I. The Crystal Structures of Trimethyl Platinum Chloride and Tetramethyl Platinum
II. The Electron Diffraction Investigation of Dimethyl Sulfone, Dimethyl Sulfoxide, and Trimethyl Amine Oxide
III. The Heat Capacity and Entropy of Arsenic Trifluoride

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I

The Crystal Structures of Trimethyl Platinum Chloride and Tetramethyl Platinum.

THE CRYSTAL STRUCTURES OF TRIMETHYL PLATINUM CHLORIDE AND TETRAMETHYL PLATINUM

All reported structures of tetravalent platinum compounds have involved octahedral coordination about platinum. Presumably, however, tetravalent platinum is capable of forming d^2sp tetrahedral bonds, and the organo--platinum compounds, tetramethyl platinum and hexamethyl diplatinum, prepared by Gilman and Lichtenwalter (1) were expected to have this configuration (8). In order to establish their structure and, if possible, to determine the tetrahedral radius of platinum, the X-ray study of these compounds was undertaken.

It early became necessary, however, to alter the plan of this research. Isolated tetrahedral molecules in the required number could not be packed into the observed unit cell of tetramethyl platinum. In addition the observed intensities, together with space group considerations, led to two non-equivalent sets of positions for the platinum atoms with identical structure factors. Finally, the scattering of the methyl groups was nearly negligible relative to that of the platinum atoms. As a result neither chemical reasoning nor X-ray data permitted further progress. Fortunately some incomplete observations of Cox and Webster (2) led to the discovery that trimethyl platinum chloride has a structure similar to that of tetramethyl platinum. In the structure of trimethyl platinum chloride the chlorine atoms could be located with some accuracy, and the platinum arrangement could be determined uniquely. This latter structure determination will therefore be discussed before the presentation of the results on tetramethyl platinum.

Trimethyl Platinum Chloride

Preparation

Trimethyl platinum chloride was prepared by the action of methyl Grignard on platinum tetrachloride after the method of Pope and Peachey (3). The platinum tetrachloride was prepared according to the procedure of Kharasch and Ashford (4), and added to the Grignard as the dry powder as suggested to us by Professor Gilman. The material obtained fitted the description of trimethyl platinum chloride by Pope and Peachey (3), and X-ray powder lines from it agreed with the measurements of Cox (2). The product was recrystallized from several solvents, rhombic dodecahedral crystals being obtained. Solutions in dibutyl ether and petroleum ether yielded the best formed crystals.

Crystal System and Unit Cell

Several crystals of trimethyl platinum chloride were mounted and goniometered. Although the quality of the reflections was good the interfacial angles determined from different crystals varied as much as thirty minutes. Within this accuracy these angles correspond with those of a rhombic dodecahedron, a form of the cubic system. Viewed between the crossed nicols of a polarizing microscope the powdered crystals appear isotropic. By the Laue method two, three, and four-fold axes were found in positions agreeing with the goniometry, and the Laue symmetry was established as O_h (Figure III).

Powder diagrams, and rotation diagrams taken about two and three-fold axes of single crystals could be indexed using a body-centered cubic unit ($a_0 = 10.55 A^0$). Very heavy exposures for such rotations were made using copper $K\alpha$ radiation and a nickel filter. (For operations of the X-ray tube at thirty-eight kilovolts peak, the exposures ran from eight hundred to a thousand milliampere hours.) In all cases the sum of the indices of the reflections obtained was even, and the layer line spacing for rotation about the three-fold axis was larger than that for rotation about the two-fold axis. The measurements of the reflections used in determining the size of the unit are recorded in Table I. The density of trimethyl platinum chloride is 3.1 gm./cm.^{3} (2). Accordingly there are eight $(CH_3)_3$ PtCl molecules per unit cell.

Space Group Discussion

Though the X-ray data indicate the Laue symmetry O_h and a body-centered lattice it is questionable whether this evidence can be considered binding for the methyl groups, whose scattering power is relatively low. We shall, however, accept it for the arrangement of platinum and chlorine atoms. Possible space groups for these atoms are then (16) T_d^3-I$\bar{4}$3m, T_d^6-I$\bar{4}$3d, O^5-I43, O^8-I$4_2$3, O_h^9-Im3m, and O_h^{10}-Ia3d. The positions (16) available for eight platinums, with a suitable choice of origin in each case, are the following:

(α) 000; $\frac{1}{2}\frac{1}{2}\frac{1}{2}$; + (000), (0 1/2 1/2), (1/2 0 1/2), (1/2 1/2 0).

(β) 000; $\frac{1}{2}\frac{1}{2}\frac{1}{2}$; + (1/8 1/8 1/8), (5/8 3/8 7/8), (7/8 5/8 3/8), (3/8 7/8 5/8).

(γ) 000; $\frac{1}{2}\frac{1}{2}\frac{1}{2}$; + (3/8 3/8 3/8), (7/8 1/8 5/8), (5/8 7/8 1/8), (1/8 5/8 7/8).

(δ) 000; $\frac{1}{2}\frac{1}{2}\frac{1}{2}$; + (uuu), $(u\bar{u}\bar{u})$, $(\bar{u}u\bar{u})$, $(\bar{u}\bar{u}u)$.

The positions (α) require that maxima with h, k, or l odd be absent. Many reflections of the type (2n+1, 2n+1, 2n) were observed to be so strong that their structure factors must necessarily involve a large platinum contribution. The positions (α) are therefore eliminated for platinum. The positions (β) and (γ) are enantiomorphs and hence have the same structure factor.

Intensities calculated on the basis of either of these sets of positions, with platinum atoms alone considered, are in rough qualitative agreement with those observed. No maxima were present of types (4n+2, 4n+2, 4n) or (4n+2, 4n, 4n). If the platinum is in (δ) the parameter u is then limited to the neighborhood of 1/8 or of 3/8. These values of u give equivalent positions, both of which have the same structure factor as (β) and (γ). The positions (β), (γ), and (δ) are therefore equally satisfactory, considering the platinum alone. (The origin of the unit cell will be assumed in what follows to be chosen so that the coordinates listed above apply to the platinum atoms, whichever set of positions they occupy.)

As we have accepted the Laue symmetry O_h and body centering for both the platinum and the chlorine atoms, the positions (α), (β), (γ), and (δ), perhaps with a change of origin, are the only positions available for the chlorine atoms. We must then consider the cases discussed below.

For the chlorine atoms in (α) the coordinates must be chosen as listed above, or else with the origin displaced by $(\frac{1}{4}\ \frac{1}{4}\ \frac{1}{4})$. In either case for the chlorines the structure factor is real and equal to $(+8f_{Cl})$. For the platinums in (β), (γ), or (δ) with u = 1/8 or 3/8, the structure factor for these reflections is $(-8f_{Pt})$

when $\sum n$ is odd. If the chlorine atoms are in arrangement (α) the chlorine term in the structure factor for reflections (4n+2, 4n+2, 4n+2) is real; if the platinum atoms are in arrangements (β), (γ), or (δ) the platinum term is imaginary. Thus if the chlorine atoms are in (α) the reflections (4n+2, 4n+2, 4n+2) should be stronger than reflections (4n, 4n, 4n) with Σn odd. In every case where such reflections occur in the same vicinity the opposite is true. The difference is too great to be accounted for by carbon contributions and the positions (α) are hence eliminated.

The combinations which remain to be considered are: (a). the platinums in (β) and the chlorines in (γ); (b). the platinums in (β) and the chlorines in (δ); (c). the platinums in (δ) with $u \cong 3/8$ and the chlorines in (β); (d). both the platinum and the chlorine atoms in (δ) with $u_{Pt} \cong 3/8$. (The arrangements enantiomorphic with (a), (b), and (c) need not be considered.) The arrangements (b) and (c) can be eliminated at once since they do not have the cubic symmetry established by the Laue method. We shall first consider (a) and (d) with u_{Cl} in (d) taken equal to 1/8. These cases can then be compared profitably for reflections of the type (2n+1, 2n'+1, 2n"). For n, n', n" even, for n, n" even, n' odd, and for n, n' odd, n" even the following structure factors are found:

$$\text{(a)}\quad S = \pm 4i\,(f_{Pt} - f_{Cl})$$

$$\text{(d)}\quad S = \pm 4\,(f_{Pt} + f_{Cl})$$

For n, n' even, n" odd, for n, n' odd, n" even, and for n, n', n" odd the structure factors become:

(a) $S = \pm 4\ (f_{Pt}+f_{Cl})$

(d) $S = \pm 4i\ (f_{Pt}-f_{Cl})$

The examination of a large quantity of reflections of the type (2n+1, 2n'+1, 2n") was made, and it was found that reflections of the first group were more intense than those in the second whenever comparisons could be made. The arrangement (a) is therefore eliminated.

That we have assumed the parameter $u_{Cl} = 1/8$ in (d) does not invalidate the elimination of (a). It is, however, easy to establish that u_{Cl} is in the neighborhood of 1/8. If u_{Cl} differs greatly from 1/8 chlorine will contribute strongly to many reflections of the type (4n+2, 4n, 4n) and (4n+2, 4n+2, 4n). In such a case it would be nearly impossible to explain their absence everywhere by interference by the carbons. In addition it is objectionable chemically to place the chlorines so close together as to be bonded, or to place them closer to the platinums than permitted by sums of their covalent radii. These considerations likewise restrict u_{Cl} to values not widely different from 1/8. We conclude therefore that the platinums are in (δ) with u_{Pt} near 3/8 and the chlorines are in (δ) with u_{Cl} near 1/8. Of the space groups listed before, only T_d^3 is permitted.

It is true, however, that the space groups T_d^1-$P\bar{4}3m$ and T_d^4-$P\bar{4}3n$ furnish the positions chosen for the platinum and the chlorine atoms. In the former case, as in T_d^3-I$\bar{4}$3m, the platinum and chlorine positions have the point symmetry C_{3v}-3m, but each set of positions is divided into two sets of four equivalent positions. No reason for supposing that all eight positions in each set are not equivalent appears. In T_d^4 the positions are all equivalent but have the point symmetry C_3-3; again it seems unnecessary to consider distorted configurations of the methyl groups which would lower the point symmetry of the platinum and chlorine positions. For these reasons T_d^3-I$\bar{4}$3m was chosen, although the X-ray evidence does not suffice to prove rigorously that the methyl groups fulfill the requirements for this space group. That a satisfactory structure is provided by T_d^3 is added justification for this choice.

Determination of the Parameters

Though approximate positions for the platinums and chlorines can be found by rough intensity considerations, refinement of the parameters requires rather accurate intensity measurements. In addition it was hoped that something could be learned concerning the carbon positions, and at best they would be expected to alter the intensities only a small amount.

Trimethyl platinum chloride possesses a high coefficient of absorption for X-radiation. Intensities must, therefore, be corrected for absorption, and to do this reliably a cylindrical crystal is necessary. The compound is so insoluble in even the most favorable solvents that it was necessary to grind the cylinder. For this purpose a small crystal was attached by shellac to a fine glass fiber with the fiber axis parallel to a two-fold axis of the crystal. The crystal was well centered on the fiber and baked until firm. It was then mounted on a goniometer head, carefully oriented, and ground without alteration of this orientation so that the crystal axis and cylinder axis were parallel. The grinding operation was carried out on a milling machine using a rotating ground glass plate as the grinding surface. Under the microscope the crystal appeared to be quite a smooth cylinder of 0.1 mm. diameter 0.14 mm. long. It was covered with a fine layer of powder which could be dusted off till in its final form the crystal gave only a trace of a powder pattern.

Using the cylinder described long exposures were made with the crystal rotating about a two-fold axis in a beam of copper $K\alpha$ radiation filtered through a nickel foil 7μ thick. The tube was operated at 38 kv. peak and exposures ran to 975 milliampere hours. The reflections produced very symmetrical, clean spots on the photographic film making possible quite good intensity estimates. These estimates were made visually using the multiple film technique (17) and are given in Table II. The absorption correction calculated by Rusterholz (6) for crystals of high absorption was used in correcting the intensities. (The linear absorption coefficient is 471 for trimethyl platinum chloride and 1.54A°).

It has been shown that the platinums must be in the positions (δ) with u_{Pt} nearly 3/8. It is now possible to set a limit on the displacement of the platinum parameter from that value. The observation (see Table II) that ($\overline{9}2\overline{9}$) is stronger than ($\overline{2}\cdot 12.\overline{2}$) requires $u_{Pt} < 0.385$. Again since ($\overline{9}2\overline{9}$) is approximately one-fourth as intense as ($\overline{6}\cdot 10.\overline{6}$), $u_{Pt} \geqslant 0.372$. These comparisons are made assuming the most unfavorable contributions of carbon and chlorine to the structure factor, and are hence independent of the carbon and chlorine parameters. Since however we have already seen that u_{Cl} is near 1/8 it can be shown immediately that $u_{Pt} = 0.375 \pm 0.002$ by the above considerations.

The reflections (4n, 4n, 4n) are more intense than reflections (4n+2, 4n+2, 4n+2) (see Table II). The contributions of platinum to the structure factor of these reflections is very closely equal in magnitude even for small variations in the platinum parameter; hence these reflections are useful in the determination of the chlorine parameter. Thus the observation ($\overline{4}\cdot 12\cdot\overline{4}$) > ($\overline{6}.10.\overline{6}$) requires that $0.105 < u_{Cl} < 0.145$ (see Table III).

Further refinement of the chlorine parameter requires that some account be taken of the positions of the carbons. These positions cannot be determined by X-ray evidence; approximate positions were therefore chosen by chemical considerations. It is expected that three methyls are bonded to each platinum. The positions determined for the platinum atoms and chlorine atoms (Figure I) show that three chlorines are already bonded to platinum in such a way that an approximately octahedral configuration about platinum seems to be demanded. To satisfy, in addition, the requirements of T_d^3 the three methyls bonded to each platinum must be symmetrically placed about the three-fold axes. They are then in the positions 24(g) of this space group. As has been pointed out in the space group discussion there appears to be no reason to consider unsymmetrical arrangements of the methyls. (The other positions in T_d^3 do not permit octahedral bonding and can be eliminated by the consideration of the methyl-methyl distances which would result from their use.) If it is assumed that the platinum-carbon distance is approximately the sum of the covalent radii for platinum and carbon (8), the carbon-platinum distance is about 2.08Å and approximate values of the carbon parameters are $u_C = 0.375$ and $v_C \doteq 0.18$. Using these parameters we shall reconsider the chlorine parameter.

We observe that $(\bar{5}.10.\bar{5}) > (\bar{1}.12.\bar{1})$. If the carbon terms are entirely neglected we find $u_{Cl} \leq 0.10$

(Table IV), in disagreement with the previous limitations set on this parameter. If, however, the contribution of the carbon terms to the structure factor is included u_{Cl} is brought back into the range of values permitted in Table III. (See Table IV). If the carbon configuration previously described is approximately maintained it appears that (5.10.5) > ($\bar{1}$.12.$\bar{1}$) requires that $u_{Cl} < 0.12$. For the carbon parameters chosen $u_{Cl} = 0.11 \pm 0.01$ seems to be the best value of this parameter. Due to the uncertainty in the carbon positions, further refinement of the chlorine parameter is not warranted.

An examination was made of the possibility of refining the carbon parameters, but it appeared very unpromising. Few reflections are influenced significantly by carbon contributions. That some general improvement does result from the inclusion of carbon terms in the structure factor can be seen by comparing columns 3, 4, and 5 of Table II.

The agreement between observed and calculated intensities for the final parameters chosen ($u_{Pt} = 0.375 \pm 0.002$, $u_{Cl} = 0.11 \pm 0.01$, $u_C \cong 0.375$, $v_C \cong 0.18$) is seen to be quite satisfactory. (For comparison, column 6 of Table II is included where the structure factor was calculated with $u_{Cl} = 0.125$). The complete structure is discussed in the section following the structure determination of tetramethyl platinum.

Tetramethyl Platinum

The tetramethyl platinum used in this determination was kindly provided by Professor Gilman. Unlike other compounds of the type Me_4M it is a crystalline material which does not melt below its decomposition point (about 100°C). It is likewise less soluble in organic solvents than other such compounds, dissolving only slowly and in but slight amounts in benzene, petroleum ether, the ethers, etc.

From benzene tetramethyl platinum crystallizes in anisotropic plates which go to pieces so quickly after removal from benzene that no further attempt was made to study their properties, but it is believed they contain benzene of crystallization.

From petroleum ether and ether the crystals obtained appear to be rhombic dodecahedra. The goniometry, as with trimethyl platinum chloride, confirmed this form. Again a mixture of petroleum ether and a higher ether proved the best solvent from which to obtain the crystals.

Unit Cell and Space Group

The crystals were studied in a manner similar to that described for trimethyl platinum chloride. Thus between crossed nicols the powdered crystals showed complete extinction in all orientations. Crystals from benzene solution also showed this property shortly after they had been removed from the mother liquor.

The Laue method was again used to establish the Laue symmetry which, as for trimethyl platinum chloride, is O_h (Figure III).

Careful measurements of high-order equatorial reflections from rotation of the crystal about the two-fold axis were made, the film was corrected for shrinkage, and the edge of the cubic unit determined to be 10.145Å ±0.003Å (Table I). Again the body-centered unit chosen was tested by the examination of a large quantity of Laue and rotation data.

The density of tetramethyl platinum was determined by flotation of the crystals in solutions of methylene iodide and methyl iodide, sedimentation being accelerated by the use of a centrifuge. Solutions having the same density as the crystals had the density 3.16 gm./cm.^{3}. The density calculated for eight molecules per unit cell is 3.23 gm./cm.^{3}.

Rotation diagrams about two and three-fold axes resembled closely those obtained from trimethyl platinum chloride (Figure II). Certain intensities were altered a significant amount, however. The most notable of such alterations was the appearance of the reflections (4n+2, 4n+2, 4n) and (4n+2, 4n, 4n). In all cases the intensity of these reflections was too weak to be comparable with others in their vicinity.

The positions available for the platinums are again (α), (β), (γ), and (δ) as discussed in the previous section. The positions (α) are eliminated on the same basis, and (β), (γ), and (δ) will furnish positions with identical structure factors if again u_{Pt} in (δ) is equal to 3/8. Rough qualitative agreement with the observed intensities is furnished by all three positions.

It was at first believed that the reflections (4n+2, 4n+2, 4n) and (4n+2, 4n, 4n) were weak enough to be explained by the carbon contributions alone. It was then impossible to decide between (β), (γ), or (δ) on X-ray evidence, and (δ) was chosen because the structure was expected to be similar to that of trimethyl platinum chloride, and no obvious structure based on (β) or (γ) presented itself. Closer examination of high order reflections indicated, however, that it is impossible to account for the reflections (4n+2, 4n+2, 4n) and (4n+2, 4n, 4n) unless some platinum contribution to these reflections is allowed. The positions (β) and (γ) are invariant for a body-centered structure and are therefore eliminated even if no similarity between tetramethyl platinum and trimethyl platinum chloride is assumed. We shall again assume the space group T_d^3-$I\bar{4}3m$ for reasons similar to those given in the previous structure determination.

Determination of the Parameters

Attempts were made to prepare cylindrical crystals as previously described. Here, however, it was found that the shellac could not be baked without complete decomposition of the crystals, long periods at low temperatures being as harmful as short periods at more elevated temperatures. Various lacquers and other materials were substituted for shellac but proved either too brittle, too soft, or would not wet the crystals sufficiently to hold them securely during the grinding operation. Each attempt cost a few crystals, and it was decided to give up this procedure before the rapidly dwindling supply was completely exhausted.

As has been seen, trimethyl platinum chloride crystallizes in the same form as tetramethyl platinum, and both substances have the same coefficient of absorption. Reflections from dodecahedral crystals of tetramethyl platinum were therefore corrected for absorption by comparing intensities of reflection from a dodecahedral crystal and the cylindrical crystal of trimethyl platinum chloride, determining an appropriate correction for each reflection. As can be seen from Table V, most reflections required no correction. For those that did it was thought advisable to under correct, rather than over correct. The corrected intensities for the equator of a two-fold rotation examination are given in Table V and are appropriately corrected for comparison with SS* in Table VI.

It cannot be claimed that a parameter determination was made for the carbons. The intensities observed agreed rather well with those calculated for the platinum scattering alone. Instead the structure was assumed to be very similar to trimethyl platinum chloride and positions for the carbons were chosen on this basis. Only the positions of the platinums will be discussed in the structure determination.

As mentioned before, reflections (4n+2, 4n+2, 4n) and (4n+2, 4n, 4n) in high orders cannot be accounted for by the scattering of carbons alone regardless of the positions assumed for them. These intensities are quite sensitive to the platinum parameter, however, requiring $u_{Pt} = 0.375 \pm 0.006$. Otherwise they become comparable in intensity with other reflections. The question as to which way the platinums must be shifted was easily decided by reflections such as $(\overline{7}0\overline{7})$ which are very weak but would be increased enormously if $u_{Pt} > 0.375$. Even though the positions of the carbons are very uncertain, the platinum term in the structure factor for all reflections is so important that good agreement between observed and calculated intensities can only be obtained if $u_{Pt} =$

0.380 ± 0.02.

As will be noted in Table VI, a few reflections such as $(\bar{3}.10.\bar{3})$ and $(\bar{3}.4.\bar{3})$ show some disagreement between observed and calculated intensities. Comparison with Table V will show that such reflections were invariably ones for which absorption corrections were unusually large and therefore rather unreliable by the method used. The weak intensities also jump around a bit in relative magnitude, but all were scarcely visible and quantitative estimates of their intensities highly inaccurate. Neither could they be corrected for absorption, so that the present agreement is believed as satisfactory as is obtainable.

Discussion of the Structures

The crystal structures of trimethyl platinum chloride and tetramethyl platinum show that in the crystal these substances are tetramers with the configuration shown in Figure I. These units are packed together in a body-centered arrangement to form the crystal. The large molecule resembles a tetrahedron with a large sphere attached to each corner. The structure is, then, a very closely packed arrangement for such molecules.

In both structures the platinums and the chlorines or methyls which fill out what is ideally a cube lie on three-fold axes, the symmetry at the points they occupy being C_{3v}-3m. Sets of three other methyls lie in a plane normal to a three-fold axis and bonded to platinum. The point symmetry for their position is C_s-m.

As has been mentioned, the carbon-platinum distance for the methyls lying out of the cube is assumed to be 2.08Å. The platinum-chlorine distance in trimethyl platinum chloride is 2.48Å ; the methyl replacing this chlorine in tetramethyl platinum is at a distance from platinum of 2.50Å for the parameter assumed, but this can be considerably reduced by pulling the methyl inside the tetramer as was found necessary for the chlorine. The calculated intensities are not appreciably changed by this alteration. The nearest platinum-platinum distance in trimethyl platinum chloride is 3.73Å ($\angle$ Pt-Cl-Pt = 99°); in tetramethyl platinum it is 3.44Å. The chlorine-chlorine distance is 3.28Å in the former compound; the methyls replacing the chlorines in the latter are not determined but must be of the same order of magnitude. Methyl-methyl distances between tetramers are slightly over 4Å in both cases.

Particularly for tetramethyl platinum the structure is very unexpected. Though structures for aluminum methyl* and diborane have been proposed where methyl and hydrogen respectively serve to bridge the other atoms together, the evidence in these cases is inconclusive. Considerable time was spent, therefore, in attempting to find other suitable structures. Any attempts to move the platinum atoms at once appeared useless. Since they are too close to permit the packing of methyls about them and too far apart for platinum-platinum bonds, a bridge structure becomes necessary. For trimethyl platinum chloride the nature of this bridging can be established, and no more suitable structure suggests itself for tetramethyl platinum.

A very high temperature factor for these compounds is indicated by the fact that only the heaviest exposures produced visible high order reflections. For compounds containing heavy atoms this is unusual and confirms, we believe, the hydrocarbon-like packing that we have found for both of these compounds. (It is interesting in this respect that the temperature factor for trimethyl platinum chloride appears to be larger than that for tetramethyl platinum.)

The type of bonding between platinum and chlorine and platinum and the methyl which replaces the

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* It is reported that recent work of L. O. Brockway on aluminum methyl indicates that an aluminum-aluminum bond is probable.

chlorine is interesting but, of course, not explained by this work. In the latter case carbon cannot violate the octet rule and hence its four orbitals must take care of six bonds. Speculation as to how it accomplishes this does not seem profitable. In trimethyl platinum chloride each chlorine atom can be bonded to three platinum atoms without this difficulty if the chlorine atom furnishes five of the six electrons involved in the three bonds. The formal charge on each chlorine atom then would be 2, and the formal charge on each platinum atom would be -2. The sum of the octahedral covalent radius of platinum and the tetrahedral covalent radius of chlorine is 2.30A^{o} as compared with 2.48A^{o}, the observed Pt-Cl distance. This difference is large enough to suggest that the platinum-chlorine bonding is not just that described. It seems possible that a chlorine atom, in order to avoid a large positive formal charge, might furnish only one or three electrons, and hence only one or two orbitals, for bond formation. The bonding would then be analogous to that in tetramethyl platinum.

Hexamethyl Diplatinum

Hexamethyl diplatinum was prepared from trimethyl platinum iodide by the method of Gilman and Lichtenwalter (1). Powder diagrams were made of the crystalline material but they appear very complicated and further study was not attempted. As it is for trimethyl platinum chloride and tetramethyl platinum, the temperature factor for hexamethyl diplatinum is unusually large.

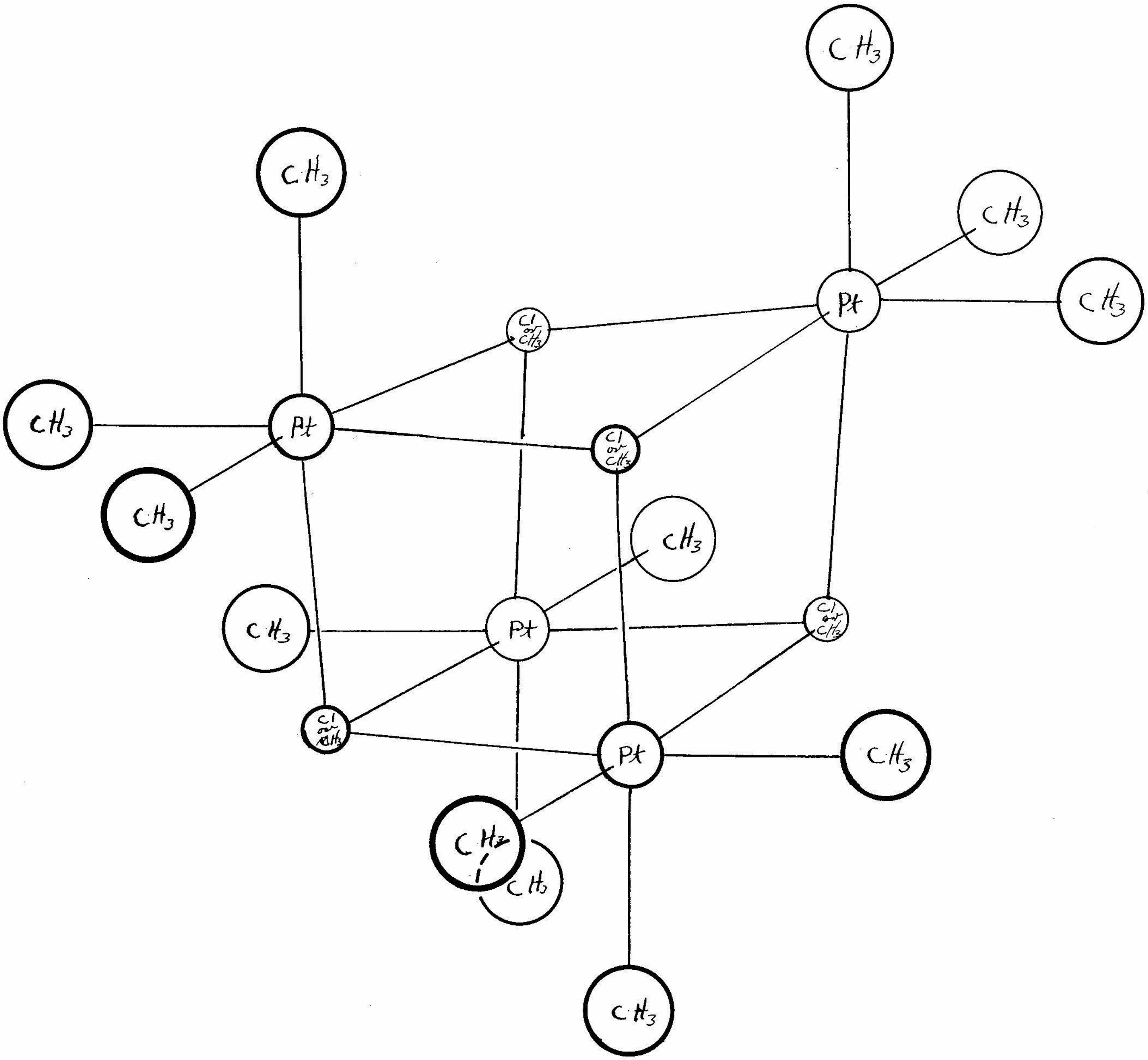


Figure I

Trimethyl Platinum Chloride and Tetramethyl Platinum,

Configuration of Tetramer

Table I

Determination of the Edge of the Cubic Unit of Trimethyl Platinum Chloride

Rotation Diagram of 5-26-'40 about $[10\bar{1}]$

Camera radius = 5.00 cm. Cu Kα = 1.5387A°

Indices	4θ (Rad.)	a_0^2	a_0
$\bar{3}6\bar{3}$	2.2620	111.32	10.55°
$\bar{1}8\bar{1}$	2.5360	111.32	10.55°
$\bar{6}2\bar{6}$	2.7570	111.26	10.55°
$\bar{4}8\bar{4}$	3.1789	111.56	10.56°
			10.55A°, Av.

Determination of the Edge of the Cubic Unit of Tetramethyl Platinum

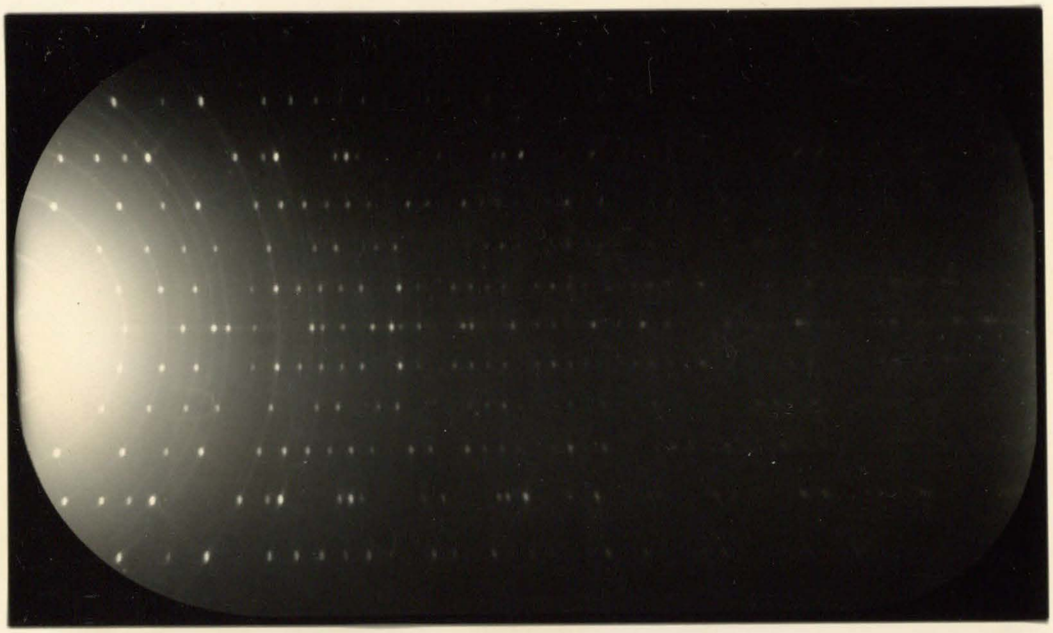
Rotation Diagram of 3-29-'39 about $[10\bar{1}]$

Camera radius = 4.993 cm. (corr. for film shrinkage).

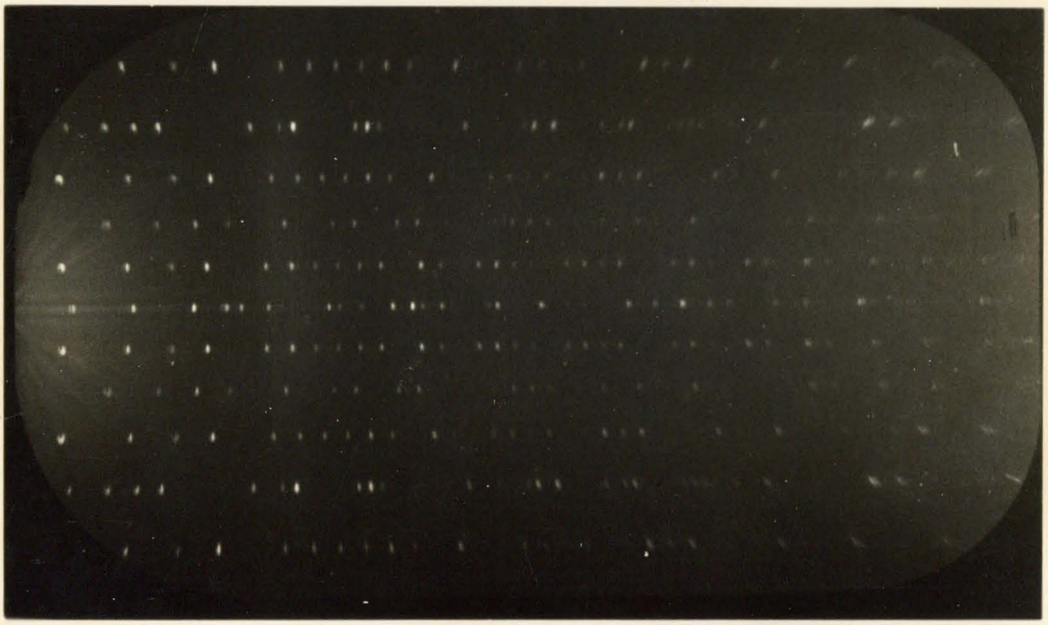
Cu Kα = 1.5387A°

Indices	θ deg.	a_0^2	a_0
$\bar{8}0\bar{8}$	59° 08'	102.89	10.143
$\bar{7}6\bar{7}$	61° 26'	102.91	10.145
$\bar{8}4\bar{8}$	65° 35'	102.87	10.142
$\bar{9}0\bar{9}$	75° 19'	103.03	10.150
			10.145A° Av.

Figure II



Trimethyl Platinum Chloride. Rotation about 101 (Table II)



Tetramethyl Platinum. Rotation about 101 (Table VI)

Table II

Trimethyl Platinum Chloride

Equatorial Reflections from Rotation about [101] 5-26-'40

Cylindrical Crystal Cu Kα = 1.5387A°.

I = directly observed intensity.

II = I K $\frac{\sin 2\theta}{1+\cos^2 2\theta}$ $e^{-k\Sigma h^2}$ x Absorption factor (6). ($k = 0.022$).

III = K'SS*J where J is the multiplicity factor and K' is a convenient constant.

S is calculated with $u_{Pt} = 0.375$, $u_{Cl} = 0.11$, $u_C = 0.375$, and $v_C = 0.18$.

IV = III but without carbon terms.

V = III but with $u_{Cl} = 0.125$.

Indices	I	II	III	IV	V
$\bar{1}0\bar{1}$	3400	151	180	180	168
020	0	0	0	0	0
$\bar{1}2\bar{1}$	2450	196	172	138	157
$\bar{2}0\bar{2}$	0	0	0	0	0
$\bar{2}2\bar{2}$	2125	254	300	445	294
$\bar{3}0\bar{3}$	1800	290	75	91	84
$\bar{1}4\bar{1}$			208	215	196
$\bar{3}2\bar{3}$	285	55	62	78	82
$\bar{2}4\bar{2}$	0	0	0	0	0
$\bar{4}0\bar{4}$	1300	366	388	344	396

Table II (cont.)

Indices	I	II	III	IV	V
$\bar{3}4\bar{3}$	425	127	116	144	137
$\bar{4}2\bar{4}$	0	0	2	2	0
$\bar{1}6\bar{1}$	330	112	98	95	82
$\bar{2}6\bar{2}$	650	267	300	330	278
$\bar{4}4\bar{4}$	1300	600	575	550	608
$\bar{5}0\bar{5}$	170	84	108	90	91
$\bar{5}2\bar{5}$	275	150	104	100	78
$\bar{3}6\bar{3}$			63	62	71
080	350	248	264	260	284
$\bar{1}8\bar{1}$	320	238	109	125	115
$\bar{5}4\bar{5}$			190	155	153
$\bar{4}6\bar{4}$	0	0	1	1	0
$\bar{6}0\bar{6}$	0	0	0	0	0
$\bar{2}8\bar{2}$			1	1	0
$\bar{6}2\bar{6}$	295	275	287	280	245
$\bar{3}8\bar{3}$	95	100	75	77	94
$\bar{5}6\bar{5}$	105	116	95	80	70
$\bar{6}4\bar{6}$	0	0	1	1	0
$\bar{4}8\bar{4}$	320	430	384	370	432
$\bar{7}0\bar{7}$	22	29	44	40	60
0.10.0	0	0	2	2	0

Table II (cont.)

Indices	I	II	III	IV	V
$\bar{7}2\bar{7}$	55	80	21	35	37
$\bar{1}.10.\bar{1}$			47	64	37
$\bar{2}.10.\bar{2}$	335	525	262	240	216
$\bar{6}6\bar{6}$			270	230	230
$\bar{7}4\bar{7}$	115	192	77	60	106
$\bar{5}8\bar{5}$			120	115	111
$\bar{3}.10.\bar{3}$	35	61	51	72	48
$\bar{8}0\bar{8}$	80	150	160	165	190
$\bar{8}2\bar{8}$	0	0	1	1	0
$\bar{4}.10.\bar{4}$			2	2	0
$\bar{7}6\bar{7}$	15	27	24	20	34
$\bar{6}8\bar{6}$	0		1	1	0
$\bar{8}4\bar{8}$	250	480	270	300	320
0.12.0			144	160	160
$\bar{1}.12.\bar{1}$	35	67	65	74	78
$\bar{5}.10.\bar{5}$	45	87	74	64	55
$\bar{2}.12.\bar{2}$	0	0	8	8	0
$\bar{3}.12.\bar{3}$	80	150	48	53	64
$\bar{7}8\bar{7}$			54	58	76
$\bar{9}0\bar{9}$			65	40	51
$\bar{9}2\bar{9}$	25	44	45	56	28
$\bar{6}.10.\bar{6}$	125	205	214	180	168
$\bar{4}.12.\bar{4}$	175	248	230	235	290

Table III

Trimethyl Platinum Chloride

Variation of u_{Cl} with $u_{Pt} = 0.375$

	(6.10.6)		(4.12.4)	
U_{Cl}	S	SS*	S	SS*
0.10	$-8if_{Pt} + 5.2f_{Cl}$	215	$-8f_{Pt} + 2f_{Cl} + 2.5if_{Cl}$	185
0.11	$-8if_{Pt} + 3if_{Cl} + 2f_{Cl}$	183	$-8f_{Pt} - 3f_{Cl}$	235
0.14	$-8if_{Pt} + 3if_{Cl} + 2f_{Cl}$	183	$-8f_{Pt} - 3f_{Cl}$	235
0.15	$-8if_{Pt} + 5.2f_{Cl}$	215	$-8f_{Pt} + 2f_{Cl} + 2.5if_{Cl}$	185

(4.12.4) observed $>$ (6.10.6)

Table IV

Trimethyl Platinum Chloride

Variation of u_{Cl} with $u_{Pt} = 0.375$, $u_C = 0.375$, and $v_C = 0.18$

Indices	u_{Cl}	S	SS*
(1.10.5)	0.14	$-4if_{Pt}-11if_C+4.3if_{Cl}$	50
(1.12.1)		$-4f_{Pt}+7f_C-1.4f_{Cl}$	62
(5.10.5)	0.125	$-4if_{Pt}-11if_C+4if_{Cl}$	55
(1.12.1)		$-4f_{Pt}+7f_C-1.4f_{Cl}$	78
(5.10.5)	0.11	$-4if_{Pt}-11if_C+0.4i_{Cl}$	73
(1.12.1)		$-4f_{Pt}+7f_C-1.4f_{Cl}$	62

Without carbon contribution

(5.10.5)	0.11	$-4if_{Pt}+0.4f_{Cl}$	59
(1.12.1)		$-4f_{Pt}-1.4f_{Cl}$	71

(5.10.5) observed > (1.12.1).

Table V

I_d = observed intensity from dodecahedron of Me_3PtCl.

I_c = observed intensity from cylinder of Me_3PtCl.

I_{obs} = observed intensity from dodecahedrons of Me_4Pt.

					Me_4Pt	
Indices	I_d	I_c	Ratio	Corr. to be applied	I_{obs}	$I_{corr.}$
$\bar{1}0\bar{1}$	2400	3400	1.41		540	540
020	0	0			0	0
$\bar{1}2\bar{1}$	2650	2450	0.93	-30%	850	600
$\bar{2}0\bar{2}$	0	0			0	0
$\bar{2}2\bar{2}$	1450	2125	1.47		1000	1000
040	2550	3730	1.46		520	520
$\bar{1}4\bar{1}$	1500	1800	1.20		350	350
$\bar{3}2\bar{3}$	260	285	1.05	-10%	300	270
$\bar{2}4\bar{2}$	0	0			15	15
$\bar{4}0\bar{4}$	1250	1300	1.04	-10%	325	290
$\bar{3}4\bar{3}$	600	425	0.71	-40%	130	80
$\bar{4}2\bar{4}$	0	0			10	10
$\bar{1}6\bar{1}$	300	330	1.10		150	150
$\bar{2}6\bar{2}$	1000	650	0.65	-40%	550	330
$\bar{4}4\bar{4}$	1540	1300	0.84	-30%	650	460
$\bar{5}0\bar{5}$	150	170	1.10		105	105
$\bar{5}2\bar{5}$	280	275	.98	-10%	240	215
080	215	350	1.63	25%	70	90
$\bar{1}8\bar{1}$	300	320	1.07		325	325

Table V (cont.)

Indices	I_d	I_c	Ratio	Corr. to be applied	I_{obs}	$I_{corr.}$
$\bar{4}6\bar{4}$	0	0			0	0
$\bar{6}0\bar{6}$	0	0			12	12
$\bar{6}2\bar{6}$	250	295	1.18		280	280
$\bar{3}8\bar{3}$	120	95	0.79	-30%	20	15
$\bar{5}6\bar{5}$	90	105	1.17		25	25
$\bar{6}4\bar{6}$	0	0			10	10
$\bar{4}8\bar{4}$	300	320	1.07		210	210
$\bar{7}0\bar{7}$	20	22	1.10		10	10
0.10.0	0	0			15	15
1.10.1	65	55	0.85	-20%	100	80
$\bar{6}6\bar{6}$	290	335	1.15		350	350
$\bar{5}8\bar{5}$	110	115	1.05		120	110
$\bar{3}.10.\bar{3}$	25	65	2.65	100%	65	130
$\bar{8}0\bar{8}$	40	65	1.63	20%	75	90
$\bar{8}2\bar{8}$	0	0			30	30
$\bar{7}6\bar{7}$	12	15	1.25		100	100
$\bar{6}8\bar{6}$	0	0			8	8
0.12.0	260	250	0.96	-10%	240	215
$\bar{1}.12.\bar{1}$	28	35	1.25		55	55
$\bar{5}.10.\bar{5}$	25	45	1.80	25%	12	15
$\bar{2}.12.\bar{2}$	0	0			10	10
$\bar{9}0\bar{9}$	90	80	0.89	-20%	170	135

Table VI

Tetramethyl Platinum

Equatorial Reflections from Rotation about [101], 3-29-'39

Dodecahedral Crystal CuKα = 1.5387A^0

I = I_{obs} (Table V) K $\frac{\sin 2\theta}{1+\cos^2 2\theta}$ x Absorption factor (6).

where K is a convenient constant.

II = I $e^{-k\Sigma h^2}$ with k = 0.0083.

III = SS*J where J is the multiplicity factor and S is calculated with u_{Pt} = 0.375, u_{C1} = 0.125, u_{C_2} = 0.375, and v_{C_2} = 0.17.

IV = III but with u_{Pt} = 0.380.

Indices	I	II	III	IV
$\bar{1}0\bar{1}$	115	120	130	135
020	0	0	0	1
$\bar{1}2\bar{1}$	210	220	220	210
$\bar{2}0\bar{2}$	0	0	0	0
$\bar{2}2\bar{2}$	530	590	600	585
040	275	315	385	380
$\bar{3}0\bar{3}$	225	260	68	42
$\bar{1}4\bar{1}$			105	150
$\bar{3}2\bar{3}$	160	190	105	150
$\bar{2}4\bar{2}$	10	12	1	7
$\bar{4}0\bar{4}$	195	255	310	305
$\bar{3}4\bar{3}$	115	150	105	65
$\bar{4}2\bar{4}$	8	10	0	3

Table VI (cont.)

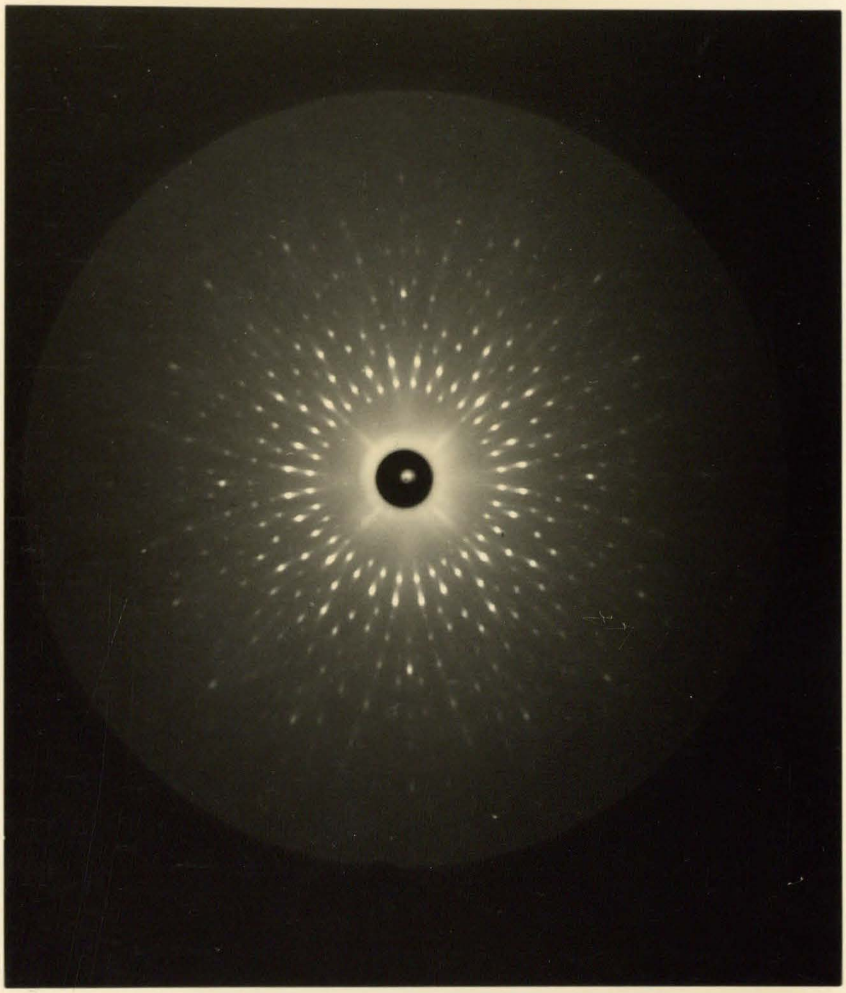
Indices	I	II	III	IV
$\bar{1}6\bar{1}$	110	150	110	89
$\bar{2}6\bar{2}$	265	380	360	350
$\bar{4}4\bar{4}$	380	570	490	475
$\bar{5}0\bar{5}$	88	130	68	110
$\bar{5}2\bar{5}$	185	290	100	64
$\bar{3}6\bar{3}$			93	130
080	84	140	215	165
$\bar{1}8\bar{1}$	285	480	85	95
$\bar{5}4\bar{5}$			115	185
$\bar{4}6\bar{4}$	0	0	0	6
$\bar{6}0\bar{6}$	10	18	0	1
$\bar{2}8\bar{2}$			0	24
$\bar{6}2\bar{6}$	240	460	324	310
$\bar{3}8\bar{3}$	12	24	67	40
$\bar{5}6\bar{5}$	21	43	88	44
$\bar{6}4\bar{6}$	7	14	0	9
$\bar{4}8\bar{4}$	160	350	330	285
$\bar{7}0\bar{7}$	14	30	44	9
0.10.0	22	45	0	16
$\bar{1}.10.\bar{1}$	57	130	53	45
$\bar{7}2\bar{7}$			53	120
$\bar{2}.10.\bar{2}$	235	560	270	250
$\bar{6}6\bar{6}$			290	260

Table VI (cont.)

Indices	I	II	III	IV
$\bar{5}8\bar{5}$	60	155	70	29
$\bar{7}4\bar{7}$			80	125
$\bar{3}.10.\bar{3}$	71	185	60	90
$\bar{8}0\bar{8}$	42	120	130	114
$\bar{8}2\bar{8}$	12	35	0	2
$\bar{4}.10.\bar{4}$			0	23
$\bar{7}6\bar{7}$	40	120	46	95
$\bar{6}8\bar{6}$	3	9	0	15
$\bar{8}4\bar{8}$	105	345	235	210
0.12.0			140	125
$\bar{1}.12.\bar{1}$	16	53	52	55
$\bar{5}.10.\bar{5}$	4	14	66	40
$\bar{2}.12.\bar{2}$	2.5	9	0	26
$\bar{3}.12.\bar{3}$	20	78	45	30
$\bar{7}8\bar{7}$			49	22
$\bar{9}0\bar{9}$			38	78

Figure III A

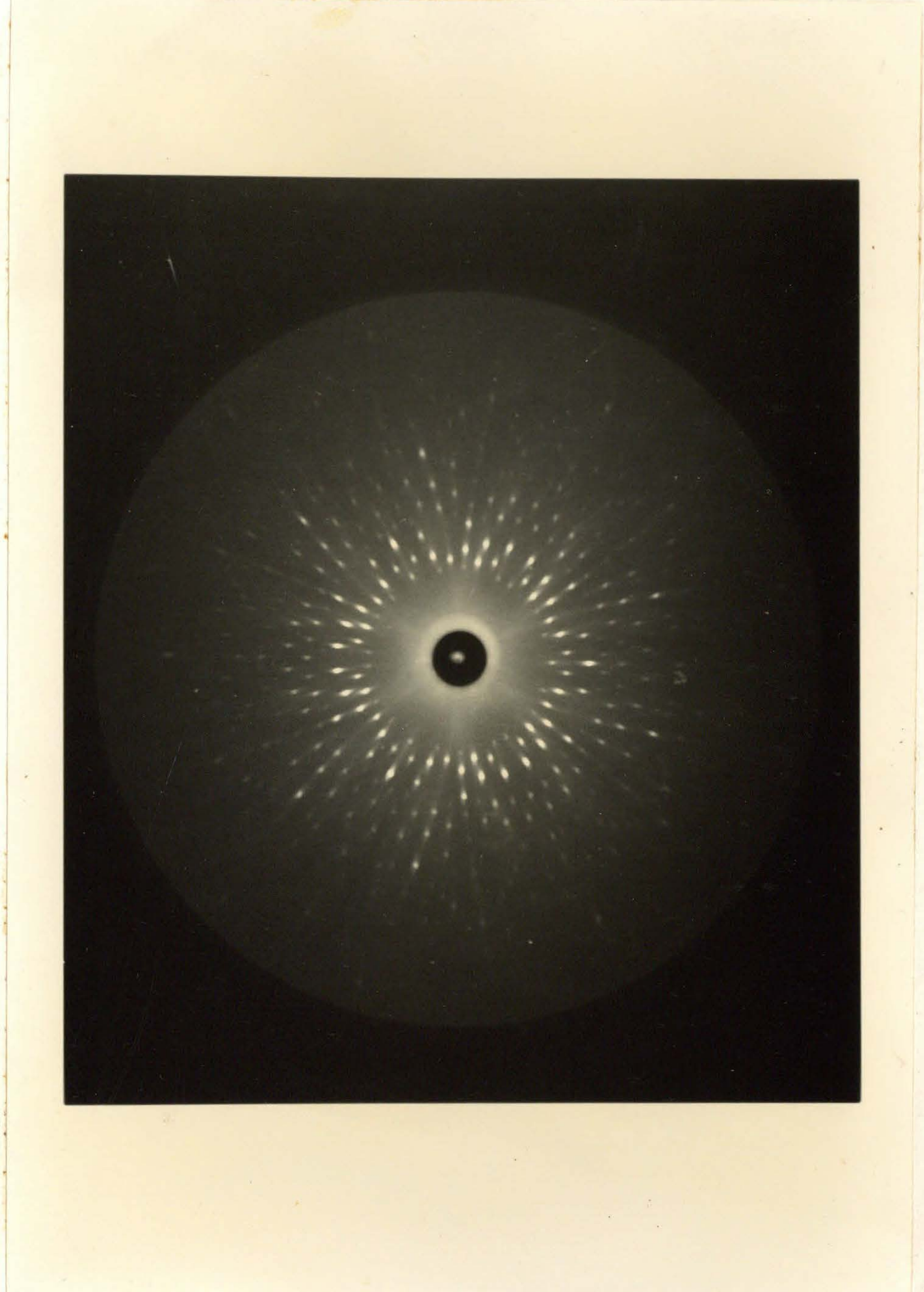
Trimethyl Platinum Chloride



Laue Diagram $\underset{\sim}{s}_0 \parallel \underset{\sim}{a}_1$

Figure III B

Trimethyl Platinum Chloride



Laue Diagram $\underset{\sim}{s}_0 \parallel [111]$

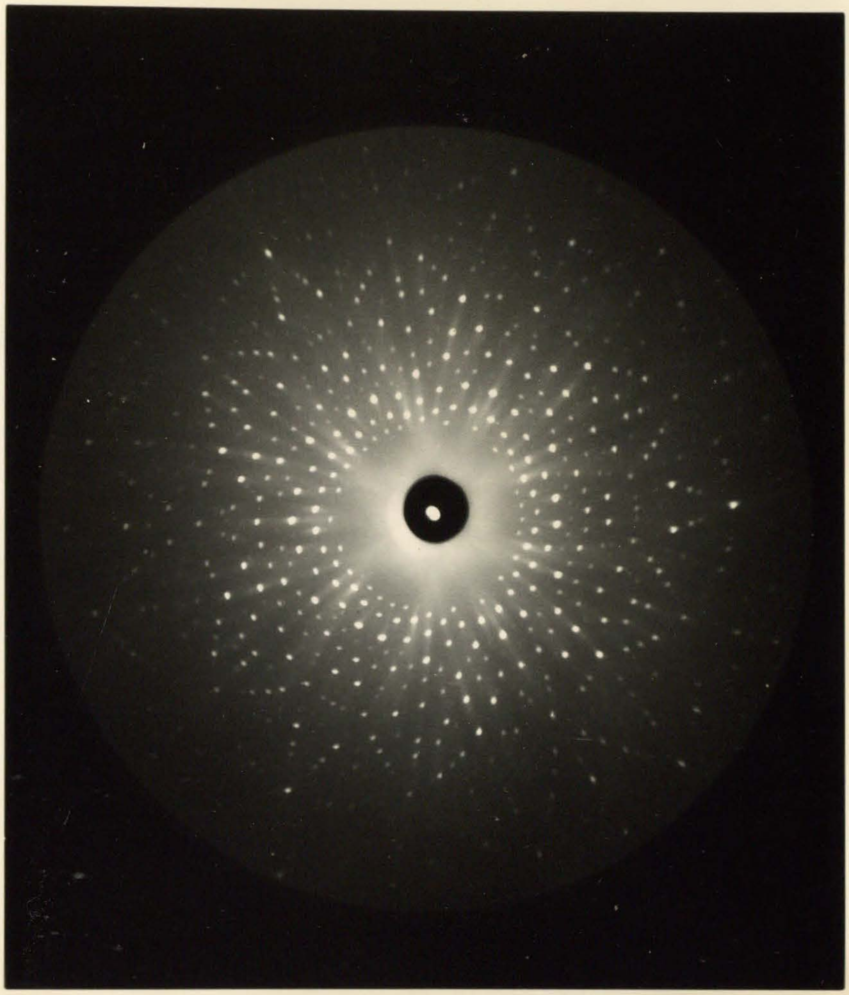
Figure IV A

Tetramethyl Platinum

Laue Diagram $\utilde{s}_0 \parallel \utilde{a}_1$

Figure IV B

Tetramethyl Platinum



Laue Diagram $\underset{\sim}{s}_0 \parallel [111]$

Summary

The structures of trimethyl platinum chloride and tetramethyl platinum have been determined by Laue and rotation methods. The edge of the cubic unit of trimethyl platinum chloride is 10.55A°, and for tetramethyl platinum it is 10.145A°. The space group of both structures is $T_d^3 - I\bar{4}3\,m$.

In the crystal both of these substances are tetramers with the configuration shown in Figure I. For tetramethyl platinum this structure requires that one of the methyls in each $(CH_3)_4Pt$ molecule be bonded to three platinums. ? The carbon of this methyl is then forming six bonds with its four available orbitals. The Pt-Cl distance in trimethyl platinum chloride (2.48A°) suggests that, similarly, a chlorine atom is forming bonds to three platinum atoms with the use of only one or two orbitals.

II

The Electron Diffraction Investigation of Dimethyl Sulfone, Dimethyl Sulfoxide, and Trimethyl Amine Oxide

THE ELECTRON DIFFRACTION INVESTIGATION OF DIMETHYL SULFONE, DIMETHYL SULFOXIDE, AND TRIMETHYL AMINE OXIDE

The electron diffraction examination (9) of molecules containing semipolar double bonds has revealed certain discrepancies between observed bond distances and those predicted by the formal charge rule of Elliott (7) and Pauling (8). In many of the cases examined, however, resonance among single-bond and double-bond structures makes difficult any unique interpretation of the results.

On the basis of the formal charge rule Pauling (8) has predicted a C-N distance of about $1.44A^{\circ}$ for trimethyl amine oxide and tetramethyl ammonium ion as compared with the value $1.47A^{\circ}$ found for this distance in trimethyl amine. As he has pointed out, these substances provide a simple test of the formal charge rule. An examination of trimethyl amine oxide has been made by Sutton and Lister (10), but their value for the C-N distance ($1.54A^{\circ}$) seems too large, and it was thought advisable to repeat their work. They have also made an electron diffraction investigation of dimethyl sulfone, but again the distances they give (C-S = $1.90A^{\circ}$) seem out of keeping with other work. Along with dimethyl sulfone dimethyl sulfoxide appears worthy of study, for here the variation of the C-N distance can be determined when the formal charge on sulfur is changed from two to one.

Dimethyl Sulfone

Experimental Method

Dimethyl sulfone was prepared by the oxidation of dimethyl sulfide with 40% hydrogen peroxide as described by Pummer (11). After recrystallization from water its melting point was 109°C (uncorr.), and it was found to distill without decomposition at atmospheric pressure (B. Pt. 238°C uncorr.).

The electron diffraction apparatus used in this investigation has been described by Brockway (12). The wave length of the electrons, determined by gold foil diffraction ($a_o = 4.070 A^o$), was 0.0611A°; pictures were taken with a camera distance of 10.86 cm. Due to the high boiling point of dimethyl sulfone it was necessary to volatilize the material in a high temperature nozzle (13).

Interpretation

The observed s values ($s = 4\pi/\lambda \sin \vartheta/2$) were treated by the modified radial distribution function (I) of V. Schomaker (14):

$$D(\ell) = \sum_n C_n \frac{\sin s_n \ell}{s_n \ell} \qquad \text{(I)}$$

In this equation $C_n = I_n s_n e^{-a s_n^2}$, I_n is the estimated intensity of the n_{th} maximum or minimum, and $e^{-a\ s_n^2}$ is the artificial temperature factor (14). The estimated values of C_n and the observed s values for dimethyl sulfone are given in Table VII.

The radi~~c~~al distribution function (R, Figure V) shows maxima at 1.43A°, 1.79 Å, and 2.55A°. The first is the value expected for the oxygen-sulfur distance, the second corresponds closely to the expected carbon-sulfur distance, and the third is a composite of the unresolved long distances in the molecule.

Theoretical intensity curves were calculated using the equation

$$I\ (s) = \sum_{i,j} Z_i Z_j e^{-a_{ij}\ s^2}\ \frac{\sin l_{ij} s}{l_{ij} s}\ , \quad \text{(II)}$$

in which Z is the atomic number, l is an interatomic distance, and $e^{-a_{ij}\ s^2}$ is the temperature factor (12). (Except for the terms involving hydrogen a_{ij} was taken as zero). The more exact equation containing (Z-f), where f is the atomic scattering function, was used in calculating curves E and F (Figure VII). As can be seen by comparing these curves with C and D in the same figure, only minor changes are made by this substitution even at small s values.

In all the models considered the carbon-hydrogen distance was assumed to be 1.09A°, and the sulfur-hydrogen distance was taken as 2.40A°. Temperature factors were applied to these terms; their weight in (II) for $s = 20$ was one-fourth the initial value.

If the two oxygens and the two carbons are assumed to be equivalent the structure has four parameters. Of these three are sufficient to determine the form of the intensity curves. These were taken as (a) the ratio of the C-S distance to the O-S distance, (b) the ratio of the C-O distance to the O-S distance, and (c) the O-S-O angle. Large variations of the angle produced no significant changes in the theoretical intensity curves, so its value had to be assumed. For the curves shown in Figure V it was taken to be 123°.

Curve A of Figure V is typical of the results obtained where the ratio (a) is smaller than that given by the radial distribution function. It is unsatisfactory because of the strong doubling of the fifth maximum. This feature is likewise inacceptable in curve B, where the C-S to S-O ratio is larger than that indicated by the radial distribution. Variation of the other parameter produced curves C and D, both equally satisfactory. The final structure selected is, therefore:

S-O = 1.43 ± 0.02A°   ∠C-S-O = 105° ± 3°
S-C = 1.80 ± 0.02A°   ∠C-S-C = 115° ± 15°
C-O = 2.58 ± 0.02A°   ∠O-S-O = 125° ± 15°

Comparison of s observed and s calculated is made in Table VII.

Dimethyl Sulfoxide

Experimental Part

Dimethyl sulfoxide was prepared by the method of Saytzeff (15), and was recrystallized from absolute methyl alcohol. It was found to distill without decomposition at 120 mm. pressure; the boiling point for this pressure was 128°C (uncorr.). The crystals melt at 16°C (uncorr.).

Diffraction patterns were obtained as described for dimethyl sulfone. In this case the camera distance was 10.83 cm. and the wave length of the electrons was 0.0618A°. The pictures had a high background, but seven maxima were visible, of which six could be measured reliably. The broad, shallow, fifth minimum was thought to have some structure, but this was so doubtful that little significance was attached to it. The observed values of s for the maxima and minima are given in Table VIII, together with the estimated values of C_n.

Interpretation

The radial distribution function (Figure VI), calculated as described for dimethyl sulfone, shows maxima at 1.47A°, 1.84A°, and 2.65A°. The first peak corresponds to the sulfur-oxygen distance, the second to the sulfur-carbon distance, and the third must be nearly that of the carbon -oxygen distance since this is by far the most important long distance in the molecule.

The visual correlation method was carried out as described for dimethyl sulfone. The carbon-hydrogen distance assumed was again 1.09A°, and the sulfur-hydrogen distance was taken as 2.44A°; temperature factors were again applied to these terms. In addition it was necessary to assume the carbon-sulfur-carbon angle, equivalent to assuming the carbon-carbon distance, since it could not be hoped to determine this parameter. The angle was chosen to be 115°, making the carbon-carbon distance 3.10A° for a carbon-sulfur distance equal to that given by the radial distribution function (1.84A°).

The three parameters remaining are then the carbon-sulfur distance, the oxygen-sulfur distance, and the carbon-oxygen distance. The ratios of these were varied in calculating the curves, some of which are shown in Figure VI. No important features appear particularly sensitive to these variations, and reliance had to be placed in the relative agreements of the observed and calculated s values for the maxima and minima. On this basis curve B was selected as the most satisfactory (Table VIII). The structure selected is:

C-S = 1.84 ± 0.02A° S-O = 1.47 ± 0.04A°

C-O = 2.65 ± 0.03A° ∠C-S-O = 106° ± 6°.

The accuracy of this determination was limited by the numerous, relatively unimportant terms which had to be included in the theoretical intensity function, and by the fact that good data at high s values were unattainable for this compound.

Trimethyl Amine Oxide

Experimental Part

Trimethyl amine oxide was prepared by the action of 3% hydrogen peroxide on trimethyl amine as described by Dunstan and Goulding (18). The anhydrous material could be sublimed at pressures of about 50 mm. without decomposition, but higher pressures could only be obtained over 200°C where some decomposition took place. The electron diffraction pictures were, therefore, quite hard to obtain and were not very clear beyond $s = 18$. For this compound diffraction photographs were made with a camera distance of 10.82 cm.; the wave length of the electrons was $0.0615A^{\circ}$. The values of q $(\frac{10s}{\pi})$ observed and of C_n estimated are given in Table IX.

Interpretation

The structure determination of trimethyl amine oxide was carried out in a manner quite analogous to that described for dimethyl sulfone, except that calculations were carried out on the International Business Machines recently lent to the California Institute by the I.B.M. Corp. The use of these machines is made easier by modification of both the radial distribution function and the theoretical scattering equation. The former becomes

$$D'(\ell) = \sum_n C_n/q \sin q_n\ell, \quad (I')$$

and the latter is modified to

$$I'(q) = \sum \frac{z_i z_j}{\ell_{ij}} e^{-a_{ij} q^2} \sin \ell_{ij} q \quad (II').$$

where $q = \frac{10s}{\pi}$.

These changes alter somewhat the character of the curves obtained. Thus in the new radial distribution function $D'(\ell)$ is equal to $D(\ell)$ calculated by equation (I) multiplied by ℓ, the variable. This causes unimportant shifts in the maxima obtained from (I'). $I'(q)$ does not have q (or s) in the denominator, and hence does not decrease in amplitude as does I(s) for high s (or q) values. $I'(q)$ is, however, quite as satisfactory in structural determinations.

The radial distribution function calculated for trimethyl amine oxide is shown in Figure VII (Curve R). The maximum at 1.49A° corresponds to the unresolved N-C and C-O distances; that at 2.42A° is due to the unresolved C-O and C-C distances.

As before, the C-H distance was assumed to be 1.09A°. Using the distance 1.49A° for C-N, the H-N distance is 2.09A° for a tetrahedral N-C-H angle. Only for the N-H and C-H terms was the temperature factor in equation II' applied.

The structure is determined by three parameters, conveniently taken as the C-N, C-O, and C-C distances. The curves shown in Figure ~~VIII~~ VII were obtained by choosing C-N to be 1.49A° and varying the other parameters. The average of the C-O and C-C distances had to be kept very nearly equal to 2.42A° to obtain quantitative agreement between observed and calculated s values. This requires that the N-O distance be nearly 1.47A° when C-N is 1.49A°.

Theoretical intensity curves calculated for various ratios of the C-O and C-C distances show important differences only in the seventh maximum. It was thought that some eccentricity in the diffraction pattern could be detected for this maximum, but structures corresponding to A and B should have made this eccentricity more marked. Curve D is unsatisfactory from the fourth maximum on. Though the structure corresponding to curve C is accepted, comparison with curve A will reveal that a fine, and therefore doubtful, choice has been made. The structure adopted is:

C-N = 1.49 ± 0.02A° N-O = 1.44 ± 0.04A°
C-O = 2.34 ± 0.03A° C-C = 2.49 ± 0.03A°
∠ O-N-C = 104° ± 5° ∠ C-N-C = 114° ± 5°

Values calculated for q are given in Table IX.

Discussion

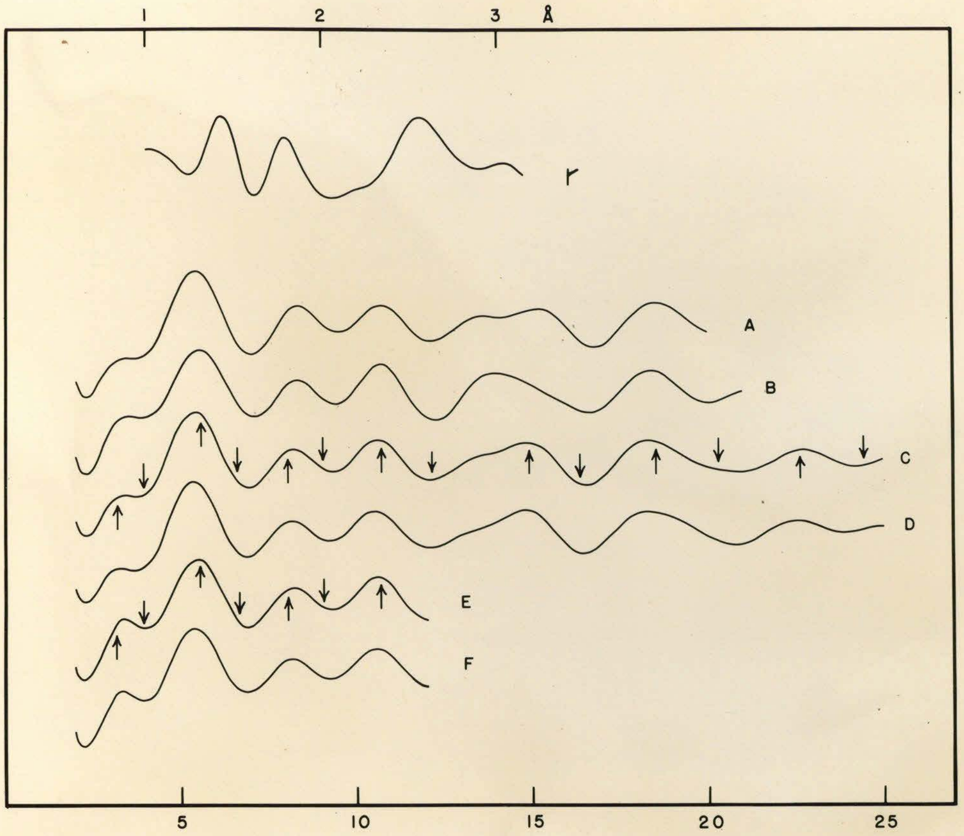
The carbon-nitrogen distance in trimethyl amine oxide (1.49 ± 0.02A°) is at least as great as that found by Brockway and Jenkins (19) for trimethyl amine (1.47 ± 0.02A°). We believe that this result is sufficient to establish the fact that the formal charge rule (8) is not generally valid.

Other exceptions to the formal charge rule have been found so that the results reported above are nor surprising. Thus for both PCl_3 and $POCl_3$ the reported P-Cl distance is 2.01A°, and for both PF_3 and POF_3 the P-F distance is found to be 1.51A° (9). Similar examples can be found among the compounds of sulfur (see below).

The S-O distances determined for dimethyl sulfone and dimethyl sulfoxide were compared with values for that distance found in other molecules. This led to the observation that if two oxygens were bonded to sulfur the distance was 1.43A°, while if but one was bonded to sulfur the distance was always greater than that value. Thus the S-O distance is 1.43A° in Cl_2SO_2 (9b), F_2SO_2 (9b), SO_2 (21), SO_3 (9b) and $(CH_3)_2SO_2$. For Cl_2SO (9b) and $(CH_3)_2SO$ it is 1.47A°, and for Br_2SO it is 1.45A° (22). This was discussed with V. Schomaker, who suggested that a formal charge of two might cause the sulfur to violate the octet rule producing more double bond character in the S-O bond. The author knows of no other sets of compounds which permit the application of this idea.

The C-S distance in dimethyl sulfone (1.80A°) is equal to that found in dimethyl sulfide (19). These values agree with the sum of the covalent radii for carbon and sulfur (1.81A°). Dimethyl sulfoxide on the other hand has a greater distance (1.84A°). This is in accord with results reported for sulfuryl chloride (9d), thionyl chloride (9b), and thionyl bromide (22). For these as well as for the methyl compounds reported in this thesis, compounds of the type X_2SO_2 have X-S bond distances equal to the sum of the covalent radii, while compounds of the type X_2SO have greater distances for this bond. No satisfactory explanation for this correlation is known.

Figure V   Dimethyl Sulfone



All curves			A	B	C	D
C-H	1.09A^{o}	S-C	1.76A^{o}	1.84	1.80	1.80
S-O	1.43	C-O	2.52	2.48	2.56	2.60
S-H	2.40	O-O	2.52	2.52	2.52	2.52
C-C	3.03	O-S-C	103°	99°	104°	107°

Curves E & F are like C & D respectively but with (Z-f) for (Z).

Table VII

Dimethyl Sulfone

Max	Min	I_o	C_n	s_o	s	s/s_o
1		5	2	3.15	3.30	(1.045)
	2	-9	-5	3.90	3.88	(0.995)
2		10	7	5.54	5.38	(0.972)
	3	-7	-7	6.57	6.82	(1.046)
3		7	8	8.01	8.09	1.009
	4	-3	-4	9.02	9.20	1.002
4		5	8	10.68	10.50	0.987
	5	-4	-9	12.11	12.01	0.992
5		4	8	14.89	14.78	0.993
	6	-5	-15	16.35	16.43	1.005
6		5	13	18.49	18.33	0.993
	7	-2	-6	20.30	20.70	1.019
7		2	5	22.62	22.50	0.995
	8	-1	-4	24.44	24.20	0.982
8		1	3	26.69	24.93	(0.934)

Av.0.999±0.011

s_o = s observed s = s calc. from model.

Model for which s is calculated:

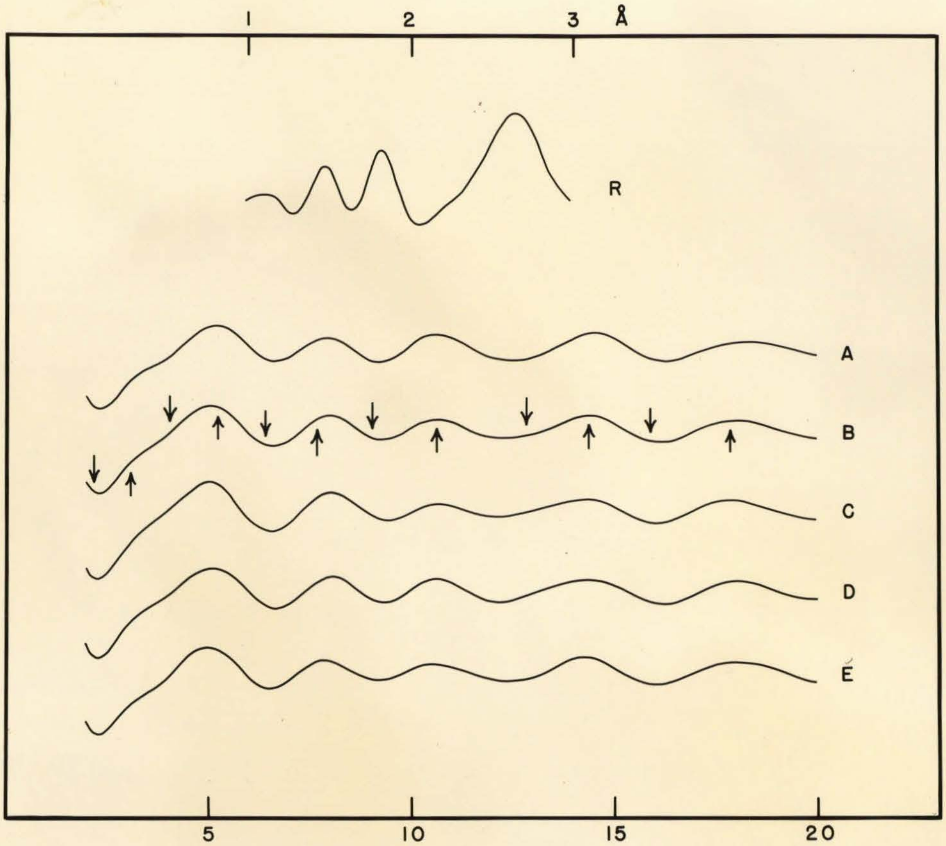
C-H = 1.09A° S-O = 1.43A° O-O = 2.52A°

S-H = 2.40A° S-C = 1.80A° C-C = 3.03A°

C-O = 2.58A°

∠O-S-O = 123° ∠C-S-C = 115° ∠O-S-C = 104°

Figure VI Dimethyl Sulfoxide



Models for which these curves were calculated are given in Table VIII.

Table VIII

Dimethyl Sulfoxide

					Curve A		Curve B		Curve C		Curve D	Curve E
Max	Min	s_o	I_o	C_n	s	s/s_o	s	s/s_o	s	s/s_o	s/s_o	s/s_o
	1	2.20	-6	-3	2.31	(1.049)	2.30	(1.045)	2.28	(1.036)	(1.059)	(1.055)
1		3.10	6	5	3.20	(1.032)	3.20	(1.032)	3.35	(1.081)	(1.065)	(1.016)
	2	4.08	-10	-7	3.90	0.956	4.00	0.982	4.03	0.988	0.993	0.931
2		5.24	10	9	5.15	0.983	5.09	0.971	5.00	0.954	0.973	0.952
	3	6.41	-10	-10	6.62	1.033	6.57	1.024	6.58	1.026	1.042	1.041
3		7.70	8	9	7.89	1.025	7.92	1.028	8.00	1.039	1.043	1.026
	4	9.06	-3	-4	9.14	1.009	9.20	1.015	9.39	1.036	1.029	1.013
4		10.62	5	6	10.53	0.992	10.58	0.996	10.51	0.990	0.998	0.993
	5	(11.31)	-1	-1								
5		(12.39)	1	1								
	6	(12.85)	-2	-2	12.53		12.29		12.00			
6		14.40	8	9	14.48	1.006	14.30	0.993	14.20	0.986	0.990	0.988
	7	15.91	-10	-10	16.28	1.023	16.00	1.005	15.93	1.002	1.018	1.004

Table VIII (cont.)

Max	Min	s_o	I_o	C_n	s	s/s_o	s	s/s_o	s	s/s_o	s/s_o	s/s_o
7		17.87	10	8	18.20	1.018	17.90	1.001	17.83	0.998	1.006	1.018
	8	(19.68)	-10	-7	(20.2)		(20.0)		(20.0)			
8		(21.60)	10	5								
					1.007 ± 0.020		1.001 ± 0.013		1.002 ± 0.020		1.010	0.996
											±0.010	±0.025

All Curves

C-H = 1.09A^{o}

S-H = 2.44A^{o}

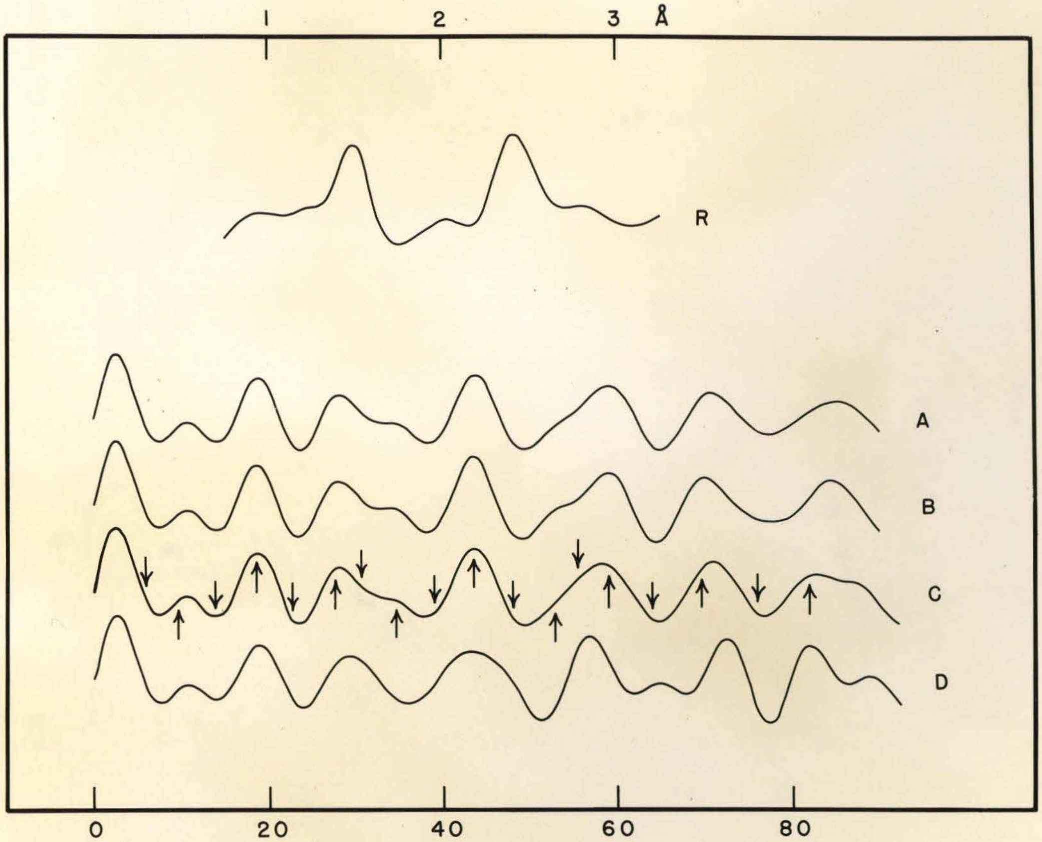
C-C = 3.10A^{o}

S-C = 1.84A^{o}

C-S-C = 115^{o}

	C - O	S - O
Curve A	2.65A^{o}	1.43A^{o}
Curve B	2.65A^{o}	1.47A^{o}
Curve C	2.65A^{o}	1.51A^{o}
Curve D	2.60A^{o}	1.47A^{o}
Curve E	2.70A^{o}	1.47A^{o}

Figure VII Trimethyl Amine Oxide



All curves			A	B	C	D
C-H	1.09A°	O-C	2.42	2.36	2.34	2.27
N-H	2.09A°	C-C	2.42	2.47	2.49	2.53
N-O	1.47A°	O-N-C	109°	106°	104°	100°

Table IX

Trimethyl Amine Oxide

Min	Max	I_o	C_n	q_o	q	q/q_o
1		-6	-12	5.92	7.50	(1.26)
	1	1	2	9.58	10.55	(1.10)
2		-10	-18	13.81	13.90	1.006
	2	10	17	18.65	18.65	1.000
3		7	-11	22.60	23.25	1.028
	3	5	7	27.56	28.00	1.015
4		---	---	30.59	(31.50)	
	4	---	---	34.70	34.50	0.994
5		-10	-10	39.02	37.90	0.971
	5	10	8	43.51	43.48	0.999
6		-8	-6	47.93	49.40	(1.031)
	6	5	3	52.9	( )	
7		-1	---	55.6	( )	
	7	4	2	59.1	58.25	0.985
8		-8	-2	64.0	64.70	1.010
	8	8	2	69.6	71.00	1.020
9		-8	-1	75.8	76.7	(1.011)
	9	8	1	82.1	82.5	(1.004)

1.003±0.013 Av.

Table IX (cont.)

Model for which q is calculated:

C-N = $1.49\mathrm{A}^{\circ}$

C-O = $2.34\mathrm{A}^{\circ}$

C-C = $2.49\mathrm{A}^{\circ}$

O-N = $1.47\mathrm{A}^{\circ}$

N-H = $2.10\mathrm{A}^{\circ}$

C-H = $1.09\mathrm{A}^{\circ}$

O-N-C = 104°

C-N-C = 114°

Summary

Structures of dimethyl sulfone, dimethyl sulfoxide, and trimethyl amine oxide, as determined by the electron diffraction of the gas molecules, are reported, and are summarized in Tables VII, VIII, and IX. The C-N distance in trimethyl amine oxide (1.49A$^{\circ}$) furnishes the best evidence to date that the formal charge rule is invalid in its present form. Both the C-S and O-S distances in dimethyl sulfoxide are longer than they are in dimethyl sulfone. This is in agreement with the reported structures of thionyl chloride (9), sulfuryl chloride (9) and thionyl bromide (22).

III

The Heat Capacity and Entropy of Arsenic Trifluoride

THE HEAT CAPACITY AND ENTROPY OF ARSENIC TRIFLUORIDE

The heat capacity, heat of vaporization, heat of fusion, vapor pressure, and entropy of arsenic trifluoride have been measured and the latter quantity has been compared with that calculated from spectroscopic (24) and structural (25) data. The usual interest in these properties was augmented by the unusual behavior of arsenic trifluoride near 100°K. Upon either heating or cooling the crystals in the neighborhood of this temperature intense emission of light, accompanied by violent sounds of cracking, occurs. Rough observations indicated that the temperature region in which this phenomenon takes place is rather narrow and the existence of a transition seemed to provide a possible explanation.* The study of the heat capacity in this region was sufficient to eliminate this possibility.

Experimental Method

The heat capacity of arsenic trifluoride from 15°K to 290°K was measured in an adiabatic calorimeter. Both the method and the apparatus have been fully de-

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* Hydrogen cyanide behaves in a similar manner in the interval 100°K to 200°K but no transition was found to take place (23).

scribed (26). The heat of fusion was likewise determined in this calorimeter. The heat of vaporization measurements were carried out in a Nernst-Giauque type non-adiabatic calorimeter which has also been described (26a). Where necessary further details will be given in discussing the determination of the various quantities here reported.

Preparation

Arsenic trifluoride was prepared by the method of Ruff (27), purified by allowing it to stand over sodium fluoride for several hours, and then distilling. Sodium fluoride removes the HF formed by hydrolysis of the crude AsF_3 and the material, after this treatment, could be distilled in a glass system with no sign of etching the glass. The distilling column used was five feet long and packed with glass helices. A reflux ratio of about seven to one was maintained during the distillation, and the temperature at the top of the column remained constant to 0.03° while eighty percent of the material distilled. Since the premelting revealed a higher purity for first fractions than for middle and end fractions, the impurities after treatment with sodium fluoride must be chiefly high boiling.

Melting Point and Estimated Impurity

Heat capacity measurements were made on an arsenic trifluoride sample at temperatures just below the melting point. From the extrapolated heat capacities for these temperatures and the total heat of fusion, the percentage melted for temperatures in the premelting range was calculated. Raoult's law was assumed and on this basis the percentage melted at each temperature could be accounted for by a melting point of $267.205 \pm 0.010^{\circ}K$ and a 0.02 mole percent impurity (Table X). This sample was used for the heat capacity and heat of fusion measurements. Treated in a similar fashion, the sample used in the heat of vaporization determinations was estimated to have an impurity of 0.04 mole percent.

Vapor Pressure of Arsenic Trifluoride

The mercury manometer used in the vapor pressure measurements has been described (26b). The measurements were carried out using a standard meter mounted in the manometer case and a Hansen cathetometer as a comparison instrument. The arsenic trifluoride was contained in the heat of vaporization calorimeter where its temperature was maintained constant to $0.002^{\circ}C$. The standard acceleration of gravity was taken as $980.665\ cm/sec^2$ and for this locality the acceleration of gravity was taken as 979.57 cm/sec^2. The measurements were corrected to international cms. by means of the density data given in the "International Critical Tables " (28).

Difficulty was experienced in obtaining reproducible measurements of the vapor pressures and the values given (Table XI) are good to about 0.3 mm. The experimental vapor pressures can be represented by the equation $\log_{10}P = A+\frac{B}{T}+C\log T$ where A = 61.37969, B = -4149.784, and C = -18.26403. These constants were found by treating the experimental data by the modified least-squares method due to D. Osborne. $\sum p^2(\log p - \log P)^2$ was minimized. A comparison between p observed and P calculated is made in Table XI. As our distilling column was poorly equipped for measurement of the boiling point, the best value we can report is that calculated from the vapor pressure equation (62.3°C at 760mm.).

The Heat Capacity of Arsenic Trifluoride

The purified arsenic trifluoride used in the heat capacity determination was distilled through a ground-glass joint into a weighed bulb equipped with a "breakoffski." The arsenic trifluoride was frozen in dry ice, and the bulb evacuated and sealed below the joint. The bulb and joint were weighed and the sample introduced into the calorimeter through the "breakoffski";

little contact with stop-cock grease was necessary by this procedure. The weight of arsenic trifluoride in the calorimeter, corrected for the vapor remaining in the line and bulb, was 237.11 gm. (1.7975 moles). Helium was admitted to the calorimeter to sweep out the end of the line, serve as a buffer against diffusion of the AsF_3 vapor, and help establish rapid equilibrium between the solid and the calorimeter in the heat capacity measurements. The calorimeter and contents were cooled to 12°K, and the heat capacity of the solid was measured adiabatically from that temperature to just below the melting point. Temperature intervals ranged from 1° at the lowest temperatures to 10° for temperatures above 150°K. The molal heat capacities, corrected for the heat capacities of the calorimeter and helium, are give in Table XII and are represented graphically in Figure VIII. Heat capacity measurements were likewise made on the liquid. Corrected for vaporization and the heat capacity of the vapor and helium, they are also given in the above mentioned table and figure. In calculating the energy input the defined calorie = 4.1833 international joules was used. The ice point is taken as 273.16°K.

For temperatures just above 100°K equilibrium was very slow, but as can be seen from the heat capacity curve (Figure VIII) there is no manifestation of a transition.

Heat of Fusion

The heat of fusion of arsenic trifluoride was measured by heating the substance from 15° below the melting point to 9° above the melting point. The correction $\int C_p dT$ for this temperature increase was made by extrapolating the heat capacity-temperature curves for the solid, the liquid, and the calorimeter to the temperature of the melting point and integrating under the curves. A slight correction was also necessary for the amount of premelting below the lower temperature. The final heat of fusion per mole is 2486.4 ± .2 cal. A summary of the data is given in Table XIII.

Heat of Vaporization

The heat of vaporization measurements were carried out (26a) by supplying electrical energy to the liquid at the desired temperature, well under room temperature, and measuring the quantity of material vaporized. To do this at constant pressure a buffer pressure of helium was applied thru a mercury bubbler attached to the collecting bulb. Though the measurements are simple in nature a number of important corrections must be made if the values are to have the required accuracy. Thus the heat capacity of the empty calorimeter and the liquid were measured, and corrections were made for the rise in temperature of the liquid and calorimeter which necessarily accompanies the vaporization as carried out. Corrections for the extra vapor space in the calorimeter after the vaporization were made using the density of arsenic trifluoride measured by Throop (29). An estimate of the temperature of the liquid surface was made from the buffer pressure and the estimated pressure drop in the line leading to the collecting bulb. The temperature of the vapor emerging from the calorimeter was measured by means of a difference thermocouple at the top of the calorimeter. As the liquid surface and emerging vapor temperatures were different a correction was made for the energy supplied to the vapor using the heat capacity of the gas calculated from spectroscopic data ($Cp_{292.5} = 15.48$ cal. deg.$^{-1}$ mole^{-1}). The collecting bulb was weighed before and after the vaporization run and the amount collected was determined by difference. Approximately five grams of material were collected in each run.

Four measurements of the heat of vaporization of arsenic trifluoride were made. These are summarized in Table XIV. It will be noted that the values fall into pairs. We believe that the difference in these sets of values arises from the fact that for the two low values the collecting bulb was evacuated without melting the collected material so that a little of the buffer gas may have been trapped in the crystals. We, therefore, have adopted the higher values for the heat of vaporization ($H^{vap.}_{292.5^o}$ = 8565 cal./mole.). The value calculated from the vapor pressure equation (Table XI) is 8376 cal./mole. This large discrepancy is probably indicative of a large gas imperfection and is not surprising for arsenic trifluoride.

The Entropy from Caliometric Data

A plot was made of the heat capacity of the solid and the liquid as a function of log T and a graphical integration was carried out to determine the entropy. Checks were made of the reproducibility of the graphical integration; deviations were found to amount to about 0.03% so that no significant error was introduced by the process of integration.

The heat capacity of arsenic trifluoride at temperatures below 17° is well represented by the Debye Function (30) with Θ = 91.1 (Table XV). The extrapolated entropy from 0°K to 13.338°K for this value of Θ is 0.454 cal./deg./mole. A summary of the entropy of AsF_3 from 0° to 292.5°K is given in Table XVI.

To compare the calorimetric value of the entropy with that calculated from spectroscopic and molecular data it is desirable to estimate the difference in entropy between the actual gas and that of the ideal gas at the same temperature and pressure. If it is assumed that the actual gas can be represented by Berthelot's equation of state then from the thermodynamic equation

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p$$

it can be shown that

$$S_{ideal} - S_{actual} = \frac{27 R T_c^3 p}{32 T^3 p_c}$$

No critical data exist for arsenic trifluoride, nor are any data available for particularly similar gases. For heavy, polar molecules with a boiling point near that of arsenic trifluoride values in the neighborhood of $T_c = 570^oK$ and $p_c = 30$ atmospheres are found. Using these values $S_{ideal} - S_{actual} = 0.09$ cal./mole./deg. H. Russell has obtained a similar value by an independent method (31); the value is probably good to 30%.

The Entropy from Spectroscopic and Structural Data.

The As-F distance measured by electron diffraction (25) is $1.72 \pm 0.02 A^o$ and the F-As-F angle is estimated to be $100^o \pm 5^o$. The principle moments of inertia of arsenic trifluoride calculated using the values above are $I_x = I_y = 86.809$ At. wt. A^{o2}, and $I_z = 131.938$ At. wt. A^{o2}. Using the equation

$$S_{trans} + S_{rot} = \tfrac{1}{2}R \ln(I_x I_y I_z) + 4R \ln T - R \ln p$$
$$- R \ln\sigma + 3/2 R \ln M - 7.6989, \quad (1)$$

obtained from statistical mechanics, the rotational and vibration entropy was calculated. In equation (1), I_x, I_y, and I_z are the principle moments of inertia in At. wt. $A^{o\,2}$, T is the absolute temperature, p is the pressure in atmospheres, σ is the symmetry number of the molecule, M is the gram molecular weight, and the constant is chosen so that R, the gas constant, must be taken in cal./deg./mole; $S_{trans.} + S_{rot.}$ is then found in cal./deg./mole. The value of R used in these calculations was 1.9871 cal./deg./mole. The symmetry number for arsenic trifluoride is 3. At 292.5°K and 141.6 mm pressure the vibration and rotational entropy is 66.898 cal./deg./mole. At 298.1°K and 760 mm pressure it is 63.675 cal./deg./mole. An error of five degrees in the F-As-F angle corresponds to an error of 0.05 cal./deg./mole. An error of 0.02A° in the As-F distance causes an error of 0.08 cal./deg./mole.

The Raman frequencies measured by Yost and Sherborne (24) permit the calculation of the vibration entropy of arsenic trifluoride. From statistical mechanics $S_v = R\left\{\ln Q + T\frac{\partial \log Q}{\partial T}\right\}$ where $Q = \sum_n \exp\left\{-(n+\frac{1}{2})hc\omega/kT\right\}$, w is the frequency in $cm.^{-1}$, k is the Boltzmann constant, h is Planck's constant, c is the velocity of light, and T is the absolute temperature. In these calculations, hc/k is taken as 1.4384 cm.deg. (32). The vibration entropy calculated for 292.5°K is 5.263

cal./mole./deg. The frequencies used were obtained from the liquid and may ~~have~~ be displaced a few wave numbers from those of the vapor. A displacement of as much as five wave numbers in the lowest frequency will, however, change the entropy calculation by but 0.10 cal./mole./deg. Changes in the other frequencies are much less important.

The entropy calculated for one mole of the perfect gas at 298.1°K and one atmosphere pressure is 69.08 ± 0.15 cal./mole./deg. as compared with 69.1 cal./mole./deg. calculated by Yost (24b). Comparison of the entropy calculated from spectroscopic and molecular data is made in Table XVI. The agreement is somewhat fortuitous but indicates that the entropy of crystalline arsenic trifluoride approaches zero at 0°K.

Table X

Melting Point and Estimated Impurity of Arsenic Trifluoride

In these estimates the following equation was assumed:

$$T_o - T = \frac{RT_o^2}{\Delta H_o^F} X$$

where T_o is the temperature at the freezing point, X is the mole fraction of solute, and H_o^F is the heat of fusion for one mole of the pure solvent at T_o.

Temperature	Cal. added	Cal. to calorimeter and solid	With T_o = 267.205°K % melted	% impurity (molal)
254.434°K			(0.246)	
	1471.81	700		0.019
267.143			17.52	
	819.12			
267.173			35.9	0.020
267.190	1091.53		60.3	0.016
267.192	1172.05		86.5	0.020

Total Heat of Fusion = 4469 cal.

With % impurity = 0.0195 and T_o = 267.205°K

% melted	$T_{calc.}$	$T_{obs.}$
17.5	267.141°K	267.143°K
35.9	267.174	267.173
60.3	267.187	267.190
86.5	267.192	267.192

Table XI

The Vapor Pressure of Arsenic Trifluoride

$$\log P = 61.37969 - \frac{4149.784}{T} - 18.26403 \log T.$$

T °K	$p_{obs.}$ mm.	Pmm.	P-$p_{obs.}$
265.019	28.90	29.00	0.10
268.235	36.15	35.85	-0.30
272.058	45.68	45.67	-0.01
275.271	55.22	55.53	0.31
280.182	74.20	73.88	-0.32
288.055	112.70	113.10	0.40
291.816	136.96	136.90	-0.06
291.879	137.46	137.30	-0.16

Calc. B.Pt. (760 mm.) = 62.3°C.

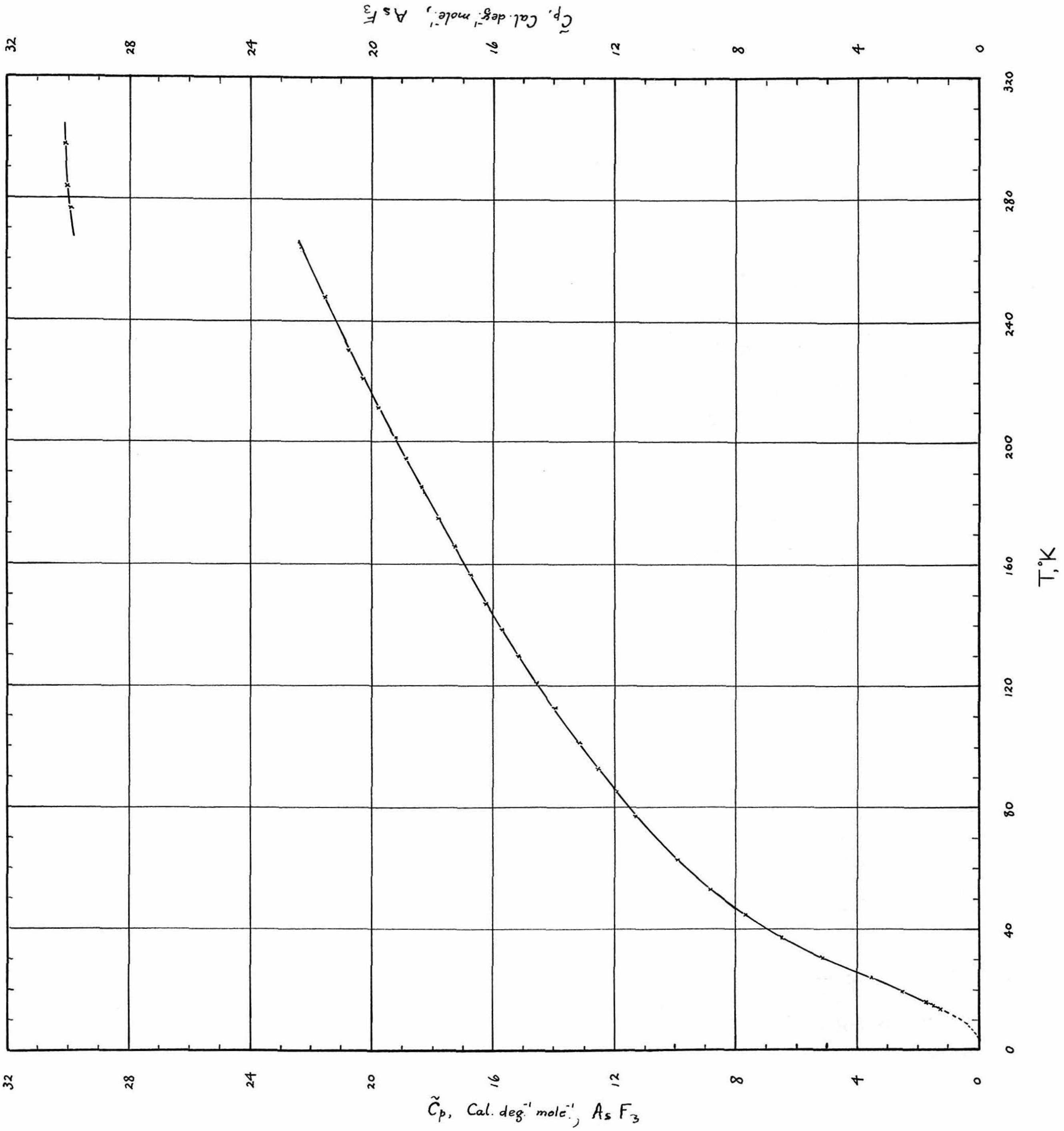
$\tilde{C}_p$, Cal. deg.$^{-1}$ mole^{-1}, As F$_3$
32
28
24
20
16
12
8
4
0
T,°K
320
280
240
200
160
120
80
40
0
32
28
24
20
16
12
8
4
0
$\tilde{C}_p$, Cal. deg.$^{-1}$ mole^{-1}, As F$_3$

Table XII

Heat Capacity of Arsenic Trifluoride

Molecular weight, 131.91 $0^\circ C = 273.16^\circ K$

T, $^\circ$K	T	C_p cal./deg./mole.
13.588	1.132	1.258
14.677	1.152	1.480
15.868	1.230	1.712
17.250	1.533	2.044
19.166	2.300	2.513
21.504	2.376	3.084
23.992	2.599	3.703
26.893	3.205	4.388
30.329	3.666	5.143
33.872	3.419	5.870
37.220	3.279	6.488
40.673	3.627	7.056
44.305	3.639	7.653
48.273	4.296	8.207
52.687	4.515	8.799
57.433	4.996	9.320
63.072	6.283	9.920
69.868	7.309	10.610
77.120	7.216	11.287
78.186	9.256	11.359
84.407	7.338	11.894

Table XII (cont.)

T, °K	T	C_p cal./deg./mole.
87.074	8.520	12.118
92.365	8.577	12.541
95.685	8.700	12.788
101.289	9.274	13.183
104.139	8.207	13.433
112.163	7.842	13.953
120.456	8.745	14.525
129.683	8.949	15.122
138.460	8.603	15.685
147.190	8.857	16.209
156.354	9.473	16.749
165.679	9.175	17.282
175.036	9.540	17.800
185.032	9.247	18.342
194.454	9.598	18.857
201.673	9.284	19.172
211.116	9.603	19.744
220.869	9.901	20.254
230.631	9.624	20.736
239.601	8.315	21.569
247.802	8.088	21.569
267.205	(Extrap.)	(22.458)
	Liquid	
276.203	3.897	29.959

Table XII (cont.)

T, °K	T	C_p cal./deg./mole.
280.091	3.877	30.020
283.958	3.857	30.068
287.810	3.847	30.071

Table XIII

Heat of Fusion of Arsenic Trifluoride

Molecular weight, 131.91 $0^\circ C = 273.16^\circ K$

Weight of $AsF_3 = 237.11$ gm. = 1.7975 moles.

$T_1 = 251.847^\circ K$ Premelting below

$T_2 = 274.255^\circ K$ $251.847^\circ = 9.184$ cal.

$T_f = 267.205^\circ K$ from extrapolated heat capacity curve.

Total energy added = 5784.37 cal.

Energy to solid and calorimeter $251.847^\circ - 267.205^\circ K$ = 839.39 cal.

Energy to liquid and calorimeter $267.205^\circ - 274.255^\circ K$ = 484.92 cal.

$\Delta\widetilde{H}_{fusion} = 4469.23/1.7975 = 2486.4 \pm 2$ cal./mole.

Table XIV

Heat of Vaporization of Arsenic Trifluoride

Molecular weight, 131.91 $0^{\circ}C = 273.16^{\circ}K$

Run I $T = 293.12^{\circ}K$

Total Energy Add = 359.22 cal. Moles collected = 0.037692

Energy to liquid and calorimeter = 36.98 cal. Moles vaporized in system = 0.000030

Energy to emerging vapor = 0.77 cal. Moles vaporized 0.037722

$H^{vap.}_{293.12^{\circ}} = 8522$ cal./mole $H^{vap.}_{292.5^{\circ}} = 8531$ cal./mole.

Run II $T = 292.48^{\circ}K$

Total Energy Added = 450.35 cal. Moles collected = 0.042382

Energy to liquid and calorimeter = 85.36 cal. Moles vaporized in system = 0.000050

Energy to emerging vapor = 1.53 cal. Moles vaporized 0.042432

$H^{vap.}_{292.5} = 8566$ cal./mole

Table XIV (cont.)

Run III $T = 292.67^{o}K$

Total Energy Added = 529.27 cal.

Energy to liquid and calorimeter = 25.82 cal.

Energy to emerging vapor = 1.77 cal.

$H^{vap.}_{292.67} = 8526$ cal./mole.

Moles collected = 0.058809

Moles vaporized in system = 0.000032

Moles vaporized = 0.058841

$H^{vap.}_{292.5} = 8529$ cal./mole.

Run IV $T = 292.20^{o}K$

Total Energy Added = 461.61 cal.

Energy to liquid and calorimeter = 43.89 cal.

Energy to emerging vapor = 1.31 cal.

$H^{vap.}_{292.2} = 8569$ cal./mole.

Moles collected = 0.048552

Moles vaporized in system = 0.000041

Moles vaporized = 0.048593

$H^{vap.}_{292.5} = 8565$ cal./mole.

Value accepted $H^{vap.}_{292.5} = 8565$ cal./mole.

Table XV

Fit of Debye Function to Arsenic Trifluoride (30)

C_p cal./deg./mole	T, °K	Θ/T	Θ, °K
1.258	13.588	6.695	91.05°
1.480	14.677	6.204	91.07°
1.712	15.868	5.759	91.38
2.044	17.250	5.228	90.18
2.513	19.166	4.577	87.74

Θ = Debye's characteristic temperature.

Value Adopted, Θ = 91.1°K.

Table XVI

Entropy of Arsenic Trifluoride

Molecular weight, 131.91   0°C = 273.16°K

	Entropy
0° - 13.338°K (Debye Extrap.)	0.454 cal./mole/deg.
13.338° - 267.205°K	30.272
Heat of Fusion = 2486.4/267.205	9.305
Liquid to 292.50°K	2.713
Heat of Vaporization = 8566/292.50	29.285
Real Gas at 141.6 mm., 292.50°K	72.03 ± 0.1
Gas correction	0.09
Ideal Gas at 141.6 mm., 292.50°K	72.12 ± 0.1
Value from Molecular Data	72.16 ± 0.15 cal./mole/deg.

Summary

The heat capacity of solid arsenic trifluoride has been measured from 14°K to the melting point, and the heat capacity of the liquid has been measured to 290°K. The melting point was found to be 267.21°K. The heat of fusion, determined calorimetrically, is 2486 cal./mole, and the heat of vaporization at 292.5°K is 8565 cal./mole.

The vapor pressure of arsenic trifluoride has been measured from the melting point to 290°K; the observed pressures have been represented by the equation

$$\log_{10} P_{mm.} = 61.37969 - \frac{4149.784}{T} - 18.26403 \log_{10} T.$$

The entropy of arsenic trifluoride vapor at 292.5°K and 141.6 mm. pressure was found to be 72.03 cal./mole/deg., and for the perfect gas under these conditions 72.12 cal./mole/deg. This is in good agreement with the spectroscopic value (72.16 cal./mole/deg.). The entropy at 298.1°K and one atmosphere pressure is 69.08 cal./mole/deg.

Heat capacity measurements in the neighborhood of 100°K show no sign of a transition in solid arsenic trifluoride. The emitted light and sounds of cracking which occur upon heating or cooling the crystals at temperatures near 100°K is probably due to static discharge produced by crystals breaking under the strain of uneven contraction or expansion.

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PROPOSITIONS

1. (a) The "thermal mutarotation" of d-galactose observed by Isbell and Pigman (1) could have been predicted quantitatively from the work of Smith and Lowry (2).

(b) The existence of furanose and other ring forms in the equilibrium mixture of solutions of the simple aldohexoses is not at all required by the kinetic studies of Isbell and Pigman (1). Likewise the heats of activation which they have calculated for these ring forms are meaningless.

2. Enough evidence is now available to establish the invalidity of the formal charge rule. It is suggested that the average shielding of an electron pair is altered by bond formation so that a simple estimate of the effective shielding is impossible.

3. Deductions concerning the molecular structure of hexamethyl diplatinum can be made from the x-ray powder diagram it produces.

4. (a) Cox and Webster (3) could have shown that their proposal of tetrahedral molecules of trimethyl platinum chloride was incorrect from the density and size of the unit cell which they found for trimethyl platinum chloride.

(b) The space group discussion of Cox and Webster (3) is so incomplete as to be erroneous.

~~5. The chlorine in trimethyl platinum chloride is bonded to the three nearest platinums using but one chlorine bond orbital.~~

6. (a) The molecular weight of hydrazine in the vapor,

contrary to the statement of Eucken and Krome (4), corresponds to the monomer.

(b) The models for the dimer proposed by Fresenius and Karweil (5) do not seem very reasonable.

6 ~~7~~. For a cylindrical crystal with a high linear coefficient of absorption for x-radiation the absorption correction for layer line reflections can be calculated using an approximation similar to that used by Rusterholz (6) for equatorial reflections.

7 ~~8~~. Heats of mutarotation calculated from polarimetric data need revision now that Isbell and Pigman (1) have obtained good values for the specific rotations of the α and β forms of the simple hexoses at several temperatures. Most of the early calculations neglected the temperature dependence of the specific rotations of the pure forms, and are therefore incorrect.

8 ~~9~~. It would be better to use oxidation potentials instead of reduction potentials in the sophomore analytical course.

9 ~~10~~. The behavior of arsenic trifluoride indicates that the solid has an abnormally high coefficient of expansion. The emission of light produced when the solid is subjected to changes in temperature ~~is~~ can be accounted for by this property.

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