Physics. — *"The structure of solid nitrous oxide and carbon dioxide."* By J. DE SMEDT and W. H. KEESOM. Communication N°. 13 from the Laboratory of Physics and Physical Chemistry of the Veterinary College at Utrecht. (Communicated by Prof. H. KAMERLINGH ONNES).

(Communicated at the meeting of March 29, 1924)*).

1. *The structure of solid nitrous oxide* [1]).

§ 1. In connection with our investigations [2]) on the diffraction of X-rays in liquefied gases, we have worked out a method to get Röntgenograms of solidified gases [3]) at low temperatures. Our first experiments were made with N_2O and CO_2, because these gases are already solid at the temperature of liquid air. Moreover they show this particularity that the molecule N_2O possesses the same number of electrons as the molecule CO_2. Hence it may be interesting to be able to compare the structures of these substances.

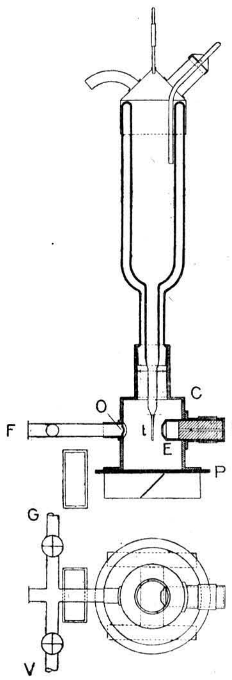

Fig. 1.

§ 2. *The apparatus.* The vacuum glass with fixed to it the camera is only little different from that which has served to the X-ray-diagrams of liquefied gases [4]). The glass tube t (wall thinner than 0.01 mm.) had a diameter of 1 mm. The glass was silvered, excepted the tube t and a vertical slit, through which the surface of the liquid could be observed.

The brass tube, which holds the diaphragm of tin (length 4 cm., diameter of the opening 2 mm.) is continued to the inside. It is closed by a small screen with an opening E, chosen in such

[1]) In this translation the results of our second communication on this subject have been taken up.

[2]) Comm. N°. 10 and N°. 12, these Proc. 25, 1922, p. 118, and 26, 1923, p. 112.

[3]) As a subject of research already mentioned in Comm. N° 1, these Proceedings 21, 1918, p. 405. Cf. Comm. N°. 10. At the same time F. SIMON and CLARA VON SIMSON independently worked out such a method, Zs. f. Phys. 21, 168, 1924.

[4]) Comm. N°. 10, these Proceedings 25, 1922, p. 118.

*) Published in these Proceedings, meeting of June 28, 1924.

a manner that the Röntgen beam, which is limited by the diaphragm, passes without striking the metal, whereas the rays, which are reflected by the tin crystals at the utmost brim of the diaphragm, are intercepted.

To the opening *O* of the camera is fixed a glass tube, which is closed at the end by a small window *F* of mirror glass.

Of the two side-tubes, one, *V*, leads to the vacuum pump, the other, *G*, to the container in which the gas to be investigated is stored.

§ 3. *Depositing the crystals.* When a sufficiently high vacuum has been formed in the apparatus, the vacuum glass is filled with liquid air. By closing the tap in *V*, the connection with the pump is broken, after which the gaseous N_2O is admitted through *G*. It condenses as a micro-crystalline powder on the narrow tube *t*. This condensation could be watched through the window *F* by means of a telescope, the crystals being illuminated by the aid of a mirror which was placed under the glass closing-plate *P*.

In order to prevent that during the depositing of the nitrous oxide the liquid in the tube *t* boils away, during this manipulation a wire of well conducting metal was let in from above.

Depositing was stopped when the crystal layer had obtained a thickness of 0.4 mm.

§ 4. *The film*, which was obtained with an exposition of $2^1/_2$ hours (30 m. A, 25 KV.) with *K*-rays of copper, showed very sharp lines and so proved that the micro-crystals had had the right dimensions. This film was made without a Ni-filter. We owe to Dr. N. H. KOLKMEIJER a second film, with Ni-filter.

The films show no trace of a diffraction ring that could be due to the liquid air in the tube *t*.

In the calculation it appeared however that there are parasitic lines on both the films. The rings namely, due to the crystal planes with the smallest indices appeared to be double. This can be explained by the fact, that the crystal powder was irradiated as a relative wide cylinder mantle, which surrounds the tube with liquid air, and not as a thin bar, as is ordinarily the case with the method of DEBIJE and SCHERRER.

In Fig. 2 the hatched ring represents a section through the cylinder mantle, formed by the crystal powder. *AB* be the incident beam. If we consider the diffracted rays *a*, *b*, which make a small angle with the direction of incidence, we see that the rays which are diffracted by the outer surface of the cylinder, have to pass through a much thinner layer of absorbing substance than those rays which pass through the centre. So the beam that is diffracted in the direction φ, is divided into two smaller ones. Of these the beam, originating from b, will have the greatest intensity. As φ is larger, the rays from a must pass through a thicker layer, and so they will finally give no more a visible impression on the film.

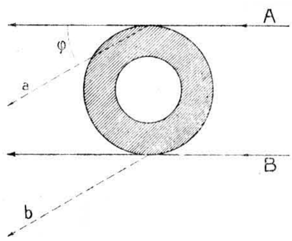

Fig. 2.

As was made first for CO_2 (cf. § 6), afterwards also for N_2O expositions were made with half of the incident Röntgen beam being screened off, in order to identify these parasitic lines indubitably [1]).

§ 5. *Results*. Table I contains the experimental results, derived from the film (*Kα*-rays of *Cu*).

The first column gives the observed intensities. In the second column the radii of the interference rings are inserted, viz. half the distances, measured on the film, of the two interference lines on both sides of the centre. The radius of the film is 27,3 mm. The third column gives $sin^2 \frac{\varphi}{2}$, the correction for the thickness of the irradiated preparation having been applied. This correction is put equal to $r \cos \frac{\varphi}{2}$, to be subtracted from the radius of the interference ring, r being the radius of the outer circumference of the preparation [2]). The fourth column is relative to the deriving of a common divisor of the values of $sin^2 \frac{\varphi}{2}$. The common divisor 0.0181 gives quotients, which oscillate about whole numbers, excepted however the numbers placed between [ ]. These are relative to parasitic lines as mentioned in § 4. The relative values of the intensities agree with the supposition about their origin made in § 4. The quotients of the fourth column show still a weak tendency to enlarge with encreasing φ. We ascribe it to the circumstance, that somewhat too large values are given to above-said correction terms.

From table I we conclude, that nitrous oxide crystallises cubically

[1]) These expositions were made in the Physical Laboratory at Leiden. Our thanks are due to Mr. V. ESBACH, assistant of this laboratory, for his help in making these expositions.

[2]) Comp. W. GERLACH und O. PAULI, Zs. f. Phys. 7, 116, 1921.

TABLE I.

Intensity [1]	Radius of the interference ring in $^1/_{10}$ mm. [2]	$10^3 . \sin^2 \frac{\varphi}{2}$ [3]	$\sin^2 \frac{\varphi}{2} : 0.0181$ [3]	*h. k. l.*
f	102	29	[1.60]	
m	115	37	[2.06] [4]	
f	123^5	44	[2.58]	
vs	136	54	2.97	111
vf	145	61^5	[3.40]	
m [5]	154	70	3.85	200
vf	161	76	[4.20]	
vs	173	88	4.88	210
s	191	108	5.95	211
m	221	145	8.02	220
f	273	219	12.10	222
m	283	234	12.94	320
m	296	255	14.08	321
vf	316	287	15.83	400
vf	329	310	17.12	322—410
s	349	344	19.05	331
vs	359	361	19.95	420
f	369	380	21.95	421
f	380	399	22.05	332
vf	399	434	24.00	422
vf	420	472	26.04	510—431
m	448	525	29.00	520—432
vf	459	545	30.05	521
s	479	582	32.15	440
s	509	635^5	35.10	531
f	519	654	36.10	600—442
m	540	691	38.15	611—532

[1]) vf = very feeble, f = feeble, m = moderate, s = strong, vs = very strong.

[2]) To the numbers given in the report about the work of the 1st International Commission of the Institut International du Froid, presented to the 4th International Congress of Refrigeration in London, the corrections for the thickness of the preparation had already been applied.

[3]) These numbers are something different from those, given in the report mentioned in note 2, on account of another calculation of the corrections for thickness of the preparation.

[4]) That this line is a parasitic one was shown by the film made with half of the incident Röntgen beam being screened off.

[5]) That this line has a mean intensity was taken from the film mentioned in footnote [4]).

with a side of the unit cube 5,72 Å [1]). In order to calculate the number of the molecules in a unit cube the density of solid nitrous oxide is not available. If we suppose 4 molecules in the unit cube the calculated density is 1,55 [1]), whereas, at the melting-point, — 90,5°, the liquid has a density 1,299.

In Fig. 3 we have drawn the structure which for the calculated intensities has given values which agree with the observed ones. On each of the four not intersecting diagonals of the cube, forming the ternary axes, we find a molecule N_2O, viz. an atom O in the middle of it, on both sides at the same distance flanked by an atom N.

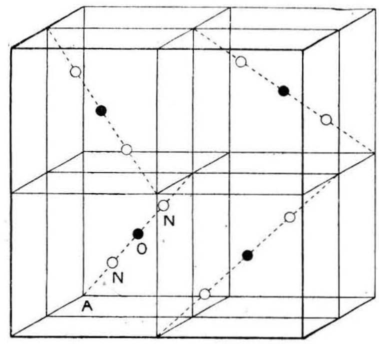

Fig. 3.

As a parameter we chose: the projection q of the distance between the atoms O and N, on the side of the unit cube.

The places of the other atoms follow then from the ternary symmetry of the axis AO. The parameter is expressed in 360th parts of the side of the elementary cube. The best agreement of calculated intensities with the observed ones (see table II) has been obtained with $q = 42$. In these calculations we have taken into consideration: 1°. the structure factor, 2°. the factor on account of the number of the planes that contribute to the diffraction, 3°. the LORENTZ-factor, 4°. the factor $\dfrac{1}{\cos\frac{\varphi}{2}}$ proposed by BIJVOET [2]).

The coordinates of the 4 atoms O are thus: $^1/_4\,a$, $^1/_4\,a$, $^1/_4\,a$; $^3/_4\,a$, $^3/_4\,a$, $^1/_4\,a$; $^3/_4\,a$, $^1/_4\,a$, $^3/_4\,a$; $^1/_4\,a$, $^3/_4\,a$, $^3/_4\,a$.

$a = 5.72$ Å. The distance between two neighbouring atoms N and O is 1.15 Å.

II. *The structure of solid carbon dioxide.*

§ 6. The expositions for solid carbon dioxide have been made in the same way as those for nitrous oxide (cf. §§ 2—4).

Also an exposition has been made at which half of the incident Röntgen beam was screened off by means of a small screen

[1]) Owing to a repeated calculation these numbers are somewhat different from those which are given in the report mentioned, p. 842, note 2.

[2]) J. M. BIJVOET, Thesis, Amsterdam 1923.

that was placed at a short distance before the preparation, in such a manner that only the right half or the left half of the preparation was irradiated. So a complete interference figure without the

TABLE II.

h. k. l.	Intensity	
	observed	calculated
100	—	0
110	—	0
111	vs	8425
200	m	2282
210	vs	3740
211	s	3230
220	m	1760
300 } 221 }	—	45
310	—	0
311	—	465
222	f	783
320	m	2020
321	m	3325
400	vf	250
322 } 401 }	vf	89
330 } 411 }	—	35
331	s	2630

parasitic lines mentioned in § 4 has been obtained on one side of the film. On the other side only the parasitic lines appeared. So we get in the first place an affirmation of the supposition mentioned there, relative to the origin of the parasitic lines. The parasitic lines could further be identified now indubitably for carbon dioxide.

Table III contains these experimental results. The columns have the same meaning as in table I. The parasitic lines have been omitted. In the fifth column two planes (311 and 420) have been inserted.

They appeared on another film than the one for which these calculations were made.

From the fact that the quotients in the 4th column oscillate about

TABLE III.

Intensity	Radius of the interference ring in $^1/_{10}$ mm.	$10^3. \sin^2 \frac{\varphi}{2}$	$\sin^2 \frac{\varphi}{2} : 0.0187$	*h. k. l.*
vs	140	56	3.0	111
f—m	160	74	3.96	200
s	177	91	4.89	201
s	196	112^5	6.02	211
f—m	228	153	8.16	220
vf	240	168	8.99	221—300
vf				311 [1])
vf	281	229	12.25	222
m	291	245^5	13.13	320
m	302	262	14.02	321
vf	349	342	18.30	330—411
m—f	358	358	19.15	331
vf				420 [1])
vf—f	376	391	21.00	421
vf	387	411^5	22.01	332
m	458	541	28.98	520—432
vf	469	563	30.09	521
m	487	595	31.85	440
vf	519	651	34.83	531

whole numbers, we conclude that carbon dioxide (just as nitrous oxide) crystallises in the cubic system. The side of the unit cube is 5,63 Å. If we admit the number of the molecules in an elementary cube to be 4, we obtain for the density 1,63, in agreement with the value, which DEWAR[2]) obtained at the temperature of liquid air.

[1]) From another film.

[2]) $\delta_{-188^\circ} = 1.63$, Chem. News 85, 277, 1902; $\delta_{-189^\circ} = 1.627$, Chem. News 91, 216, 1905.

Hence the structure of carbon dioxide is given by Fig. 3, just as that of nitrous oxide, if O has been replaced by C and N by O. The parameter q was chosen in the same way as for nitrous

TABLE IV.

h. k. l.	Intensity	
	observed	calculated
111	vs	6420
200	f—m	1735
201	s	3070
211	s	3100
220	f—m	940
221—300	vf	148
310	—	—
311	vf	102
222	vf	370
320	m	2700
321	m	3400
400	—	430
322—410	—	365
330—411	vf	218
331	m	1520
420	vf	176

oxide. As the line 110 is absent it follows that the atom C lies in the middle of the diagonal. The best agreement between calculated and observed intensities was obtained for $q = 39$ (see table IV).

So the coordinates of the C-atoms are $^1/_4\,a$, $^1/_4\,a$, $^1/_4\,a$; $^3/_4\,a$, $^3/_4\,a$, $^1/_4\,a$; $^1/_4\,a$, $^3/_4\,a$, $^3/_4\,a$; $^3/_4\,a$, $^1/_4\,a$, $^3/_4\,a$, a being 5,63 Å. The O-atoms are at the same distance on both sides of a C-atom. That distance CO is 1.05^5 Å.

It is an agreeable duty to us to thank Miss IRM. DESMET, who has made most of the intensity calculations.