculating Messrs. Liveing and Dewar's numbers for liquid ethylene, we obtain the molecular refraction of 17·2 for the line D. But Professor Dewar has kindly furnished me with a more recent determination of what he believes to be a purer specimen. The refractive index, at the boiling-point, for the line C is 1·3445, and for the line F is 1·3528, the specific gravity being 0·55. These figures give 17·53 as the molecular refraction for the line C, and 17·92 for the line F. These will indicate about 17·41 for the line A. The theoretical value for ethylene, for the line A, is 17·4.

$$\begin{array}{rcl}
 \text{C}_2 & . & . & . & . & = 10\cdot0 \\
 \text{H}_4 & . & . & . & . & = 5\cdot2 \\
 \text{Double-linking} & . & . & . & & = 2\cdot2 \\
 & & & & & \hline
 & & & & & 17\cdot4
 \end{array}$$

The coincidence between experiment and theory is very striking.