

CRYSTAL STRUCTURE OF SOLIDIFIED GASES

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The crystal structures of substances existing at ordinary temperatures in the gaseous or liquid state is of great interest because of the possibility of obtaining some information regarding the molecular structure. The investigation of crystal structure, if carried out completely, leads to information on the exact positions of the atoms with respect to one another and gives, therefore, direct information regarding the binding forces. By comparing the molecular arrangement for different states it is possible to determine the change of valence angle and of atomic distance and, consequently, of the free energy.

We have investigated carbon disulfide to compare its structure with the structure of carbon dioxide, which shows a completely symmetrical molecule, viz., a carbon atom in the center of the straight line joining the oxygen atoms, and the whole system in a cubic arrangement. Both carbon and sulphur belong to the same group in the periodic table and have the same distribution of outer electrons, but the polarizability is different.

We have investigated acetylene (C_2H_2) and ethylene (C_2H_4), since in this way one can obtain information regarding the arrangement of the triple and double bound carbon atoms. Moreover, the optical investigation of Wahl¹ seems to indicate that acetylene has a simple structure near its sublimation point, and it was, therefore, considered possible that even at -185° (liquid air temperature) this structure would be only slightly distorted.

Experimental Procedure

Two different methods have been used to obtain diffraction patterns from the solidified gases. The first method adapted to low temperature work, by K. Lark-Horovitz², consists of an arrangement in which slit, crystals, and photographic film are placed on the circumference of the same cylinder. Focusing of the diffracted beam is obtained in this way, and, since a large amount of crystal material reflects, the time of exposure is shortened. In this device the gas is solidified on the carefully ground bottom part of a liquid air container held in the vacuum camera by a ground joint so as to avoid contamination by grease vapor. This ground joint is developed according to Siegbahn³, the camera being protected by a rectangular groove in the wall, this groove being evacuated through an auxiliary tube. This focusing method gives twice the resolution of the ordinary powder camera but has the disadvantage of cutting out reflections at small angles which are particularly important for the interpretation of complicated structures.

For this reason another camera has been used, in which the gas is condensed on a metallic capillary tube or a wire which is carefully centered, and in this way the small angles of diffraction are obtained. Since most of the gases used are of low molecular weight as compared with

*Now with Division of Optics, Bureau of Standards, Washington, D. C.

¹Proc. Roy. Soc. London A89:327. 1913.

²K. Lark-Horovitz, 1925. Science 64:303.

³Spectroscopy of X-rays, p. 61.

the metal capillary, standard lines from the metal are produced on the film for measurement.

The camera is pumped down to a good vacuum. The liquid air container is then filled with liquid air, and, if there are no impurities present, the metal will remain clean, and no solid deposit of foreign gases will be produced on it. The gases to be investigated are carefully purified and admitted in small quantities to the camera. A solidified deposit of the gas to be investigated is then formed on the metal and continued until a uniform coating has been obtained. X-rays produced in a special high power tube developed in this laboratory¹ enter through the aluminum window and are diffracted from the crystallites. The $K\alpha$ radiation of chromium, iron, and copper has been used. In most cases filtered radiation was applied. Recently some experiments have been carried out with strictly monochromatic radiation so as to make it possible to apply Fourier analysis to the diffraction pattern.

For the purification of the carbon disulfide, a process described by Obach² has been used. By this process water and any residue containing free sulphurated hydrogen or other decomposition products are removed. The product was repeatedly distilled, and the final substance investigated

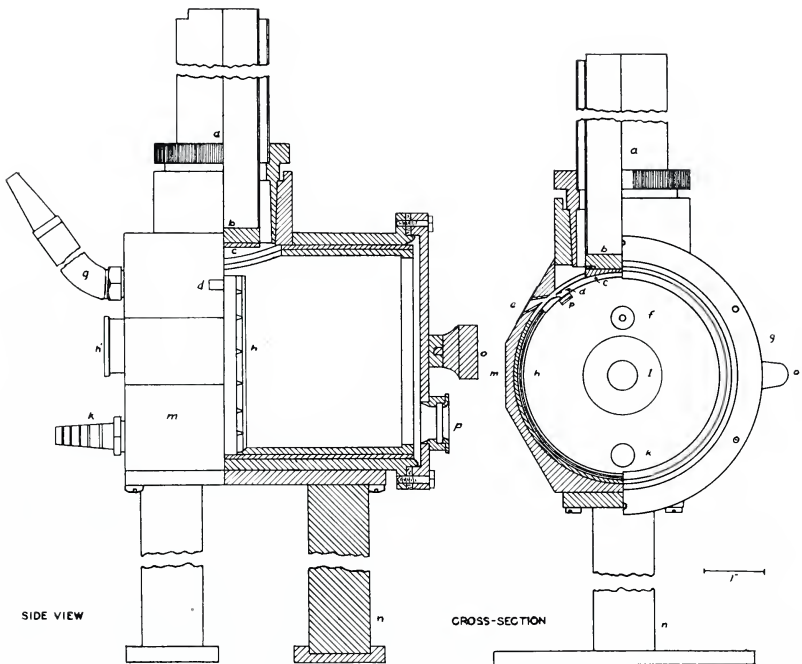


FIG. 1. Focusing low temperature X-ray camera. Side view and cross-section showing Dewar flask *a* with copper bottom *b*; crystal face *c*, (made of aluminum block to minimize background due to scattering), film holder *h* and gold slit *d* (0.001" wide) being on the same circumference; *p* is an additional inner shield to cut out radiation scattered from the slit. The front plate carries a window *P* for observation of the crystal formation. Evacuation is effected through tube *k*, while gas can be admitted through *g*.

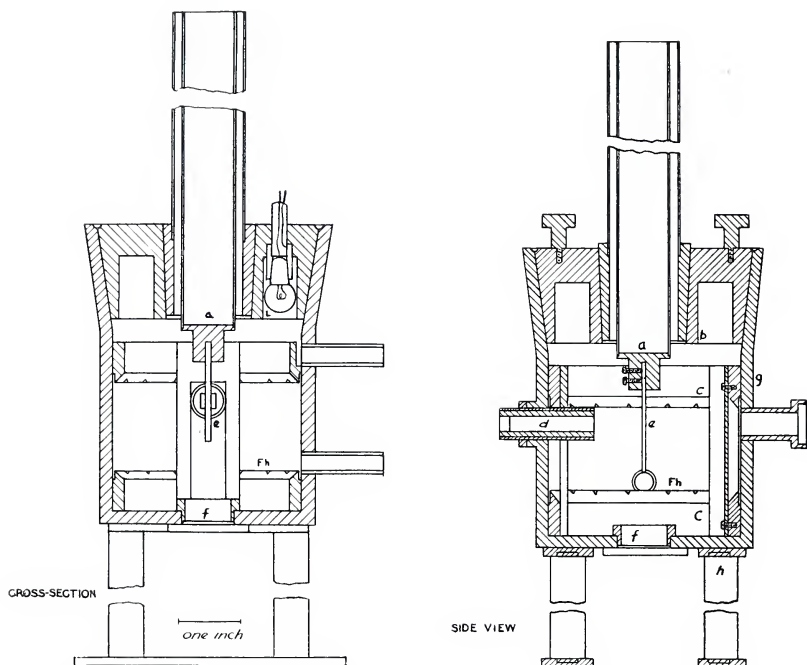


FIG. 2. Low temperature powder camera, cross-section and side view. Dewar flask *a* carries capillary *e* through which liquid air can stream and then return through a different capillary back into the container, thus securing equal temperature over the whole length of the capillary. Filmholder *h* showing triangular cuts to give standard mark on the film. Capillary *e* can be replaced by a silver wire or other type of specimen holders. Observation can be made through window *f* by using a mirror, the sample being illuminated by light from top of the camera.

was almost odorless. It was used, if possible, immediately after distillation and was kept in a pyrex container coated with black paint on the outside to avoid photochemical action of light. This liquid carbon disulfide was kept in a long pyrex tube, and, to seal it to the camera system, the carbon disulfide was frozen so as to avoid any possibility of explosion. The carbon disulfide container was connected with the camera system by a greaseless metal valve as described by Bodenstein.⁶ All the connections up to the camera are greaseless, and copper to glass seals are used wherever metal is connected to the glass system. Any flexible connections to the camera are made with sylphon tubing so as to avoid the use of rubber hose, which may be attacked by the gas.

The acetylene and ethylene used were purified in the manner described by Smyth⁷ when used by this author for the determination of the dipole moment.

All the gases are first admitted to a container filled with purest and redistilled potassium to eliminate traces of water and carbon dioxide and

⁴K. Lark-Horovitz and E. P. Miller, 1932. Phys. Rev. 42:915. E. P. Miller, 1933. Rev. Sci. Insts. 4:379.

⁵Obach, Journal Prakt. Chem. 26:281-287.

⁶Bodenstein, 1924. Z. f. Phys. Chem. 110:399.

⁷Smyth, 1925. Journal Am. Chem. 47:2501.

are then led to a small vessel, which can be cooled with liquid air if necessary. The first portions of the gas are passed through the camera without condensing them so as to remove any volatile impurities taken up by the gas stream in passing through the system. Liquid air is then applied to the Dewar flask of the camera, and condensation takes place on the crystal holder.

TABLE I
Carton Disulfide Patterns

Film No. 348. CS₂ (purified) deposited on Al—Cu K-alpha. Focusing camera. Computations based on standard lines of Al at —185°C. (a = 4.025)

Film No. 436. CS₂ (purified) deposited on Ag—Cu K-alpha. Debye-Scherrer camera. Computation based on standard lines of silver at —185°C.

Int.	No.	Sin θ	Spacing	Int.	No.	Sin θ	Spacing
v st	1	.3823	002 A1	st	1	.2091	3.682
m	2	.4321	1.781	v st	2	.2504	3.073
m	3	.4523	1.698	v st	3	.2555	3.012
m	4	.4756	1.618	m	4	.2868	2.683
m	5	.4960	1.551	m	5	.2988	2.575
m	6	.5105	1.507	st	6	std 111 Ag	
st	7	.5407	022 A1	st	7	std 002 Ag	
f	8	.5712	1.347	f	9	.4070	1.891
m	9	.5764	1.335	f	10	.4176	1.842
v f	10	.5906	1.303	f	8	.3891	1.965
v f	11	.5990	1.285	st	11	.4329	1.778
v f	12	.6111	1.259	f	12	.4418	1.742
v st	13	.6340	113 A1	m	13	.4540	1.695
m	14	.6578	1.170	f	14	.4759	1.617
m	15	.6622	222 A1	f	15	.4972	1.548
f	16	.6711	1.147	m	16	.5058	1.521
v f	17	.7059	1.090	f	17	.5115	1.504
m	18	.7294	1.055	st	18	std 022 Ag	
f	19	.7509	1.025	f (d)	19	.5676	1.356
st	20	.7647	004 A1	f (d)	20	.5901	1.304
f	21	.7965	.966	f	21	.6097	1.262
f	22	.8095	.951	v st	22	std 113 Ag	
v st	23	.8333	133 A1	f	23	.6410	1.201
st	24	.8361	.920	v st	24	std 222 Ag	
v st	25	.8549	024 A1	v f	25	.6702	1.148
st	26	.8576	.897	v f	26	.6831	1.126
v f	27	.8984	.857	v f	27	.7030	1.095
v f	28	.9313	.826	v f	28	.7250	1.061
v f	29	.9325	.825	v f	29	.7433	1.035
v st	30	.9365	224 A1	st	30	std 004 Ag	
				v f	31	.7898	.974
				v f	32	.8047	.956
				v st	33	std 313 Ag	
				v st	34	std 024 Ag	
				v f	35	.8584	.897
				v f	36	.8838	.871
				v st	37	std 224	

TABLE I—Continued
Carbon Disulfide Patterns

Film No. 350. CS₂ (purified) deposited on Al—Fe K-alpha (Mn f—Al f). Computations are based on standard lines of Al. Focusing camera.

Int.	No.	Sin Θ	Spacing
st	1	.3713	2.602
m	2	std 111 Al.	
m	3	std 002 Al.	
m	4	.5684	1.700
f	5	.5963	1.620
f	6	.6410	1.507
st	7	std 022 Al.	
f	8	.7216	1.339
f	9	.7658	1.261
m	10	.7813	1.236
m	11	.7867	1.228
st	12	std 113 Al.	
m	13	std 222 Al.	
f	14	.8399	1.150
f	15	.8829	1.094
f	16	.8864	1.090
f	17	.9396	1.028
f	18	.9409	1.027
f	19	.9491	1.018
f	20	std 004 Al.	
f	21	.9614	1.005

Film No. 361. CS₂ (purified) deposited on A 1. Cr K-alpha (Va f—A1 f) Line No. 4, (111) of Al used as base of computations, with film constant from No. 350 = 3.3274° per cm. Focusing camera.

Int.	No.	Sin Θ	Spacing
st	1	.3690	3.099
st	2	.4229	2.704
m	3	.4396	2.601
f	4	.4920	std 111 Al.
f	5	.6382	1.792
f	6	.6677	1.713
f	7	.7027	1.627
f	8	.7563	1.512
f	9	.9037	1.265
f	10	.9176	1.246

Results

The results, as given in Tables 1, 2, and 3, contain measurements with both methods and with different radiations.

While this work was being carried out, information regarding the same substances was obtained in the Cryogenic laboratory in Leyden, Holland. The results by Keesom and de Smedt⁸ on carbon disulfide have been interpreted by these authors as evidence for a tetragonal structure. We have found, however, due to the better resolving power of our equipment, that some of the lines reported by these authors have not been correctly interpreted and also, that some lines which they have found do not appear at all if purest carbon disulfide is used. They appear only if the gas can react with stopcock grease and is therefore contaminated. We have not been able to interpret the pattern by assuming a cubic, tetragonal, or hexagonal structure and therefore must assume a structure of a lower symmetry.

In the case of acetylene and ethylene our results agree with the main

⁸Smedt, ——. *Physica* 10:1931.

TABLE II
Acetylene Patterns

Film No. 418. C_2H_2 (purified) deposited on Ag—Cu K-alpha (ni-f). Computations based on standard lines of Ag. at $-185^\circ C$. Debye-Scherrer camera.

Film No. 294. C_2H_2 (purified) deposited on Al—Fe K-alpha (mn-f). Computations based on standard lines of Al. at $-185^\circ C$. Focusing camera.

Int.	No.	Sin θ	Spacing	Int.	No.	Sin θ	Spacing
m	1	.2047	3.759	v st	1	std 111 Al.	
m	2	.2134	3.606	st	2	.4640	2.082
v st	3	.2251	3.419	st	3	.4712	2.050
m	4	.2755	2.793	v st	4	std 002 Al.	
f	5	.2994	2.570	v st	5	std 022 Al.	
f	6	.3110	2.474	m	6	.7334	1.317
v st	7	std 111 Ag.		v st	7	std 113 Al.	
f	8	.3451	2.230	v st	8	std 222 Al.	
v st	9	std 002 Ag.		m	9	.8626	1.120
f	10	.4037	1.906	f	10	.8793	1.099
m	11	.4468	1.722	f	11	.8861	1.090
f	12	.4813	1.599	f	12	.8875	1.089
f	13	.4913	1.566	f	13	.9603	1.006
v st	14	std 022 Ag.					
f	15	.5681	1.355				
f	16	.5863	1.313				
v st	17	std 113 Ag.					
v st	18	std 222 Ag.					
f	19	.6859	1.122				
f	20	.7058	1.090				
f	21	.7465	1.031				
m	22	std 004 Ag.					
f	23	.7834	.982				
f	24	.7932	.970				
v st	25	std 133 Ag.					
v st	26	std 024 Ag.					
f	27	.8607	.894				
m	28	.9660	.889				

lines given by Mooney, but again some of the lines which we have found are missing in his pattern. We have not been able to assign a high symmetry structure to these crystals but come to the conclusion that a rhombic or still lower symmetry has to be assumed to explain the complicated diffraction pattern.

For this reason we have been carrying out some experiments with completely monochromatic radiation. In this case it is possible, as has been shown recently, to find distances between the neighbors of any atom by Fourier analysis, and in this way to gain a basis for the interpretation of the quadratic form. These experiments are being continued.

This investigation has been carried out at the suggestion of and under the direction of K. Lark-Horovitz, 1929-1935, whom we wish to

TABLE III
Ethylene Patterns

C_2H_4 (purified) deposited on Cu-Fe K-alpha. Manganese filter. Debye-Scherrer camera. Computations based on standard lines from copper.

Int.	Sin θ	Spacing
f	.2275	4.396?*
m	.2418	4.136?*
m	.2492	3.882
st	.2647	3.655
m	.2796	3.460
f	.3029	3.194
f	.3291	2.940
f	.3382	2.861
f	.4307	2.246
m	.3820	2.532
st	.4226	2.289
v st	std 111 Cu.	
m	.4783	2.023
m	.4890	1.979
m	.5063	1.911
v st	std 002 Cu.	1.581
f	.6118	1.520
f	.6364	1.463
f	.6614	1.403
f	.6894	
f	.7092	1.364
v st	std 022 Cu.	
m	.8088	1.196
f		

*possibly due to K-beta

thank also for his continuous help and interest. We also wish to thank Mr. A. I. May and the other members of the instrument maker's shop at the Physics Department for the precise workmanship in building the necessary equipment.