The principal results of the optical determinations are: $\alpha = 1.563$; $\beta = 1.612$; $\gamma = 1.631$; optical character, negative; elongation, commonly negative; system, orthorhombic.

The density at 30° is 1.40 g. per cc.

The dissociation pressure in the range 60 to 90° is expressed by the equation $\log P_{\text{mm.}} = 9.308 - (2313/T_K)$. The "decomposition temperature" is consequently 87°, and the heat of dissociation–vaporization 69 calories per gram of carbon tetrachloride.

WASHINGTON, D. C. RECEIVED FEBRUARY 17, 1937

[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 584, AND THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

The Crystal Structure of Selenium Dioxide

BY JAMES D. MCCULLOUGH

Quoting measurements made by C. F. Rammelsburg, Groth[1] describes selenium dioxide as monoclinic prisms with $a:b:c = 1.292:1:1.067$. He states that the measurements were only approximate, however, due to the extreme hygroscopic nature of the crystals, which made rapid work necessary. All crystals examined in the present work were found to be tetragonal needles with the axial ratio $a:c = 1:0.6047$.

Method of Preparation.—Pure selenium dioxide was dried at approximately 200° in a stream of oxygen which had been passed first through a tube containing phosphorus pentoxide. After drying for several hours, the Pyrex tube containing the selenium dioxide was sealed off at both ends and the substance was sublimed very slowly in an electric furnace. The atmosphere of oxygen prevented the decomposition which sometimes accompanies sublimation of the oxide in the open. The tube was opened inside a moisture-free box and selected crystals were mounted in moisture-proofed gelatine capsules. Except when being photographed they were kept in a desiccator. These precautions were found necessary in order to preserve the crystal faces and prevent lines due to selenious acid appearing on the photographs.

The crystals were transparent, colorless needles about 2–10 mm. long and 0.2–0.5 mm. thick with (100), (110) and (111) principally developed.

The Unit Cell and Space-Group

Laue photographs prepared with the incident beam perpendicular to a (100) face showed a vertical as well as a horizontal plane of symmetry as did the photographs normal to a (110) face. The tetragonal nature of the crystals was established by noting that a rotation of 90° about the needle axis gave a Laue photograph indistinguishable from the original one. Further evidence was furnished by the fact that the photographs prepared with the x-ray beam parallel to the needle axis showed a fourfold axis and four planes of symmetry at 45° intervals. The Laue symmetry thus indicated is that of D_{4h}.

A complete set of 15° oscillation photographs was prepared using unfiltered copper radiation with a 5-cm. camera. The oscillation was about the c-axis. One 30° oscillation photograph was prepared using [110] as an axis but was not very satisfactory for intensity considerations due to the shape of the crystal. Attempts to cleave the crystals across the needle or c-axis were unsuccessful and resulted in shattering.

From these photographs the unit edges $a_0 = 8.353 \pm 0.005$ Å. and $c_0 = 5.051 \pm 0.010$ Å. were calculated. Using these dimensions, values of $n\lambda$ were calculated for a completely indexed Laue photograph in which the x-ray beam made an angle of about 2° with the a-axis. The smallest value thus found was $n\lambda = 0.245$ Å. from (810), the short wave length limit being 0.24 Å.

The oscillation photographs and the first order reflections on the indexed Laue photograph showed all varieties of (hkl) and ($hk0$) reflections. The lattice is accordingly simple. Reflections of the type (hhl) were not observed for l odd although many such planes were in position to reflect, especially on the oscillation photograph about [110]. Further, ($h0l$) was not observed for h odd. These conditions indicate $D_{4h}^{13} - P4/mbc$ or $C_{4v}^{8} - C4cb$ as probable space groups. Attempts to detect a pyroelectric effect failed, but this may have been due to the hygroscopic

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(1) P. Groth, "Chemische Kristallographie," Vol. I, 1906, p. 93.

nature of the crystals. Hence, no further choice of space group can be made at this point.

The Atomic Arrangement

The density of selenium dioxide is given by Clausnizer[2] as 3.95. This value requires 7.59 molecules in the unit. On the assumption of 8 molecules of selenium dioxide in the unit cell, the calculated density is 4.17 g./cc. We have, therefore, to place 8Se and 16O within the cell. Since the selenium atoms will do most of the scattering, to a first approximation we may overlook the oxygen. By means of simple considerations, all positions[3] were excluded to selenium except 8*g* and 8*h* of D_{4h}^{13} and 8*c* of C_{4v}^{8}. At this point some difficulty was encountered so it was considered advisable to resort to the two-dimensional Patterson method[4] in view of the excellent (*hk*0) data available.

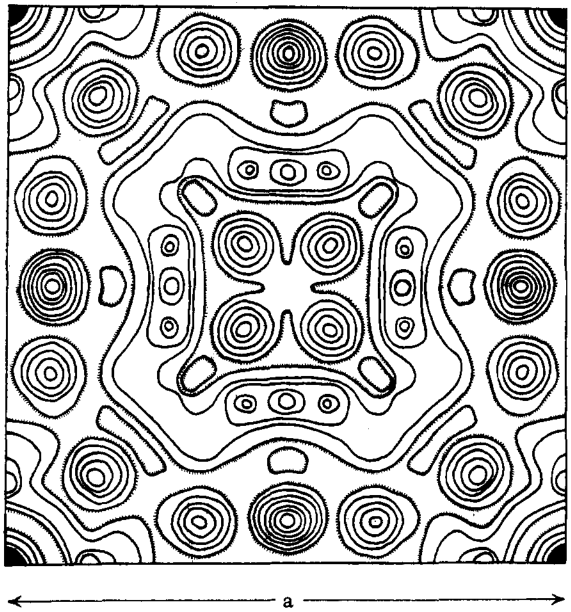

Fig. 1.—Plot of the function $p\ (x, y)$. Maxima represent the projection of interatomic distance vectors on the plane (001).

The two dimensional Fourier series

$$p(x,\ y) = \text{constant}\ \Sigma_h \Sigma_k\ |F_{hk0}|^2 \cos 2\pi(hx + ky) \quad (1)$$

will have maxima corresponding to the projection of the interatomic distance vectors on the (001) face of the unit cell. In evaluating this series the values of $|F_{hk0}|^2$ shown in Table I were used. These values were obtained from the visually estimated intensities by use of the equation

$$|F_{hk0}|^2 = \frac{2I_{hk0} \sin 2\theta}{1 + \cos^2 2\theta} \quad (2)$$

In estimating the intensities a graduated comparison film of timed exposures was used. The function was evaluated at intervals of x and y corresponding to $1/48\ a_0$. The result is plotted in Fig. 1. The principal maxima are without doubt due to selenium–selenium interactions and correspond to the positions 8*h* of D_{4h}^{13} or 8*c*

TABLE I

EQUATORIAL REFLECTIONS FOR SELENIUM DIOXIDE

hkl	Intensity of reflection Obsd.	Calcd.	Obsd. $\lvert F_{hkl}\rvert^2$	Obsd. F_{hkl}
110	47	66	13	3.6
200	350	410	135	−11.6
210	150	216	65	− 8.1
220	0	0	0	0
310	50	67	34	− 5.8
320	45	48	35	− 5.9
330	36	63	35	5.9
400	100	106	91	− 9.6
410	0	0.4	0	0
420	49	65	51	7.2
430	19	14	23	− 4.8
440	35	22	51	− 7.2
510	40	31	50	7.1
520	28	20	37	6.1
530	13	7	19	− 4.4
540	25	21	45	− 6.7
550	35	44	68	− 8.3
600	8	13	12	3.5
610	150	152	245	15.7
620	1	0.8	1.5	− 1.2
630	0	.1	0	0
640	2.5	.2	5	− 2.2
650	33	22	66	− 8.1
660	0	0.2	0	0
710	11	9.0	21	− 4.6
720	1.5	5.0	3.0	1.7
730	9	6.4	17	4.1
740	8	7.3	15	− 3.9
750	45	42	82	9.1
760	1.0	2.1	1.5	− 1.2
770	100	126	103	−10.2
800	3.0	2.4	6.0	2.5
810	35	38	70	− 8.4
820	18	11	34	− 5.8
830	5	3.3	9	− 3.0
840	20	20	34	5.8
850	20	21	26	5.1
860	0	0	0	0
910	7	4.7	11.5	3.4
920	23	28	34	− 5.8
930	22	21	29	− 5.4
940	33	33	36	6.0
10·0·0	2	2	2	1.4
10·1·0	14	17	14	− 3.7
10·2·0	10	5	8	2.8

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[2] Clausnizer, *Ann.*, **196**, 272 (1879).

[3] R. W. G. Wyckoff, "The Analytical Expression of the Results of the Theory of Space-Groups," Publication of the Carnegie Institute of Washington, 1922.

[4] A. L. Patterson, *Z. Krist.*, **90**, 517 (1935).

of C_{4v}^8 with parameters $x = 0.13$ and $y = 0.21$. Maxima due to selenium–oxygen interactions with a separation of 1.25 Å. on the projection occur along the edges of the plot. Because of the symmetry properties of the space-groups under consideration, each crystallographically different set of atoms must produce one or more maxima along the diagonal of the plot. In order to increase the probability of finding the oxygen atoms and in order to get better values of the selenium parameters, the diagonal was evaluated in units corresponding to 1/240 a_0. The result is shown in Fig. 2. The larger selenium–selenium peaks occur at $x_1 = 0.161$ and $x_2 = 0.427$. Since

$$\begin{aligned} x_{Se} + y_{Se} &= \tfrac{1}{2} - x_1, \text{ and} \\ x_{Se} - y_{Se} &= \tfrac{1}{2} - x_2 \end{aligned} \qquad (3)$$

the selenium parameters are $x = 0.133$ and $y = 0.206$. The smaller maximum at $x = 0.284$ was considered to be due to 8O in the positions $8g$ of D_{4h}^{13} or the equivalent in C_{4v}^8. The corresponding parameter x_O is obtained by the relationship $2x_O = 1 - x$, from which $x_O = 0.358$. This assumption was considered reasonable since it also accounts for the previously mentioned selenium–oxygen separation both in direction and in magnitude.

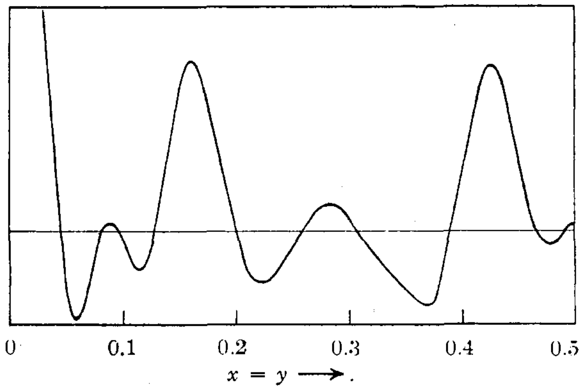

Fig. 2.—Half-diagonal of the function $p\ (x,\ y)$.

This still leaves 8O unaccounted for and maxima due to them are either hidden by the larger interactions already mentioned or they fail to appear due to inaccuracies in the intensity data or because of an insufficient number of terms in the summation. In order to locate these oxygen atoms and to further verify the results already obtained, a two-dimensional Fourier synthesis was made using the series

$$\rho\ (x,\ y) = \text{constant}\ \Sigma_h \Sigma_k\ F_{hk0} \cos 2\pi(hx + ky) \qquad (4)$$

The maxima in this case will correspond to the projection of the atomic positions on the plane (001). In carrying out this summation, intervals corresponding to 1/96 a_0 were employed in x and y. The algebraic sign of F_{hk0} was determined in each case from the selenium parameters already given, on the assumption that all the scattering was due to selenium. These signs were later checked and only one minor change was needed. The F_{hk0} values are shown in Table I.

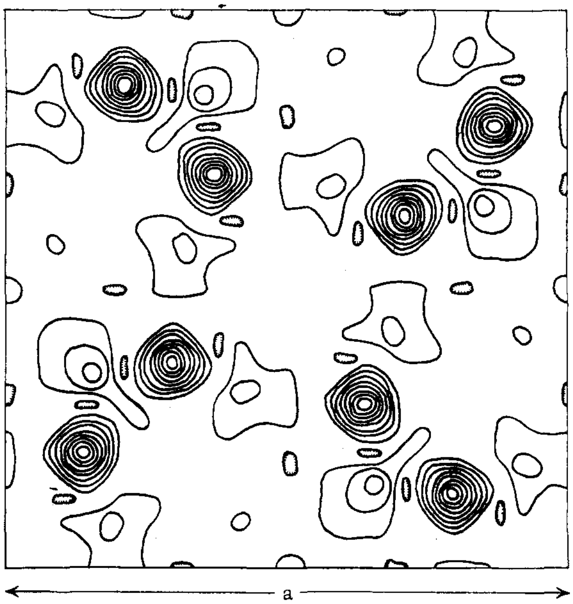

Fig. 3.—Plot of the function $\rho\ (x,\ y)$ for selenium dioxide. Projection of scattering matter on (001).

The result of the Fourier summation is shown in Fig. 3. It is seen that the previous findings are confirmed and the remaining oxygens located. The whole projection can be interpreted in terms of either D_{4h}^{13} or C_{4v}^8 with similar x and y parameters. The final choice was made by means of the layer line intensities which are accounted for nicely by the structure based on D_{4h}^{13} having the following atomic positions

8Se in $8h$

$x,\ y,\ 0;\ \bar{x},\ \bar{y},\ 0;\ \tfrac{1}{2} + x,\ \tfrac{1}{2} - y,\ 0;\ \tfrac{1}{2} - x,\ \tfrac{1}{2} + y,\ 0;$
$\bar{y},\ x,\ \tfrac{1}{2};\ y,\ \bar{x},\ \tfrac{1}{2};\ \tfrac{1}{2} + y,\ \tfrac{1}{2} + x,\ \tfrac{1}{2};\ \tfrac{1}{2} - y,\ \tfrac{1}{2} - x,\ \tfrac{1}{2}.$

$8O_I$ in $8g$

$x,\ \tfrac{1}{2} + x,\ \tfrac{1}{4};\ \bar{x},\ \tfrac{1}{2} - x,\ \tfrac{1}{4};\ \tfrac{1}{2} + x,\ \bar{x},\ \tfrac{1}{4};\ \tfrac{1}{2} - x,\ x,\ \tfrac{1}{4};$
and corresponding positions with $z = \tfrac{3}{4}$.

$8O_{II}$ in $8h$.

with parameter values from the Fourier plot
$x_{Se} = 0.133 \pm 0.001;\ y_{Se} = 0.207 \pm 0.002$
$x_{O_I} = .358 \pm .005$
$x_{O_{II}} = .425 \pm .010;\ y_{O_{II}} = .320 \pm .010$

These parameter values are seen to be in good agreement with those obtained by the Patterson method.

Intensities were calculated for the equator and first two layer lines by means of the equation

$$I_{hkl} = \text{constant}\ [\Sigma_j f_j\, e^{2\pi i(hx_j + ky_j + lz_j)}]^2\ \frac{1 + \cos^2 2\Theta}{2 \sin 2\Theta} \qquad (5)$$

The Pauling–Sherman f-values[5] were used for f_j and the atomic coördinates x_j, y_j, z_j are the parameter values given above. No temperature factor was introduced. The observed and calculated equatorial intensities are given in Table I, while those for the layer lines occur in Table II. The agreement is believed sufficiently good to establish the structure as correct.

TABLE II

LAYER-LINE REFLECTIONS FOR SELENIUM DIOXIDE

	First layer line Intensity			Second layer line Intensity	
hkl	Obsd.	Calcd.	*hkl*	Obsd.	Calcd.
201	205	240	312	88	96
211	190	263	322	80	73
311	41	36	332	115	116
321	31	26	402	2.4	4.8
401	195	213	412	7.3	7.6
411	77	74	422	37	30.4
421	62	70	432	33	15.9
431	2.6	2.1	442	64	51.5
511	42	56	512	14	14.4
521	1.5	3.0	522	57	55
531	71	114	532	3.3	2.2
541	35	30	542	40	28
601	1	0.04	552	40	33
611	3	2.9	602	0	1.3
621	3.5	2.2	612	55	71
631	51	47	622	0	0.1
641	5	2.1	632	2.4	1.6
651	40	34	642	4	1.7
711	21	21	652	8	6.1
721	0	0	662	1.6	1.7
731	46	46	712	1.6	1.0
741	1.4	0.8	722	3.1	4.8
751	2.6	2.5	732	0	0
761	10	4.2	742	8	7.3
801	41	55	802	0	0
811	1	1.0	812	33	21
821	14	11	822	16	15
831	24	17	832	0	0.9
841	0	0.2	842	57	42
851	31	17			
861	0	0.02			
911	2.6	2.5			
921	0	0.2			
931	10	4.0			
941	9	4.4			
951	10	12			
10·0·1	57	79			
10·1·1	62	69			

Discussion of the Structure

The structure found for selenium dioxide is shown in Figs. 4 and 5. It is to be noted that the oxygen atoms are of two kinds, both crystallographically and chemically. Accepting small interatomic distances as showing bonds, we see that the oxygen atoms of the first type are bonded to two selenium atoms while those of the second type are bonded to only one. Since each selenium atom is bonded to two oxygen atoms of type one and to one of type two, the result is a series of flat chains parallel to the c-axis of the crystal. The selenium atoms in a given chain all lie in a plane which is parallel to (110). The oxygen atoms of the second type lie in another plane also parallel to (110), while the remaining oxygen atoms are in between, somewhat closer to the plane of the oxygen atoms of type two than to the selenium plane. This causes a difference in charge on either side of the chain, the selenium surface being positive and the oxygen surface negative. The chains are probably held together by the electrostatic attraction of the oxygen atoms in one chain for the selenium atoms in a neighboring chain, which effect would be enhanced by the staggering of atoms which occurs. The chain structure ties in with observance of a fair prismatic cleavage parallel to (100) and (110), and the lack of cleavage parallel to (001).

The observed interatomic distances are 1.78 ± 0.03 Å. for Se–O_I and 1.73 ± 0.08 Å. for Se–O_{II}. The sum of the normal single bond radii is 1.83 Å., taking 1.17 Å. for selenium and 0.66 Å. for oxygen.[6] The nearest approach of two oxygen atoms is 2.53 Å. for O_I–O_I and 2.67 Å. for O_I–O_{II}, while the distance between selenium atoms in the same chain is 3.16 Å. The observed bond angles are 98 ± 2° for O_I–Se–O_{II}, 90° ± 30′ for O_I–Se–O_I and 125° ± 30′ for Se–O_I–Se.

The observed Se–O_I distance is in fairly good agreement with the value expected for a single covalent bond, but one would expect the oxygen atoms of the second type to be doubly bonded to selenium with a separation of approximately 1.64 Å. When O_{II} parameters are chosen to satisfy this double bond distance, the calculated intensities are not quite as satisfactory in general, although the changes are not great. The O_{II} parameters given were taken as the

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[5] L. Pauling and J. Sherman, *Z. Krist.*, **81**, 1 (1932).

[6] L. Pauling and M. L. Huggins, *ibid.*, **87**, 205 (1934).

highest points due to these atoms on the Fourier plot. Actually the closeness of the large selenium maxima may be of influence here and perhaps one should take the highest point above the sloping selenium maximum in the background. Efforts to get a good estimate of this influence were without success due to the ever-present fluctuations introduced when one evaluates an infinite series of this kind by means of a finite number of terms. Further, the estimated intensities used in the summation may have been somewhat in error.

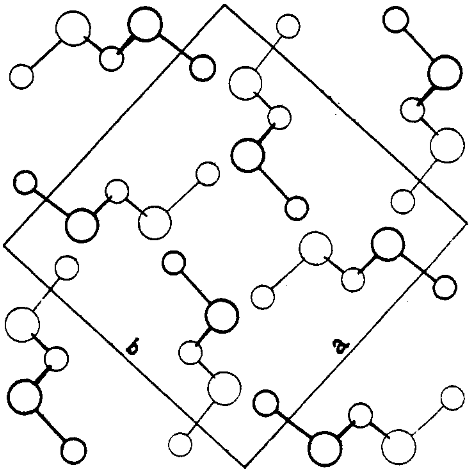
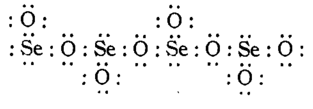


Fig. 4.—Projection of the selenium dioxide structure on the (001) face of the unit. The chains are seen end-on. Large circles indicate selenium atoms, while small circles represent oxygen.

It is interesting to note that selenium dioxide molecules as such do not exist in the solid. However, only one single covalent bond must be broken per selenium dioxide molecule produced in the vapor state. This may account for the relatively high vapor pressure of the solid as shown by its ease of sublimation. The probable electron configuration is



$$\begin{array}{cccccccc} :\ddot{\mathrm{O}}: & & & & :\ddot{\mathrm{O}}: & & & \\ :\underset{\cdot\cdot}{\mathrm{Se}}: & \underset{\cdot\cdot}{\ddot{\mathrm{O}}}: & \underset{\cdot\cdot}{\mathrm{Se}}: & \underset{\cdot\cdot}{\ddot{\mathrm{O}}}: & \underset{\cdot\cdot}{\mathrm{Se}}: & \underset{\cdot\cdot}{\ddot{\mathrm{O}}}: & \underset{\cdot\cdot}{\mathrm{Se}}: & \underset{\cdot\cdot}{\ddot{\mathrm{O}}}: \\ & & :\underset{\cdot\cdot}{\mathrm{O}}: & & & & :\underset{\cdot\cdot}{\mathrm{O}}: & \end{array}$$

with an unshared pair of electrons occupying the fourth tetrahedral position of selenium. The shortening of the selenium–oxygen bonds, especially that for oxygen of the second type, may be attributed to partial double bond character brought about by an unshared pair from oxygen swinging into the bonding position for a fraction of the time. This gives selenium more than eight electrons in its valence shell, and it is probably the resistance to this breaking of the octet rule which prevents permanent double bonds from selenium to oxygen. Assuming a relationship between interatomic distance and percentage of double bond character similar to that for the carbon–carbon bond,[7] it is estimated that the Se–$\mathrm{O_I}$ bonds have 10–15% and the Se–$\mathrm{O_{II}}$ bonds 20–25% of double bond character.

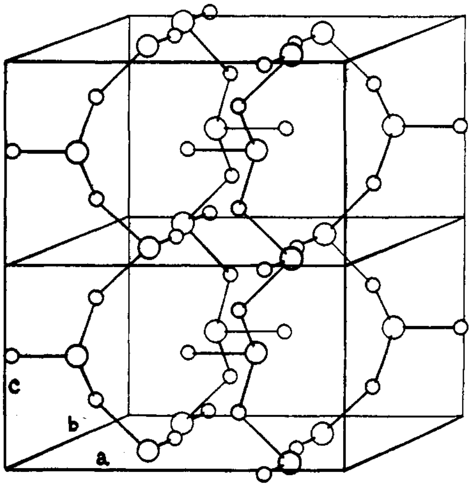


Fig. 5.—Atomic arrangement of selenium dioxide showing two unit cells. Large circles represent selenium atoms and small circles oxygen.

Another feature of the structure worth-while mentioning is that each selenium atom is surrounded by an irregular octahedron of six oxygen atoms. This octahedron consists of two $\mathrm{O_I}$ at a distance of 1.78 Å., one $\mathrm{O_{II}}$ at 1.73 Å., one $\mathrm{O_{II}}$ at 2.63 Å. and two $\mathrm{O_{II}}$ at 3.00 Å. The first three atoms belong to the same chain as the selenium while the remaining three belong to neighboring chains.

The author wishes to express thanks to Professor Linus Pauling for his helpful suggestions during the structure determination and to Dr. James H. Sturdivant for much valuable advice and assistance in preparing the X-ray photographs.

Summary

By means of an X-ray investigation, sublimed selenium dioxide has been shown to crystallize in the tetragonal system with unit edges a_0 = 8.353 ± 0.005 Å. and c_0 = 5.051 ± 0.010 Å. The unit of structure contains eight selenium

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(7) L. Pauling, L. O. Brockway and J. Y. Beach, This Journal, **57**, 2705 (1935).

and sixteen oxygen atoms in the following positions of the space group D_{4h}^{13}:

$8Se$ in $8h$ with $x = 0.133$ and $y = 0.207$
$8O_I$ in $8g$ with $x = 0.358$
and $8O_{II}$ in $8h = 0.425$ and $y = 0.320$

The structure consists of chains of alternating selenium and oxygen atoms along the *c*-axis, with oxygen of a second kind bonded to each selenium atom. The observed separations are 1.78 ± 0.03 Å. for $Se–O_I$ and 1.73 ± 0.08 Å. for $Se–O_{II}$ with bond angles of 98 ± 2° for $O_I–Se–O_{II}$, 90° ± 30′ for $O_I–Se–O_I$ and 125° ± 30′ for $Se–O_I–Se$.

LOS ANGELES, CALIF. RECEIVED FEBRUARY 17, 1937

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA]

The Validity of Raoult's Law for Paraffin Molecules of Very Different Length

BY JOEL H. HILDEBRAND

An interesting and fundamental question was raised during the recent symposium of the Faraday Society by Guggenheim,[1] who pointed out that the ordinarily accepted validity of Raoult's law for solutions whose components possess equal molecular fields has no sure foundation in statistical mechanics except for cases which correspond to the simple model in which molecules are spherical and "sufficiently alike so that each molecule of either species is directly surrounded by the same number of other molecules. Up to the present no one has succeeded in applying statistical mechanics to a more general model." In the discussion which followed the presentation of this paper the writer called attention to various pieces of experimental evidence indicating that the effect, if it exists, is probably a small one, as indeed the formulation by Guggenheim indicated; nevertheless, the modern treatment of solutions on the basis of their deviations from Raoult's law makes the theoretical support of this law a matter of considerable importance. The purpose of this paper is to follow up a suggestion, made during the discussion, of a model which does lend itself to statistical treatment and which, fortunately, corresponds to the actual solutions most appropriate for experimental tests of the matter: those of normal paraffins of different molecular weight. These furnish, moreover, the cases likely to be of greatest practical importance.

Our model will consist of two molecular species of identical cross section but different lengths, close-packed with their axes parallel. The longer paraffin chains are evidently parallel in the solid state and are probably not much disturbed from a similar "cybotactic" grouping in the liquid state.[2] Furthermore, the field strength of such molecules is surely the same function of the distance from the axis, *e. g.*, to separate a decane molecule from another decane molecule, parallel and in "contact," requires the same energy as to separate it from two pentane molecules, except for a slight effect due to the ends, which becomes proportionally still less for longer chains. The intermolecular distances are not strictly the same for the longer and the shorter molecules at the same temperature, for the latter possess a greater amplitude of motion for the same thermal energy. This difference, however, can be minimized by using longer molecules or lower temperatures. This point will be evident from the lower curve in Fig. 1, where the heat of vaporization per gram, $\Delta H/m$, is plotted against the temperature. The values are all evidently asymptotic to a common line as temperature is lowered. The divergence appears to be almost entirely due to more rapid expansion for the lighter species with rising temperature, as shown by the upper curve in Fig. 1, in which $V\Delta E/m^2$ is plotted against temperature, where V is the molal volume, ΔE, the molal energy of vaporization and m, the molecular weight. This is equivalent to the product of the volume and heat of vaporization per gram. The departures from a common line appear to be within the experimental errors.

Raoult's law is most often written in the form $p_1 = p_1^0 N_1$, where p_1 is the partial vapor pressure of one component, p_1^0 its vapor pressure in the pure liquid state and N_1 its mole fraction. For the present purpose we shall substitute fugacity, f, for vapor pressure. Raoult's law is then

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[1] E. A. Guggenheim, *Trans. Faraday Soc.*, **33**, 151 (1937).

[2] G. W. Stewart, *Phys. Rev.*, **31**, 174 (1928); A. Müller, *Trans. Faraday Soc.*, **29**, 990 (1933); R. Rigamonti, *Gazz. chim. ital.*, **66**, 174 (1936).