

AN ABSTRACT OF THE THESIS OF

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Title: ELECTRON DIFFRACTION INVESTIGATIONS. I. THE
MOLECULAR STRUCTURES OF THE GASEOUS GROUP III
HALIDES Al_2Cl_6 , Al_2Br_6 , Al_2I_6 - AlI_3 , Ga_2Cl_6 , AND
 Ga_2Br_6 - GaBr_3 ; II. THE GASEOUS EQUILIBRIA $2\text{NO} \rightleftharpoons \text{N}_2\text{O}_4$
AND $2\text{GaBr}_3 \rightleftharpoons \text{Ga}_2\text{Br}_6$

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Kenneth Hedberg

The molecular structures of dimeric aluminum chloride, aluminum bromide, aluminum iodide, gallium chloride, and gallium bromide have been investigated by electron diffraction. The results for all these molecules are consistent with a model of D_{2h} symmetry having two bridging halogen atoms above and below the plane of the remaining atoms and undergoing intramolecular motion of large magnitude corresponding to a "bending" around an axis through the two bridging atoms. The electron diffraction analyses led to the following values for the principal distances (in Å) and bond angles (in degrees); the parenthesized values are 2σ : aluminum chloride,

$\text{Al}-\text{Cl}_t = 2.065$ (.002), $\text{Al}-\text{Cl}_b = 2.252$ (.004), $\angle \text{Cl}_b \text{AlCl}_b = 91.0$ (.5),
 and $\angle \text{Cl}_t \text{AlCl}_t = 123.4$ (1.6); aluminum bromide, $\text{Al}-\text{Br}_t = 2.222$ (.005),
 $\text{Al}-\text{Br}_b = 2.414$ (.007), $\angle \text{Br}_b \text{AlBr}_b = 92.3$ (.9), and $\angle \text{Br}_t \text{AlBr}_t =$
 122.8 (3.3); aluminum iodide, $\text{Al}-\text{I}_t = 2.449$ (.013), $\text{Al}-\text{I}_b = 2.634$
 (.030), $\angle \text{I}_b \text{AlI}_b = 99.6$ (4.5), and $\angle \text{I}_t \text{AlI}_t = 115.0$ (7.4); gallium
 chloride, $\text{Ga}-\text{Cl}_t = 2.099$ (.002), $\text{Ga}-\text{Cl}_b = 2.300$ (.002), $\angle \text{Cl}_b \text{GaCl}_b =$
 88.3 (.8), and $\angle \text{Cl}_t \text{GaCl}_t = 124.6$ (1.8); gallium bromide, $\text{Ga}-\text{Br}_t =$
 2.245 (.003), $\text{Ga}-\text{Br}_b = 2.446$ (.009), $\angle \text{Br}_b \text{GaBr}_b = 91.1$ (2.2), and
 $\angle \text{Br}_t \text{GaBr}_t = 128.1$ (3.0). In the cases of aluminum iodide and
 gallium bromide the samples contained monomeric as well as dimeric
 molecules. The D_{3h} symmetry of these monomers was verified.
 The bond distance and angle values are: aluminum triiodide, $\text{Al}-\text{I} =$
 2.449 (.013), and $\angle \text{I Al I} = 120.1$ (4.0); and gallium tribromide,
 $\text{Ga}-\text{Br} = 2.243$ (.040), and $\angle \text{BrGaBr} = 120.0$ (1.2). These parameter
 values agree very well with those expected based on the view that
 the metal atoms use sp^2 hybrids in the monomer and sp^3 in the
 dimer. The terminal bonds in the dimer seem to be about as strong
 as the bonds in the monomer. The double-bond characters of the
 terminal bonds are fairly large and prevail even in the cases of
 bromides and iodide. The bridge bonds in the gallium halides are
 weaker than the corresponding ones in aluminum halides. Unlike
 the trimethyl aluminum dimer and trimethyl aluminum hydride dimer,
 metal-metal bonds do not seem to be indicated by the structures of

the dimeric aluminum and gallium halides.

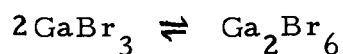
The dependence of the equilibrium constant for the system $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$ and the knowledge of the effective temperatures and pressures of the sample at the diffraction zone (required in the calculation of dissociation equilibrium constants and thermodynamic quantities) were studied. The several experiments fall into two sets: i) those with nozzle temperatures of 104, 25, 2, -12, -25, and -35°C and the sample bath temperatures at -42 - -44°C, and ii) those with nozzle temperature at -12°C and bath temperatures of -26, -36, and -43°C. In these studies the values obtained for the bond distances and angles are as follows: dinitrogen tetroxide, N-O = 1.191 (.002), N-N = 1.774 (.005), and $\angle\text{ONO} = 134.8$ (.4), and nitrogen dioxide, N-O = 1.199 (.001), and $\angle\text{ONO} = 134.0$ (.5). The compositions at three different sample bath temperatures (N_2O_4 : 49.7 (2.6)%, -43°C; 61.5 (2.5)%, -36°C; and 71.6 (2.0)%, -26°C) and five different nozzle temperatures (N_2O_4 : 4.5 (0.7)%, 25°C; 30.3 (1.7)%, 2°C; 49.7 (2.6)%, -12°C; 68.2 (1.8)%, -25°C; and 76.3 (2.9)%, -35°C) reveal that within experimental accuracy the vapor pressure provided by the sample bath may be taken as representing the effective pressure and the nozzle temperature as representing the effective temperature. The enthalpy and entropy of dissociation of N_2O_4 are $\Delta H^\circ = 13.7$ (1.3) kcal mole⁻¹, and $\Delta S^\circ = 42.8$ (5.3) cal mole⁻¹ deg⁻¹.

Using the results about the effective temperature and pressure derived from the N_2O_4 - NO_2 experiments, the equilibrium constant of gallium bromide was evaluated at 163, 192, and 226°C. The dimer concentrations were found to be 47.4 (5.1)%, 25.5 (5.4)%, and 7.6 (5.7)%, respectively, from which the enthalpy and entropy of dissociation of Ga_2Br_6 are calculated to be $\Delta H^\circ = 19.5$ (3.5) kcal mole⁻¹, and $\Delta S^\circ = 35.3$ (6.5) cal deg⁻¹ mole⁻¹.

Electron Diffraction Investigations. I. The Molecular
Structures of the Gaseous Group III Halides Al_2Cl_6 ,

Al_2Br_6 , Al_2I_6 - AlI_3 , Ga_2Cl_6 , and Ga_2Br_6 - GaBr_3 ;

II. The Gaseous Equilibria $2\text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_4$ and



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Professor of Chemistry 0
in charge of major

Redacted for privacy

Chairman of Department of Chemistry

Redacted for privacy

Dean of Graduate School

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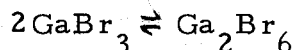
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ELECTRON DIFFRACTION INVESTIGATIONS. I. THE MOLECULAR
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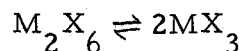
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INTRODUCTION

The aluminum and gallium halides in the gaseous state exist in the form of dimeric and monomeric molecules in equilibrium:



At pressures equal to their vapor pressures aluminum chloride and bromide exist predominantly as dimers below about 250°C (20) gallium chloride and bromide as dimers below about 200°C (21), and the iodides predominantly as monomers. The fluorides are very nonvolatile and the vapors are apparently nearly entirely monomeric. The existence of dimer molecules of the group III halides presents some interesting problems in bonding theory. The simple valence-bond picture of the monomers suggests molecules of D_{3h} symmetry with bonds from the central atom of the hybridized sp^2 type. The formation of dimers requires a different view of the metal atom bonds inasmuch as the p-orbital on these atoms remaining for dimer formation is empty. Such a bonding situation has led to the term "electron-deficient compounds".

During the past four decades the group III halides have attracted many investigators. The following is a summary of work related to the molecular structures of these compounds.

1938: Palmer and Elliott (38) used the electron diffraction method to study the configurations of gaseous aluminum chloride, bromide, and iodide which were found to be composed mainly of dimeric Al_2X_6 species of D_{2h} symmetry with halogen bridges as shown in Figure 1.

1940: Brode (17) studied aluminum chloride and iodide, and gallium chloride and bromide by electron diffraction. He concluded that the configuration of these dimers was that of two regular tetrahedra joined by a common edge. These data were later interpreted by Schomaker (45) to be consistent with the model reported by Palmer and Elliott.

1941: The infrared and Raman spectra of liquid and solid aluminum chloride, bromide, and iodide were studied by Gerding and Smit (22), who concluded that the D_{2h} model gave the best agreement with the observed bands.

1944-45: Normal coordinate calculations on dimeric aluminum chloride, bromide and iodide based on the D_{2h} model were made by Bell et al. (10, 11)

1951: Harris et al. (26) used the X-ray technique to study the structure of aluminum chloride in the liquid state. The radial

distribution curve showed five peaks at 2.20, 3.60, 4.74, 5.57 and 6.52 Å. Their conclusions about the structure were similar to those of Palmer and Elliott.

1956: Klemperer (32) used a D_{2h} model for the assignment of the infrared absorption bands he observed for gaseous Al_2Cl_6 ($\approx 180^\circ C$).

1959: Akishin et al. (3, 4) employed electron diffraction to investigate the molecular structures of gaseous gallium chloride and bromide and four aluminum halides (F, Cl, Br, I). Except for aluminum fluoride and iodide, the experimental radial distribution curves for these halides showed four peaks; for aluminum fluoride and iodide only two peaks were observed. These authors concluded that for the latter compounds the major species at the scattering zone were monomeric AlF_3 and AlI_3 molecules with D_{3h} symmetry, and for the other four compounds dimeric species M_2X_6 with D_{2h} symmetry.

1956-66: An X-ray crystallographic study by Wallwork and Worrall (50) revealed that gallium chloride has a triclinic crystal structure with each unit containing two gallium and six chlorine atoms. However, the structure of the molecule was not determined. Balls et al. (5) concluded from the infrared and Raman spectra that dimeric gallium chloride, bromide, and iodide possessed D_{2h} symmetry. Their data included infrared spectra of benzene

solutions and Nujol mulls of gallium chloride, bromide and iodide, and Raman spectra of liquid gallium chloride and bromide.

1967-69: A series of papers by Beattie and coworkers (8, 9, 10) reported on the vibration spectra of aluminum and gallium trihalides: aluminum chloride, Raman (gaseous); aluminum bromide, infrared (benzene solution, Nujol mull) and Raman (gaseous, melt, solid); aluminum iodide, infrared (benzene solution, Nujol mull) and Raman (gaseous, melt, solid); gallium chloride, infrared (hexafluorobenzene, perfluorokerosene, melt, gaseous) and Raman (gaseous, solid); gallium bromide, infrared (benzene solution, Nujol mull) and Raman (gaseous, melt, solid); and gallium iodide, infrared (Nujol mull) and Raman (gaseous, melt and solid). The spectroscopic assignments were made according to a model with D_{2h} symmetry. Through these authors' extensive temperature studies of the vibrational spectra of the gaseous trihalides (Cl, Br, I) of aluminum and gallium, they were able to identify some bands which were attributed to the monomeric species of D_{3h} symmetry. By measurements of the relative intensities of ν_1 of $AlBr_3$ and ν_3 of Al_2Br_6 as a function of temperature a value of 23 ± 3 Kcal/mole was obtained as the heat of dissociation for Al_2Br_6 . However, for the others the accurate measurements of the intensity of ν_1 of the monomers were obscured by effects attributed to possible Fermi resonance involving an overtone of a

low-lying fundamental of the dimer.

1970: The symmetry of gaseous aluminum chloride dimer, D_{2h} , was again confirmed by Raman spectroscopy by Maroni et al. (35).

Many of the spectroscopic investigators based their conclusions on the agreement between the experimentally observed frequencies and ones calculated by using one assumed force field together with the geometrical parameters provided by Palmer et al. (38), Brode (17) and Akishin et al. (3, 4). A study of the radial distribution curves for aluminum and gallium chloride and bromide reported by Akshin and coworkers reveals that the peaks to be expected for the longer distances in the molecules ($X_3 \dots X_7$, $X_3 \dots X_6$ particularly), are either distorted or missing (the radial distribution curves from earlier works were too poor to reveal these details). A possible explanation could be the existence of large-amplitude motions in these molecules which would tend to "wash out" the expected peaks and make them difficult to detect. Because improvement in the electron diffraction experiment and in the methods of structure analysis since the early investigations have been so great, it seemed certain that very much more accurate measurements of the structures of some of the group III halides could now be made. Those chosen for study were the chlorides and bromides of aluminum and gallium, and aluminum iodide. The fluorides could not be included because their very low volatilities

require temperatures too high for our present nozzling system. Further, they and gallium iodide are known to exist almost entirely as monomers in the vapor phase and hence were of less interest to us.

Our initial interest in the group III halides was primarily the structures of the dimer molecules. It was clear, of course, that in the cases of aluminum iodide and gallium bromide it would be necessary to consider the structures of the monomers also. As the work progressed, the gallium bromide system took on an additional, special interest when it developed that the temperature dependence of the equilibrium could be measured (one of the results of the diffraction analyses is the composition of the vapor). Accordingly, the scope of the work with this compound was expanded to include studies at a total of three different temperatures. Aluminum iodide could not be similarly studied because the temperature range of the nozzling system was too small.

Equilibrium studies offer the possibility of determining certain thermodynamic quantities for the reaction through the temperature dependence of the equilibrium constant K_p . Unfortunately, the electron-diffraction experiment measures not the partial pressures of the components of the mixture but their mole fractions X . In terms of the gallium bromide system we have



$$K_p = \frac{p_{\text{GaBr}_3}^2}{p_{\text{Ga}_2\text{Br}_6}} = \frac{x_{\text{GaBr}_3}^2}{x_{\text{Ga}_2\text{Br}_6}} \cdot P_T \quad (2)$$

It is thus seen that a necessary quantity is the total pressure P_T which, since the diffraction process takes place in a jet of gas being expanded into a high vacuum, is unknown.

In addition to the value of P_T there exists a related question, the value of the temperature of the mixture at the diffraction point; that is, the temperature at a point in a rapidly expanding jet. Because the compositions of mixtures measured by electron diffraction are observed to change with the temperature of the nozzle tip, it is certain that an "effective" temperature, and likewise an effective pressure, exist that will adequately describe the equilibrium under consideration. Ryan and Hedberg (43) have given some theoretical justification for the view that the nozzle-tip temperature is a good representation of the effective temperature of the vapor, and as these authors point out, implicit verification exists in the good agreement between observed and calculated amplitudes of vibration. No similar information is available for P_T , however.

The requirement for knowing P_T in order to evaluate the thermodynamic properties of the gallium bromide system, as well as others sure to be studied in the future, seemed to require the

study of a well-understood equilibrium. For example, the compositions of the system measured by electron diffraction combined with the known values of K_p would permit evaluation of the effective pressure P_T and, incidentally, the effective temperature. Hopefully the P_T values would be equal to the vapor pressure or to some definite fraction of it which could be extended to other systems.

Additional requirements from the side of the diffraction experiment are that the structures of the molecules of the mixture be simple and that the composition be altered substantially by temperature changes over the range permitted by the nozzling apparatus. A system which meets all these requirements admirably is the $\text{NO}_2\text{-N}_2\text{O}_4$ system. First, its composition can be varied over the large, approximate range $0.95 > X_{\text{N}_2\text{O}_4} > 0.05$ by changing the temperature of the tube through which the gas passes in the range $-15^\circ\text{C} < T < 100^\circ\text{C}$. Second, the total pressure can easily be increased several-fold by changing the bath temperature over a range numerically no larger than 30°C , a value at which substantial amounts of both molecular species exist. Third, this system has been very thoroughly studied by other methods (23, 28, 47), providing a reliable basis for interpretation of the electron-diffraction results. Accordingly, the work of this thesis was expanded to include the temperature and pressure dependent behavior of the $\text{NO}_2\text{-N}_2\text{O}_4$ system.

The remainder of this thesis is arranged in three parts.

The first contains details of the experiments and the analysis procedures common to all the molecules studied. The second, divided into several sections, describes the structure determinations of the individual halide molecules. The first of these sections, that on Al_2Cl_6 , contains details of the handling of intramolecular motion, one form of which was found to account nicely for the diffraction data for all the dimeric molecules. Those sections concerned with the remaining halides draw on the Al_2Cl_6 description. The last section is a discussion of the structural results. The third part of the thesis is concerned with the equilibria problems. The investigation of the effective total pressure and the effective temperature in conjunction with the $\text{NO}_2\text{-N}_2\text{O}_4$ equilibrium is first described, followed by the application of these results to the $\text{GaBr}_3\text{-Ga}_2\text{Br}_6$ system.

The method of electron diffraction for all the determination of molecular structures and the general structural analysis procedures employed in this laboratory are given in Appendix A.

THE EXPERIMENT AND TREATMENT OF DATA

The purity and sources of samples used were as follows:

nitrogen dioxide (99.5%), Matheson Gas Products, Cucamonga, California; anhydrous aluminum chloride (99.4%), Mallinckrodt Chemical Works, New York; anhydrous aluminum bromide (98 %), Fischer Scientific Co., Chicago, Illinois; anhydrous aluminum iodide (97%), Alfa Inorganic Co., Winton, Mass.; anhydrous gallium chloride (99.99%) and gallium bromide (99.99%), Research Org. / Inorg. Co., Sun Valley, California.

For all samples except aluminum iodide the standard nozzling system was used. This system, a diagram of which is shown in Figure 2, can be used over the approximate temperature range -80°C to $+220^{\circ}\text{C}$. The sample containers were Pyrex glass tubes or bulbs fitted with stopcocks and standard taper joints lubricated with Kel F or Apiezon H grease. For the aluminum iodide sample, which required temperatures somewhat higher than those obtainable with the standard nozzle, the oven-nozzle described by L. Eddy (19) was used. In brief, this apparatus consists of a graphite oven with a fine tip (Fig. 3) located inside the diffraction apparatus and heated resistively.

The halides were loaded into the sample containers in a "dry bag" filled with dry nitrogen, a procedure deemed advisable because of

the samples' hygroscopic nature. After attachment to the diffraction apparatus each container of halide was heated for several minutes under vacuum to a temperature near that later employed in the diffraction experiments in order to remove possible volatile impurities. The nitrogen dioxide-dinitrogen tetroxide sample was distilled into the sample container from a cold trap which had been filled from the original cylinder. Before loading the sample container the material in the cold trap was pumped for several hours while being maintained at -80°C .

Suitable vapor pressures of the samples mounted exterior to the apparatus were obtained by immersing the containers in a heated oil bath (the halides) or a cooled acetone bath ($\text{NO}_2\text{-N}_2\text{O}_4$). In the case of the halides the portion of the sample train from the sample container to the nozzle joint was heated with a hot air gun to prevent sample condensation. The temperature of the nozzle itself was controlled by directing a stream of heated or cooled (the latter in most of the N_2O_4 experiments) nitrogen or air into the annular space as shown in Figure 2. The temperatures of the gaseous samples were measured with thermocouples fastened to the nozzle tips.

The general conditions common to all the diffraction experiments were as follows. The electron-diffraction photographs were made in the O. S. U. apparatus using a rotating sector with angular

opening approximately proportional to r^3 and using 8x10 inch Kodak lantern slide (medium) plates. The electron beam currents were between 0.30-0.60 μA and the exposure times ranged from 30 sec-5 min. The electron wavelengths were 0.057039-0.057442 $\text{\AA}$ as determined by calibration against gaseous CO_2 in separate experiments (41). Detailed experimental data for each plate used in structure analyses are summarized in Tables 1, 4, 7, 10, 13 and 21.

The photographic plates obtained from each experiment were carefully examined and the best selected for analysis, which was carried out following the usual procedures described in Appendix A. For aluminum chloride and bromide, smooth hand-drawn backgrounds were subtracted from the data-reduced curves and multiplied by s to obtain molecular intensity curves in the form corresponding to Equation A6. For the remaining molecules these curves were obtained by use of the background-constructing computer program in which the adjusted background function consisted of a combination of the function $s^4 (I_a + I_i)$ and a fourth-degree polynomial. Averages of these individual sI_m curves from a given nozzle-to-plate distance and composites of the average curves were used in certain stages of the refinement procedure and in the calculation of radial distribution curves. For the latter purpose average curves from two or more camera distances had to be placed on the same scale.

This was done in either of two ways: Before a least squares refinement had been attempted the amplitudes of average curves were simply compared in the overlapping region to obtain scale constants. After a least squares refinement the scale constants were available as one of the refinement results.

The radial distribution curves were calculated from I_m' curves obtained by multiplying the composite curves by $Z_M Z_X / A_M A_X$ (15), where $M = \text{Al, Ga, or N}$ and $X = \text{Cl, Br, I, or O}$. For these calculations data in the regions $0 \leq s \leq 1.75$ for Al_2Cl_6 , Al_2Br_6 , and N_2O_4 ; and $0 \leq s \leq 2.75$ for Ga_2Cl_6 and Ga_2Br_6 ; and $0 \leq s \leq 3.50$ for Al_2I_6 were taken from theoretical curves. The convergence coefficient B was given the value 0.0025 in all cases. Because the method employed to take into account the intramolecular motion in these molecules (a description of the method is included in the aluminum chloride section), requires much expensive computer time, different types of intensity curves were used in the least square analysis. Composite curves were used during the preliminary refinements of Al_2Cl_6 , Al_2Br_6 , and Al_2I_6 . Average curves (long and middle) were used during the final refinements of Al_2I_6 , and Ga_2Br_6 . Individual curves were used in the final refinements of Al_2Cl_6 and Al_2Br_6 , parts of the preliminary refinements of Al_2I_6 and Ga_2Br_6 (163°), and all of the refinements for Ga_2Cl_6 and N_2O_4 . Detailed descriptions of the refinements for each molecule are included in later sections.

STRUCTURE DETERMINATIONS

(I) Aluminum Chloride

The structure determination of aluminum chloride was carried out with data obtained from seven photographic plates, four from the 75 cm. and three from the 30 cm. camera distances. These intensity data in the form of sI_m are given in Appendix B, and the curves are shown in Figure 4. The preliminary experimental radial distribution curve showed strong peaks at 2.1 and 3.5 Å and weak, broader peaks at 4.6 and 6.2 Å (Fig. 5 shows a later radial distribution curve; the appearance of this curve is similar to that of the preliminary curve). Both the first and the second peaks had shoulders on them. The first peak with its strong shoulder (at 2.2-2.3 Å) is indicative of two slightly different interatomic distances of about the same weight with the longer distance having a larger vibration amplitude which tends to diminish the height of its contribution. Since the Al-Cl bonds are expected to be the shortest bonds in the molecule, it seemed likely that there were two different kinds of Al-Cl bonds. This and the areas and positions of the rest of the peaks were found to be compatible with the expected halogen bridged D_{2h} model (Fig. 1). Accordingly, a model of this symmetry with Al-Cl bridge bonds ($Al-Cl_b$) longer than the Al-Cl

terminal bonds (Al-Cl_t) was selected as the trial structure. The geometrical parameters chosen to describe the structure were

$\langle \text{Al-Cl} \rangle = (r_{\text{Al-Cl}_t} + r_{\text{Al-Cl}_b}) / 2 = (r_{23} + r_{25}) / 2$ (the average of the Al-Cl bridge and terminal bond lengths), $\Delta \text{Al-Cl} =$

$r_{\text{Al-Cl}_b} - r_{\text{Al-Cl}_t} = r_{25} - r_{23}$ (the difference between the length of the two types of bonds), $\angle \text{Cl}_3\text{Al}_2\text{Cl}_4 = \angle \text{Cl}_t\text{Al Cl}_t$ and $\angle \text{Cl}_5\text{Al}_2\text{Cl}_8 = \angle \text{Cl}_b\text{Al Cl}_b$. Using $2.1\text{\AA}$ as a value for $\langle \text{Al-Cl} \rangle$, $\Delta \text{Al-Cl} = 0.2\text{\AA}$, $\angle \text{Cl}_b\text{Al Cl}_b = 90^\circ$, and $\angle \text{Cl}_t\text{Al Cl}_t = 120^\circ$, all the distances of the molecule were calculated and assigned as follows: r_{23} and r_{25} the first peak and shoulder ($2.1\text{-}2.2\text{\AA}$); r_{12} and r_{58} the inside shoulder of the second peak ($3.1\text{\AA}$); r_{34} and r_{53} the second peak ($3.5\text{\AA}$); r_{13} the third peak ($4.6\text{\AA}$); r_{37} the broad feature ($5.5\text{\AA}$); and r_{36} the $6.2\text{\AA}$ peak (the vertical bars in Figure 5 and in all other RD curves indicate the weighed average positions and relative weights of the distances calculated from the final models.)

Using the D_{2h} model, preliminary least-squares refinements were carried out and the background curves were improved in the usual way (see Appendix A). The refinements gave fair agreement in the first and second peaks of the RD curve, but for the longer non-bonded interatomic distances the agreement was unsatisfactory. The major discrepancy came in the broad feature around $5.5\text{\AA}$

where a substantial peak appeared in the theoretical curves unless an unreasonably large amplitude of vibration of the molecular frame was used. Also, the asymmetry of the peaks assigned to r_{36} and r_{13} was not matched by using this "static" model. Accordingly, attention was turned to a model which specifically incorporated a bending motion about an axis joining the bridging halogen atoms.

For many molecules studied by electron diffraction the effect of intramolecular motion may be satisfactorily taken into account by applying an exponential vibration factor (Eq. A6) to the distances calculated for a rigid geometry. In these cases the effect of the vibration is to broaden the peak of the RD curve corresponding to the affected distance but to leave its position unchanged. When the magnitude of the vibration is large, the effect can be so great that the peaks smear out over a large distance range and only very broad features are observed; such peaks are often termed "washed out" (42, 52). For some types of motions, as the bending of a linear molecule such as CO_2 or the out-of-plane motion of a coplanar molecule as AlCl_3 , the positions (as well as the shapes) of peaks will be affected in a way to give an apparent distance in the RD curve shorter than the expected value. This kind of apparent shortening due to intramolecular motion is called the "shrinkage effect" (7). When the magnitudes of the motions are small, shrinkage corrections (often calculated theoretically or estimated from known

values for similar compounds) can be applied directly to the affected distances.

In aluminum chloride the appearance of the RD curve indicates clearly that intramolecular motion plays an important role. The peak corresponding to r_{37} is nearly completely washed out, and asymmetries are apparent in the peaks corresponding to r_{13} and r_{36} . In order to account for the washed out features a plausible model of molecular motion had to be incorporated into the model of D_{2h} symmetry. One of the simplest is the ring-puckering mode of the four-membered ring formed by the two aluminum and the two bridging chlorine atoms. This ring-puckering motion is the lowest frequency mode in this type of D_{2h} compound (8, 9, 10). The motion consists principally of the wagging of the two $-AlCl_2$ terminal groups at the hinge line joining the two bridging chlorine atoms. This motion introduced a large variation in distances r_{37} compared to those experienced by the distances r_{12} , r_{13} and r_{36} and could, therefore, account for the washed out feature in the region of the RD curve corresponding to r_{37} .

If the bending motion just described is taken to be harmonic in the bending-angle displacement, its effect on the distance distribution can be described by use of a single parameter δ , the root-mean-square bending-angle amplitude. As suggested above, the motion affects the interatomic distances r_{12} , r_{13} , r_{37} and r_{36} .

The positions of these peaks may be regarded as a number average over all instantaneous molecular conformations in the gas sample, or a time average of the instantaneous conformations of a single molecule. Assuming this puckering (bending) motion to be harmonic (40) in the angle displacement, θ , one may carry out the averaging by calculating the dependence of r_{12} , r_{13} , r_{37} and r_{36} on θ , choosing a suitable number of conformations defined by θ_i , and weighting each conformation according to

$$W_i = N g_i \exp (\theta_i^2 / 2\delta^2) \quad (3)$$

Here δ is the root-mean-square (rms) amplitude of the bending vibration, g_i is the multiplicity factor, and N is a normalization constant. The multiplicity factors (g_i) for θ_i greater than 0° are two and for θ_i equal to 0° , unity. The normalization constant N is merely the inverse of the sum $g_i \exp (\theta_i^2 / 2\delta^2)$ for all conformations (thus the sum of the W_i gives unity). Experience has shown an adequate approximation of distance distributions arising from bending motions similar to those envisioned for Al_2Cl_6 may be obtained by using intervals $\Delta\theta$ equal to $0.25\delta - 0.30\delta$ and assigning to the distances derived from each configuration vibrational amplitudes judged to be normal were that configuration one corresponding to a molecule not undergoing the bending motion. (Vibrations of this type, namely ones from which large amplitude bendings or torsions have been excluded, are called "frame

vibrations.")

Tests of the D_{2h} model with a large bending amplitude of the type described above were immediately successful and accordingly least-squares refinements of this model of the structure were undertaken. Six different conformations were included to represent the bending motion. The frame vibration for a pair of nuclei was assumed to be the same for the different conformations. Since only a small portion of the total molecular scattering was sensitive to the bending motion, it was next to impossible to refine simultaneously both δ and the amplitudes of frame vibrations for the distances sensitive to the bending motion. A survey of the approximate value of δ was carried out as follows. Refinements with $\delta = 25^\circ$, 45° and 15° were first done. In these three calculations (LS1-1, 2, and 3, Table 2) the same set of geometrical and vibrational parameters was varied. The R values were 0.1105, 0.1164 and 0.1117, revealing $\delta = 25^\circ$ to be a slightly better model. (R is an index reflecting the agreement between the theoretical curve for the model and the experimental curve. The smaller the value the better the agreement. The formula for R is given in the reference in Table 2). Therefore, $\delta = 25^\circ$ was used in all Al_2Cl_6 refinements except LS1-6. In all of the refinements except LS1-4 the four geometrical parameters were refined. In LS1-4, $\Delta Al-Cl = 0.188\overset{\circ}{\text{\AA}}$ (an averaged value obtained from earlier refinements) was assumed and both l_{25} and l_{23}

were refined. (The parameters $\Delta\text{Al-Cl}$, l_{23} and l_{25} are highly correlated and could not be refined simultaneously. Practically speaking, this correlation meant that about equally good agreement was given by a manifold of models for which $\Delta\text{Al-Cl}$ is increased, say, and l_{23} and l_{25} simultaneously decreased. This method of refining this particular group of highly correlated parameters was employed in the case of all the group III halides.) For reasons similar to those just mentioned, it was necessary to limit the number of refinable frame vibrational amplitudes. The amplitude parameters were as follows except in some special cases (e. g., LS1-4, LS1-6): $l_{23} = l_{25} + \Delta_1$, $l_{12} = l_{58}$, l_{35} , l_{13} and $l_{37} = l_{36} + \Delta_2$ where the Δ 's are constants). The values of l_{12} and l_{58} were set equal (as in this and many other cases) because distance r_{12} was of low weight, and in general bonds of about the same lengths have similar amplitudes of vibration. The values of l_{37} and l_{36} were refined as a group because the corresponding distances gave only a weak contribution to the scattering. The scattering was further damped out by the large magnitude intramolecular motion and made an independent determination of these two amplitudes (especially l_{37}) very unlikely.

The magnitude of the δ value was investigated in LS1-6, after the relative frame vibration values for the non-bond distances were known fairly accurately. In this refinement, the vibrational

parameters were grouped as follows: $l_{36} = l_{37} + \Delta_1 = l_{13} + \Delta_2$, $l_{12} = l_{58}$, l_{34} , $l_{23} = l_{25} + \Delta_4$, and l_{35} . The geometrical parameters obtained were essentially the same as those resulting from refinements LS1-4 and LS1-5. The value of δ was determined to be $23.6 (6^\circ)$.

Although at temperatures equal to those measured at the nozzle in the electron diffraction experiments aluminum chloride is known (3, 20, 38) to be essentially completely dimeric, we felt compelled to test for the presence of monomer in the sample. Monomeric aluminum trichloride with D_{3h} symmetry was introduced into the model and the composition of the gas mixture included as a refinable parameter, α_D , the mole fraction of dimer. Since if any monomer was present the amount was sure to be small, it was clearly impossible to refine its structural parameters. Accordingly, the assumptions (see Fig. 1) $r_{9,10} = r_{23}$, $\angle \text{Cl}_{10}\text{Al}_9\text{Cl}_{11} = 120^\circ$, $l_{9,10} = l_{23}$, and $l_{10,11} = l_{34}$ were made. These assumptions were felt to be reasonable, first because in many cases (e. g., Al_2Me_6 and Al_2Cl_6) it had been shown that the lengths of the peripheral bonds in the dimers were very similar to those in the monomers, and second because later analyses monomeric AlI_3 and GaBr_3 were found to be essentially planar. The results indicated that the sample was essentially pure dimer ($\alpha_D > 99\%$)(LS1-5).

It is felt that the results of LS1-6 are a fair statement for

Al_2Cl_6 . The theoretical intensity and radial distribution curves for this model and the corresponding difference curves are shown in Figures 4 and 5. The correlation matrix is shown in Table 3.

(II) Aluminum Bromide

A total of six plates were selected for the structure analysis of aluminum bromide, three from the 75 cm and three from the 30 cm camera distances. The intensity curves in the form of sI_m are shown in Figure 6, and the data are given in Appendix B. As for Al_2Cl_6 , the preliminary RD curves (a later one is shown in Fig. 7) showed only four strong peaks; they were located at 2.30, 3.80, 4.95 and 6.65 Å. The shoulders on the first two peaks and the relative positions and shapes of the other peaks were very similar to the ones observed for Al_2Cl_6 . It was obvious from the number, positions and shapes of these peaks that D_{2h} was the symmetry of the molecule, and from the broad feature around 5.5-6.0 Å (corresponding to the expected r_{37} value) that incorporation of the ring puckering molecular motion was needed. The R values resulting from LS2-1 ($\delta = 25^\circ$) and LS2-2 ($\delta = 45^\circ$) revealed no significant difference between these two models (see Table 5). However, in the case of the latter, the r_{37} value in some high-angle conformers (large θ_i) was much less than twice the van der Waal's radius for bromine. Therefore, $\delta = 25^\circ$ was assumed in the

analyses. In all refinements shown except LS2-3, all four geometrical parameters were varied independently. In LS2-1 and LS2-2 l_{25} and l_{23} were being refined in the following fashion. In cycle 1 l_{25} was assumed at a reasonable value and l_{23} refined; then in the next cycle l_{25} was refined with l_{23} held at the value obtained in cycle 1. The other l -values being refined were l_{58} , l_{34} , l_{35} , l_{13} , and $l_{37} = l_{36} + \Delta_1$. The amplitude l_{12} was kept constant at a value close to that of l_{58} for the same reasons given in the case of Al_2Cl_6 .

As in the case of Al_2Cl_6 , planar monomeric molecules were introduced into the model (LS2-3). The refinement revealed α_D to be 95 (20)%. In this refinement $\Delta\text{Al-Br}$ was given a value of 0.184Å (a value obtained in some preliminary refinements similar to LS2-2 and 1), and both l_{23} and l_{25} were refined. The reason for keeping $\Delta\text{Al-Br}$ constant was briefly explained in the last section. All other amplitudes except l_{12} were refined.

In LS2-4 the parameter δ and the amplitudes $l_{23} = l_{25} + \Delta_1$, $l_{12} = l_{58}$, $l_{13} = l_{37} + \Delta_2 = l_{36} + \Delta_3$, l_{35} , and l_{34} were refined together with all four geometrical parameters. The value of Δ_1 was taken from the difference between l_{25} and l_{23} obtained from LS2-3, and Δ_2 and Δ_3 were values judged to be reasonable differences between those l -values. This analysis yielded a value of 23.3 (14.0) for δ . It was felt that this set of values represented

the best statement of the structure of Al_2Br_6 . The theoretical intensity and RD curves corresponding to this model are shown in figures 6 and 7, and the correlation matrix is tabulated in Table 6.

(III) Aluminum Iodide

As mentioned in the experimental section, the photographic plates were obtained using the high temperature apparatus designed by Eddy (19). Eight plates were selected for the structure refinement. Five 75 cm plates and three 30 cm plates were used for the analysis. These intensity data (sI_m) are tabulated in Appendix B and the curves are shown in Figure 8. The preliminary RD curves revealed four peaks at 2.5, 4.2, 5.3 and 7.1 Å, respectively (a later one is shown in Fig. 9). Except for the expected difference due to the greater scattering power of the iodine atoms relative to bromine and chlorine, the features in the RD curves were similar to those for Al_2Cl_6 and Al_2Br_6 but the ratios of the areas of the long non-bond peaks to the first two peaks were slightly less in Al_2I_6 . This was felt to be due either to a larger amplitude of motion in Al_2I_6 than in Al_2Br_6 and Al_2Cl_6 , or to the presence of the monomeric species expected under the electron diffraction experimental conditions (3), or to both.

A trial model consisting only of dimer having D_{2h} symmetry

and with the puckering motion ($\delta = 25^\circ$) was first tested. Several preliminary refinements were made (not shown here) and the results suggested that neither l_{23} nor l_{25} could be refined simultaneously with the four geometrical parameters. These two l -values were assumed to be 0.060 (l_{23}) and 0.087 (l_{25}). Except for l_{34} and l_{35} , the remaining amplitudes were held at reasonable values (LS3-1, 2, and 3 in Table 8) taken from the results obtained in the studies of Al_2Cl_6 and Al_2Br_6 . Each one of these values was adjusted after each refinement if the RD difference curves indicated that an improvement on the agreement could be achieved.

The value obtained for $\angle \text{I}_b \text{Al} \text{I}_b$ was unreasonably small (see LS3-1, Table 8) compared to the corresponding values for aluminum chloride and bromide. Also, the difference between the experimental and theoretical RD curves in the region of the first and second peaks strongly implied the presence of monomeric species which was known to exist under the electron-diffraction experimental conditions (3). (The area of the first peak is proportional to the number of terminal and bridge Al-I bonds. Since the experimental curve had excess area, relatively, at the point corresponding to the terminal bond, the presence of monomer, which has no bridge bonds, was indicated.) A fixed amount (30%) of monomeric aluminum iodide was introduced into the model. The assumptions imposed on the planar monomer were similar to those

assumed for AlCl_3 and AlBr_3 , namely, $r_{9,10} = r_{23}$, $\angle \text{I}_{10}\text{AlI}_{11} = 120^\circ$, $\angle_{9,10} = \angle_{23}$, and $\angle_{10,11} = \angle_{34}$. The R value dropped from a value of 0.1650 obtained on the assumption of 100% dimer to 0.1440.

In LS3-2 the composition parameter α_D was refined to a value of 42.8 (7.3%) ($R=0.1260$). It was pleasing that the value of $\angle \text{I}_b\text{AlI}_b$ increased to $98.7 (3.7^\circ)$, in better agreement with those obtained for the other dimeric aluminum halides.

The presence of monomer diminished the possibility of refining δ since the percentage of scattering sensitive to the ring puckering motion was now very small. Thus, $\delta = 25^\circ$ was assumed in all refinements.

A series of refinements was devoted to testing of the validity of the assumption $r_{9,10} = r_{23}$, that is, the equality of the lengths of the terminal bonds in monomer and dimer. An additional parameter $D-M = r_{23} - r_{9,10}$ was introduced and refined. In the most revealing refinement LS3-3 (Table 8), r_{23} was found to be 0.025 (0.09Å) longer than $r_{9,10}$. This small difference was clearly insignificant compared to experimental error and lent support to the assumption $r_{23} = r_{9,10}$ made in the cases of aluminum chloride and bromide. Refinements LS3-3 and LS3-4 were carried out on individual curves ($s_{\text{max}} = 21.0$) with the assumption that the monomer molecule had symmetry D_{3h} . Recently AlCl_3 has been reported (34) to be a pyramidal molecule of

C_{3v} symmetry and accordingly this possibility was tested in LS3-5.

At the same time, since the experimental data in the region $21.0 \leq s \leq 30.0$ in the form of individual curves appeared to be rather noisy, average curves from each camera distance were formed with the hope that a part of the noise would be eliminated.

Refinement LS3-5 (Table 8) was then carried out (s range

$2.00 \leq s \leq 30.00$) with the amplitude groupings $l_{12} = l_{58} = 0.120$,

$l_{23} = l_{25} + \Delta_1$, $l_{34} = l_{35} + \Delta_2$ and $l_{13} = l_{37} + \Delta_3 = l_{36} + \Delta_4$. In

addition to the four geometrical parameters of the dimer and α_D

(the composition parameter), $\angle I_{10} Al_9 I_{11}$ was refined subject

to the assumption $r_{23} = r_{9,10}$. The value for $\angle I_{10} Al_9 I_{11}$ was

found to be $120.1 (4.0^\circ)$ and for α_D $42.0 (16.0\%)$. The intensity

and RD curves for this model and their corresponding difference

curves are shown in Figures 8 and 9. The parameter values for

$Al I_3$ are tabulated in Table 19. The correlation matrix correspond-

ing to LS3-5 is tabulated in Table 9.

(IV) Gallium Chloride

A total of eight plates were selected (five long camera, and three middle camera) for the structure determination. These intensity data in the form of sl_m are tabulated in Appendix B, and the curves are shown in Figure 10.

The experimental RD curve showed four peaks at 2.15, 3.63,

4.70, and 6.35Å, respectively. The relative positions and shapes of these peaks were similar to the ones observed for the dimeric aluminum halides and were in accord with the D_{2h} model with bending motion. The value of δ was assumed to be 25° in all the refinements except LS4-3. In LS4-1 (Table 11) the parameter $\Delta_{\text{Ga-Cl}}$ was held constant at the value 0.198Å (found from preliminary refinements) and the two amplitudes l_{25} and l_{23} were refined as independent parameters. (The difference between the two l -values found here was used as Δ_1 in the later refinements LS4-2, and LS4-3). All other amplitudes were refined except for the weak parameter l_{12} which was assumed to be 0.08Å, a value obtained from preliminary refinements. For reasons similar to those given in the Al_2Cl_6 case, l_{36} and l_{37} were refined as a single parameter with a fixed split.

Refinement LS4-2 was carried out to investigate the amount of monomeric species present in the sample. During this refinement the parameters of the monomer were given assumed values deduced from the results of the aluminum iodide investigation: $\angle \text{Cl}_{10}\text{Ga}_9\text{Cl}_{11} = 120.0$, $r_{9,10} = r_{23}$, $l_{9,10} = r_{23}$ and $l_{10,11} = l_{34}$. The result showed that the sample was essentially pure dimer ($\alpha_D = 99.1$ (1.5%)). The amplitudes were refined in a way similar to LS4-1, except that l_{25} was grouped with l_{23} , and l_{58} was assumed to be 0.077Å.

The magnitude of the rms value of the bending motion (δ) was refined in LS4-3. In this refinement the amplitudes $l_{25} = l_{23} + \Delta_1$, $l_{12} = l_{58}$, l_{34} , l_{35} and $l_{37} = l_{36} + \Delta_2 = l_{13} + \Delta_3$ were refined. A value of $20.5 (3.3^\circ)$ was obtained for δ .

The intensity and RD curves corresponding to LS4-3, which represents the best model for Ga_2Cl_6 , are shown in Figures 10 and 11. The correlation matrix is shown in Table 12.

(V) Gallium Bromide

Electron diffraction photographs at nozzle-tip temperatures of 163° , 192° , and 226° C were taken for reasons discussed in the introduction. For each temperature four plates from the 75 cm and three from the 30 cm camera distances were used for analysis. The intensity data in forms of sI_m are given in Appendix B, and the composite curves for the three temperatures are shown in Figure 12.

Data from the lowest nozzle temperature ($\text{TN}=163^\circ$) were analyzed first. The preliminary RD curve showed four peaks with features similar to the ones observed for the other group III halides. The D_{2h} model with $\delta=25^\circ$ was used in the refinements. In LS5-1, the sample was assumed to be pure dimer. The difference between the experimental and the theoretical curves showed negative areas in the region $2.4\text{-}2.5\text{\AA}$. As described for aluminum iodide, these discrepancies were attributed to the possible presence

of monomer, and to test this hypothesis planar monomeric molecules were introduced into the model. The results, summarized in LS5-2, showed substantial improvement (reflected by the R values); the value obtained for the composition parameter α_D was 49.8 (4.3%). In this refinement, because of the measured large amount of monomer present, a successful determination of the non-bond amplitudes of the dimer was thought unlikely and only $l_{23} = l_{25} + \Delta_1 = l_{9,10}, l_{58}, l_{34} = l_{10,11}$, and l_{35} were refined. Later, several refinements on these 163° data were devoted to the study of the symmetry of the monomer as before through refinement of the monomer parameters $\angle \text{Br}_{10} \text{Ga}_9 \text{Br}_{11}$ and $D-M = r_{23} - r_{9,10}$. Analyses LS5-3 and LS5-4 (Table 14), where no restriction on the symmetry of the monomer was imposed, yielded $118.3 (6.7^\circ)$ and $121.2 (1.6^\circ)$ as values for $\angle \text{Br}_{10} \text{Ga}_9 \text{Br}_{11}$, respectively. These results together with the ones obtained from the higher temperature experiments showed that the monomers were essentially planar. The evident similarity in the r_{23} and $r_{9,10}$ values, prevented the accurate measurement of each and instead allowed the determination of only an average value. However, the large R value from LS5-3 where the assumption $D-M = 0.04\text{\AA}$ was made, suggests that the difference $D-M$ should be less than $0.04\text{\AA}$. (This point was further supported by the results from the 226°C analyses. With 92.7%

monomer present the average value was 2.243 (0.003)Å. Comparing this value with the one (2.245 (0.005)Å) obtained at 163° (52.6% monomer) it was clear that 0.01Å could be taken as the upper limit of the difference. In these two analyses (LS5-3 and 4) the vibrational parameters refined were $l_{23} = l_{25} + \Delta_1 = l_{9,10}$, $l_{34} = l_{10,11}$, l_{35} , and $l_{13} = l_{37} + \Delta_2 = l_{36} + \Delta_3$. Throughout these studies (LS5-2, 3, 4, as well as later ones) the value of α_D remained fairly constant: the values from LS5-2, LS5-3, and LS5-4 were 49.8 (4.3)%, 44.5 (5.0)%, and 47.4 (5.1)%, respectively.

Due to the presence of significant amounts of monomer which diminishes the inherently weak scattering contribution from the ring puckering motion, accurate determinations of δ were felt to be unlikely and its value was assumed to be 25° in all refinements.

In the analyses of the data from the higher temperatures, the monomer was found to be planar ($\angle \text{Br}_{10}\text{Ga}_9\text{Br}_{11} = 119.9 (1.1)^\circ$ (192°C) and $120.0 (1.2)^\circ$ (226°C)) and present to the extent of 74.5 (5.4)% (192°), and 92.4 (5.7)% (226°C). The small amount of dimer at these elevated temperatures made determination of the l -values for the long non-bond interatomic distances impossible. Therefore, only $l_{23} = l_{25} + \Delta_1 = l_{9,10}$, and $l_{34} = l_{10,11}$ were refined (LS5-5 and LS5-6). The magnitude of the non-bond amplitudes (l_{34} , l_{35} , l_{12} , l_{36} , and l_{37}) were kept at reasonable

values (5-10% higher than the corresponding ones obtained at 163°C); however, l_{12} and l_{58} were assumed to be 0.1208 Å throughout because the corresponding distances contribute only very weakly to the scattering.

The final results are summarized as LS5-4 (163), LS5-5 (192), and LS5-6 (226°C) in Table 14. The consistency of the geometrical parameter values at different temperatures is good. Since almost pure (92%) monomer was present at the highest temperature, and 47% dimer was present at the lowest temperature, it was felt that results from LS5-6 may be taken as representing the structure of monomer GaBr_3 . By combining these values with those from LS5-4 one may deduce the structure of the dimer in a straight-forward manner. One of the pertinent points has to do with the value of $r_{9,10}$ from LS5-6 (2.243 (0.003) Å) and say, r_{23} from LS5-5 and LS5-4 (2.246 (0.003) Å, and 2.245 (0.003) Å). The nearly identical values for these distances over a large change in composition can only be interpreted as indicative of an accurately measured terminal Ga-Br bond length in the dimer. Another point concerns the trend in the values of dimer bond angles and in their associated errors as the amount of dimer increases: they are clearly well determined in LS5-4. The results of LS5-4 may be taken as a good description of the structure of the dimer Ga_2Br_6 . Theoretical intensity and RD curves corresponding to these three refinements are shown

in Figures 12 and 13, and the correlation matrices are given in Table 15.

DISCUSSION

Results

The results of previous electron-diffraction (3, 4, 38) studies of the group III halides are shown in Tables 16 and 18. The present work generally confirms the equilibrium geometry of these compounds. However, a close comparison of these sets of geometrical parameters reveals discrepancies in the values of the $M-X_b$ distances and the X_bMX_b and X_tMX_t bond angles. The most pronounced differences come in the cases of aluminum iodide and gallium bromide, the two substances found in the present study to contain substantial amounts of monomer. The possible presence of monomer was not taken into account in the earlier work, where under the experimental conditions required for electron diffraction (the temperatures are not given but must have been sufficient to provide at least 10-20 torr of vapor pressure) it is practically certain that monomeric species were present. In the case of gallium bromide this circumstance may be invoked to account for the differences between the earlier (4) and the present results as follows. The unrecognized monomer with a bond distance very close to that of the terminal bonds of the dimer ($Ga-Br_t$) contributes to the bond-distance peak of the RD curve in a way to

shift the average distance ($\langle \text{Ga-Br} \rangle$) to smaller values. Table 18 reveals that the earlier work does indeed have a smaller average Ga-Br distance ($2.30\text{\AA}$) than does the present work ($2.345\text{\AA}$). The second discrepancy is seen to lie in the value of the terminal bond angle ($\angle \text{Br}_t \text{GaBr}_t$) which is much smaller (110°) in the earlier work. Inspection of the RD curve suggests that the distance $\text{Br}_t \dots \text{Br}_t$ (i. e., r_{34}) has been mis-assigned to a small peak on the inside of what is probably the correct peak. Using the center of gravity of the correct peak together with the value $2.25\text{\AA}$ for the Ga-Br_t distance led to an angle value of 120° , considerably closer to that from this work. The discrepancy in the case of aluminum iodide does not find the same type of explanation, for the average bond distances in the two studies are about the same. However, the early work (38) was from visual estimates of intensity rather than from microdensitometer measurements and the errors are correspondingly much higher. Moreover, the data are for only a very limited range of scattering angle ($s < 13.0$).

Bonding.

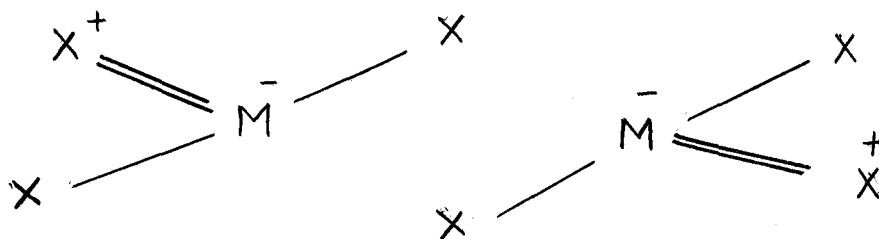
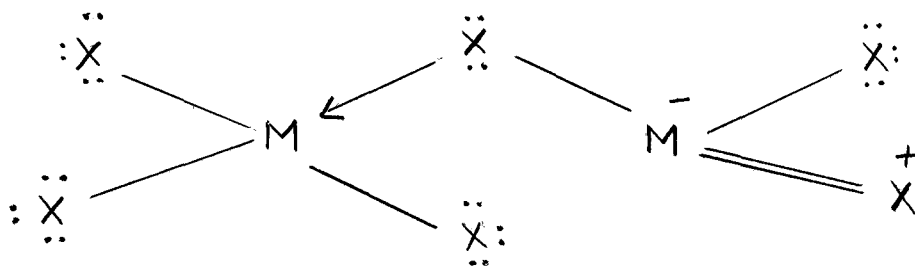
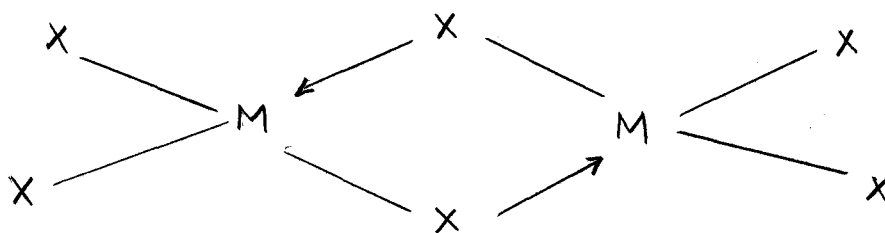
The empirical equation proposed by Pauling (39) $D(n) = D(1) - k \log (n)$ may be applied to calculate the bond numbers of the terminal and bridge M-X bonds in all of the halides investigated. ($D(n)$ is the interatomic distance for a fractional bond (in which case

k equals 0.60) or a multiple bond (where $k=0.70$), $D(1)$ is the length of a covalent single bond and n is the bond number of the bond of interest. A suitable set of covalent radii (39) are $Al = 1.265\text{\AA}$, $Ga = 1.265\text{\AA}$, $Cl = 0.99\text{\AA}$, $Br = 1.14\text{\AA}$, and $I = 1.33\text{\AA}$. The covalent single-bond lengths for these halides are calculated with correction for the electronegativity differences (39) using the Schomaker-Stevenson (46) formula $D_{A-B}(1) = r_A + r_B - 0.08 |x_A - x_B|$, where $D_{A-B}(1)$ is the length of the covalent single bond for A-B, r_A and r_B are the covalent radii of atom A and B, and x_A and x_B are their electronegativities. The bond numbers for the dimeric species are shown in Table 20.

The ratio of n_{M-X_b} / n_{M-X_t} are 0.508, 0.502 and 0.511 for aluminum chloride, bromide and iodide. The similarity of these ratios is consistent with the almost constant difference of about $0.18\text{-}0.19\text{\AA}$ between r_{25} and r_{23} . For the gallium compounds the ratios are 0.47 (Ga_2Cl_6) and 0.48 (Ga_2Br_6) corresponding to a distance difference about $0.20\text{\AA}$. Evidently the bridge bonds are only very slightly weaker in the gallium compounds.

The terminal bond numbers in the aluminum and gallium halides indicate that these bonds are larger than those for a covalent single bond. The sums of the bond numbers are 7.57 (Al_2Cl_6), 7.76 (Al_2Br_6), 7.49 (Al_2I_6), 6.80 (Ga_2Cl_6), and 7.29 (Ga_2Br_6) each substantially greater than the value 6.00 to be

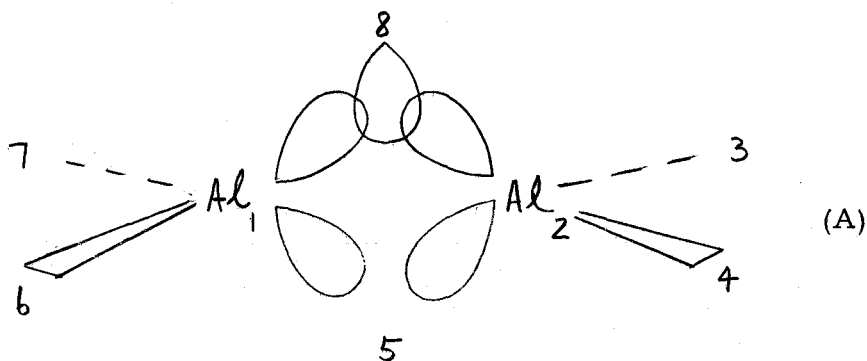
expected from a total of 12 valence shell electrons, one from each halogen atoms and three from each aluminum atom. This excess in bond number and the lengths of the individual bond types suggest contributions from resonance structures like the ones shown below.

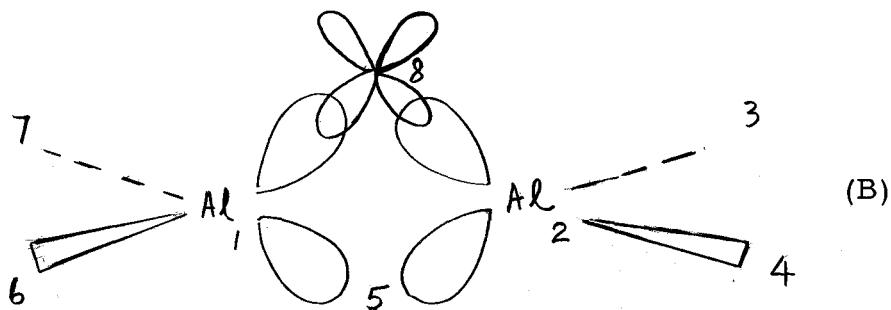


The bond numbers in Table 20 correlate very well with the ability of the X_t and X_b atoms to use their available valence electrons to form bonds with the empty orbitals of the metal in accordance with these diagrams. It is clear that in Al_2Me_6 the sp^3 carbon atom is a poor electron donor since the terminal and bridge bond numbers are very close to unity and to one-half, respectively. In $Al_2Me_4H_2$ the $Al-C_t$ bond number is also close to unity, but the $Al-H_b$ bond is rather greater than one-half. This has been observed in other compounds as well, and may have something to do with the small size of the hydrogen atom. However, in the dimeric aluminum halides, where lone pair valence electrons are available from the halogen atoms, the bond numbers for the terminal and bridge bonds are greater than 1.23 and 0.63, respectively.

Due to the absence of a low-energy valence lone pair on the sp^3 carbon, the bonding in Al_2Me_6 and $Al_2Me_4H_2$ are substantially different from that in Al_2X_6 . The most conspicuous difference is in the Al-Al bond distances. Haaland and co-workers reported values of 2.617 (0.006) ($Al_2Me_4H_2$) (2) and 2.619 (0.005) (Al_2Me_6) (1) for the Al-Al distance. These values are about 0.24 Å shorter than the Al-Al distance in the metal (46). Their report supported the view of direct bonding between metal atoms in Al_2Me_6 and $Al_2Me_4H_2$. The Al...Al bond distances obtained in this study for the halides are 3.102 (0.036) (Cl), 3.288 (0.078) (Br) and 3.335 (.180) (I).

They are at least $0.25 \text{ \AA}$ longer than the Al-Al distance in the metal, and a metal-metal bond is highly unlikely. The configurations of these molecules are also quite different (see Table 17). For Al_2Me_6 and $\text{Al}_2\text{Me}_4\text{H}_2$, the C_tAlC_t angles are 117.3° and 118.5° ; and the C_bAlC_b and H_bAlH_b angles are 104.5° and 77.4° , respectively. For the aluminum halides, the X_tAlX_t angles vary from 115° (I) to 123° (Cl) depending on the values of $\angle \text{X}_b\text{AlX}_b$: 99° (I), and 91° (Cl). These differences may be interpreted as follows. For Al_2Me_6 and $\text{Al}_2\text{Me}_4\text{H}_2$ a three-center bond can be formed by two aluminum atoms (using sp^3 or $\text{sp}^2 + \text{p}$ orbitals) and the carbon atom (sp^3) or the hydrogen atom (see A). A direct metal bond does figure in this picture. For the aluminum halides, each halogen atom can use two p orbitals to overlap with the aluminum sp^3 hybrids as shown in (B). Since p orbitals are at approximately 90° to each other direct interaction of the metal atoms is minimal.





Further, with this orientation of the p orbitals, the bonding in (B) will tend to give AlX_bAl angles about equal to 90° ; the values measured are $89.0 (0.5^\circ)$ (Al_2Cl_6), $87.7 (0.8^\circ)$ (Al_2Br_6), and $80.4 (4.5^\circ)$ (Al_2I_6). The values become smaller as the size of the bridge atoms increases. This trend is in accord with the idea that in order to increase r_{58} to prevent the bulky bridge atoms from interfering with one another, $\angle\text{AlX}_b\text{Al}$ has to decrease. In any event, since the AlX_bAl angle is close to 90° and the four central atoms are coplanar, the X_bAlX_b angle has to be about 90° with the result that X_tAlX_t angle becomes considerably greater than tetrahedral. The $\angle\text{X}_t\text{AlX}_t$ values observed are $123.4 (1.6^\circ)$ (Cl) $122.8 (3.3^\circ)$ (Br), and $115.0 (7.4)$ (I). Thus the sp^3 hybridization concept provides a consistent picture of the structures of the dimeric aluminum halide.

A similar kind of picture also applies to the gallium halides. The terminal and bridge bond numbers are greater than 1.15 and 0.54, respectively. The $\text{Ga}\dots\text{Ga}$ bond distances obtained are $3.256 (0.022)$ (Ga_2Cl_6) and $3.358 (0.067)$ (Ga_2Br_6). The GaX_bGa

angles are $91.7 (0.8^\circ)(\text{Cl})$, and $88.9 (2.2^\circ)(\text{Br})$ very close to a right angle. These angles also follow the trend of being smaller for a larger halogen atom as in the aluminum halides.

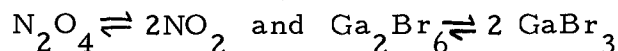
The Structures of Monomeric Aluminum Iodide and Gallium Bromide

The monomers of aluminum iodide and gallium bromide are planar to within experimental error. The AlI_3 structural parameter values compare very well with the ones reported by Akishin *et al.* (4). No previous structural result has been reported for GaBr_3 .

The $r_{9,10}$ (monomer) values are close to the r_{23} (dimer) values. A similar circumstance exists in the cases of Al_2Me_6 and AlMe_3 (1). These very similar bond lengths make accurate determination of each value impossible because they are very highly correlated. In aluminum iodide the difference was measured to be $0.02 (0.09)\text{\AA}$ with the dimer value being the longer. The R values calculated for the gallium bromide refinements revealed the difference to be within $0.04\text{\AA}$; however, as described in the gallium bromide section, there is reason to believe the difference may be much smaller.

The longer r_{23} values are in accord with the view that the empty p orbital on the aluminum atom in the monomer is used to form sp^3 hybrids in the dimer: sp^2 type bonds are known to be shorter than sp^3 bonds.

THE STUDY OF EQUILIBRIUM SYSTEMS


Structure and Composition Determination of N_2O_4 - NO_2

The experiments fall into two sets. One was designed to measure the effect of temperature at constant pressure on the sample composition, the other to measure the effect of pressure at constant temperature. The first set of experiments was made at nozzle temperatures of 104, 25, 2, -12, -25 and -35°C with the sample bath temperature maintained at -42 to -44°C. The second set of experiments was made with nozzle temperature at -12°C and sample bath temperatures of -26, -36, and -44°C. The analysis of the data from each experiment was based upon two plates from the long and two from the intermediate camera distances. The composite final intensity and corresponding RD curves are shown in Figures 15 and 16 together with the difference curves.

Since N_2O_4 is known to have symmetry D_{2h} (36), the model of the system is completely described by a composition parameter α_D (the mole fraction of dimer), five geometrical parameters and seven vibrational parameters. The geometrical and vibrational parameters were $r_{78}, r_{89}, l_{78}, l_{89}$ for NO_2 ; and $r_{12}, r_{23}, \angle \text{O}_3\text{N}_2\text{O}_4, l_{12}, l_{23}, l_{34}, l_{45}$ and l_{35} for N_2O_4 . (See Fig. 14 for

the atom numbering.) In the analyses of the 104°C data where it was known (14) that only the monomer was present, only the four NO₂ structural parameters were refined. Since the structure of the -NO₂ group in N₂O₄ and NO₂ itself are so similar the parameters of each cannot be determined in mixtures. Accordingly the values of the two geometrical parameters obtained from this NO₂ analysis were later introduced into the analyses of the 2, -12, -25, and -35°C data as known quantities. None of the experiments yielded a mixture composition corresponding to pure N₂O₄; however, the results concerning the N₂O₄ structure from the lowest temperatures (-35, -25°C) were judged to be sufficiently accurate to permit their being inserted as known quantities in the analysis of the 25°C data. This particular analysis was concerned with the four NO₂ parameters mentioned above and the composition parameter. With the values of r_{78} and r_{89} determined as mentioned and assumed known, the parameters left to be determined in all the other cases were r_{23} , r_{12} , $\angle \text{O}_3\text{N}_2\text{O}_4$, $l_{23}=l_{78}$, $l_{34}=l_{89}$, l_{12} , l_{45} , l_{35} , and α_D . The final results are summarized in Table 22.

The consistency of the geometrical parameters resulting from these studies is excellent. Either of the sets of results from the 104 and 25°C refinements shown in Table 22 is a satisfactory description of the structure of NO₂, and the results from any one of the lower-temperature refinements in Table 22 are satisfactory

descriptions of the structure of N_2O_4 . All these values are in good agreement with the results reported earlier (13, 14, 36) (see Tables 25 and 26). The correlation matrices for N_2O_4 (25, 2, -12, -25, -35°C) and NO_2 (104°C) are given in Tables 23 and 24, respectively.

Effective Nozzle-Tip Temperature and Sample Pressure

The problems connected with the temperature and pressure measurements, which describe the equilibria to be discussed here, have been outlined in the introduction. For the equilibrium

$\text{N}_2\text{O}_4 \rightleftharpoons 2 \text{NO}_2$ one may write

$$K_p = \frac{x_{\text{NO}_2}^2}{x_{\text{N}_2\text{O}_4}} P_T \quad (4)$$

If the effective total pressure (P_T) of the system at the diffraction zone is proportional to the vapor pressure P_{TB} of the sample determined by the oil bath temperature, K_p can be rewritten

$$K_p = \frac{x_{\text{NO}_2}^2}{x_{\text{N}_2\text{O}_4}} C P_{TB} \quad (5)$$

and

$$P_{TB} = \frac{K_p}{C} \frac{x_{\text{N}_2\text{O}_4}}{x_{\text{NO}_2}^2} \quad (6)$$

where C is a proportionality constant.

The three experiments carried out at different bath temperatures with constant nozzle temperature (-12°C) were designed to give information about the effective total pressure P_T , i. e., the proportionality constant C . The mole fractions of the two species at each bath temperature were first measured (see Table 27) and the corresponding vapor pressures calculated with the formula $\log p_{\text{cm Hg}} = 2460.0/T + 9.58149 + 7.6172 \times 10^{-3} T - 1.51335 \times 10^{-5} T^2$ reported by Giaque et al. (23). A plot of P_{TB} vs $X_{\text{N}_2\text{O}_4}/X_{\text{NO}_2}^2$ was made and the best straight line passing through the origin was drawn (Fig. 17). The slope, K_p/C , has the value of $5.26 (0.5) \times 10^{-3}$ atm. This together with the value 5.31×10^{-3} atm. for K_p at -12°C (calculated from the formula (47) $\log K_p = 9.0179 - 2947.4/T$) led to $C = 1.01 (0.15)$ where the error is 2σ excluding any error in the measurement of the nozzle-tip temperature. Inclusion of such an error estimated at $\sigma = 1^{\circ}$ will give $C = 1.01 (0.26) (2\sigma)$. The agreement with the ideal value $C = 1.00$ is pleasing because it suggests that the nozzle-tip temperature may be taken to represent the effective temperature of the system, in accord with other agreements presented earlier (43). The calculation described above does not, of course, prove anything about the relation between the effective and the measured values of the temperature and pressure. For example, had one assumed that the effective temperature was lower than that measured, the

value calculated for C would also be smaller. Some idea of the connection between the effective temperature and pressure may be seen in the following values for $T_N - T$ and P_T / P_{TB} which are calculated from the known values of K_p at T and the measured sample compositions: 0 and 1.01, 10 and 0.35, 20 and 0.12, 40 and 0.01. The circumstances suggested by these pairs of numbers agree with one's intuition about the physics of the process (i.e., that cooling will attend the expansion and a pressure drop will attend the passage of the gas through the nozzle-tip). Although all these pairs of values are compatible with the experimental results at the nominal nozzle-tip temperature of -12°C , it turns out that only small values of $T_N - T$ (and correspondingly values of P_T / P_{TB} close to one) are compatible with the results from all experiments. Consider the relationship between equilibrium constants and thermodynamic functions which are given by the formulas.

$$-RT \ln K_p = \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (7)$$

$$\ln K_p = \ln \left(\frac{X_{\text{NO}_2}^2}{X_{\text{N}_2\text{O}_4}} P_T \right) = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (8)$$

Plots of $\ln K_p$ as a function of $1/T$ for assumed values of $\Delta T = T_N - T$ were made using the measured compositions and the connection between T and P_T described above. These are shown in Figure 18 with straight lines fit to them by least-squares. Also shown in

Figure 18 are the results obtained by more conventional methods, which are seen to be in strikingly good agreement with the curve calculated for $\Delta T=0$. It is clear from Figure 18 that the agreement of these results with those from diffraction becomes progressively worse as the values assumed for ΔT increase, and it remains only to set a limit on the magnitude of ΔT . This is obtained from a comparison of the calculated standard deviation in the slope of the straight line corresponding to $\Delta T=0$ with the slopes of curves for $\Delta T>0$ such as those in Figure 18. The former is $\sigma = 321.0$ deg. (the line has the equation $\ln K_p = -6,976.5/T + 21.562$). The smooth variation Δm in the slopes of the lines is expressible by the formula $\Delta m = -53.4\Delta T - 7.0$ from which one calculates $\Delta T = (321.0 + 7.0)/53.4 = 6.1^\circ$ corresponding to $\sigma = 321.0$ deg. From the normal curve of error one may conclude that ΔT is less than 5° at the 58% confidence level and less than 10° at the 90% confidence level.

It is interesting to compare values for the thermodynamic functions themselves derived from electron diffraction with those gotten by other methods. From electron diffraction they are $\Delta H^\circ = 13.7 (1.3) \text{ kcal mole}^{-1}$ and $\Delta S^\circ = 42.8 (5.2) \text{ cal deg.}^{-1} \text{ mole}^{-1}$; from spectrophotometry they are $\Delta H^\circ = 13.65 (0.2) \text{ kcal mole}^{-1}$ and $\Delta S^\circ = 41.92 (0.15) \text{ cal deg.}^{-1} \text{ mole}^{-1}$ (47); and from vapor pressure measurements $\Delta H^\circ = 13.69 \text{ kcal mole}^{-1}$ and $\Delta S^\circ = 42.2$

cal deg.⁻¹ mole⁻¹ (23). Although much less accurate, the electron diffraction results are in excellent agreement with the earlier results.

The Dissociation Enthalpy and Entropy of Ga₂Br₆

The compositions of dimeric gallium bromide at the three nozzle temperatures 163, 192 and 226°C were 47.4 (5.1), 25.5 (5.4) and 7.6 (5.7)%, respectively. Sample vapor pressures were calculated from the measured sample bath temperatures of 146, 149, and 156°C, using the formula $\log P_{\text{mm Hg}} = -(14300/4.57T) + 8.554$ reported by Fischer (21). Equilibrium constant values $K_p = [(X_{\text{GaBr}_3}^2 / X_{\text{Ga}_2\text{Br}_6}) \times P_T]$ were calculated assuming $P_{\text{TB}} = P_T$ as suggested by the N₂O₄ experiments and a plot of $\ln K_p$ vs $1/T$ was made. The equilibrium constant values are shown in Table 28 and the plot in Figure 19.

The error limits for the composition measurements are approximately equal. However, that for the 226°C experiment translates into a relatively very large error in the quantity $\ln K_p$. The weighting of the three experiments for the purpose of determining the standard enthalpy and entropy of the reaction, done conventionally as $1/\sigma^2$, leads to the values $\Delta H^\circ = 19.5$ (3.5) kcal mole⁻¹ and $\Delta S^\circ = 35.3$ (6.5) cal deg.⁻¹ mole⁻¹. The assignment of weights in the ration 6:3:1 (approximately $1/\sigma$) for

experimentals at 163, 192, and 226 °C led to the values $\Delta H^\circ = 21.8$ (5.0) kcal mole⁻¹ and $\Delta S^\circ = 40.8$ (9.0) cal deg.⁻¹ mole⁻¹.

The results $\Delta H^\circ = 18.5$ kcal mole⁻¹ for the dissociation of Ga₂Br₆ has been reported (22) in good agreement with the electron-diffraction values. No value of ΔS° for Ga₂Br₆ is known, but ΔS° values of 31.9 (0.5) and 30.8 (0.2) e. u. for Al₂Cl₆ (49) and Ga₂Cl₆ (33) suggested the electron diffraction result from Ga₂Br₆ to be a little high. It may be noted that ΔH° for Ga₂Br₆ is lower than that for Al₂Cl₆ (27.7 (0.9) kcal mole⁻¹) (49) and for Ga₂Cl₆ (20.0 (0.2) kcal mole⁻¹) (33).

The two equilibrium studies (N₂O₄-NO₂ and Ga₂Br₆-GaBr₃) clearly demonstrate that electron diffraction can be successfully used as a tool for the investigation of gaseous chemical equilibria when the compositions of the mixtures are not too complicated. Before placing too much reliance on the method, however, it should be further tested with well-understood systems in which the K_p's are not dependent on pressure.

Table 1. Al_2Cl_6 . Experimental data for electron-diffraction photographs used in the structure analysis.

Plate Identification	Plate size (in)	Accelerating voltage (volts)	Electron wave length (Å) ^a	Beam current (μ a)	Exposure time (min)	Bath temperature (°C)	Nozzle temperature (°C)	Run in pressure (mm Hg)	Camera height (cm)	s range
2-58-1	8x10	44314	0.057035	0.30	2.0	129	150	3.4×10^{-6}	74.99	1.0-13.0
2-58-3	8x10	44320	0.057031	0.35	2.5	123	148	3.2×10^{-6}	74.99	1.0-13.0
2-58-4	8x10	44318	0.057032	0.45	3.0	122	148	3.1×10^{-6}	74.99	1.0-13.0
2-58-5	8x10	44322	0.057029	0.46	3.5	119	147	3.0×10^{-6}	74.99	1.0-13.0
2-60-3	8x10	44310	0.057037	0.46	3.5	124	150	4.2×10^{-6}	29.99	8.0-31.75
2-60-4	8x10	44311	0.057037	0.46	4.0	123	150	4.0×10^{-6}	29.99	8.0-31.75
2-60-5	8x10	44312	0.057036	0.46	4.0	120	150	3.8×10^{-6}	29.99	8.0-31.75

^a The wavelengths were calculated from the accelerating voltage, which was calibrated against gaseous CO_2 using $r_a(\text{C-O}) = 1.1642 \text{ Å}$ and $r_a(\text{O} \dots \text{O}) = 2.3244 \text{ Å}$. See ref. (41) for details.

Table 2. Al_2Cl_6 . Structural results from least-squares refinements. ^{a, b}

Parameters	LS1-1				LS1-2				LS1-3			
	r		1 ^d		r		1 ^d		r		1 ^d	
< Al-Cl >	2.160 (0.003)				2.160 (0.004)				2.161 (0.003)			
$\Delta\text{Al-Cl}$	0.189 (0.004)				0.189 (0.004)				0.189 (0.004)			
$\angle\text{Cl}_5\text{Al}_2\text{Cl}_8$	90.9 (0.6)				90.7 (0.6)				91.3 (0.6)			
$\angle\text{Cl}_3\text{Al}_2\text{Cl}_4$	123.7 (2.2)				123.8 (2.1)				123.4 (2.6)			
δ^e	25.0				45.0				15.0			
Al_2-Cl_3 (4) ^c	2.066 (0.003)	0.050	(0.003)		2.066 (0.003)	0.050	(0.003)		2.066 (0.003)	0.050	(0.003)	
Al_2-Cl_5 (4)	2.255 (0.005)	0.075			2.255 (0.005)	0.075			2.255 (0.005)	0.075		
$\text{Cl}_5\cdots\text{Cl}_8$ (1)	3.215 (0.017)	0.078	(0.014)		3.208 (0.017)	0.075	(0.013)		3.224 (0.019)	0.081	(0.016)	
$\text{Al}_1\cdots\text{Al}_2$ (1)	3.101 (0.018)	0.075			2.971 (0.018)	0.075			3.132 (0.020)	0.075		
$\text{Cl}_3\cdots\text{Cl}_4$ (2)	3.643 (0.017)	0.105	(0.022)		3.645 (0.037)	0.103	(0.021)		3.638 (0.045)	0.107	(0.023)	
$\text{Cl}_3\cdots\text{Cl}_5$ (8)	3.526 (0.015)	0.138	(0.013)		3.526 (0.015)	0.140	(0.013)		3.528 (0.018)	0.139	(0.014)	
$\text{Al}_1\cdots\text{Cl}_3$ (4)	4.444 (0.026)	0.135	(0.006)		4.285 (0.027)	0.131	(0.053)		4.489 (0.030)	0.194	(0.085)	
$\text{Cl}_3\cdots\text{Cl}_7$ (2)	5.059 (0.070)	0.185	(0.046)		4.798 (0.070)	0.227	(0.050)		5.078 (0.078)	0.021	(0.047)	
$\text{Cl}_3\cdots\text{Cl}_6$ (2)	6.155 (0.034)	0.155			5.892 (0.030)	0.197			6.232 (0.039)	0.018		
% dimer	100				100				100			
R^f	0.111 ^h				0.116 ^h				0.112 ^h			

Continued

Table 2 (cont.). Al_2Cl_6 . Structural results from least-squares refinements. ^{a, b}

Parameters	LS1-4		LS1-5		LS1-6*	
	r	l^d	r	l^d	r	l^d
$\langle \text{Al}-\text{Cl} \rangle$	2.160 (0.003)		2.160 (0.003)		2.159 (0.003)	
$\Delta \text{Al}-\text{Cl}$	0.188		0.188 (0.003)		0.188 (0.003)	
$\angle \text{Cl}_5\text{Al}_2\text{Cl}_8$	90.9 (0.5)		90.9 (0.5)		91.0 (0.5)	
$\angle \text{Cl}_3\text{Al}_2\text{Cl}_4$	123.0 (2.1)		123.0 (2.1)		123.4 (1.6)	
δ^e	25.0		25.0		23.4 (6.0)	
Al_2Cl_3 (4) ^c	2.065 (0.003)	0.050 (0.003)	2.065 (0.002)	0.050 } 0.003	2.065 (0.002)	0.049 } (0.003)
Al_2-Cl_5 (4)	2.254 (0.003)	0.076 (0.004)	2.254 (0.004)	0.076 }	2.252 (0.004)	0.075 }
$\text{Cl}_5 \dots \text{Cl}_8$ (1)	3.213 (0.014)	0.079 (0.011)	3.213 (0.015)	0.079 (0.012)	3.214 (0.015)	0.075 } (0.013)
$\text{Al}_1 \dots \text{Al}_2$ (1)	3.099 (0.015)	0.075	3.100 (0.016)	0.075	3.102 (0.036)	0.075 }
$\text{Cl}_3 \dots \text{Cl}_4$ (2)	3.631 (0.037)	0.109 (0.017)	3.631 (0.037)	0.109 (0.017)	3.636 (0.103)	0.103 (0.014)
$\text{Cl}_5 \dots \text{Cl}_3$ (8)	3.530 (0.014)	0.141 (0.010)	3.530 (0.014)	0.141 (0.010)	3.525 (0.011)	0.140 (0.009)
$\text{Al}_1 \dots \text{Cl}_3$ (4)	4.449 (0.020)	0.137 (0.040)	4.450 (0.020)	0.137 (0.041)	4.451 (0.089)	0.143 }
$\text{Cl}_3 \dots \text{Cl}_7$ (2)	5.031 (0.060)	0.192 } (0.058)	5.031 (0.039)	0.193 }	5.027 (0.170)	0.199 } (0.034)
$\text{Cl}_3 \dots \text{Cl}_6$ (2)	6.163 (0.029)	0.162 }	6.164 (0.029)	0.163 } (0.059)	6.168 (0.066)	0.169 }
% dimer	100.0		100.4 (4.7)		100.0	
R^f	0.155 ^g		0.155 ^g		0.142 ^g	

Table 2--Footnotes.

- * Best model.
- a Distances (r) and root-mean-square amplitudes (l) in Angstroms; angles in degrees.
- b Parenthesized values indicated are 2σ and include estimates of systematic error, otherwise the values are held constant during the refinement.
- c Parenthesized values are the multiplicities of the different distances.
- d Bracketed quantities were refined, with constant differences as a group.
- e Root-mean-square amplitude of bending motion, in degree.
- f $R = [\sum W_i \Delta_i^2 / (\sum W_i I_i^2 (\text{obs}))]^{1/2}$ where $\Delta_i = I_i (\text{obs}) - I_i (\text{cal})$.
- g Value obtained from refinement on individual plates.
- h Value obtained from refinement on composite curves.
- i Value obtained from refinement on average curves.

Table 3. Al_2Cl_6 . Correlation matrix from LS1-6. ^a

	$\langle \text{Al-Cl} \rangle$	$\Delta \text{Al-Cl}$	$\angle 5, 2, 8$	$\angle 4, 2, 3$	δ	l_{23}	l_{58}	l_{34}	l_{35}	l_{37}	r_{23}	r_{25}	r_{34}	r_{35}	r_{13}
σ^b	0.0006	0.0010	0.189	0.562	0.860	0.0006	0.0043	0.0047	0.0028	0.0117	0.0005	0.0010	0.0097	0.0038	0.0066
	1.000	0.642	-0.101	0.233	-0.162	0.188	0.098	0.065	-0.314	0.020	0.630	0.928	0.284	0.040	0.069
		1.000	-0.190	0.153	-0.093	0.438	0.157	0.099	-0.094	0.021	-0.191	0.882	0.134	0.050	0.155
			1.000	-0.308	-0.181	-0.092	-0.575	0.006	0.150	0.035	0.063	-0.155	-0.298	0.104	-0.473
				1.000	0.128	0.008	-0.130	-0.701	-0.841	-0.036	0.144	0.218	0.996	-0.945	-0.668
					1.000	-0.008	-0.229	-0.036	0.091	-0.181	-0.113	-0.145	0.116	-0.145	-0.022
						1.000	0.128	0.173	0.152	0.031	-0.203	0.328	-0.010	0.062	0.113
							1.000	0.208	0.173	0.025	-0.033	0.137	-0.130	0.279	0.572
								1.000	0.603	0.002	-0.017	0.088	-0.692	0.766	0.675
									1.000	0.011	-0.307	-0.239	-0.854	0.785	0.622
										1.000	0.004	0.022	-0.035	0.036	0.012
											1.000	0.295	0.228	0.001	-0.069
												1.000	0.240	0.049	0.118
													1.000	-0.930	-0.663
														1.000	0.827
															1.000

^a Distances (r) and root-mean-square amplitudes (l) in Angstroms, angles in degrees.

^b Standard deviations from least squares.

Table 4. Al_2Br_6 . Experimental data for electron-diffraction photographs used in the structure analysis.

Plate identification	Plate size (in)	Accelerating voltage (volts)	Electron wave ^a length (Å)	Beam current (μa)	Exposure time (sec)	Bath temperature (°C)	Nozzle temperature (°C)	Run in pressure (mmHg)	Camera height (cm)	s range
2-68-2	8x10	44262	0.057070	0.48	17	128	160	6.0×10^{-6}	75.35	2.0-13.0
2-68-4	8x10	44264	0.057068	0.48	20	128	160	5.0×10^{-6}	75.35	2.0-13.0
2-68-5	8x10	44265	0.057068	0.48	10	128	160	4.0×10^{-6}	75.35	2.0-13.0
2-76-2	8x10	44234	0.057088	0.48	120	93	163	1.0×10^{-5}	30.01	6.0-31.50
2-76-3	8x10	44235	0.057088	0.46	180	92	161	8.0×10^{-6}	30.01	6.0-31.50
2-76-4	8x10	44237	0.057086	0.48	180	92	161	6.0×10^{-6}	30.01	6.0-31.50

^a The wavelengths were calculated from the accelerating voltage, which was calibrated against gaseous CO_2 using $r_a(\text{C}-\text{O}) = 1.1642 \text{ Å}$ and $r_a(\text{O} \dots \text{O}) = 2.3244 \text{ Å}$. See ref. (41) for details.

Table 5. Al_2Br_6 . Structural results from least-squares refinements.^{a, b}

Parameters	LS2-1				LS2-2			
	r		l^d		r		l^d	
<Al-Br>	2.318 (0.006)				2.318 (0.006)			
$\Delta\text{Al-Br}$	0.192 (0.009)				0.193 (0.009)			
$\angle\text{Br}_5\text{Al}_2\text{Br}_8$	92.6 (0.9)				92.6 (0.9)			
$\angle\text{Br}_3\text{Al}_2\text{Br}_4$	120.5 (4.2)				119.8 (3.3)			
δ^e	25.0				45.0			
$\text{Al}_2\text{-Br}_3$ (4) ^c	2.222 (0.005)	0.054	(0.005)		2.222 (0.005)	0.054	(0.006)	
$\text{Al}_2\text{-Br}_5$ (4)	2.414 (0.010)	0.087			2.415 (0.010)	0.087		
$\text{Br}_5\cdots\text{Br}_8$ (1)	3.489 (0.031)	0.105	(0.026)		3.491 (0.036)	0.109	(0.031)	
$\text{Al}_1\cdots\text{Al}_2$ (1)	3.272 (0.029)	0.075			3.131 (0.028)	0.075		
$\text{Br}_3\cdots\text{Br}_4$ (2)	3.858 (0.081)	0.117	(0.027)		3.844 (0.062)	0.114	(0.031)	
$\text{Br}_5\cdots\text{Br}_3$ (8)	3.800 (0.030)	0.151	(0.022)		3.806 (0.028)	0.155	(0.022)	
$\text{Al}_1\cdots\text{Br}_3$ (4)	4.759 (0.043)	0.186	(0.176)		4.593 (0.044)	0.165	(0.008)	
$\text{Br}_3\cdots\text{Br}_7$ (2)	5.433 (0.130)	0.187	(0.083)		5.229 (0.120)	0.220	(0.090)	
$\text{Br}_3\cdots\text{Br}_6$ (2)	6.621 (0.061)	0.157			6.345 (0.080)	0.190		
% dimer	100				100			
R^f	0.188 ^h				0.189 ^h			

Continued

Table 5 (cont.). Structural results from least-squares refinements.^{a, b}

Parameters	LS2-3				LS2-4*			
	r	l ^d			r	l ^d		
<Al-Br>	2.318 (0.005)				2.318 (0.005)			
ΔAl-Br	0.184				0.192 (0.007)			
∠Br ₅ Al ₂ Br ₈	92.4 (0.7)				92.3 (0.9)			
∠Br ₃ Al ₂ Br ₄	122.7 (2.7)				122.8 (3.3)			
δ ^e	25.0				23.3 (14.0)			
Al ₂ -Br ₃ (4) ^c	2.226 (0.005)	0.050	(0.006)		2.222 (0.005)	0.055	} (0.006)	
Al ₂ -Br ₅ (4)	2.409 (0.005)	0.080	(0.011)		2.414 (0.008)	0.085		
Br ₅ ...Br ₈ (1)	3.480 (0.023)	0.097	(0.020)		3.481 (0.026)	0.099	} (0.021)	
Al ₁ ...Al ₂ (1)	3.270 (0.021)	0.100			3.288 (0.078)	0.099		
Br ₃ ...Br ₂ (2)	3.905 (0.055)	0.105	(0.020)		3.901 (0.063)	0.114	(0.024)	
Br ₅ ...Br ₄ (8)	3.784 (0.016)	0.139	(0.165)		3.784 (0.021)	0.143	(0.016)	
Al ₁ ...Br ₃ (4)	4.734 (0.025)	0.307	(0.270)		4.751 (0.100)	0.166	} (0.060)	
Br ₃ ...Br ₇ (2)	5.363 (0.080)	0.179	} (0.046)		5.379 (0.350)	0.216		
Br ₃ ...Br ₆ (2)	6.590 (0.034)	0.149			6.607 (0.186)	0.186		
% dimer	95 (20)				100			
R ^f	0.207 ^g				0.263 ^g			

Table 5--Footnotes.

- * Best model
- a Distances (r) and root-mean-square amplitudes (l) in Ångstroms; angles in degrees.
- b Parenthesized values indicated are 2σ and include estimates of systematic error, otherwise the values are held constant during the refinement.
- c Parenthesized values are the multiplicities of the different distances.
- d Bracketed quantities were refined, with constant differences as a group.
- e Root-mean-square amplitude of bending motion, in degree.
- f $R = [\sum W_i \Delta_i^2 / (\sum W_i I_i^2(\text{obs}))]^{1/2}$ where $\Delta_i = I_i(\text{obs}) - I_i(\text{cal})$.
- g Value obtained from refinement on individual plates.
- h Value obtained from refinement on composite curves.
- i Value obtained from refinement on average curves.

Table 6. Al_2Br_6 . Correlation matrix from LS2-4.^a

<Al-Br> Δ Al-Br		$\angle 5, 2, 8$	$\angle 4, 2, 3$	δ	l_{23}	l_{58}	l_{34}	l_{35}	l_{37}	l_{23}	r_{25}	r_{34}	r_{35}	r_{13}	
σ^b	0.0017	0.0026	0.30	1.16	2.00	0.0017	0.0073	0.0083	0.0053	0.0210	0.0014	0.0027	0.0222	0.0073	0.0096
	1.000	0.600	-0.067	0.398	-0.118	0.068	-0.202	0.081	-0.505	0.033	0.682	0.925	0.459	-0.078	-0.105
		1.000	-0.223	0.241	-0.072	0.235	-0.082	0.128	-0.176	0.037	-0.175	0.859	0.213	-0.013	0.135
			1.000	-0.635	-0.366	-0.120	0.192	0.360	0.416	0.119	0.121	-0.149	-0.599	0.560	-0.009
				1.000	0.093	0.016	-0.457	-0.706	-0.890	-0.053	-0.269	0.369	0.994	-0.937	-0.713
					1.000	0.012	-0.117	-0.198	0.078	-0.364	-0.080	-0.110	0.081	-0.093	0.140
						1.000	-0.006	0.171	0.140	0.031	-0.131	0.155	0.001	0.030	0.123
							1.000	0.245	0.522	0.058	-0.174	-0.168	-0.460	0.438	0.407
								1.000	0.591	0.089	-0.018	0.113	-0.683	0.819	0.734
									1.000	-0.009	-0.462	-0.407	-0.909	0.802	0.712
										1.000	0.007	0.039	-0.050	0.055	-0.015
											1.000	0.353	0.370	-0.084	-0.252
												1.000	0.395	-0.056	-0.003
													1.000	-0.913	-0.716
														1.000	0.822
															1.000

^a Distances (r) and root-mean-square amplitudes (l) in Angstroms, angles in degrees.

^b Standard deviations from least squares.

Table 7. $\text{Al}_2\text{I}_6 - \text{AlI}_3$. Experimental data for electron-diffraction photographs used in the structure analysis.

Plate identification	Plate size (in)	Accelerating voltage (volts)	Electron wave length ($\text{\AA}$) ^a	Beam current (μa)	Exposure time (min)	Nozzle temperature ($^{\circ}\text{C}$)	Run in pressure (Torr)	Camera height (mm)	s range
2-88-1	8x10	44210	0.057105	0.46	2.0	221	2.0×10^{-6}	749.31	1.00-13.00
2-88-2	8x10	44206	0.057107	0.46	2.5	226	2.0×10^{-6}	749.31	1.00-12.75
2-88-3	8x10	44206	0.057107	0.46	2.0	230	4.0×10^{-6}	749.31	1.00-12.75
2-88-4	8x10	44211	0.057104	0.46	1.0	234	3.6×10^{-6}	749.31	1.00-12.75
2-88-5	8x10	44211	0.057104	0.46	1.0	235	4.0×10^{-6}	749.31	1.00-12.75
2-89-3	8x10	44201	0.057111	0.40	3.5	221	3.8×10^{-6}	298.53	7.00-30.00
2-89-4	8x10	44206	0.057107	0.40	4.0	228	3.8×10^{-6}	298.53	7.00-30.00
2-89-5	8x10	44214	0.057102	0.40	4.0	230	4.0×10^{-6}	298.53	7.00-30.00

^a The wavelengths were calculated from the accelerating voltage, which was calibrated against gaseous CO_2 using $r_a(\text{C-O}) = 1.1642 \text{ \AA}$ and $r_a(0 \dots 0) = 2.3244 \text{ \AA}$. See ref. (41) for details.

Table 8. Al_2I_6 - AlI_3 . Structural results from least-squares refinements.^{a, b}

Parameters		LS3-1		LS3-2	
		r	l^d	r	l^d
Dimer					
$\langle \text{Al-I} \rangle$		2.507 (0.008)		2.546 (0.009)	
$\Delta \text{Al-I}$		0.153 (0.022)		0.193 (0.019)	
$\angle \text{I}_5\text{Al}_2\text{I}_8$		83.0 (3.1)		98.7 (3.7)	
$\angle \text{I}_4\text{Al}_2\text{I}_3$		120.8 (1.7)		115.6 (4.9)	
δ^e		25.0		25.0	
D-M		--		0.0	
$\text{Al}_2\text{-I}_3$	(4) ^c	2.430 (0.101)	0.060	2.450 (0.006)	0.060
$\text{Al}_2\text{-I}_5$	(4)	2.583 (0.016)	0.087	2.643 (0.018)	0.087
$\text{I}_5\cdots\text{I}_8$	(1)	3.424 (0.108)	0.227 (0.091)	4.011 (0.109)	0.130
$\text{Al}_1\cdots\text{Al}_2$	(1)	3.793 (0.087)	0.100	3.375 (0.130)	0.130
$\text{I}_3\cdots\text{I}_4$	(2)	4.227 (0.035)	0.123 (0.016)	4.146 (0.107)	0.128 (0.023)
$\text{I}_5\cdots\text{I}_3$	(8)	4.150 (0.023)	0.201 (0.022)	4.181 (0.058)	0.231 (0.038)
$\text{Al}_1\cdots\text{I}_3$	(4)	5.398 (0.086)	0.210	5.095 (0.170)	0.230
$\text{I}_3\cdots\text{I}_7$	(2)	6.146 (0.115)	0.240	5.934 (0.290)	0.260
$\text{I}_3\cdots\text{I}_6$	(2)	7.413 (0.082)	0.230	7.193 (0.220)	0.260
Monomer					
$\text{Al}_9\text{-I}_{10}$	(3)	--		2.450 (0.060)	0.060
$\text{I}_{10}\cdots\text{I}_{11}$	(3)	--		4.011 (0.109)	0.130
$\angle \text{I}_{10}\text{Al}_9\text{I}_{11}$		--		120.0	
% Dimer		100		42.8 (7.3)	
R^f		0.165 ^h		0.126 ^h	

Continued

Table 8 (cont.). Al_2I_6 - AlI_3 . Structural results from least-squares refinements. ^{a, b}

Parameters		LS3-3		LS3-4		LS3-5*	
Dimer		r	l^d	r	l^d	r	l^d
<Al-I>		2.549 (0.019)		2.544 (0.007)		2.542 (0.017)	
$\Delta\text{Al-I}$		0.171 (0.056)		0.185 (0.014)		0.184 (0.030)	
$\angle \text{I}_5\text{Al}_2\text{I}_8$		98.9 (2.4)		99.2 (1.8)		99.6 (4.5)	
$\angle \text{I}_4\text{Al}_2\text{I}_3$		115.8 (4.3)		114.5 (3.2)		115.0 (7.4)	
δ^e		25.0		25.0		25.0	
D-M		0.025 (0.091)		0.0		0.0	
$\text{Al}_2\text{-I}_3$	(4) ^c	2.463 (0.046)	0.061	2.451 (0.005)	0.061	2.449 (0.013)	0.069
$\text{Al}_2\text{-I}_5$	(4)	2.634 (0.015)	0.082	2.636 (0.013)	0.082	2.634 (0.029)	0.090
$\text{I}_5\cdots\text{I}_8$	(1)	4.004 (0.073)	0.120	4.015 (0.053)	0.120	4.022 (0.114)	0.120
$\text{Al}_1\cdots\text{Al}_2$	(1)	3.357 (0.086)	0.120	3.351 (0.070)	0.120	3.335 (0.180)	0.120
$\text{I}_3\cdots\text{I}_4$	(2)	4.173 (0.160)	0.133 (0.023)	4.123 (0.070)	0.121 (0.019)	4.132 (0.169)	0.124 (0.054)
$\text{I}_5\cdots\text{I}_3$	(8)	4.182 (0.037)	0.225 (0.028)	4.182 (0.034)	0.231 (0.026)	4.173 (0.069)	0.238 (0.059)
$\text{Al}_1\cdots\text{I}_3$	(4)	5.087 (0.110)	0.230	5.087 (0.088)	0.230	5.065 (0.187)	0.256
$\text{I}_3\cdots\text{I}_7$	(2)	5.924 (0.200)	0.260	5.951 (0.160)	0.260	5.915 (0.310)	0.296
$\text{I}_3\cdots\text{I}_6$	(2)	7.200 (0.130)	0.260	7.188 (0.093)	0.260	7.169 (0.194)	0.276
Monomer							
$\text{Al}_9\text{-I}_{10}$	(3)	2.438 (0.045)	0.061	2.451 (0.005)	0.061	2.449 (0.013)	0.069
$\text{I}_{10}\cdots\text{I}_{11}$	(3)	4.224 (0.078)	0.133 (0.023)	4.245 (0.008)	0.121 (0.019)	4.245 (0.068)	0.124
$\angle \text{I}_{10}\text{Al}_9\text{I}_{11}$		120.0		120.0		120.1 (4.0)	
% dimer		42.6 (5.3)		42.1 (4.7)		42.0 (16.3)	
R^f		0.183 ^g		0.183 ^g		0.207 ⁱ	

Table 8--Footnotes.

* Best model.

a Distances (r) and root-mean-square amplitudes (l) in Angstroms; angles in degrees.

b Parenthesized values indicated are 2σ and include estimates of systematic error, otherwise the values are held constant during the refinement.

c Parenthesized values are the multiplicities of the different distances.

d Bracketed quantities were refined, with constant differences as a group.

e Root-mean-square amplitude of bending motion, in degree.

f $R = [\sum W_i \Delta_i^2 / (\sum W_i I_i^2(\text{obs}))]^{1/2}$ where $\Delta_i = I_i(\text{obs}) - I_i(\text{cal})$.

g Value obtained from refinement on individual plates.

h Value obtained from refinement on composite curves.

i Value obtained from refinement on average curves.

Table 9. $Al_2I_6-AlI_3$. Correlation matrix from LS3-5. ^a

	<Al-I>	$\Delta Al-I$	$\angle 5, 2, 8$	$\angle 4, 2, 3$	$\angle 10, 9, 11$	l_{23}	l_{34}	l_{35}	l_{37}	α_D	r_{23}	r_{25}	r_{35}	r_{13}	$r_{10, 11}$
σ^b	0.0059	0.0106	1.57	2.62	1.38	0.0078	0.0192	0.0205	0.0953	0.0576	0.0046	0.0103	0.0246	0.0659	0.0239
	1.000	0.667	-0.634	0.104	-0.604	0.110	0.384	0.115	0.009	-0.417	0.530	0.924	0.546	0.639	-0.560
		1.000	-0.336	0.174	-0.032	-0.263	0.098	0.275	0.056	0.163	-0.279	0.901	0.255	0.326	-0.133
			1.000	-0.037	0.614	-0.122	-0.296	0.230	0.039	0.485	-0.435	-0.541	-0.581	-0.876	0.605
				1.000	-0.477	-0.120	0.831	-0.280	0.012	0.056	-0.063	0.150	-0.731	-0.423	-0.605
					1.000	-0.334	-0.828	0.275	0.051	0.743	-0.741	-0.367	-0.084	-0.356	0.972
						1.000	0.163	0.332	-0.016	-0.470	0.441	-0.071	0.180	0.163	-0.261
							1.000	-0.357	-0.028	-0.460	0.384	0.274	-0.394	-0.094	-0.884
								1.000	0.076	0.210	-0.165	0.208	0.186	-0.015	0.281
									1.000	0.084	-0.052	0.034	-0.020	-0.033	0.045
										1.000	-0.723	-0.159	-0.382	-0.471	0.665
											1.000	0.165	0.413	0.453	-0.570
												1.000	0.449	0.539	-0.394
													1.000	0.901	0.036
														1.000	-0.284
															1.000

^a Distances (r) and root-mean-square amplitudes (l) in Angstroms, angles in degrees.

^b Standard deviation from least-squares.

Table 10. Ga_2Cl_6 . Experimental data for electron-diffraction photographs used in the structure analysis.

Plate identification	Plate size (in)	Accelerating voltage (volts)	Electron wave length ($\text{\AA}$)	Beam current (μa)	Exposure time (min)	Bath temperature ($^{\circ}\text{C}$)	Nozzle temperature ($^{\circ}\text{C}$)	Run in pressure (mm Hg)	Camera height (cm)	s range
2-87-6	8x10	44189	0.057120	0.48	1.0	66	112	6×10^{-6}	74.97	1.0-13.00
2-87-7	8x10	44194	0.057115	0.48	1.0	66	117	6×10^{-6}	74.97	1.0-13.00
2-87-8	8x10	44192	0.057117	0.48	0.75	66	120	6×10^{-6}	74.97	1.0-13.00
2-87-9	8x10	44192	0.057117	0.48	0.50	65	121	6×10^{-6}	74.97	1.0-13.00
2-87-10	8x10	44194	0.057115	0.48	0.75	66	121	4×10^{-6}	74.97	1.0-13.00
2-87-1	8x10	44186	0.057122	0.50	4.0	65	117	4×10^{-6}	29.97	7.0-30.75
2-87-4	8x10	44192	0.057117	0.50	3.0	64	118	4×10^{-6}	29.97	7.0-30.75
2-87-5	8x10	44193	0.057116	0.50	3.5	63	118	4×10^{-6}	29.97	7.0-30.75

^a The wavelengths were calculated from the accelerating voltage, which was calibrated against gaseous CO_2 using $r_a(\text{C-O}) = 1.1642 \text{ \AA}$ and $r_a(0 \dots 0) = 2.3244 \text{ \AA}$. See ref. (41) for details.

Table 11. Ga_2Cl_6 . Structural results from least-squares refinements.^{a, b}

Parameters	LS4-1			LS4-2			LS4-3*		
	r	1^d		r	1^d		r	1^d	
$\langle \text{Ga}-\text{Cl} \rangle$	2.199 (0.002)			2.200 (0.003)			2.200 (0.003)		
$\Delta \text{Ga}-\text{Cl}$	0.198			0.200 (0.002)			0.201 (0.002)		
$\angle \text{Cl}_5\text{Ga}_2\text{Cl}_8$	87.9 (0.5)			88.0 (0.4)			88.3 (0.8)		
$\angle \text{Cl}_4\text{Ga}_2\text{Cl}_3$	125.3 (1.0)			125.5 (1.1)			124.6 (1.8)		
δ^e	25.0			25.0			20.5(3.3)		
Ga_2-Cl_3 (4) ^c	2.010 (0.002)	0.050	(0.002)	2.100 (0.002)	0.051	(0.003)	2.099 (0.002)	0.052	(0.003)
Ga_2-Cl_5 (4)	2.297 (0.003)	0.084	(0.004)	2.300 (0.003)	0.084		2.300 (0.003)	0.085	
$\text{Cl}_5 \dots \text{Cl}_8$ (1)	3.190 (0.015)	0.077	(0.006)	3.194 (0.012)	0.077		3.205 (0.023)	0.091	(0.014)
$\text{Ga}_1 \dots \text{Ga}_2$ (1)	3.243 (0.014)	0.080		3.245 (0.011)	0.080		3.256 (0.022)	0.091	
$\text{Cl}_3 \dots \text{Cl}_4$ (2)	3.730 (0.018)	0.106	(0.018)	3.734 (0.019)	0.106	(0.019)	3.717 (0.031)	0.110	(0.021)
$\text{Cl}_5 \dots \text{Cl}_3$ (8)	3.589 (0.009)	0.135	(0.009)	3.590 (0.009)	0.134	(0.009)	3.594 (0.013)	0.138	(0.011)
$\text{Ga}_1 \dots \text{Cl}_3$ (4)	4.582 (0.018)	0.154	(0.031)	4.582 (0.016)	0.154	(0.031)	4.609 (0.038)	0.154	(0.025)
$\text{Cl}_3 \dots \text{Cl}_7$ (2)	5.135 (0.036)	0.181	(0.063)	5.130 (0.037)	0.182	(0.062)	5.154 (0.099)	0.189	
$\text{Cl}_3 \dots \text{Cl}_6$ (2)	6.305 (0.021)	0.151		6.303 (0.020)	0.152		6.350 (0.019)	0.159	
% dimer	100			99.1 (1.5)			100		
R^f	0.119 ^g			0.118 ^g			0.106 ^g		

Table 11--Footnotes.

- * Best model.
- a Distances (r) and root-mean-square amplitudes (l) in Ångstroms; angles in degrees.
- b Parenthesized values indicated are 2σ and include estimates of systematic error, otherwise the values are held constant during the refinement.
- c Parenthesized values are the multiplicities of the different distances.
- d Bracketed quantities were refined, with constant differences as a group.
- e Root-mean-square amplitude of bending motion, in degree.
- f $R = [\sum W_i \Delta_i^2 / (\sum W_i I_i^2(\text{obs}))]^{1/2}$ where $\Delta_i = I_i(\text{obs}) - I_i(\text{cal})$.
- g Value obtained from refinement on individual plates.
- h Value obtained from refinement on composite curves.
- i Value obtained from refinement on average curves.

Table 12. Ga₂Cl₆ correlation matrix from LS4-3. ^a

	< Ga-Cl >	ΔGa-Cl	∠5, 2, 8	∠4, 2, 3	δ	l ₂₃	l ₅₈	l ₃₄	l ₃₅	l ₃₇	r ₂₃	r ₂₅	r ₃₄	r ₃₅	r ₁₃
^b															
σ	0.00047	0.0074	0.277	0.643	0.471	0.00039	0.0048	0.0073	0.0033	0.0084	0.0003	0.0008	0.0109	0.0043	0.0069
	1.000	0.734	0.180	0.078	0.027	0.292	0.101	0.035	-0.070	0.010	0.610	0.946	0.109	0.048	-0.108
		1.000	0.166	0.047	0.052	0.441	0.087	0.044	0.016	0.012	-0.090	0.914	0.042	0.040	-0.090
			1.000	-0.528	-0.626	0.038	0.860	0.388	0.605	0.214	0.070	0.187	-0.522	0.376	-0.439
				1.000	0.619	0.038	-0.681	-0.847	-0.880	-0.228	0.060	0.069	0.999	-0.972	-0.519
					1.000	0.063	-0.754	-0.420	-0.502	-0.293	-0.022	0.041	0.615	-0.532	-0.013
						1.000	0.035	0.057	0.058	0.035	-0.086	0.384	0.034	0.001	-0.026
							1.000	0.490	0.712	0.244	0.047	0.102	-0.675	0.566	-0.142
								1.000	0.755	0.171	0.000	0.042	-0.843	0.856	0.518
									1.000	0.205	-0.122	-0.034	-0.883	0.821	0.312
										1.000	0.000	0.012	-0.227	0.203	0.026
											1.000	0.322	0.111	0.024	-0.053
												1.000	0.085	0.048	-0.107
													1.000	-0.966	-0.520
														1.000	0.667
															1.000

^a Distances (r) and root-mean-square amplitudes (l) in Angstroms, angles in degrees.

^b Standard deviations from least squares.

Table 13. $\text{Ga}_2\text{Br}_6\text{-GaBr}_3$. Experimental data for electron-diffraction photographs used in the structure analyses of $\text{Ga}_2\text{Br}_6\text{-GaBr}_3$ mixtures.

Plate identification	Plate size (in)	Accelerating voltage (volts)	Electron wave length ($\text{\AA}$) ^a	Beam current (μa)	Exposure time (min)	Bath temperature ($^{\circ}\text{C}$)	Nozzle temperature ($^{\circ}\text{C}$)	Run in pressure (torr)	Camera height (mm)	s range
2-97-2	8x10	44188	0.057119	0.50	0.75	147	163	3.0×10^{-6}	749.706	2.00-12.75
2-97-3	8x10	44187	0.057120	0.50	1.00	148	163	3.0×10^{-6}	749.706	2.00-12.75
2-97-4	8x10	44187	0.057120	0.50	1.00	148	163	3.0×10^{-6}	749.706	2.00-12.75
2-97-5	8x10	44187	0.057120	0.50	0.75	148	163	3.0×10^{-6}	749.706	2.00-13.25
2-96-3	8x10	44208	0.057106	0.40	3.50	145	163	1.0×10^{-5}	299.780	8.00-31.00
2-96-4	8x10	44200	0.057111	0.40	2.50	145	163	1.0×10^{-5}	299.780	8.00-31.00
2-96-5	8x10	44196	0.057114	0.40	3.25	145	163	1.0×10^{-5}	299.780	8.00-31.00
2-119-7	8x10	44104	0.057176	0.38	0.50	149	192	5.4×10^{-6}	749.650	2.00-12.75
2-119-8	8x10	44105	0.057175	0.38	0.65	148	192	5.4×10^{-6}	749.650	2.00-12.75
2-119-9	8x10	44105	0.057175	0.38	0.40	148	192	5.4×10^{-6}	749.650	2.00-12.75
2-119-10	8x10	44106	0.057174	0.38	0.40	148	192	5.4×10^{-6}	749.650	2.00-12.75
2-119-1	8x10	44086	0.057188	0.38	1.50	150	192	3.8×10^{-6}	299.634	8.00-31.00
2-119-4	8x10	44095	0.057182	0.38	1.75	150	192	3.8×10^{-6}	299.634	8.00-31.00
2-119-5	8x10	44095	0.057182	0.38	2.00	149	192	3.8×10^{-6}	299.634	8.00-31.00
2-111-1	8x10	44072	0.057198	0.38	1.00	156	225	5.0×10^{-6}	749.658	2.00-12.75
2-111-2	8x10	44076	0.057195	0.38	0.75	155	226	5.0×10^{-6}	749.658	2.00-12.75
2-111-3	8x10	44081	0.057192	0.38	1.00	155	227	5.0×10^{-6}	749.658	2.00-12.75
2-111-4	8x10	44081	0.057192	0.37	0.75	154	226	5.0×10^{-6}	749.658	2.00-12.75
2-112-2	8x10	44142	0.057150	0.38	3.00	159	226	4.0×10^{-6}	299.530	8.00-31.00
2-112-4	8x10	44148	0.057146	0.38	2.50	157	225	4.0×10^{-6}	299.530	8.00-31.00
2-112-5	8x10	44150	0.057145	0.38	2.50	157	225	4.0×10^{-6}	299.530	8.00-31.00

^a The wavelengths were calculated from the accelerating voltage, which was calibrated against gaseous CO_2 using $r_a(\text{C-O}) = 1.1642 \text{ \AA}$ and $r_a(0 \dots 0) = 2.3244 \text{ \AA}$. See ref. (41) for details.

Table 14. Ga_2Br_6 - GaBr_3 . Structural results from least-squares refinements. ^{a, b}

Parameters	LS5-1 (163°C)		LS5-2 (163°C)		LS5-3 (163°C)	
	r	l^d	r	l^d	r	l^d
Dimer						
< Ga-Br >	2.334 (0.005)		2.343 (0.005)		2.356 (0.005)	
Δ Ga-Br	0.186 (0.007)		0.195 (0.007)		0.183 (0.009)	
$\angle \text{Br}_5\text{GaBr}_8$	90.2 (4.6)		90.3 (3.2)		91.6 (2.9)	
$\angle \text{Br}_3\text{Ga}_2\text{Br}_4$	121.6 (4.8)		127.4 (7.8)		122.5 (22.8)	
D-M	--		0.0		0.04	
δ^e	25.0		25.0		25.0	
$\text{Ga}_2\text{-Br}_3$ (4) ^c	2.241 (0.004)	0.053	2.245 (0.003)	0.051	2.265 (0.004)	0.049
		(0.005)		(0.004)		(0.004)
$\text{Ga}_2\text{-Br}_5$ (4)	2.427 (0.008)	0.087	2.440 (0.008)	0.085	2.448 (0.009)	0.083
$\text{Br}_5\cdots\text{Br}_8$ (1)	3.439 (0.141)	0.144	3.459 (0.096)	0.121	3.509 (0.085)	0.1208
$\text{Ga}_1\cdots\text{Ga}_2$ (1)	3.358 (0.131)	0.100	3.375 (0.099)	0.100	3.348 (0.090)	0.1208
$\text{Br}_3\cdots\text{Br}_4$ (2)	3.913 (0.090)	0.114	4.025 (0.135)	0.086	3.971 (0.432)	0.209
$\text{Br}_5\cdots\text{Br}_3$ (8)	3.829 (0.035)	0.168	3.798 (0.052)	0.137	3.853 (0.171)	0.094
$\text{Ga}_1\cdots\text{Br}_3$ (4)	4.841 (0.119)	0.270	4.790 (0.065)	0.200	4.839 (0.260)	0.194
$\text{Br}_3\cdots\text{Br}_7$ (2)	5.502 (0.200)	0.261	5.327 (0.200)	0.180	5.485 (0.760)	0.244
$\text{Br}_3\cdots\text{Br}_6$ (2)	6.708 (0.140)	0.231	6.630 (0.088)	0.150	6.727 (0.370)	0.214
		(0.266)				(0.169)
Monomer						
$\text{Ga}_9\text{-Br}_{10}$ (3)	--		2.245 (0.003)	0.051	2.225 (0.004)	
$\text{Br}_{10}\text{-Br}_{11}$ (3)	--		3.889 (0.005)	0.121	3.820 (0.133)	
$\angle \text{Br}_{11}\text{Ga}_9\text{Br}_{10}$	--		120.0		118.3 (6.7)	
% Dimer	100.0		49.8 (4.3)		44.5 (5.0)	
R^f	0.289 ^g		0.182 ^g		0.193 ⁱ	

Continued

Table 14 (cont.) . Ga_2Br_6 - GaBr_3 . Structural results from least-squares refinements. ^{a, b}

Parameters	LS5-4 (163°C) *			LS5-5 (192°C)*			LS5-6 (226°C)*		
	r	1 ^d		r	1 ^d		r	1 ^d	
Dimer									
< Ga-Br >	2.345 (0.005)			2.346 (0.010)			2.346 (0.033)		
Δ Ga-Br	0.201 (0.008)			0.200 (0.018)			0.206 (0.064)		
$\angle \text{Br}_5\text{Ga}_2\text{Br}_8$	91.1 (2.2)			89.1 (9.6)			88.5 (17.4)		
$\angle \text{Br}_3\text{Ga}_2\text{Br}_4$	128.1 (3.0)			128.8 (5.7)			137.6 (16.8)		
δ^e	25.0			25.0			25.0		
$\text{Ga}_2\text{-Br}_3$ (4) ^c	2.245 (0.003)	0.052	(0.004)	2.246 (0.003)	0.051	(0.004)	2.243 (0.003)	0.050	(0.005)
$\text{Ga}_2\text{-Br}_5$ (4)	2.446 (0.009)	0.087		2.446 (0.019)	0.085		2.450 (0.065)	0.084	
$\text{Br}_5\cdots\text{Br}_8$ (1)	3.492 (0.069)	0.120		3.431 (0.292)	0.121		3.418 (0.540)	0.126	
$\text{Ga}_1\cdots\text{Ga}_2$ (1)	3.358 (0.067)	0.120	(0.040)	3.420 (0.284)	0.121		3.441 (0.516)	0.126	
$\text{Br}_3\cdots\text{Br}_4$ (2)	4.038 (0.052)	0.084	(0.042)	4.053 (0.096)	0.110	(0.023)	4.183 (0.236)	0.122	(0.017)
$\text{Br}_5\cdots\text{Br}_3$ (8)	3.793 (0.021)	0.126	(0.026)	3.796 (0.038)	0.143		3.725 (0.129)	0.150	
$\text{Ga}_1\cdots\text{Br}_3$ (4)	4.765 (0.052)	0.200	(0.180)	4.813 (0.223)	0.204		4.718 (0.415)	0.210	
$\text{Br}_3\cdots\text{Br}_7$ (2)	5.284 (0.089)	0.250		5.321 (0.230)	0.260		5.031 (0.590)	0.273	
$\text{Br}_3\cdots\text{Br}_6$ (2)	6.603 (0.050)	0.220		6.641 (0.180)	0.230		6.492 (0.380)	0.243	
Monomer									
$\text{Ga}_9\text{-Br}_{10}$ (3)	2.245 (0.003)	0.052	(0.004)	2.246 (0.003)	0.051	(0.004)	2.243 (0.003)	0.050	(0.005)
$\text{Br}_{10}\cdots\text{Br}_{11}$ (3)	3.912 (0.031)	0.084	(0.040)	3.890 (0.021)	0.110	(0.023)	3.887 (0.024)	0.122	(0.017)
$\angle \text{Br}_{10}\text{Ga}_9\text{Br}_{11}$	121.2 (1.6)			119.9 (1.1)			120.0 (1.2)		
% dimer	47.4 (5.1)			25.5 (5.4)			7.6 (5.7)		
R ^f	0.115 ⁱ			0.130 ⁱ			0.139 ⁱ		

Table 14--Footnotes.

* Best model.

- a Distances (r) and root-mean-square amplitudes (l) in Ångstroms; angles in degrees.
- b Parenthesized values indicated are 2σ and include estimates of systematic error, otherwise the values are held constant during the refinement.
- c Parenthesized values are the multiplicities of the different distances.
- d Bracketed quantities were refined, with constant differences as a group.
- e Root-mean-square amplitude of bending motion, in degree.
- f $R = [\sum W_i \Delta_i^2 / (\sum W_i I_i^2(\text{obs}))]^{1/2}$ where $\Delta_i = I_i(\text{obs}) - I_i(\text{cal})$.
- g Value obtained from refinement on individual plates.
- h Value obtained from refinement on composite curves.
- i Value obtained from refinement on average curves.

Table 15. $\text{Ga}_2\text{Br}_6\text{-GaBr}_3$. Correlation matrix from LS5-4,^a

<Ga-Br> ΔGaBr		∠5, 2, 8	∠3, 2, 4	∠10, 9, 11	l ₂₃	l ₃₄	l ₃₅	l ₃₇	α _D	r ₂₃	r ₂₅	r ₃₅	r ₁₃	r _{10, 11}	
σ ^b	0.0017	0.0030	0.792	1.071	0.562	0.0008	0.0148	0.0088	0.0635	0.0182	0.0006	0.0032	0.0072	0.0183	0.0108
	1.000	0.935	0.072	0.183	0.071	0.426	-0.054	-0.075	0.004	0.047	0.482	0.986	0.141	0.009	0.119
		1.000	0.041	0.188	0.088	0.476	-0.050	-0.054	0.003	0.083	0.140	0.981	0.125	0.033	0.102
			1.000	-0.534	-0.190	-0.039	0.370	0.281	-0.019	-0.131	0.101	0.058	0.225	-0.799	-0.180
				1.000	0.505	0.150	-0.913	-0.747	-0.022	-0.060	0.046	0.188	-0.881	-0.046	0.508
					1.000	-0.003	-0.446	-0.834	-0.029	-0.194	-0.200	0.081	-0.488	-0.123	0.995
						1.000	-0.019	0.070	0.022	0.141	0.016	0.457	0.006	0.039	-0.002
							1.000	0.758	0.032	-0.022	-0.027	-0.053	0.900	0.210	-0.448
								1.000	0.042	0.221	-0.076	-0.066	0.734	0.192	-0.839
									1.000	0.058	0.003	0.004	0.036	0.040	-0.029
										1.000	-0.074	0.065	0.147	0.215	-0.201
											1.000	0.327	0.086	-0.058	0.079
											1.000	0.136	0.021	0.113	
												1.000	0.405	-0.478	
													1.000	-0.129	
														1.000	

Continued

Table 15 (cont.). $\text{Ga}_2\text{Br}_6\text{-GaBr}_3$. Correlation matrix from LS5-5.^a

$\langle \text{Ga-Br} \rangle$	ΔGaBr	$\angle 8, 1, 5$	$\angle 3, 2, 4$	$\angle 10, 9, 11$	l_{23}	l_{67}	α_D	r_{23}	r_{25}	r_{34}	r_{35}	r_{13}	$r_{10, 11}$
σ^b 0.003	0.006	3.40	2.02	0.385	0.001	0.008	0.019	0.0007	0.0065	0.0340	0.0135	0.0803	0.0074
1.000	0.980	-0.051	0.171	-0.038	0.522	0.085	0.121	0.450	0.995	0.187	0.258	0.113	0.035
	1.000	-0.054	0.178	0.004	0.541	0.079	0.138	0.265	0.995	0.188	0.243	0.113	0.047
		1.000	-0.619	-0.263	-0.064	0.121	-0.055	-0.004	-0.053	-0.618	-0.232	-0.967	-0.269
			1.000	0.596	0.242	-0.670	0.124	0.027	0.175	0.999	-0.549	0.418	0.612
				1.000	0.170	-0.436	0.189	-0.201	-0.018	0.587	-0.487	0.112	0.987
					1.000	0.011	0.207	0.103	0.534	0.245	-0.015	0.055	0.190
						1.000	-0.198	0.056	0.082	-0.667	0.734	0.082	-0.435
							1.000	-0.036	0.130	0.123	-0.048	0.038	0.187
								1.000	0.363	0.064	0.157	0.042	-0.041
									1.000	0.188	0.252	0.114	0.041
										1.000	-0.542	0.419	0.610
											1.000	0.472	-0.470
												1.000	0.121
													1.000

Continued

Table 15 (cont.). $\text{Ga}_2\text{Br}_6\text{-GaBr}_3$. Correlation matrix from LS5-6.^a

$\langle \text{Ga-Br} \rangle$	$\Delta \text{Ga-Br}$	$\angle 5, 2, 8$	$\angle 3, 2, 4$	$\angle 10, 9, 11$	l_{23}	l_{34}	α_D	r_{23}	r_{25}	r_{34}	r_{35}	r_{13}	$r_{10, 11}$
σ^b 0.0116	0.0226	6.157	5.932	0.425	0.0013	0.0058	0.020	0.0008	0.0229	0.0833	0.0455	0.1487	0.0082
1.000	0.998	0.034	0.205	0.091	0.556	0.112	0.203	0.400	1.000	0.211	0.169	0.053	0.155
	1.000	0.034	0.205	0.101	0.559	0.112	0.205	0.344	1.000	0.210	0.169	0.052	0.157
		1.000	-0.428	-0.464	0.032	0.096	0.088	0.010	0.034	-0.427	0.053	-0.880	-0.465
			1.000	0.526	0.188	-0.492	-0.057	0.078	0.205	1.000	-0.849	-0.016	0.542
				1.000	0.163	-0.318	0.244	-0.122	0.096	0.523	-0.348	0.255	0.987
					1.000	0.098	0.311	0.170	0.558	0.191	0.006	-0.024	0.191
						1.000	-0.213	0.049	0.112	-0.490	0.556	0.178	-0.312
							1.000	0.036	0.204	-0.057	0.110	-0.027	0.251
								1.000	0.373	0.095	0.073	0.024	0.036
									1.000	0.211	0.169	0.052	0.156
										1.000	-0.847	-0.015	0.542
											1.000	0.428	-0.339
												1.000	0.261
													1.000

^a Distances (r) and root-mean-square amplitudes (l) in Angstroms, angles in degrees.

^b Standard deviations from least squares.

Table 16. Comparison of geometrical parameter values for aluminum halides.^a

	This work	Akishin et al. ^b	Elliott and Palmer ^c
Al-Cl _t	2.065 (0.002)	2.04 (0.02)	2.06 (0.04)
Al-Cl _b	2.252 (0.004)	2.24 (0.02)	2.21 (0.04)
Al ₂ Cl ₆ ∠Cl _b Al Cl _b	91.0 (0.5)	87.0 (3.0)	79.5
∠Cl _t Al Cl _t	123.4 (1.6)	122.0 (3.0)	117.0
δ	23.4 (6.0)	--	--
Al-Br _t	2.222 (0.005)	2.22 (0.02)	2.21 (0.04)
Al-Br _b	2.414 (0.007)	2.38 (0.02)	2.33 (0.04)
Al ₂ Br ₆ ∠Br _b Al Br _b	92.3 (0.9)	82.0 (3.0)	87.0
∠Br _t Al Br _t	122.8 (3.3)	118.0 (3.0)	114.0
δ	23.3 (14.0)	--	--
Al-I _t	2.449 (0.017)		2.53 (0.04)
Al-I _b	2.634 (0.03)		2.58 (0.04)
Al ₂ I ₆ ∠I _b Al I _b	99.6 (4.5)		68.5
∠I _t Al I _t	115.0 (7.4)		112.0
δ	25		--

^a Distances in Angstroms, angles and δ in degrees. Parenthesized values are error estimates (2σ).^b Ref. (3).^c Ref. (38).

Table 17. Comparison of geometrical parameter values for aluminum halide dimers and related compounds.^a

	Al_2Cl_6^b	Al_2Br_6^b	Al_2I_6^b	Al_2Me_6^c	$\text{Al}_2\text{Me}_4\text{H}_2^d$
$\text{Al}-\text{X}_t$	2.065 (0.002)	2.222 (0.005)	2.449 (0.017)	1.957 (0.003)	1.947 (0.003)
$\text{Al}-\text{X}_b$	2.252 (0.004)	2.414 (0.007)	2.634 (0.029)	2.140 (0.004)	1.676 (0.019)
$\angle \text{X}_b\text{AlX}_b$	91.0 (0.5)	92.3 (0.9)	99.6 (4.5)	104.5 (3.0)	77.4 (1.6)
$\angle \text{X}_t\text{AlX}_t$	123.4 (1.6)	122.8 (3.3)	115.0 (7.4)	117.3 (1.5)	118.5 (0.9)
$\text{Al}\dots\text{Al}$	3.102 (0.036)	3.288 (0.078)	3.335 (0.180)	2.619 (0.005)	2.617 (0.006)
δ	23.4 (6.0)	23.3 (14.0)	25.0	--	--
Method	ED	ED	ED	ED	ED

^a Distances in Angstroms, and angles in degrees, errors in 2σ .

^b This work.

^c Ref. (1), error estimates are standard deviations.

^d Ref. (2), error estimates are standard deviations.

Table 18. Comparison of structural parameter values for gallium halide dimers.^a

	Ga_2Cl_6		Ga_2Br_6	
	This work	Akishin <i>et al.</i> ^b	This work	Akishin <i>et al.</i> ^b
Ga-X_t	2.099 (0.002)	2.09 (0.02)	2.245 (0.003)	2.25 (0.02)
Ga-X_b	2.300 (0.002)	2.29 (0.02)	2.446 (0.009)	2.35 (0.02)
$\angle \text{X}_b \text{GaX}_b$	88.3 (0.8)	89.0 (3.0)	91.1 (2.2)	87.0 (3.0)
$\angle \text{X}_t \text{GaX}_t$	124.6 (1.8)	112.0 (3.0)	128.1 (3.2)	110.0 (3.0)
δ^c	20.5 (3.3)	--	25.0	--
r_{23}	2.099 (0.002)	2.09	2.245 (0.003)	2.25
r_{25}	2.300 (0.003)	2.29	2.446 (0.009)	2.35
r_{58}	3.205 (0.023)	3.21	3.492 (0.069)	3.23
r_{34}	3.717 (0.031)	3.51	4.038 (0.052)	3.68
r_{12}	3.256 (0.022)	3.28	3.358 (0.067)	3.41
r_{35}	3.594 (0.013)	3.66	3.793 (0.021)	3.88
r_{13}	4.609 (0.038)	4.75	4.765 (0.052)	5.05
r_{37}	5.154 (0.099)	5.56	5.284 (0.089)	5.99
r_{36}	6.350 (0.019)	6.57	6.603 (0.050)	7.04
l_{23}	0.052	0.049	0.052	0.054
l_{25}	0.085	0.049	0.087	0.054
l_{58}	0.091 (0.014)	0.066	0.121	0.080
l_{34}	0.110 (0.021)	0.076	0.084 (.004)	0.080
l_{12}	0.091 (0.014)	0.076	0.121	0.080
l_{35}	0.138 (0.011)	0.076	0.126 (0.026)	0.080
l_{13}	0.154	0.116	0.200	0.111
l_{37}	0.189	0.090	0.250	0.120
l_{36}	0.159	0.097	0.220	0.128

^a Distances (r) and root-mean-square amplitudes (l) in Angstroms, angles in degrees. Parenthesized values for this work are 2σ , otherwise, the values are held in constant during the refinement. Bracketed values were refined, with constant differences as a group.

^b Ref (4), error in distances (r) is 0.5-1.0%.

^c Root-mean-square amplitude of bending motion, in degree.

Table 19. Comparison of structural parameter values for AlI_3 and GaBr_3 .^{a, b}

		This work	Akiskin et al. ^c
AlI_3	$r_{\text{Al-I}}$	2.449 (0.013)	2.44 (0.02)
	$\angle \text{IAlI}$	120.1 (4.0)	120.0 (assumed)
	$r_{\text{I...I}}$	4.245 (0.068)	
	$l_{\text{Al-I}}$	0.069 (0.022)	
	$l_{\text{I...I}}$	0.124 (0.055)	
GaBr_3	$r_{\text{Ga-Br}}$	2.243 (0.04)	
	$\angle \text{BrGaBr}$	120.0 (1.2)	
	$r_{\text{Br...Br}}$	3.887 (0.024)	
	$l_{\text{Ga-Br}}$	0.050 (0.005)	
	$l_{\text{Br...Br}}$	0.122 (0.017)	

^a Distances (r) and root-mean-square amplitudes (l) in Angstroms; angles in degrees.

^b Parenthesized values are error estimated (2σ).

^c Ref. (3).

Table 20. Bond numbers for group III halides and related compounds. ^a

Compounds	D(1)	$\bar{n}_{M-X_t}$	$\bar{n}_{M-X_b}$	$\bar{n}_{M-X_b} / \bar{n}_{M-X_t}$	$\bar{n}_{total}$
Al_2Cl_6	2.135	1.255 (0.01)	0.638 (0.005)	0.508	7.57 (0.06)
Al_2Br_6	2.301	1.292 (0.02)	0.648 (0.020)	0.502	7.76 (0.16)
Al_2I_6	2.515	1.239 (0.04)	0.633 (0.040)	0.511	7.49 (0.30)
Ga_2Cl_6	2.143	1.153 (0.01)	0.547 (0.005)	0.474	6.80 (0.06)
Ga_2Br_6	2.309	1.231 (0.01)	0.591 (0.007)	0.480	7.29 (0.07)
$Al_2Me_6^b$	1.955	1.000 (0.01)	0.495 (0.007)	0.495	5.98 (0.40)
$Al_2Me_4H_2^c$	1.955	1.003 (0.01)	0.711 (0.050)	0.566	6.97 (0.25)

^a Parenthesized values indicated are 2σ .

^b Ref. (1).

^c Ref. (2).

Table 21. N_2O_4 - NO_2 . Experimental data for electron-diffraction photographs used in the structure analyses of N_2O_4 - NO_2 mixtures.

Plate identification	Plate size (in)	Accelerating voltage (volts)	Electron wave length ($\text{\AA}$) ^a	Beam current (μa)	Exposure time (min)	Bath temperature ($^{\circ}\text{C}$)	Nozzle Temperature ($^{\circ}\text{C}$)	Run in pressure (Torr)	Camera height (mm)	s range
2-143-9	8x10	43773	0.057401	0.44	1.75	-36.0	104	3.4×10^{-6}	749.838	1.00-12.75
2-143-10	8x10	43766	0.057405	0.44	1.75	-35.5	105	3.8×10^{-6}	749.838	1.00-12.75
2-142-6	8x10	43783	0.057394	0.42	4.50	-38.0	104	5.5×10^{-6}	300.273	8.00-30.00
2-142-8	8x10	43787	0.057391	0.42	4.50	-35.0	104	6.2×10^{-6}	300.273	8.00-30.00
2-143-6	8x10	43715	0.057440	0.40	1.50	-39.5	25.0	2.8×10^{-6}	749.838	2.00-13.00
2-143-7	8x10	43719	0.057437	0.40	1.75	-39.0	26.0	3.6×10^{-6}	749.838	2.00-12.75
2-142-9	8x10	43809	0.057376	0.42	4.50	-39.0	25.5	5.0×10^{-6}	300.273	8.00-31.00
2-142-11	8x10	43821	0.057368	0.42	4.50	-40.0	23.5	4.0×10^{-6}	300.273	8.00-31.00
2-143-4	8x10	43806	0.057378	0.40	1.75	-44.0	2.0	2.4×10^{-6}	749.838	2.00-12.75
2-143-5	8x10	43808	0.057377	0.40	2.00	-44.0	2.0	2.5×10^{-6}	749.838	2.00-12.75
2-142-4	8x10	43832	0.057360	0.40	4.50	-43.5	2.0	3.5×10^{-6}	300.273	8.00-31.50
2-142-5	8x10	43825	0.057365	0.40	4.50	-42.0	2.0	3.8×10^{-6}	300.273	8.00-31.50
2-143-1	8x10	43794	0.057386	0.38	1.25	-43.0	-25.0	3.2×10^{-6}	749.838	2.00-12.75
2-143-2	8x10	43794	0.057386	0.38	1.50	-43.0	-25.0	3.2×10^{-6}	749.838	2.00-12.75
2-142-1	8x10	43797	0.057384	0.40	4.00	-43.0	-25.0	5.4×10^{-6}	300.273	8.00-31.25
2-142-2	8x10	43797	0.057382	0.40	4.00	-42.0	-25.0	5.0×10^{-6}	300.273	8.00-31.25
2-148-8	8x10	43735	0.057427	0.40	1.50	-43.0	-35.0	3.5×10^{-6}	749.758	2.00-12.50
2-148-9	8x10	43732	0.057429	0.40	1.50	-43.0	-35.0	3.5×10^{-6}	749.758	2.00-12.75
2-149-8	8x10	43766	0.057405	0.40	4.50	-44.0	-35.0	3.0×10^{-6}	299.756	8.00-30.75
2-149-9	8x10	43771	0.057402	0.40	5.00	-48.0	-35.0	2.0×10^{-6}	299.756	8.00-30.75
2-148-2	8x10	43769	0.057403	0.39	1.50	-44.0	-12.0	2.9×10^{-6}	749.758	2.00-12.50
2-148-3	8x10	43764	0.057407	0.39	1.50	-44.0	-11.5	2.9×10^{-6}	749.758	2.00-12.50
2-149-4	8x10	43764	0.057407	0.40	4.50	-45.0	-13.0	2.8×10^{-6}	299.756	8.00-31.00
2-149-5	8x10	43757	0.057412	0.40	4.75	-45.0	-13.0	2.6×10^{-6}	299.756	8.00-31.00

Continued

Table 21 (cont.). N_2O_4 - NO_2 . Experimental data for electron-diffraction photographs used in the structure analyses of N_2O_4 - NO_2 mixtures.

Plate identification	Plate size (in)	Accelerating voltage (volts)	Electron wave ^a length (Å)	Beam current (μa)	Exposure time (min)	Bath temperature (°C)	Nozzle temperature (°C)	Run in pressure (Torr)	Camera height (mm)	s range
2-148-6	8x10	43712	0.057442	0.32	1.25	-35.5	-12.0	5.2×10^{-6}	749.758	2.00-12.25
2-148-7	8x10	43714	0.057441	0.32	1.25	-35.5	-12.0	4.8×10^{-6}	749.758	2.00-12.50
2-149-2	8x10	43744	0.057421	0.40	4.00	-36.0	-12.0	4.5×10^{-6}	299.756	8.00-30.50
2-149-3	8x10	43748	0.057418	0.40	4.25	-36.0	-12.0	3.9×10^{-6}	299.756	8.00-30.75
2-148-4	8x10	43772	0.057401	0.36	0.50	-26.5	-12.0	7.0×10^{-6}	749.758	2.00-12.25
2-148-5	8x10	43778	0.057397	0.36	0.50	-26.5	-11.5	7.0×10^{-6}	749.758	2.00-12.25
2-149-6	8x10	43759	0.057410	0.44	3.00	-26.5	-12.0	4.0×10^{-6}	299.756	8.00-30.50
2-149-7	8x10	43764	0.057407	0.44	3.50	-26.5	-12.0	3.8×10^{-6}	299.756	8.00-30.50

^a The wavelengths were calculated from the accelerating voltage which was calibrated against gaseous CO_2 using $r_a(\text{C-O}) = 1.1642 \text{ Å}$ and $r_a(0 \dots 0) = 2.3244 \text{ Å}$. See ref (41) for details.

Table 22. N_2O_4 - NO_2 . Structural results from least-squares refinements. ^a, ^b, ^c

Nozzle temp. (°C)	104	25	2	-12	-25	-35	-12	-12
Bath temp. (°C)	-38	-40	-43	-43	-43	-43	-26	-36
% dimer	100	4.5 (0.7)	30.3 (1.7)	49.7 (2.6)	68.2 (1.8)	76.3 (2.9)	71.6 (2.0)	61.5 (2.5)
Monomer								
$\text{N}_7\text{-O}_8$	1.199 (.001)	1.1980 (.0015)	1.1986	1.1986	1.1986	1.1986	1.1986	1.1986
$\angle\text{O}_9\text{N}_7\text{O}_8$	134.0 (.5)	133.9 (.5)	134.0	134.0	134.0	134.0	134.0	134.0
l_{78}	0.0416 (.0021)	0.046 (.002)	0.043 (.002)	0.046 (.002)	0.042 (.002)	0.044 (.002)	0.038 (.002)	0.038 (.002)
l_{89}	0.0530 (.0037)	0.057 (.004)	0.055 (.004)	0.055 (.005)	0.052 (.003)	0.050 (.003)	0.047 (.003)	0.048 (.003)
Dimer								
$\angle\text{O}_3\text{N}_2\text{O}_4$		134.5	134.4 (.9)	134.5 (.8)	134.7 (.3)	134.8 (.4)	134.3 (.3)	134.1 (.4)
$\text{N}_1\text{-N}_2$		1.773	1.772 (.011)	1.773 (.011)	1.775 (.004)	1.774 (.005)	1.771 (.004)	1.767 (.006)
$\text{N}_2\text{-O}_3$		1.192	1.191 (.002)	1.194 (.002)	1.193 (.001)	1.191 (.002)	1.192 (.001)	1.193 (.002)
$\text{O}_3\cdots\text{O}_4$		2.196	2.195 (.007)	2.201 (.006)	2.202 (.003)	2.199 (.004)	2.197 (.003)	2.197 (.004)
$\text{N}_1\cdots\text{O}_3$		2.489	2.489 (.008)	2.491 (.008)	2.491 (.004)	2.488 (.005)	2.489 (.004)	2.488 (.005)
$\text{O}_3\cdots\text{O}_6$		2.695	2.696 (.014)	2.697 (.013)	2.694 (.005)	2.689 (.007)	2.697 (.006)	2.697 (.008)
$\text{O}_3\cdots\text{O}_5$		3.478	3.477 (.009)	3.481 (.009)	3.479 (.005)	3.473 (.005)	3.478 (.008)	3.479 (.005)
$l_{2,3}$		0.046 (.002)	0.044 (.002)	0.046 (.002)	0.042 (.002)	0.044 (.002)	0.038 (.002)	0.038 (.002)
$l_{3,4}$		0.057 (.004)	0.055 (.004)	0.055 (.004)	0.052 (.003)	0.050 (.003)	0.047 (.003)	0.048 (.003)
$l_{1,2}$		0.072	0.069 (.020)	0.087 (.021)	0.077 (.008)	0.074 (.010)	0.076 (.008)	0.073 (.011)
$l_{1,3}$		0.073	0.077 (.009)	0.085 (.010)	0.079 (.005)	0.079 (.006)	0.082 (.005)	0.079 (.006)
$l_{3,6}$		0.100	0.099 (.021)	0.102 (.019)	0.102 (.008)	0.101 (.008)	0.099 (.008)	0.099 (.012)
$l_{3,5}$		0.075	0.077 (.016)	0.080 (.015)	0.073 (.006)	0.076 (.007)	0.084 (.007)	0.083 (.010)
R^d	0.0674 ^e	0.0749 ^e	0.0766 ^e	0.0902 ^e	0.0441 ^e	0.0642 ^e	0.0453 ^e	0.0625 ^e

Table 22--Footnotes.

- a Distances (r) and root-mean-square amplitudes (l) in Angstroms, α angles in degrees.
- b Parenthesized values indicated are 2σ and include estimates of systematic error, otherwise the values are held constant during the refinement.
- c Bracketted quantities were refined, with constant differences as a group.
- d $R = [\sum W_i \Delta_i^2 / (\sum W_i I_i^2 (\text{obs}))]^{1/2}$ where $\Delta_i = I_i (\text{obs}) - I_i (\text{cal})$.
- e Values obtained from refinement on individual curves.

Table 23. N_2O_4 - NO_2 . Correlation matrix for N_2O_4 (2, -43°C).^a

r_{23}	$\angle 3, 2, 4$	r_{12}	l_{23}	l_{34}	l_{12}	l_{13}	l_{36}	l_{35}	α_D	r_{34}	r_{13}	r_{36}	r_{35}
^b σ 0.007	0.3153	0.0039	0.0005	0.0012	0.0071	0.0033	0.0073	0.0056	0.0176	0.0023	0.0027	0.0049	0.0030
1.000	-0.406	-0.364	0.019	-0.166	0.147	0.379	0.086	0.239	0.573	0.141	0.053	0.325	0.474
	1.000	0.620	0.030	0.100	0.007	-0.162	-0.085	-0.094	-0.252	0.848	-0.070	-0.784	-0.568
		1.000	-0.022	0.075	-0.081	-0.113	-0.003	-0.090	-0.191	0.461	0.726	-0.006	0.219
			1.000	-0.167	0.134	-0.034	-0.024	0.039	-0.008	0.044	-0.048	-0.053	-0.045
				1.000	-0.077	-0.286	-0.167	-0.092	-0.227	0.011	-0.015	-0.082	-0.096
					1.000	0.231	0.108	0.128	0.301	0.093	-0.081	-0.057	-0.026
						1.000	0.479	0.267	0.644	0.045	0.058	0.153	0.212
							1.000	0.124	0.181	-0.042	0.081	0.112	0.120
								1.000	0.368	0.037	0.006	0.071	0.170
									1.000	0.059	0.069	0.225	0.310
										1.000	-0.046	-0.661	-0.340
											1.000	0.674	0.824
												1.000	0.931
													1.000

Continued

Table 23 (cont.). N_2O_4 - NO_2 . Correlation matrix for N_2O_4 ($-12, -43^\circ\text{C}$).

r_{23}	$\angle 3, 2, 4$	r_{12}	l_{23}	l_{34}	l_{12}	l_{13}	l_{36}	l_{35}	α_D	r_{34}	r_{13}	r_{36}	r_{35}
σ^b 0.0006	0.2700	0.0038	0.0005	0.0014	0.0075	0.0033	0.0065	0.0051	0.0306	0.0020	0.0027	0.0043	0.0028
1.000	-0.426	-0.364	-0.015	-0.160	0.130	0.288	0.104	0.199	0.448	0.086	-0.003	0.297	0.399
	1.000	0.597	0.041	0.080	-0.029	-0.232	-0.143	-0.141	-0.323	-0.865	-0.003	-0.720	-0.486
		1.000	-0.016	0.089	-0.112	-0.122	0.012	-0.096	-0.186	0.455	0.792	0.121	0.357
			1.000	0.180	0.135	0.000	0.011	0.022	-0.073	0.037	-0.051	-0.065	-0.062
				1.000	-0.054	-0.291	-0.191	-0.106	-0.261	-0.001	0.031	-0.035	-0.043
					1.000	0.222	0.140	0.126	0.288	0.041	-0.100	-0.050	-0.043
						1.000	0.598	0.300	0.667	-0.096	0.053	0.202	0.202
							1.000	0.192	0.316	-0.100	0.130	0.193	0.190
								1.000	0.392	-0.044	0.009	0.106	0.109
									1.000	-0.107	0.061	0.272	0.282
										1.000	-0.004	-0.628	-0.313
											1.000	0.696	0.848
												1.000	0.935
													1.000

Continued

Table 23 (cont.). N_2O_4 - NO_2 . Correlation matrix for N_2O_4 (-12, -26°C).^a

r_{23}	$\angle 3, 2, 4$	r_{12}	l_{23}	l_{34}	l_{12}	l_{13}	l_{36}	l_{35}	α_D	r_{34}	r_{13}	r_{36}	r_{35}
σ^b 0.0002	0.0997	0.0015	0.0003	0.0008	0.0027	0.0014	0.0026	0.0024	0.0213	0.0008	0.0011	0.0018	0.0012
1.000	-0.404	-0.305	-0.028	-0.145	0.157	0.335	0.120	0.203	0.533	0.163	0.053	0.291	0.409
	1.000	0.499	0.085	0.067	0.034	-0.162	-0.093	-0.107	-0.253	0.837	-0.093	-0.712	-0.504
		1.000	-0.004	0.020	-0.075	-0.062	0.009	-0.057	-0.115	0.356	0.807	0.247	0.439
			1.000	0.286	0.184	-0.064	-0.045	-0.009	-0.148	0.075	-0.061	-0.098	-0.086
				1.000	-0.016	-0.315	-0.214	-0.108	-0.263	-0.015	-0.041	-0.071	-0.090
					1.000	0.184	0.096	0.099	0.257	0.131	-0.082	-0.082	-0.044
						1.000	0.562	0.278	0.648	0.026	0.080	0.159	0.198
							1.000	0.171	0.278	-0.028	0.085	0.119	0.130
								1.000	0.357	0.006	0.032	0.090	0.109
									1.000	0.046	0.106	0.234	0.296
										1.000	-0.069	-0.594	-0.299
											1.000	0.765	0.881
												1.000	0.945
													1.000

Continued

Table 23 (cont.). N_2O_4 - NO_2 . Correlation matrix for N_2O_4 (-12, -36°C).^a

r_{23}	$\angle 3, 2, 4$	r_{12}	l_{23}	l_{34}	l_{12}	l_{13}	l_{36}	l_{35}	α_D	r_{34}	r_{13}	r_{36}	r_{35}
σ^b 0.004	0.1516	0.0021	0.0004	0.0010	0.0038	0.0019	0.0039	0.0035	0.0252	0.0012	0.0016	0.0026	0.0017
1.000	-0.366	-0.298	-0.017	-0.141	0.153	0.310	0.078	0.183	0.486	0.168	0.055	0.272	0.403
	1.000	0.505	0.081	0.062	0.047	-0.137	-0.077	-0.087	-0.214	0.856	-0.118	-0.742	-0.530
		1.000	-0.010	0.015	-0.066	-0.053	0.001	-0.053	-0.098	0.370	0.787	0.198	0.404
			1.000	0.248	0.185	-0.041	-0.023	-0.004	-0.125	0.076	-0.067	-0.099	-0.088
				1.000	-0.056	-0.310	-0.191	-0.103	-0.254	-0.013	-0.045	-0.070	-0.091
					1.000	0.201	0.090	0.101	0.272	0.134	-0.082	-0.088	-0.049
						1.000	0.506	0.267	0.642	0.027	0.077	0.141	0.183
							1.000	0.147	0.214	-0.038	0.064	0.094	0.098
								1.000	0.347	0.009	0.024	0.073	0.092
									1.000	0.044	0.103	0.208	0.271
										1.000	-0.095	-0.635	-0.338
											1.000	0.754	0.878
												1.000	0.942
													1.000

Continued

Table 23 (cont.). N_2O_4 - NO_2 . Correlation matrix for N_2O_4 (-25, -43°C).^a

r_{23}	$\angle 3, 2, 4$	r_{12}	l_{23}	l_{34}	l_{12}	l_{13}	l_{36}	l_{35}	α_D	r_{34}	r_{13}	r_{36}	r_{35}
σ^b 0.0002	0.1051	0.0014	0.0003	0.0007	0.0026	0.0012	0.0026	0.0019	0.0182	0.0008	0.0010	0.0017	0.0011
1.000	-0.426	-0.363	-0.054	-0.0178	0.120	0.313	0.091	0.210	0.477	0.088	0.029	0.320	0.435
	1.000	0.600	0.060	0.041	0.001	-0.180	-0.099	-0.113	-0.294	0.863	-0.050	-0.756	-0.537
		1.000	0.002	0.038	-0.083	-0.092	0.031	-0.085	-0.175	0.458	0.759	0.064	0.293
			1.000	0.166	0.125	0.022	0.024	0.031	-0.113	0.035	-0.050	-0.076	-0.078
				1.000	-0.079	-0.286	-0.175	-0.099	-0.255	-0.054	-0.014	-0.037	-0.071
					1.000	0.229	0.125	0.132	0.280	0.068	-0.084	-0.057	-0.040
						1.000	0.538	0.282	0.638	-0.024	0.071	0.174	0.204
							1.000	0.151	0.235	-0.058	0.128	0.155	0.650
								1.000	0.379	-0.008	0.012	0.088	0.106
									1.000	-0.057	0.078	0.260	0.295
										1.000	-0.039	-0.654	-0.348
											1.000	0.691	0.840
												1.000	0.937
													1.000

Continued

Table 23 (cont.). N_2O_4 - NO_2 . Correlation matrix for N_2O_4 (-35, -43°C).^a

r_{23}	$\angle 3, 2, 4$	r_{12}	l_{23}	l_{34}	l_{12}	l_{13}	l_{36}	α_D	r_{34}	r_{13}	r_{36}	r_{35}
σ^b .0003	0.139	0.0018	0.0004	0.0010	0.0034	0.0016	0.0023	0.0291	0.0010	0.0013	0.0023	0.0015
1.000	-0.439	-0.369	-0.045	-0.175	0.153	0.376	0.221	0.550	0.147	0.055	0.337	0.473
	1.000	0.580	0.088	0.062	0.024	-0.191	-0.153	-0.306	0.824	-0.090	-0.763	-0.563
		1.000	0.009	0.036	-0.079	-0.117	-0.048	-0.178	0.407	0.747	0.077	0.275
			1.000	0.214	0.151	-0.018	-0.011	-0.144	0.068	-0.061	-0.101	-0.093
				1.000	-0.049	-0.299	-0.202	-0.276	-0.043	-0.034	-0.064	-0.096
					1.000	0.199	0.130	0.258	0.122	-0.085	-0.073	-0.036
						1.000	0.539	0.679	0.027	0.066	0.174	0.223
							1.000	0.423	-0.029	0.094	0.167	0.190
								1.000	0.010	0.107	0.281	0.345
									1.000	-0.064	-0.628	-0.322
										1.000	0.712	0.839
											1.000	0.939
												1.000

Continued

Table 23 (cont.). $\text{N}_2\text{O}_4\text{-NO}_2$. Correlation matrix for NO_2 (25, -40°C).^a

	r_{78}	$\angle 8, 7, 9$	l_{78}	l_{89}	D	r_{89}
^b						
σ 0.0003		0.1743	0.0004	0.0011	0.0071	0.0013
1.000		-0.397	-0.017	-0.076	0.266	0.035
		1.000	0.047	-0.006	-0.017	0.903
			1.000	0.197	0.045	0.043
				1.000	-0.020	0.042
					1.000	0.106
						1.000

^a Distances (r) and root-mean-square amplitudes (l) in Angstroms, angles in degrees.

^b Standard deviations from least-squares.

Table 24. N_2O_4 - NO_2 correlation matrix for NO_2 (104, -38°C).^a

r_{78}	r_{89}	l_{78}	l_{89}
σ^b 0.0003	0.0010	0.0005	0.0011
1.000	0.029	0.037	-0.022
	1.000	0.037	-0.026
		1.000	0.335
			1.000

^a Distances (r) and root-mean-square amplitudes (l) in Angstroms, angles in degrees.^b Standard deviations from least-squares.Table 25. Comparison of geometrical parameter values for NO_2 .^a

	This work	Blank	Bird
$r_{\text{N-O}}$	1.199 (0.001)	1.202 (0.0026)	1.197
$\angle\text{ONO}$	134.0 (0.5)	134.02 (1.30)	134.25
Method	ED	ED	Microwave
Ref.	--	(14)	(13)

^a Distances in Angstroms, angles in degrees.Table 26. Comparison of geometrical parameter values for N_2O_4 .^a

	This work	McClelland <i>et al.</i>
$r_{\text{N-O}}$	1.191 (0.002)	1.190 (0.0018)
$r_{\text{N-N}}$	1.774 (0.005)	1.782 (0.0083)
$\angle\text{ONO}$	134.8 (0.40)	135.4 (0.58)
Ref.	--	(36)

^a Distances (r) Angstroms, angles in degrees.

Table 27. Equilibrium constants for the N_2O_4 - NO_2 system obtained at different nozzle and bath temperatures.^a

Nozzle-tip temp. (° K)	$1/T \times 10^3$	Sample bath temp. (° K)	P_{TB} (mm Hg)	% dimer	K_P	$\ln K_P$
261	3.831	247	38.03	0.716	5.65×10^{-3}	-5.175 (0.31)
261	3.831	237	14.35	0.615	4.55×10^{-3}	-5.392 (0.34)
261	3.831	230	6.873	0.497	4.60×10^{-3}	-5.381 (0.35)
238	4.200	230	6.873	0.763	6.69×10^{-4}	-7.309 (0.30)
248	4.032	230	6.873	0.682	1.34×10^{-3}	-6.616 (0.28)
275	3.640	230	6.873	0.303	1.45×10^{-2}	-4.234 (0.20)
298	3.356	233	9.478	0.045	2.53×10^{-1}	-1.376 (0.30)

^a Parenthesized values indicated are 2σ .

Table 28. Equilibrium constants for Ga_2Br_6 - GaBr_3 system obtained at different temperatures.^a

Nozzle-tip temp (° K)	$1/T \times 10^3$	Sample bath temp. (° K)	P_{TB} (mm Hg)	% dimer	K_P	$\ln K_P$
438	2.294	419	12.19	0.474	9.36×10^{-3}	-4.671 (0.10)
465	2.151	421	13.23	0.255	3.789×10^{-2}	-3.273 (0.24)
499	2.004	429	18.21	0.076	2.692×10^{-1}	-1.312 (0.60)

^a Parenthesized values indicated are 2σ .

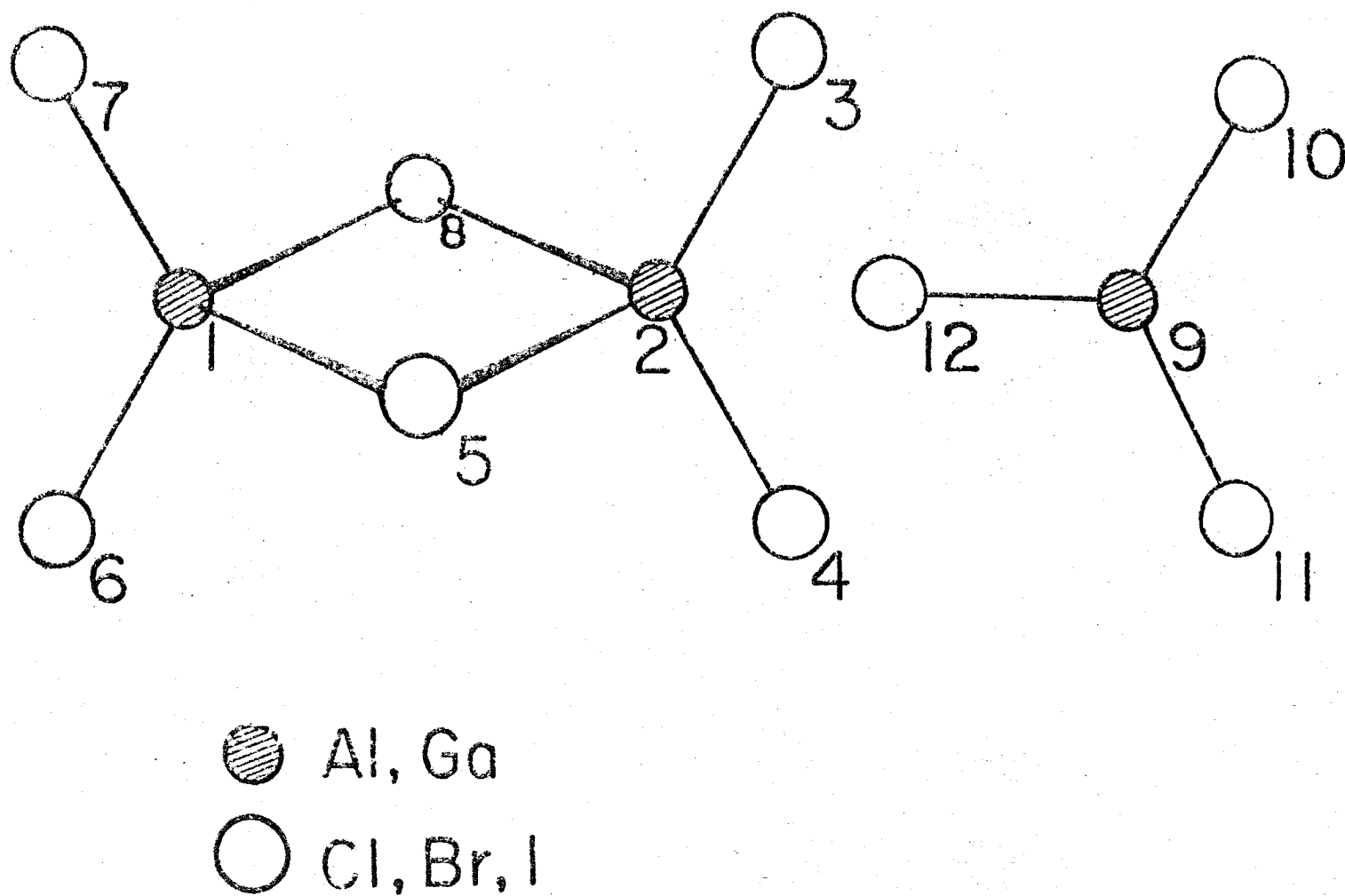


Figure 1. Configurations and atom numbering of M_2X_6 and MX_3 .

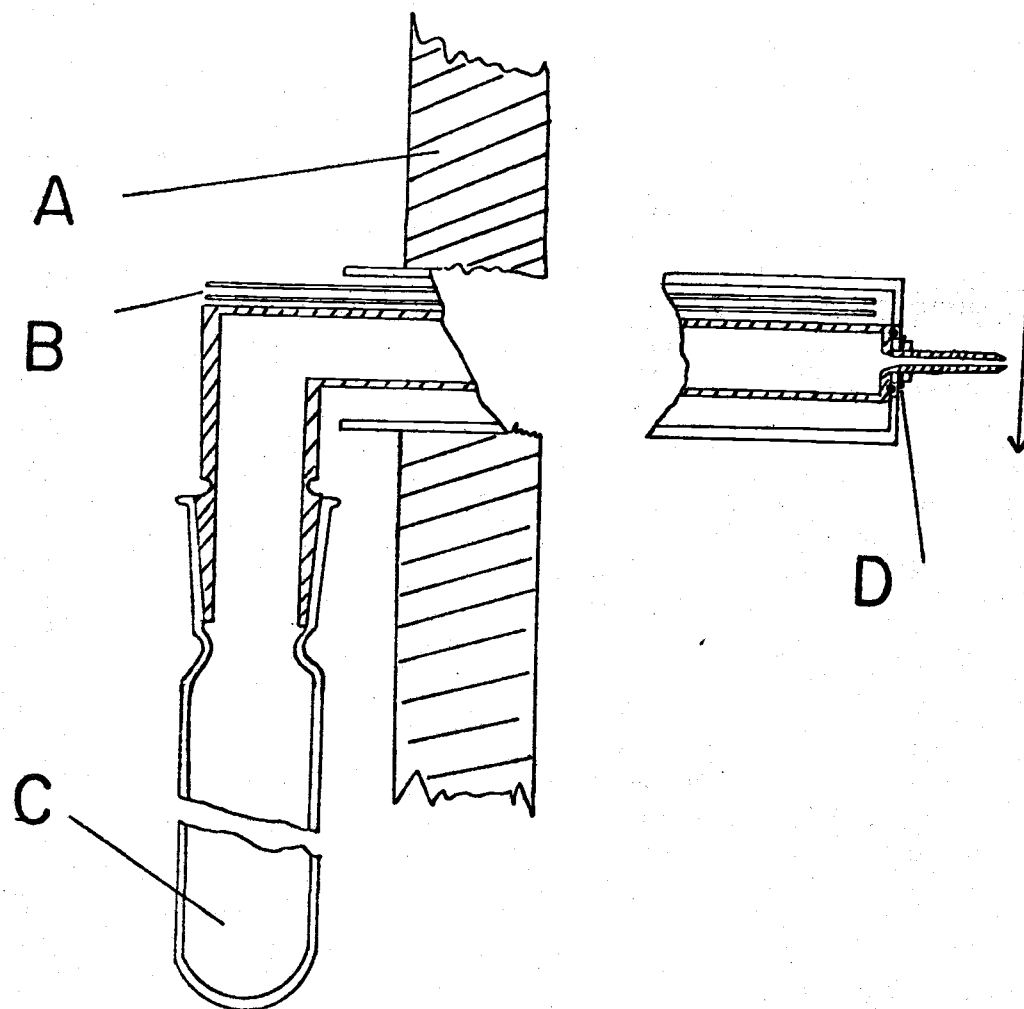


Figure 2. Cross section of standard nozzling system. A. Vacuum chamber wall. B. Heated air inlet. C. Sample container. D. Thermocouple contact.

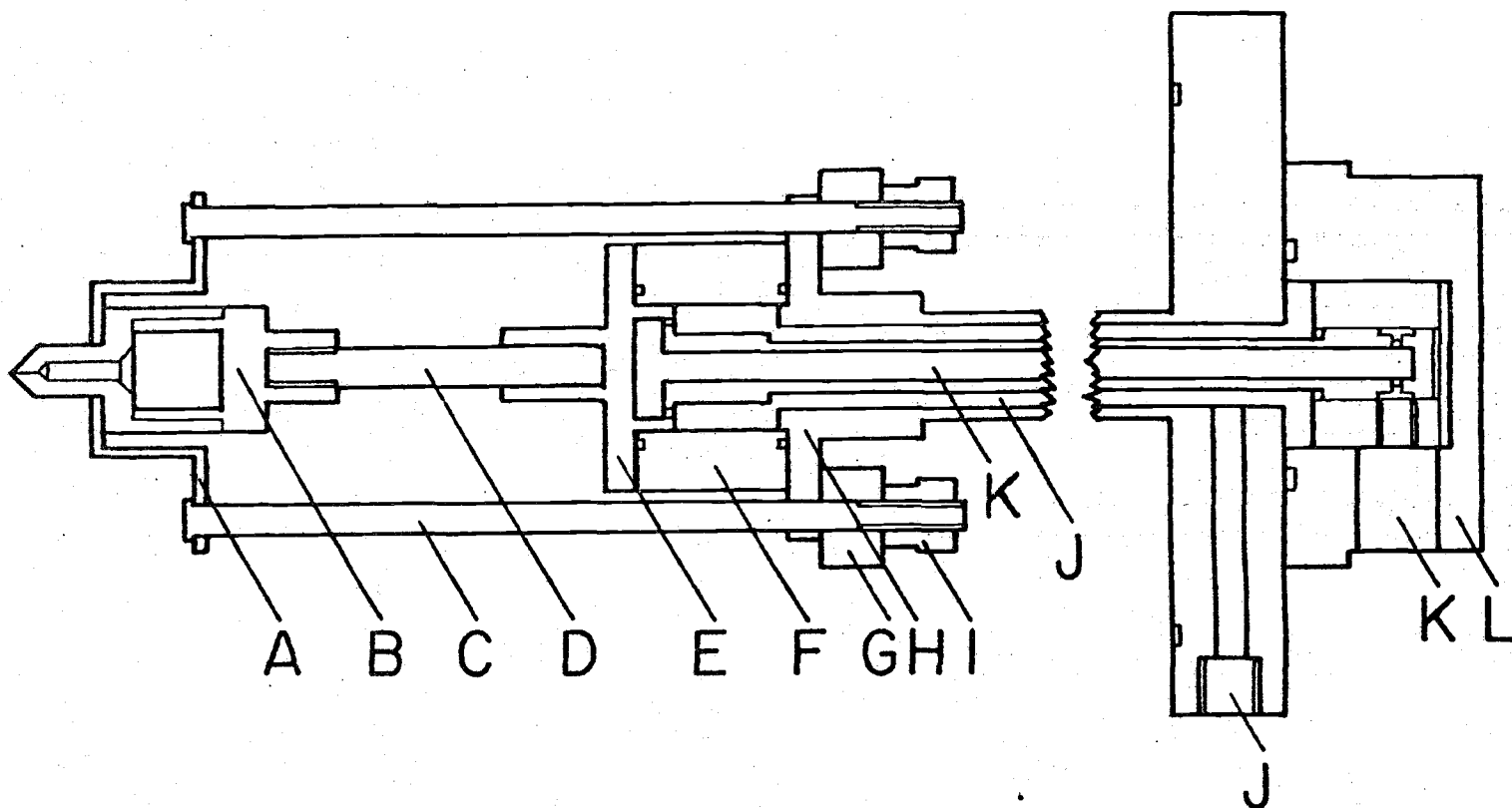


Figure 3. Cross section of high-temperature nozzle. Key for lettered parts on following page.

KEY FOR LETTERED PARTS ON HIGH-TEMPERATURE NOZZLE.*

- A. Current output collar (tantalum).
- B. High-temperature cell (graphite).
- C. Current output rods (tantalum).
- D. Connecting rod for current input (tantalum).
- E. Current input. Also serves as water inlet container (copper).
- F. Insulator between current input and output (Delrin plastic).
- G. Spacers to provide for good surface area in current output path (graphite).
- H. Current output. Also serves as water outlet container (aluminum).
- I. Nut used for tightening current output rods (stainless steel).
- J. Water outlet path. Water flows between current input (E) and current output (H).
- K. Water inlet path. Water flows inside current input (E).
- L. Current input and water inlet support block (Delrin plastic).

* All parts except for A are cylindrical cross sections.

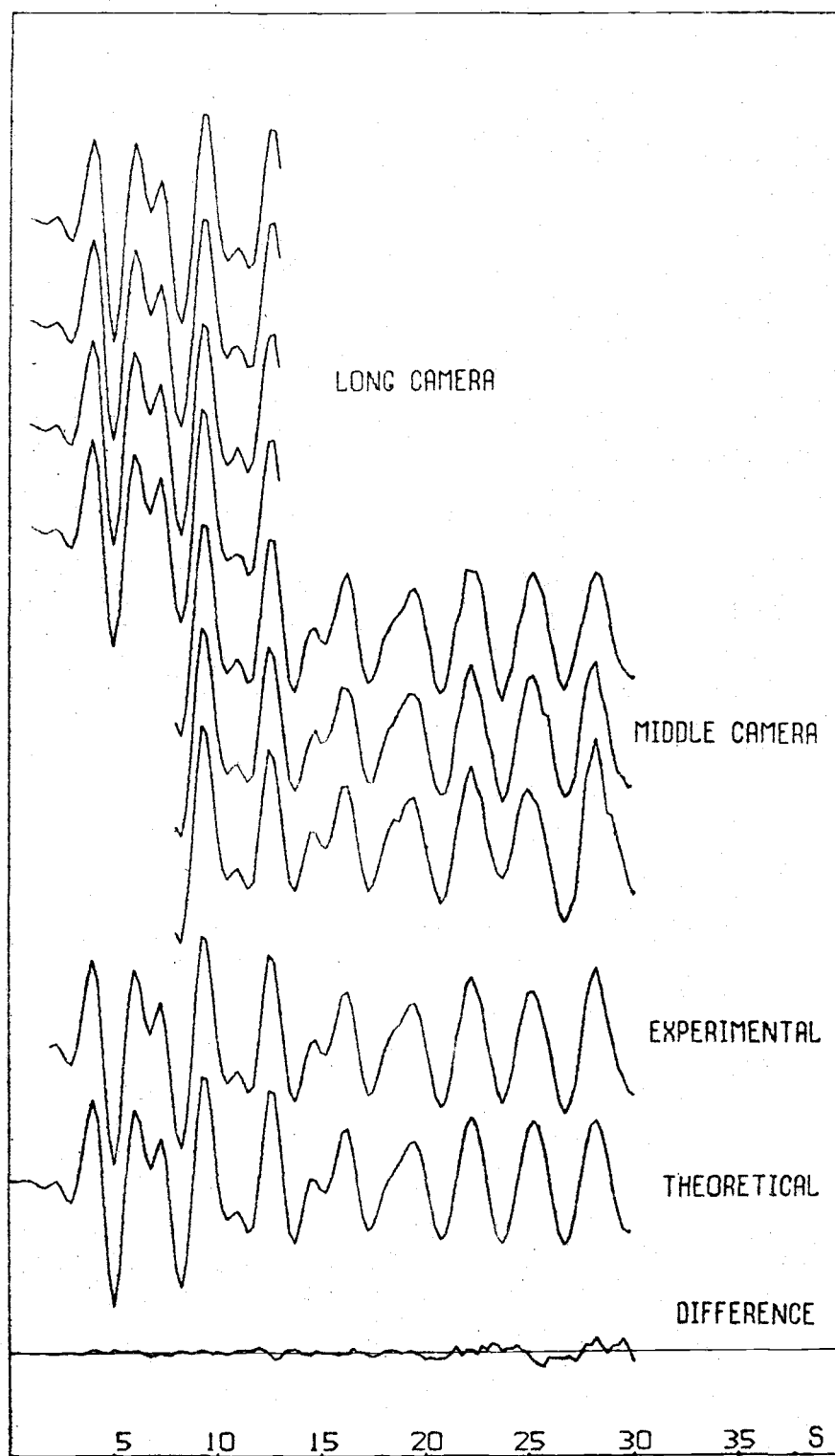


Figure 4. Al_2Cl_6 . Intensity curves ($sI_m(s)$).

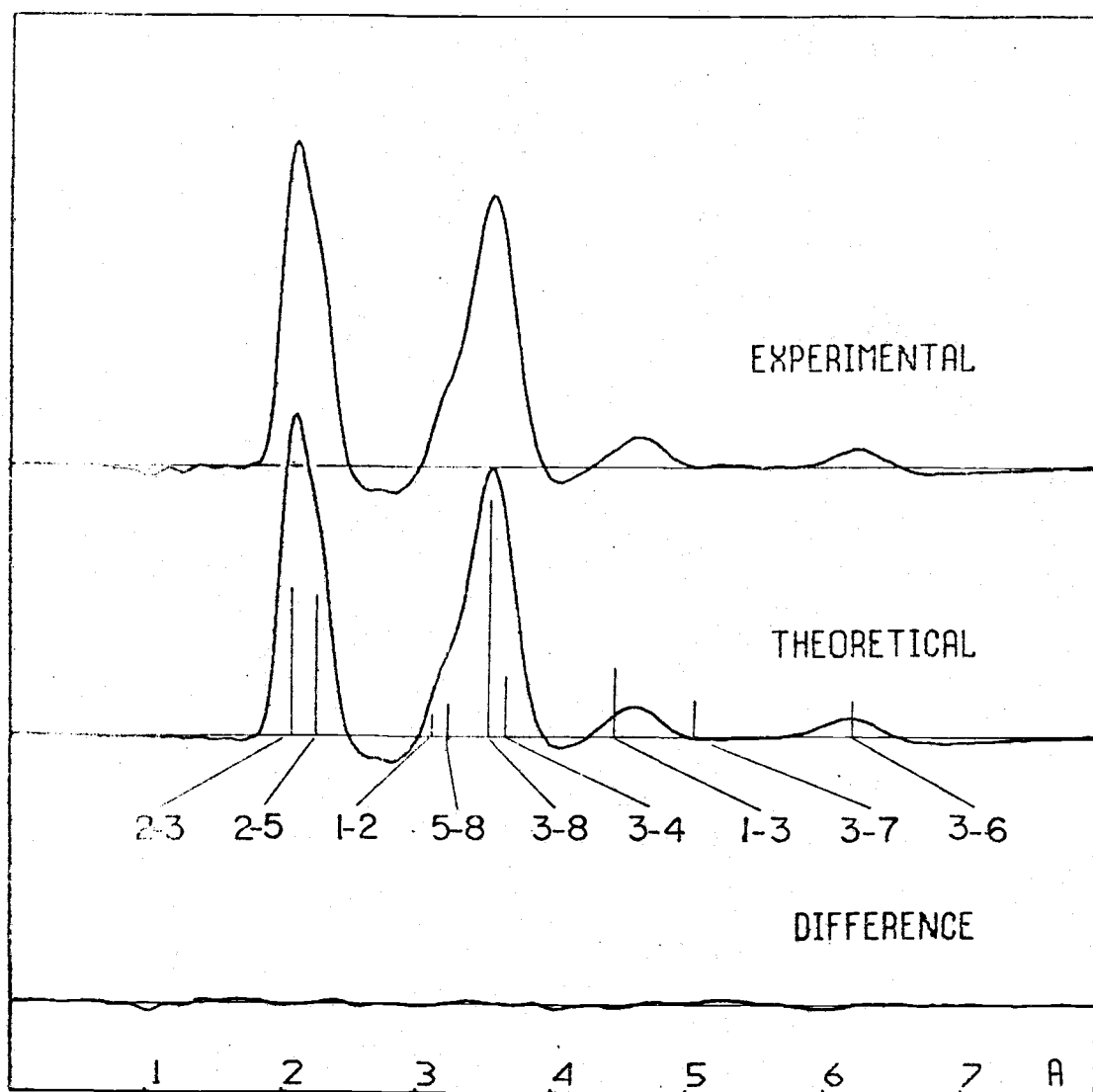


Figure 5. Al_2Cl_6 . Final radial distribution curves calculated from the composite and theoretical curves of Figure 4.
 $B = 0.0025$.

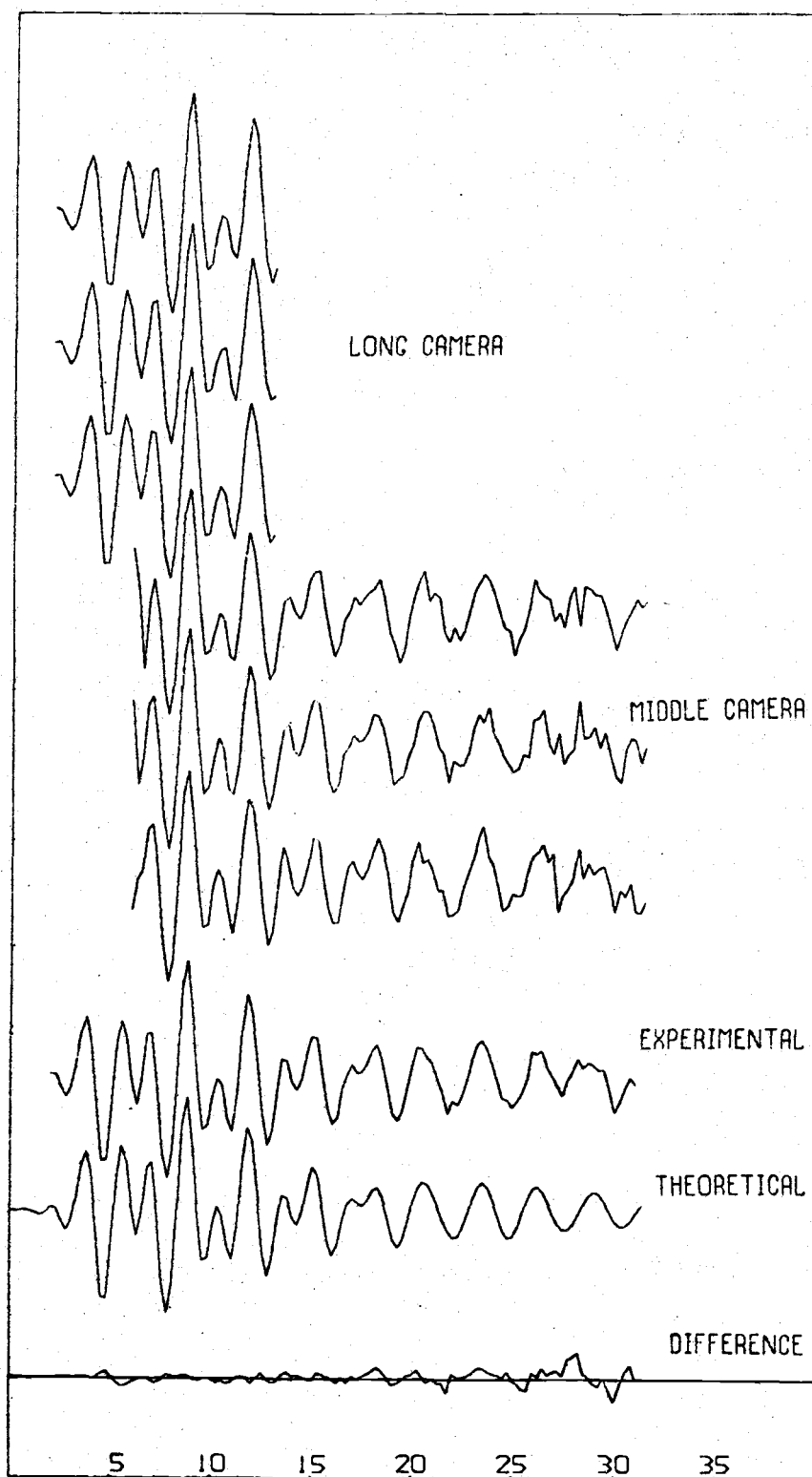


Figure 6. Al_2Br_6 . Intensity curves ($sI_m(s)$).

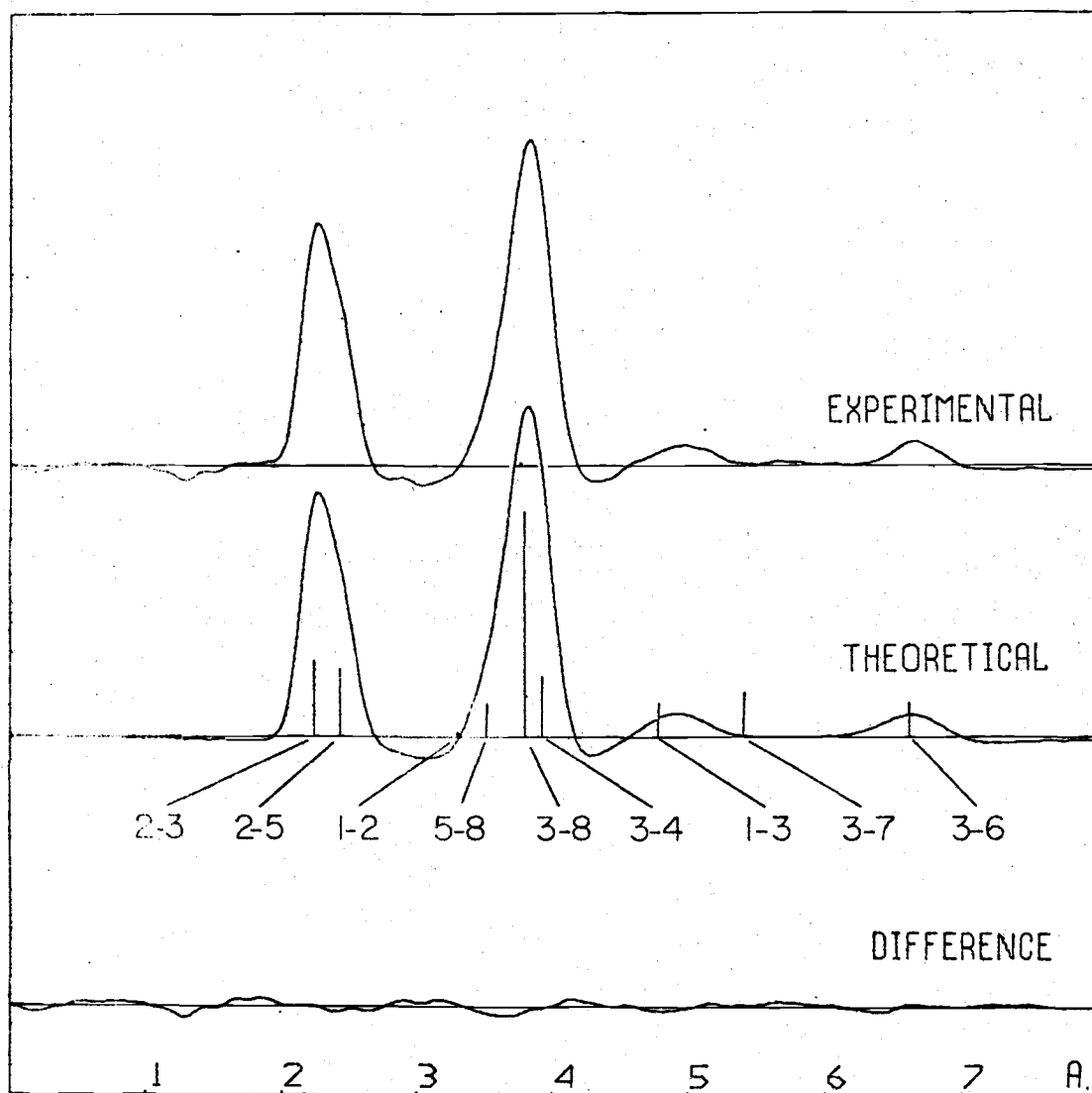


Figure 7. Al_2Br_6 . Final radial distribution curves calculated from the composite and theoretical curves of Figure 6.
 $B = 0.0025$.

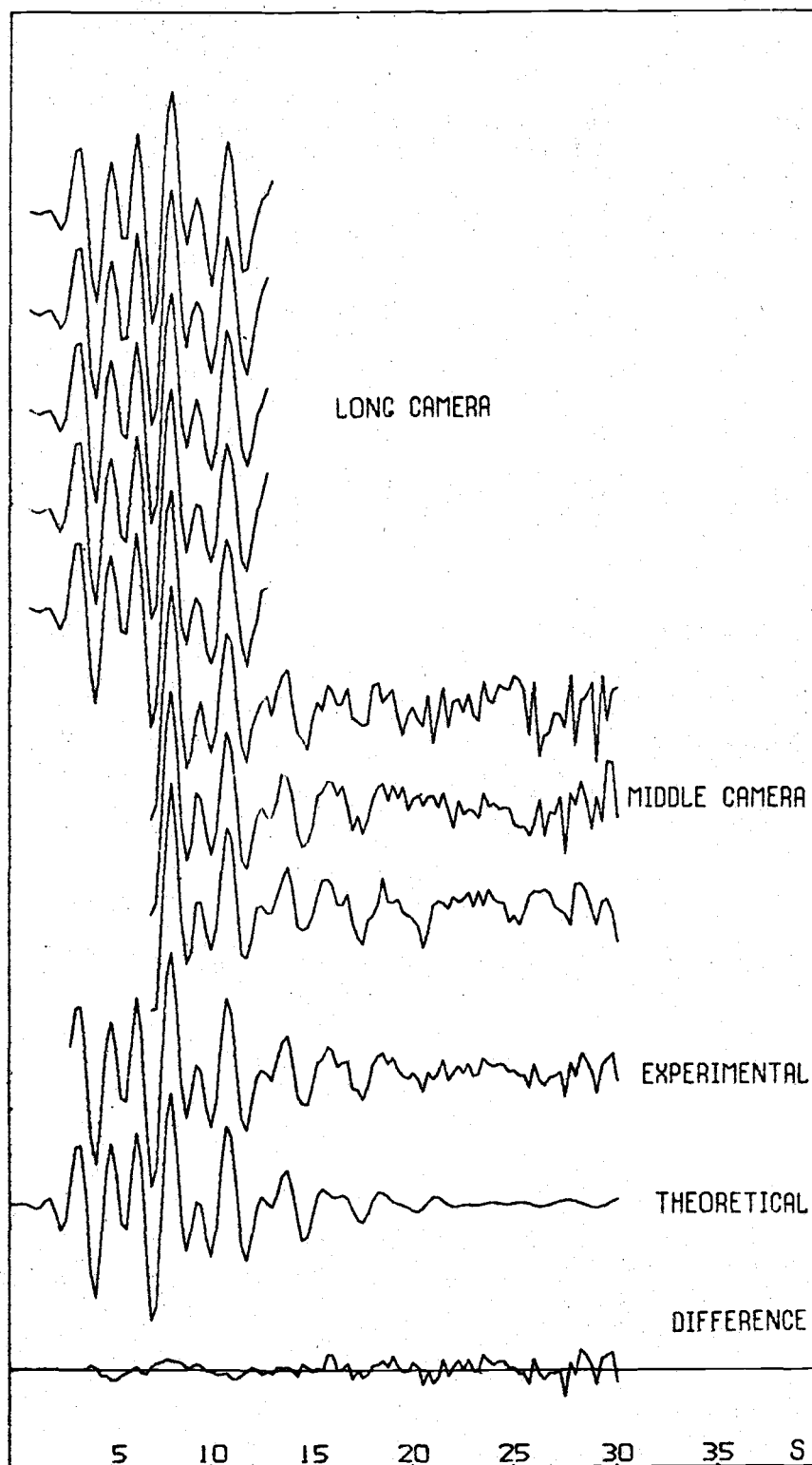


Figure 8. $\text{Al}_2\text{I}_6\text{-AlI}_3$. Intensity curves ($sI_m(s)$).

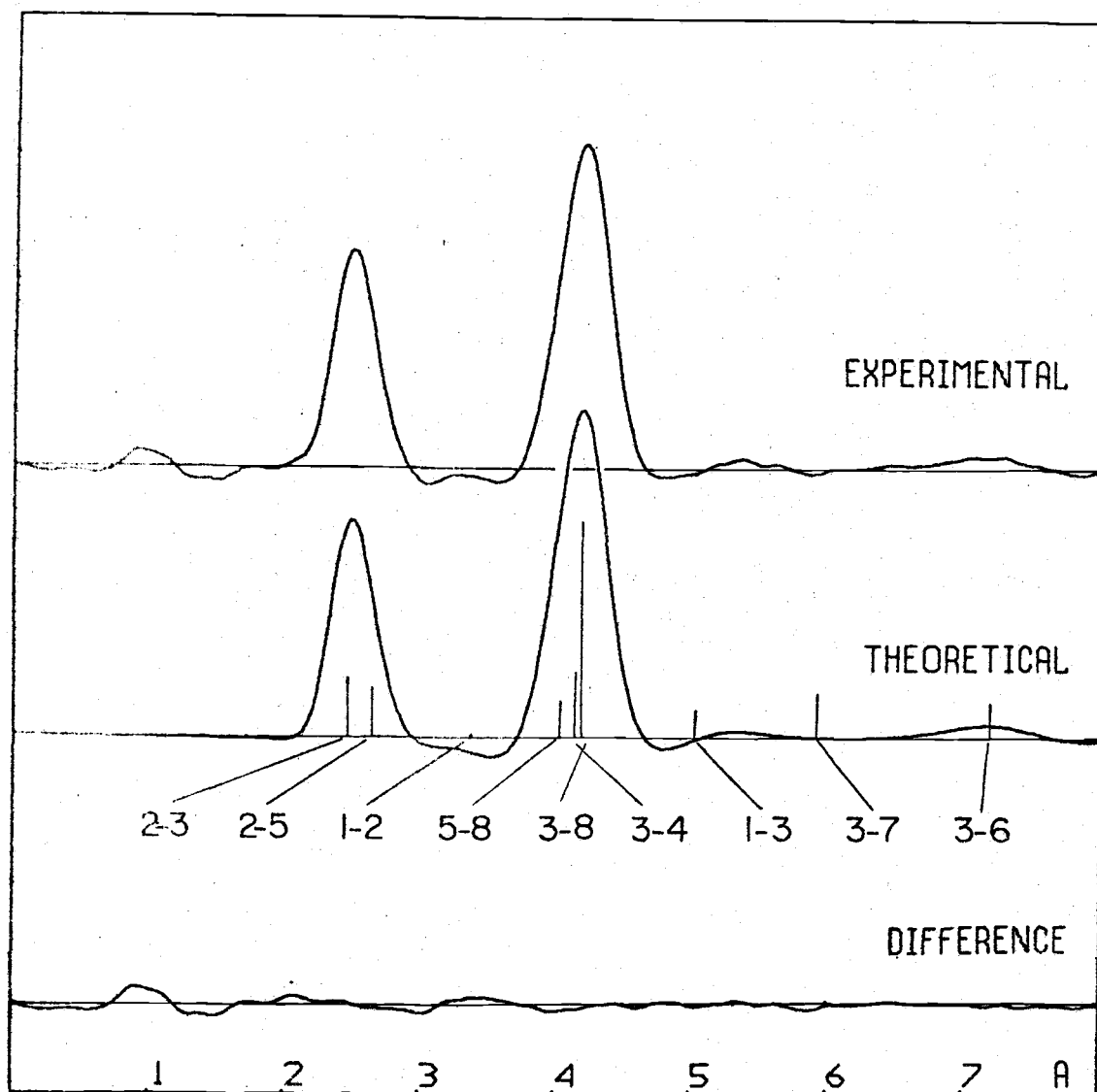


Figure 9. $\text{AlI}_{26}\text{-AlI}_3$. Final radial distribution curves calculated from the composite and theoretical curves of Figure 8. $B = 0.0025$.

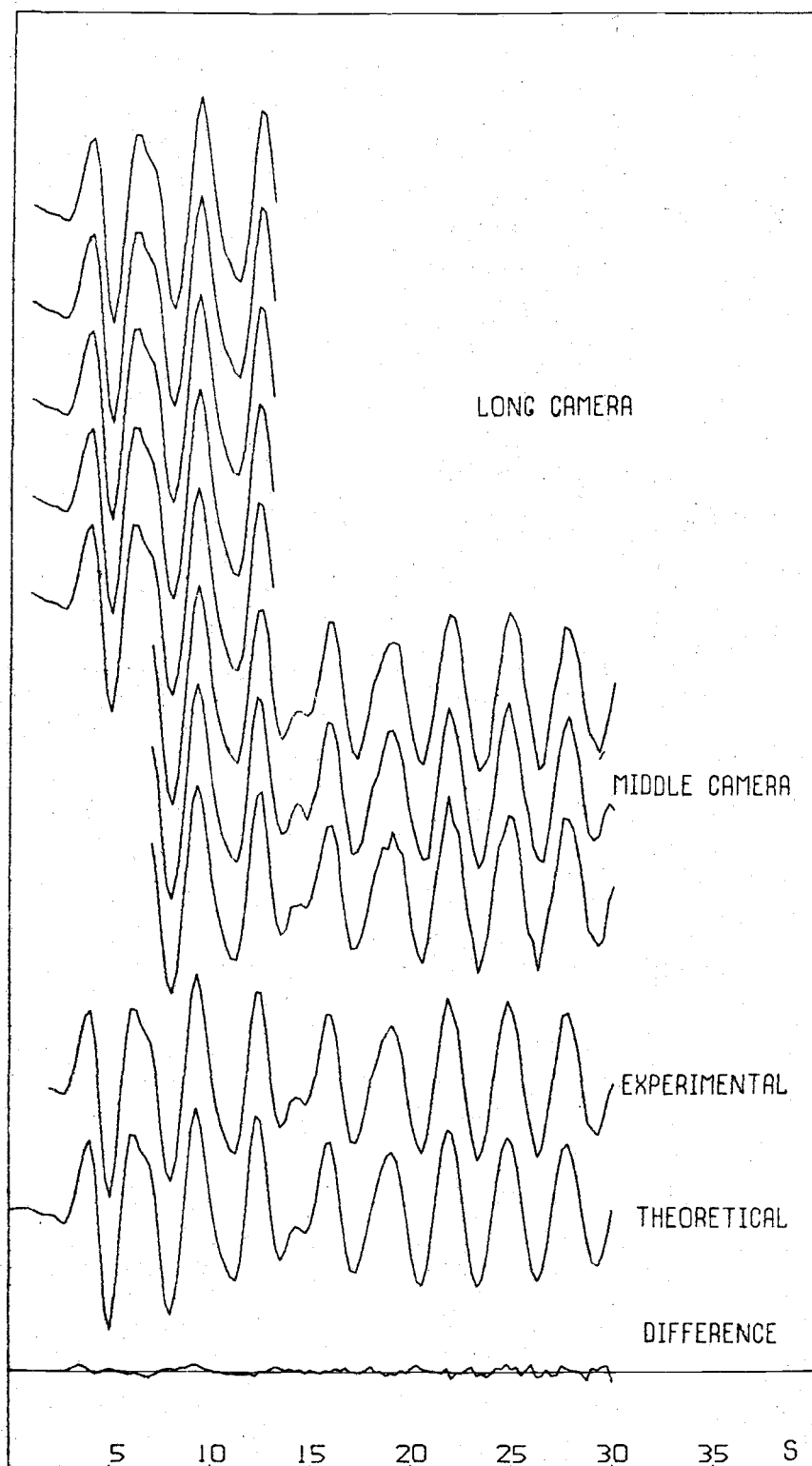


Figure 10. Ga_2Cl_6 . Intensity curves ($sl_m(s)$).

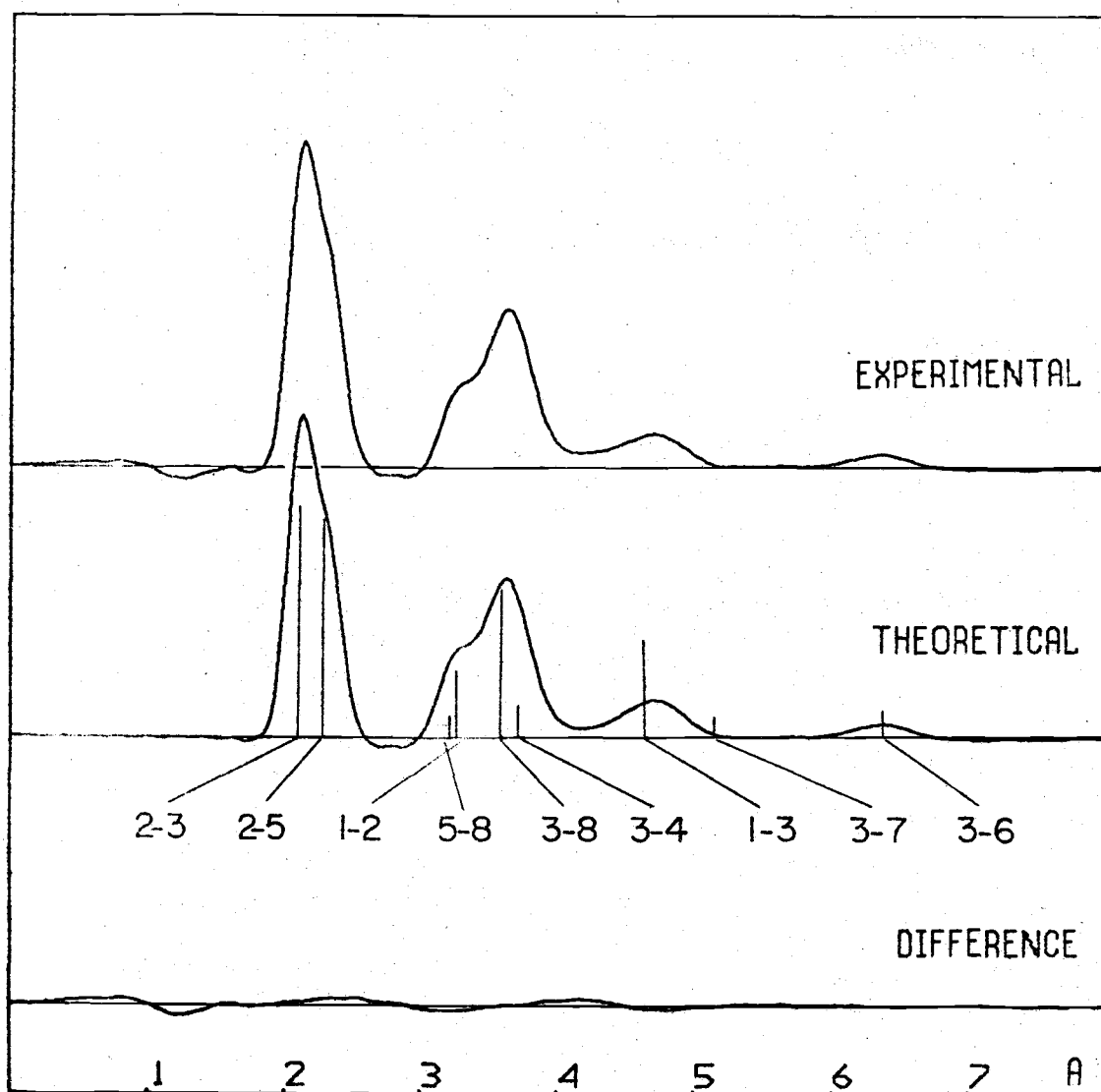


Figure 11. Final radial distribution curves calculated from the composite and theoretical curves of Figure 10. $B = 0.0025$.

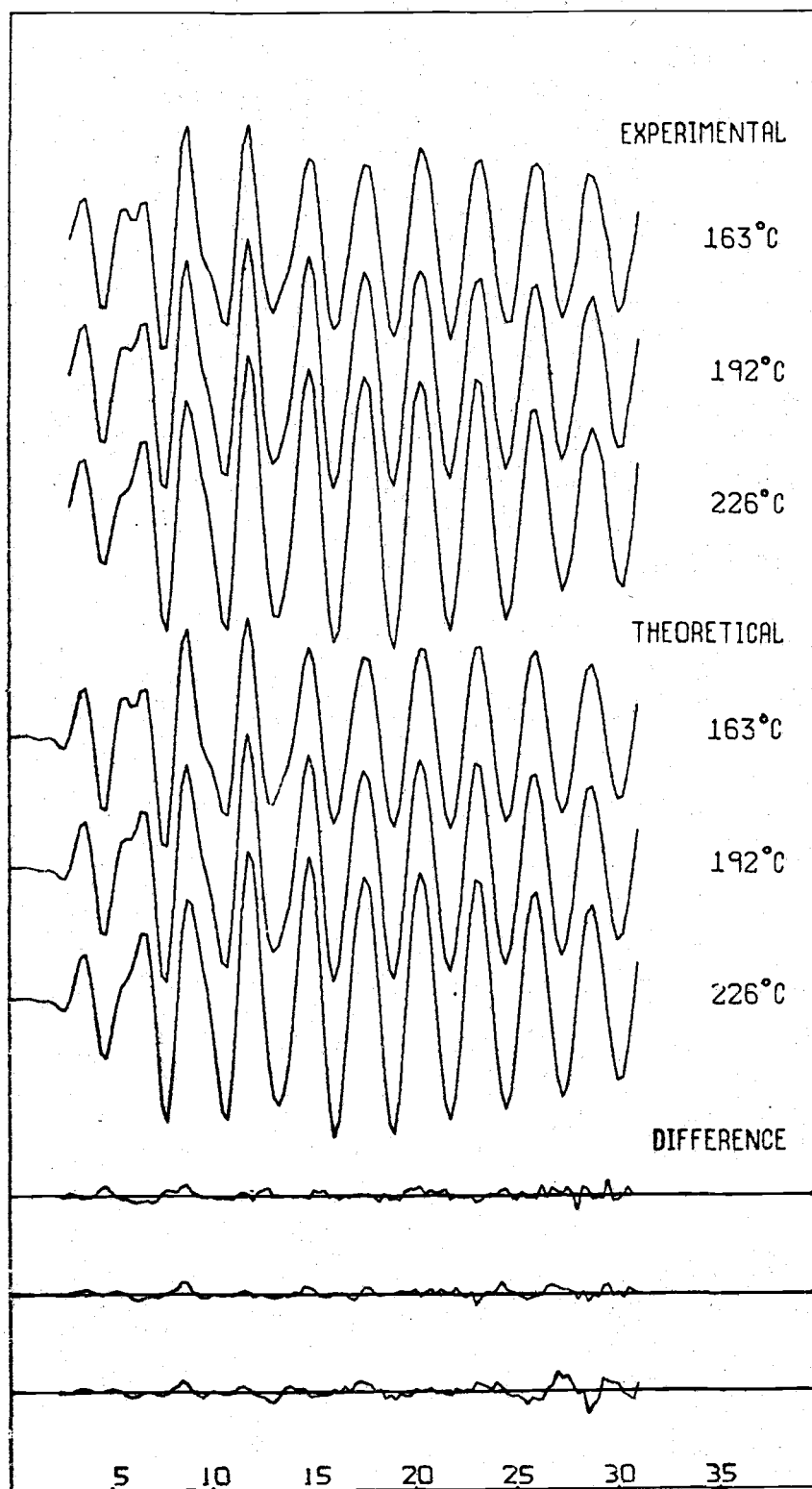


Figure 12. $\text{Ga}_2\text{Br}_6\text{-GaBr}_3$. Experimental composite and theoretical intensity curves ($\text{sl}_m(s)$).

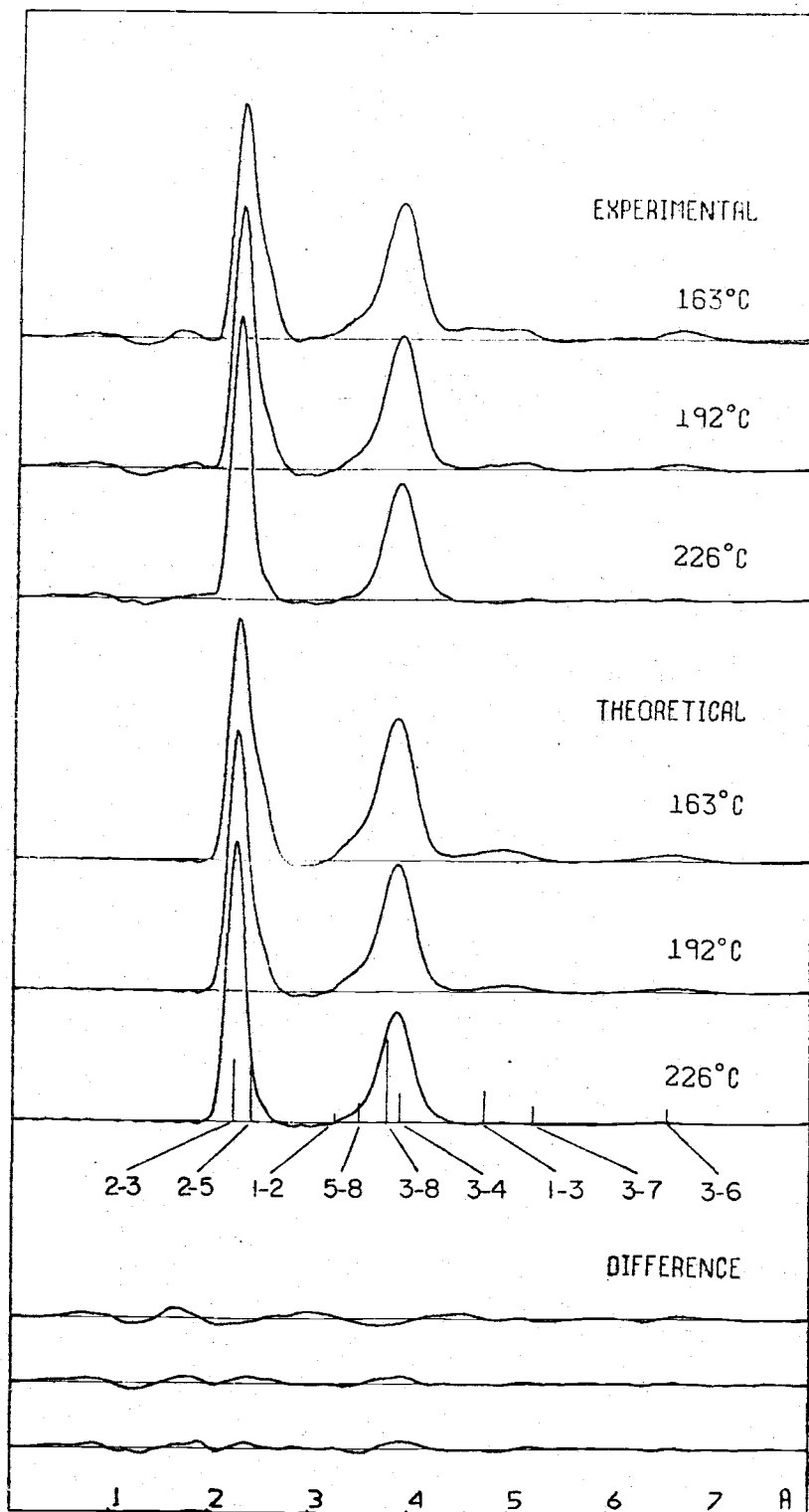


Figure 13. $\text{Ga}_2\text{Br}_6\text{-GaBr}_3$. Final radial distribution curves₆ calculated from the curves of Figure 12. $B = 0.0025$.

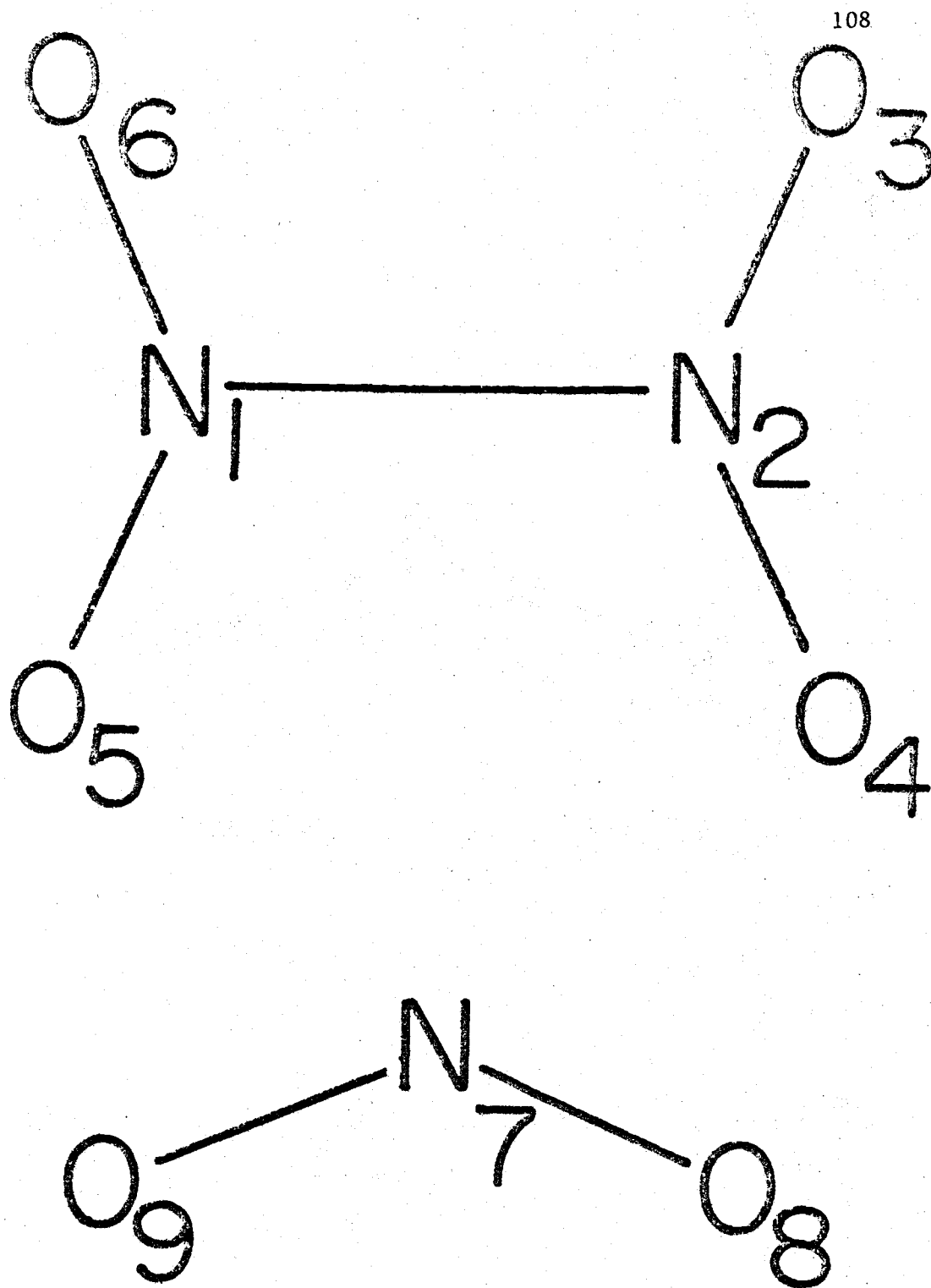


Figure 14. Configurations and atom numbers of N_2O_4 and NO_2 .

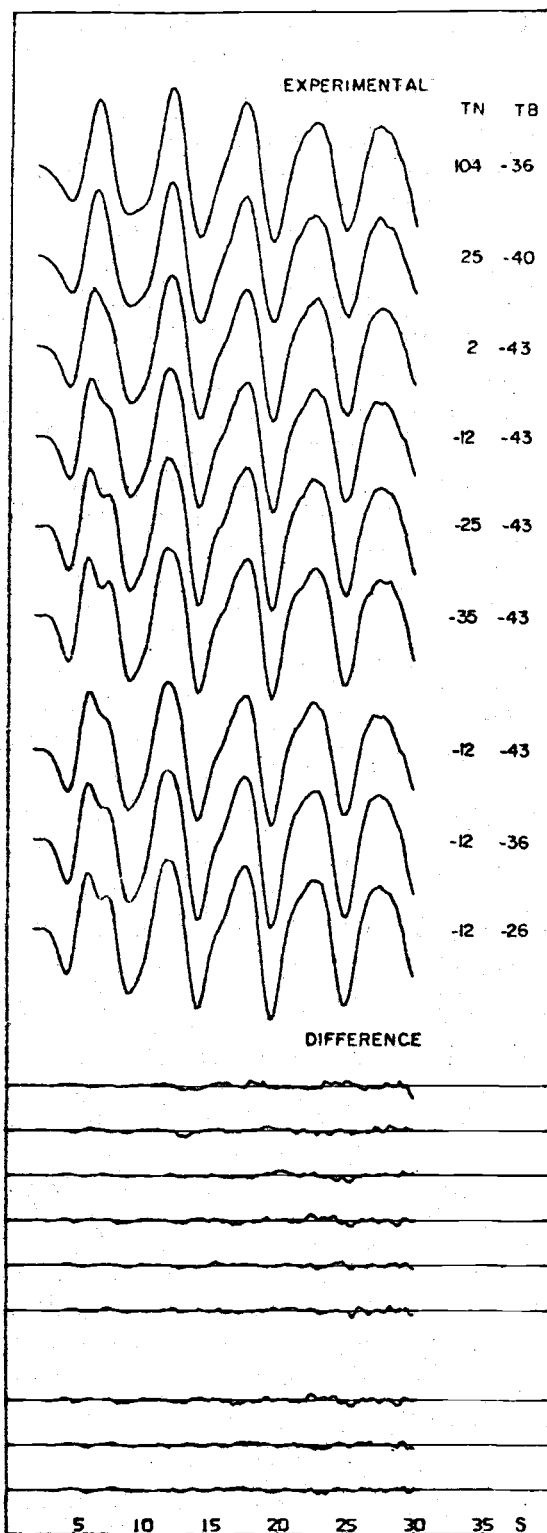


Figure 15. $\text{N}_2\text{O}_4\text{-NO}_2$. Experimental composite and theoretical intensity curves ($sl_m(s)$). TN = nozzle temp., and TB = sample bath temp.

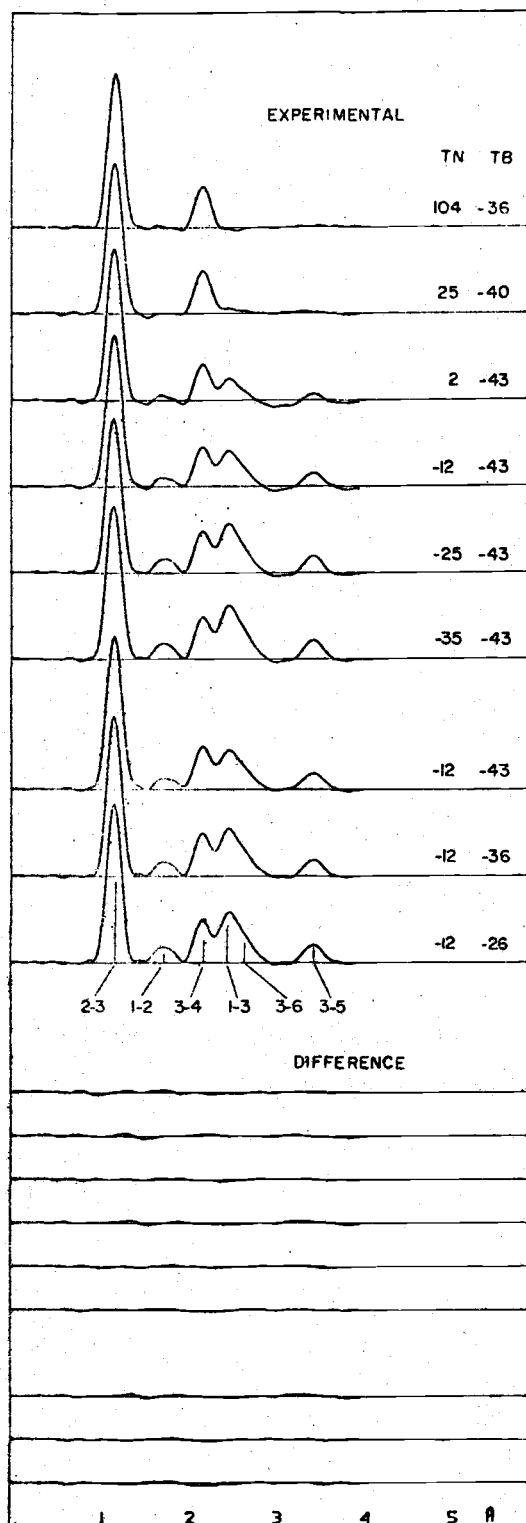


Figure 16. $N_2O_4-NO_2$. Final radial distribution curves calculated from the curves of Figure 15. $B = 0.0025$. (TN = nozzle temp., and TB = sample bath temp.)

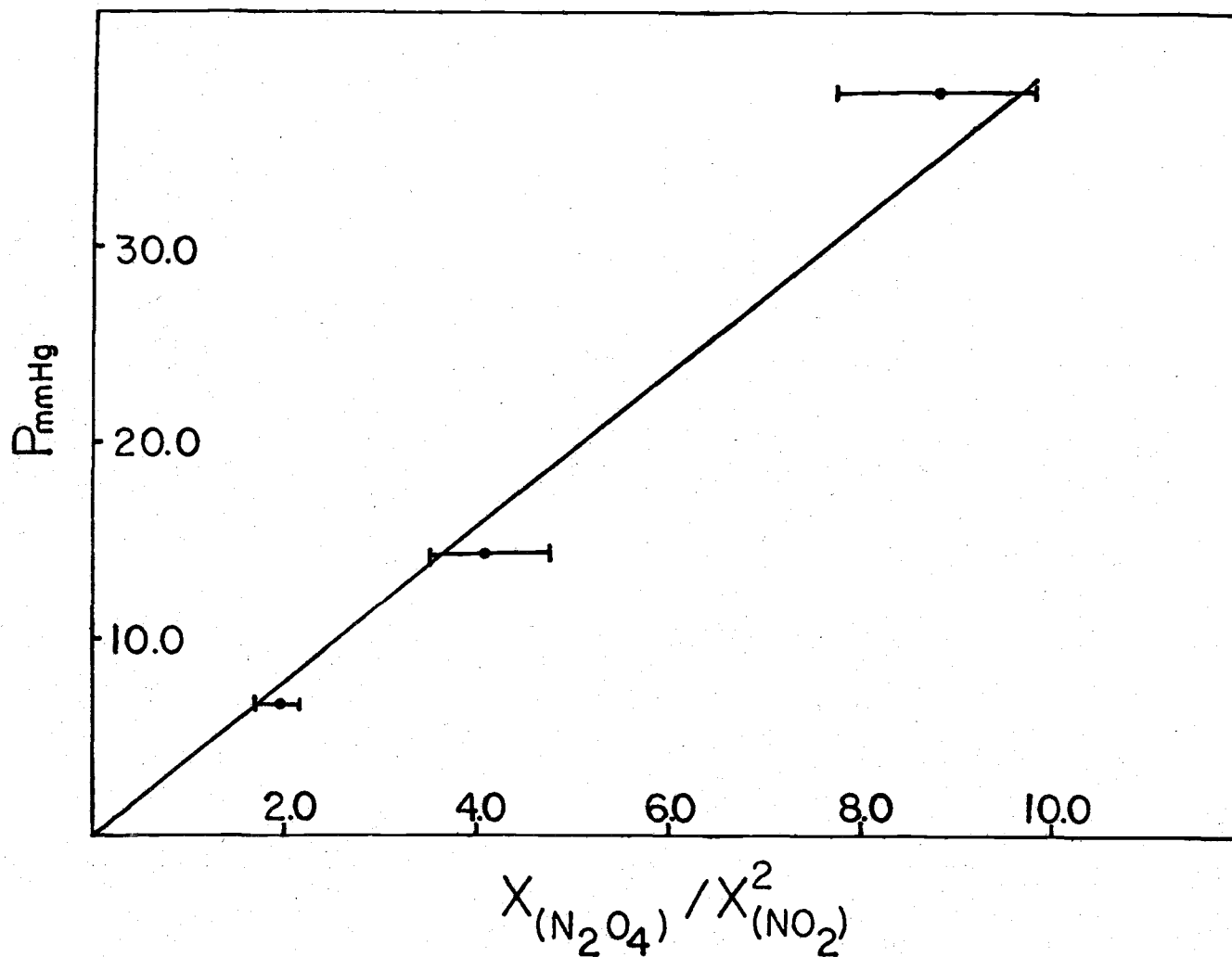


Figure 17. N_2O_4 - NO_2 . P_{TB} vs $X_{\text{N}_2\text{O}_4} / X_{\text{NO}_2}^2$ plot.

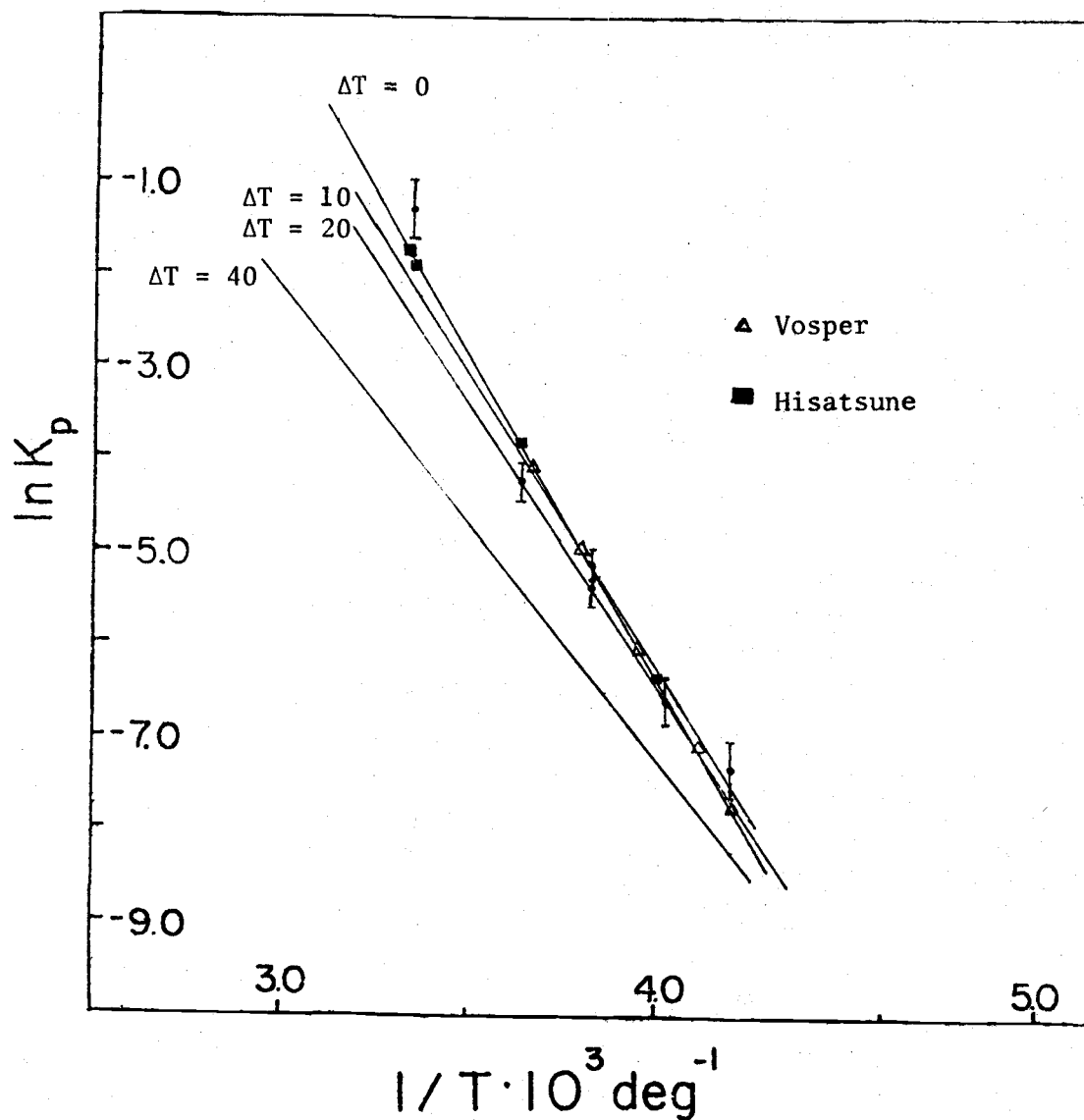


Figure 18. N_2O_4 - NO_2 . Arrhenius plot of mixture-composition data. The half-lengths of the vertical bar indicates 2σ . Least-squares straight line.

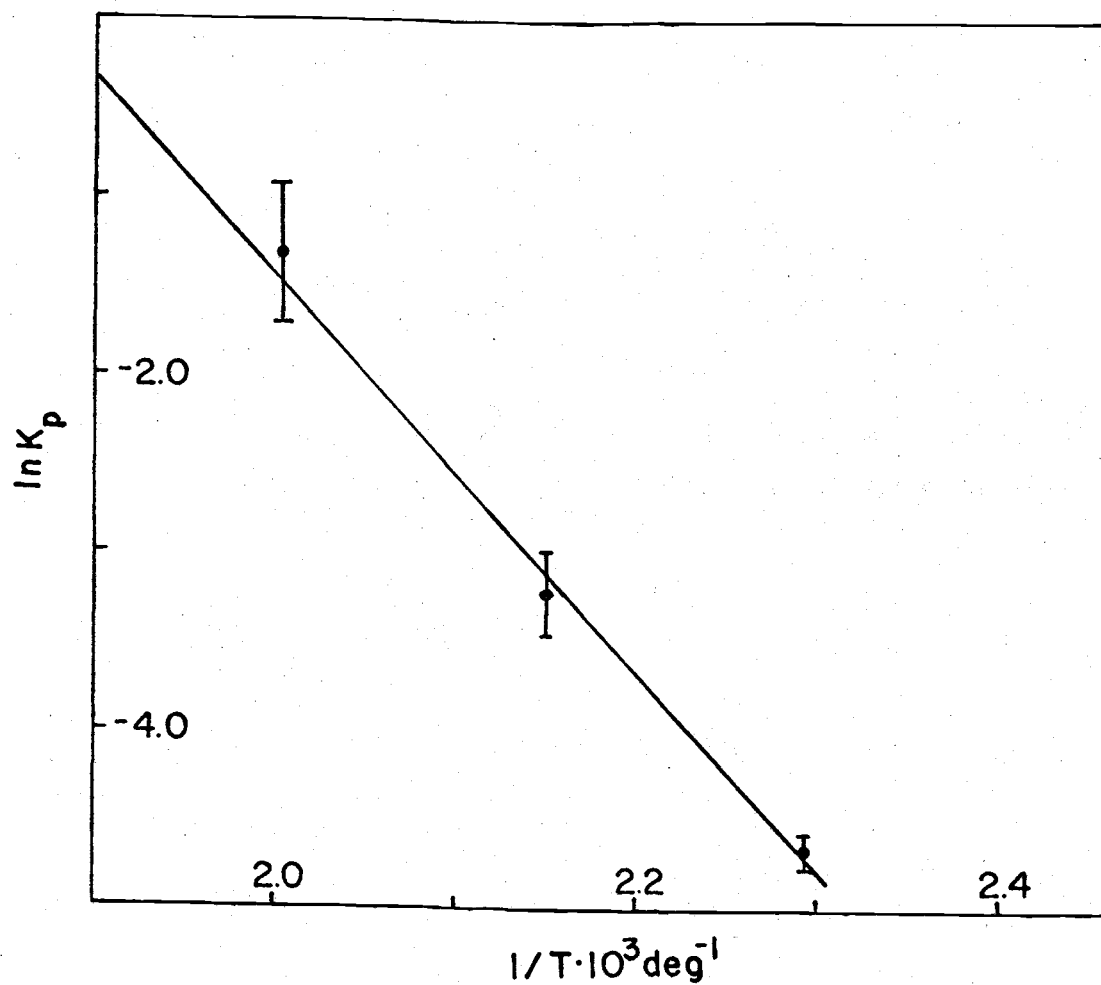


Figure 19. $\text{Ga}_2\text{Br}_6\text{-GaBr}_3$. Arrhenius plot of mixture-composition data. The half-lengths of the vertical bar indicates 2σ . Least-squares straight line.

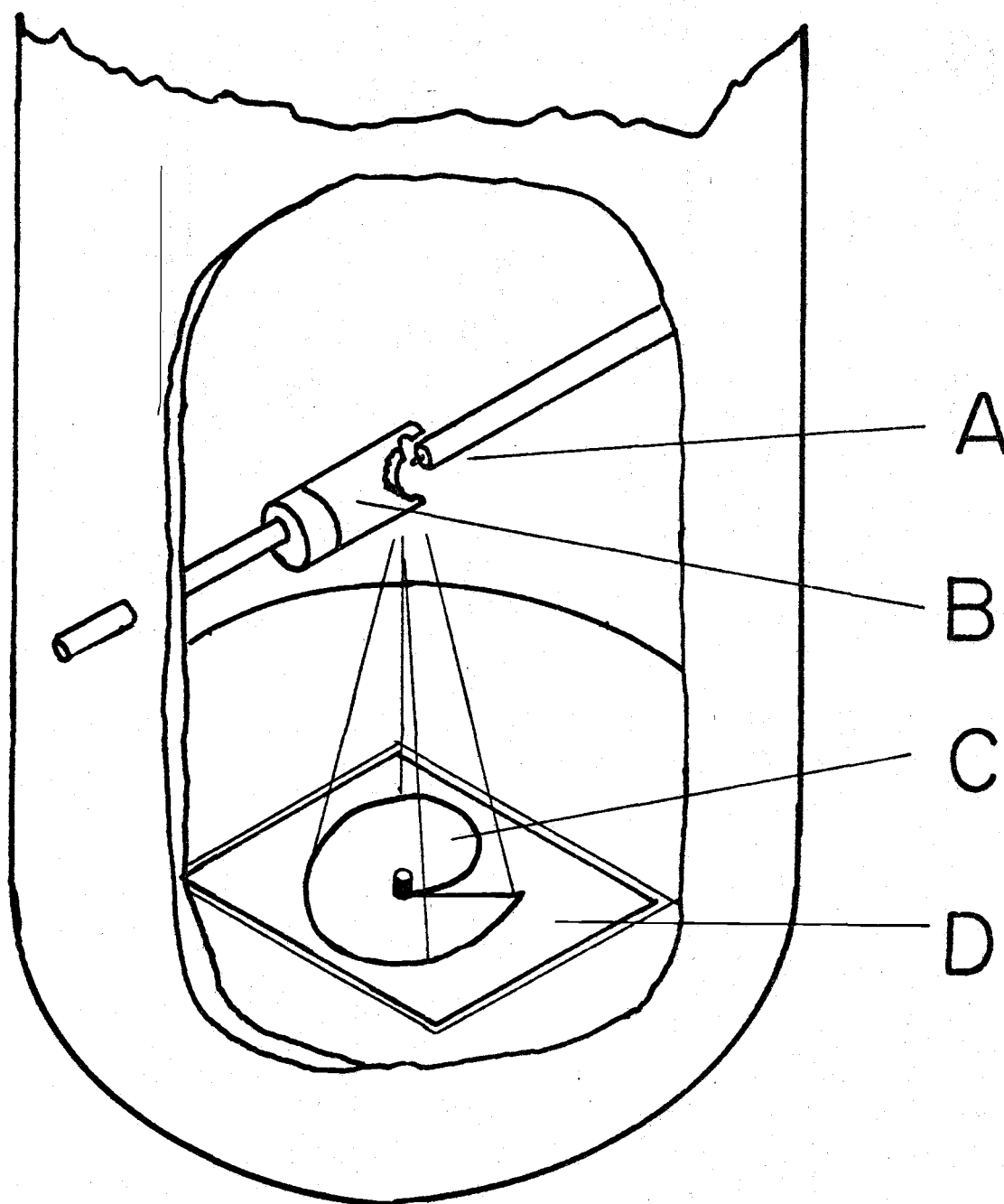


Figure 20. Diagram of the simplified electron diffraction apparatus.
A. Nozzle. B. Cold trap. C. Rotating sector. D.
Photographic plate.

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APPENDICES

APPENDIX A

Theory

Only a brief outline of the well-known theory of electron diffraction and the technique of molecular structure determination by this method will be given here since details are available in several publications and theses from Oregon State University (6, 16, 18, 24, 51).

When a beam of high energy (40-50 KV) monochromatic electrons intersects a stream of gas in a highly evacuated chamber (10^{-5} - 10^{-6} torr, diffraction effects are observed. The electrons are scattered by the potential field of the randomly oriented molecules to produce a radially symmetric (around the undiffracted electron beam) diffraction pattern which is normally allowed to impinge on a photographic plate perpendicular to the incident electron beam. Figure 20 shows the geometry of the experiment. There are four main components in the total scattered intensity, I_t : atomic scattering, I_a ; inelastic scattering, I_i ; extraneous scattering (scattering from parts of the diffraction apparatus such as apertures, etc.), I_{ext} ; and molecular scattering, I_M . The relationships between these intensities, and between intensity striking the plate (I_p) and the total scattering (I_t) are given by the equations

$$I_t(\theta) = I_M + I_a + I_i + I_{\text{ext}} \quad (\text{A1})$$

$$I_p(\theta) = I_t \cdot \alpha(s) \cdot \cos^3 2\theta, \quad (\text{A2})$$

where 2θ is the scattering angle and $\alpha(s)$ is a function characteristic of the rotating sector. The sector is a spiral-shaped metal cam cut to have an angular opening θ such that $\theta = kr^3$, where r is a radial coordinate measured on the sector. It is mounted on a plane parallel to and just above the photographic plate with its axis coincident with the undiffracted electron beam. Because I_t diminishes very rapidly with increasing 2θ , the sector serves the purpose of reducing the intensity striking the plate at small angles relative to that at large angles, thus yielding more even exposure to the photographic plate. A single photographic plate provides useful intensity data over a many-fold larger range of scattering angle than could otherwise be attained. The $\cos^3 2\theta$ term in Equation A2 is a factor which takes into account the fact that the photographic plate is flat and not everywhere equidistant from the scattering point. Using the theoretical expressions for each of the components of Equation A1, it becomes

$$I_t = K \sum_{i \neq j} \frac{|A_i| |A_j|}{s^5 r_{ij}} e^{-1_{ij} s^2 / 2} \cos(\Delta\eta_{ij}) \sin(r_{ij} - k^2 s^2)s$$

$$+ K \sum \frac{|A_i|^2}{s^4} + K \sum \frac{Z_i S_i}{s^4} + I_{\text{ext}} \quad (\text{A3})$$

where

- r_{ij} = interatomic distance between atoms i and j
- $|A_i|$ = modified electron scattering amplitude for atom i
- l_{ij} = root-mean-square amplitude of vibration between atoms i and j
- S = inelastic scattering factor
- $s = \frac{4\pi}{\lambda} \sin \theta$; 2θ is the scattering angle.
- $\Delta\eta_{ij}$ = phase shift difference between atom i and j
($\Delta\eta_{ij} = \eta_i - \eta_j$)
- K = an anharmonicity constant

Since the last three terms in Equation A3 have nothing to do with the structure of the molecule, they may be regarded as experimental background. It is convenient to multiply Equations A1 and A3 by s^4 to yield the following expression for the molecular structure sensitive part of the scattered intensity.

$$I_m(s) = s^4 I_M = s^4 (I_t - I_a - I_i - I_{\text{ext}}) = s^4 I_t - B_E \quad (\text{A4})$$

where B_E is the "experimental background" and

$$I_m = s^4 I_M = K \sum_{i \neq j} \frac{|A_i| |A_j|}{r_{ij} s} e^{-1_{ij} s^2 / 2} \cos \Delta \eta_{ij} \sin (r_{ij} - k s^2) s \quad (A5)$$

This is generally used in the form

$$s I_m = K \sum_{i \neq j} \frac{|A_i| |A_j|}{r_{ij}} e^{-1_{ij} s^2 / 2} \cos \Delta \eta_{ij} \sin (r_{ij} - k s^2) s \quad (A6)$$

To summarize then, the data in the form of I_p (the intensity of scattered electrons striking the photographic plate) may be manipulated to obtain $s I_m(s)$ in the way suggested by the equations.

$$s I_m(s) = s [s^4 I_p / (\alpha(s) \cdot \cos^3 2\theta) - B_E] \quad (A7)$$

Determination of the molecular structure of the molecule in question now consists of analyzing the molecular intensity curve ($s I_m$). In usual practice a trial structure for the molecule is deduced from a preliminary radial distribution (RD) curve (51) calculated from the experimental intensity distribution. In order that the peaks of the RD curve can be interpreted easily, the intensity curve $s I_m$ is converted to a "constant coefficient" curve I'_m by multiplying with $Z_r Z_s / |A_r| |A_s|$ to give

$$I'_m = K \sum_{i \neq j} \frac{|A_i|}{|A_r|} \frac{|A_j|}{|A_s|} \frac{Z_r Z_s}{r_{ij}} e^{-s^2_{ij}/2} \cos \Delta \eta_{ij} \sin (r_{ij} - \frac{1}{2} s^2) s \quad (A8)$$

Equation A8 can be rewritten as if the distribution of atoms were continuous over all space

$$I'_m = \int_0^\infty \frac{P(r)}{r} \sin r s \, dr \quad (A9)$$

Here $P(r)$ is the probability distribution of interatomic distances.

Using the well-known Fourier integral theorem the probability distribution becomes

$$\frac{P(r)}{r} = \frac{2}{\pi} \int_0^\infty I'_m \sin r s \, ds \quad (A10)$$

$$\frac{P(r)}{r} \approx \frac{2}{\pi} \sum_{s=0}^\infty I'_m \sin r s \, \Delta s \quad (A11)$$

For better series convergence (the experimental data do not extend over the range $0 \leq s \leq \infty$), the intensity curve I'_m is usually multiplied by the factor e^{-Bs^2} where B is calculated from the relationship $e^{-Bs^2} = 0.1$ at $s = s_{\max}$. Thus Equation A11

becomes

$$\frac{P(r)}{r} = \frac{2}{\pi} \sum_{s_{\min}}^{s_{\max}} I'_m e^{-Bs^2} \sin r s \, \Delta s \quad (A12)$$

The theoretical form of $P(r)/r$ is gotten by integration of Equation A11 into which Equation A7 has been substituted. For the cases of interest here the k_s^2 term may be neglected and Equation A7 has the approximate form

$$I'_m = \sum \frac{Z_i Z_j}{r_{ij}} e^{s^2 l_{ij} / 2} \sin r_{ij} s \quad (A13)$$

from which

$$\frac{P(r)}{r} = \frac{1}{\sqrt{2\pi}} \sum \frac{Z_i Z_j}{r_{ij}} \frac{1}{\sqrt{l_{ij}^2 + 2B}} e^{-(r_o - r)_{ij}^2 / (2l_{ij}^2 + 4B)} \quad (A14)$$

The radial distribution curve thus is a sum of Gaussians, each centered at an interatomic distance r_o and with a shape dependent on l_{ij} . The l_{ij} can be estimated from the following expression

$$\frac{1}{2} = \exp \left[-\Delta r_{1/2}^2 / (2 l_{ij}^2 + 4B) \right] \quad (A15)$$

where $\Delta r_{1/2}$ is the half-width of the peak at half-height.

Procedure of Structure Analysis

The photographic plates chosen for structure analysis are scanned along a diameter of the diffraction rings using a Joyce-Loebl microdensitometer while being at the same time rotated about the center of the rings. Digitalized data are punched into a paper tape at intervals corresponding to 0.3514 mm on the plate. The

results are read from the paper tape into the O.S. U. CDC 3300 computer via teletype for use by the "data reduction" program (25).

The data reduction program, written by Lise Hedberg, performs the following tasks. It

- (1) converts each datum on the tape (in the form of counts per second which are proportional to photographic density) to photographic density.
- (2) applies a "blackness" correction (an empirically determined correction for the non-linear response of a photographic emulsion to the scattered electron intensity) (37).
- (3) locates the precise center of the diffraction rings by a least squares method applied to the first derivatives of the two branches of the trace.
- (4) calculates the s value corresponding to each measured point and interpolates the densities at even intervals $\Delta s = 0.25$.
- (5) applies geometrical corrections (Eq. A2), compensates for use of the sector, and multiplies the density I_t by s^4 .
- (6) averages the two branches of the scan.

The curves resulting from this program are called "data reduced" curves, and correspond to the supposition of molecular scattering on a smooth background ($s^4 I_t$). These intensity curves with increment $\Delta s = 0.25$ can be plotted by hand and smooth hand-drawn background curves can be inserted, following which

the molecular intensity curves $I_m(s)$ (later to be multiplied by s) are obtained by difference.

In 1972 a computer program to calculate the backgrounds was developed by Lise Hedberg (27). It is based on the assumption that the background scattering is due to (1) "non-molecular scattering", which can be expressed as a sum of the coherent atomic (I_a) and inelastic (I_i) scattering amplitudes, and (2) apparatus scattering which may be accounted for by introducing a polynomial, usually of 3rd or 4th degree. The coefficients of the polynomial as well as a scale factor for the "non-molecular" scattering is determined by a least squares procedure. If no information about the molecular model is available, the background function is determined by minimizing the differences between the background and the data reduced curve itself. This is not necessarily a good criterion, especially at either end of the curve, and is used only as a first approximation. When a molecular model has been deduced and a theoretical intensity curve calculated, the background is determined by minimizing the differences between the background and the difference curve which results when the theoretical curve is subtracted from the data-reduced curves. The program contains an option to calculate the background using a polynomial only. This may be useful for data gathered at large scattering angles. The program subtracts the calculated background from the data reduced curve and multiplies

the resulting curve by s to yield the molecular intensity curves $sI_m(s)$.

The individual molecular intensity curves, from each camera distance (long, 70 cm; middle, 30 cm; and short, 12 cm) can be weighted and summed together to form average curves which extend over the approximate ranges $2.00 \leq s \leq 13.00$ (long); $8.00 \leq s \leq 30.0$ (middle); and $25.0 \leq s \leq 45.0$ (short). A single overall composite curve can be obtained by scaling and averaging the just-mentioned average curves in their respective overlap regions (usually $8.0 \leq s \leq 12.0$ between long and middle and $25.0 \leq s \leq 30.0$ between middle and short). (The composite intensity curve can also be formed directly by combination of the individual curves. This is especially convenient when structure refinements are being done using the uncombined intensity curves.)

Preliminary structural information is usually obtained from the experimental radial distribution curve calculated from the composite experimental curve using Equation A14. Data in the unobserved region $s < s_{\min}$ are at first often ignored, and later taken from theoretical intensity curves. Since the composite intensity is in the form sI_m , it is first multiplied by $Z_r Z_s |A_r|^{-1} |A_s|^{-1}$ to give I'_m . From the RD curve most of the important interatomic distances and root-mean-squares amplitudes can be estimated and a preliminary model can be constructed. Such a model is refined

by calculating the theoretical intensity curve sI_m corresponding to it and adjusting the curve to the experimental curve(s) by a least squares procedure (29, 30, 31). The adjustment can be based on the composite, the average curves, or on the many uncombined intensity curves gotten from each of the photographic plates (individual curves). During the course of the refinement the background abstracting program may be used again in order to correct small errors. The results of the refinement are values for geometrical parameters of the molecule, amplitudes of vibration, and in the case of mixtures, the mole fractions of the components.

From the least squares refinements, error estimates are presently calculated from the following equations:

$$2\sigma = 2[2\sigma_{LS}^2 + (0.0005r)^2]^{1/2} \quad (A16)$$

$$2\sigma_l = 2[2\sigma_{LS}^2 + 0.021]^2]^{1/2} \quad (A17)$$

$$2\sigma_{\text{angle}} = 2\sqrt{2\sigma_{LS}} \quad (A18)$$

The σ_{LS} 's are obtained from the least squares process, the factor 2 takes into account possible correlation among the observations, and the coefficients (0.0005 and 0.02) follow from estimates of possible systematic error (29).

APPENDIX B

EXPERIMENTAL INTENSITY CURVES FOR ALUMINUM CHLORIDE DIMER
CURVE 1 (2-58-1)

	0.00	0.25	0.50	0.75
1.00	.41	-2.41	-5.57	-6.77
2.00	-2.78	1.47	-5.87	-21.63
3.00	-27.26	-6.71	27.03	69.67
4.00	93.70	71.43	-10.63	-107.95
5.00	-145.85	-100.50	-15.43	55.11
6.00	89.44	68.90	27.07	6.18
7.00	25.74	44.80	19.02	-48.75
8.00	-107.66	-125.32	-94.62	-26.51
9.00	65.10	123.39	121.52	66.00
10.00	2.84	-38.55	-49.52	-41.65
11.00	-34.17	-42.67	-58.12	-51.70
12.00	-7.24	64.67	105.54	104.38
13.00	60.33			

CURVE 2 (2-58-3)

	0.00	0.25	0.50	0.75
1.00	.74	-1.30	-3.65	-4.76
2.00	-3.03	-0.81	-5.18	-13.99
3.00	-16.79	-3.56	20.33	47.27
4.00	63.02	46.79	-6.21	-69.94
5.00	-91.48	-67.32	-12.45	34.85
6.00	54.68	43.61	17.68	4.08
7.00	15.68	27.85	10.08	-31.41
8.00	-69.26	-81.29	-63.42	-17.65
9.00	39.23	78.61	76.34	40.83
10.00	6.25	-21.36	-27.89	-20.19
11.00	-18.48	-23.89	-34.84	-33.69
12.00	-0.79	43.34	74.30	75.72
13.00	49.31			

CURVE 3 (2-58-4)

	0.00	0.25	0.50	0.75
1.00	.42	-1.70	-3.99	-5.20
2.00	-3.25	-0.61	-4.89	-14.26
3.00	-16.88	-3.41	22.16	49.92
4.00	65.51	50.70	-4.94	-76.42
5.00	-95.16	-76.25	-11.26	35.71
6.00	56.68	47.12	20.56	7.66
7.00	19.04	31.34	12.91	-30.24
8.00	-71.98	-86.58	-67.28	-19.05
9.00	38.86	78.53	75.04	42.83
10.00	3.61	-22.73	-31.59	-27.24
11.00	-17.71	-26.30	-37.45	-28.24
12.00	2.25	46.43	69.44	71.35
13.00	45.01			

CURVE 4 (2-58-5)

	0.00	0.25	0.50	0.75
1.00	.79	-1.33	-3.28	-4.45
2.00	-2.92	-1.06	-4.58	-12.42
3.00	-15.03	-4.22	18.18	46.12
4.00	62.67	44.42	-9.84	-64.66
5.00	-85.34	-62.75	-13.61	32.07
6.00	51.70	43.04	19.11	9.87
7.00	21.94	35.00	16.96	-24.58
8.00	-57.30	-67.90	-51.45	-8.93
9.00	46.16	84.39	79.83	45.48
10.00	8.97	-16.76	-23.50	-20.51
11.00	-18.66	-21.63	-34.36	-29.28
12.00	-1.56	35.02	61.66	62.05
13.00	33.77			

CURVE 5 (2-60-3)

	0.00	0.25	0.50	0.75
8.00	-252.15	-288.30	-213.14	-42.12
9.00	154.23	286.61	281.85	159.80
10.00	14.68	-84.20	-115.91	-97.24
11.00	-77.34	-98.54	-142.67	-130.73
12.00	-12.18	139.21	246.01	243.99
13.00	118.49	-10.91	-138.41	-167.63
14.00	-122.34	-37.17	-0.14	7.67
15.00	-25.75	-37.41	5.08	65.82
16.00	124.98	157.74	109.92	-3.91
17.00	-94.19	-142.63	-131.79	-89.59
18.00	-27.20	-0.55	28.28	45.79
19.00	64.10	105.53	114.72	81.76
20.00	20.03	-44.72	-143.21	-171.60
21.00	-155.14	-81.05	14.21	62.79
22.00	165.33	159.65	157.96	115.22
23.00	14.36	-74.51	-149.85	-189.94
24.00	-143.46	-97.11	1.93	57.98
25.00	133.75	157.90	128.45	92.29
26.00	2.84	-64.28	-135.00	-162.60
27.00	-126.62	-67.26	-5.86	57.79
28.00	127.07	156.24	143.29	74.70
29.00	-8.26	-75.76	-100.90	-120.88
30.00	-132.23	-89.25	-11.70	65.15
31.00	123.24	127.49	138.07	40.65

CURVE 6 (2-60-4)

	0.00	0.25	0.50	0.75
8.00	-248.53	-275.40	-203.58	-40.40
9.00	149.66	273.63	257.90	148.51
10.00	11.85	-72.91	-107.12	-89.60
11.00	-79.63	-104.91	-126.79	-107.13
12.00	1.85	147.18	229.60	205.33
13.00	106.85	-18.01	-119.62	-150.10
14.00	-124.17	-54.84	-14.23	10.96
15.00	-23.83	-18.39	9.77	60.98
16.00	123.12	119.52	98.84	7.69
17.00	-84.70	-128.31	-129.25	-74.62
18.00	-31.44	12.17	27.42	60.36
19.00	81.64	106.02	104.28	84.79
20.00	10.64	-72.20	-136.09	-161.95
21.00	-157.90	-104.53	11.63	69.70
22.00	145.23	181.92	137.33	89.04
23.00	-3.24	-50.96	-132.23	-179.33
24.00	-153.86	-79.74	5.65	81.90
25.00	142.65	154.39	123.53	51.73
26.00	46.32	-73.32	-134.04	-169.91
27.00	-156.30	-113.75	8.94	118.78
28.00	168.14	189.13	109.41	54.69
29.00	-35.75	-101.32	-115.52	-145.87
30.00	-131.48	-70.12	36.82	84.24
31.00	145.98	107.91	90.89	52.97

CURVE 7 (2-60-5)

	0.00	0.25	0.50	0.75
8.00	-199.31	-220.49	-157.12	-25.15
9.00	120.11	228.84	213.87	113.15
10.00	10.73	-65.95	-88.18	-73.62
11.00	-65.96	-58.56	-106.97	-94.26
12.00	2.97	104.65	181.96	160.47
13.00	86.96	-19.32	-93.26	-112.04
14.00	-76.89	-26.37	10.85	9.18
15.00	-15.87	-23.73	1.02	56.38
16.00	103.26	105.52	65.93	-16.29
17.00	-71.75	-111.65	-97.50	-59.75
18.00	-18.26	16.19	36.67	31.71
19.00	63.17	77.50	79.72	36.57
20.00	-16.72	-63.72	-109.14	-137.81
21.00	-121.92	-62.16	7.34	65.34
22.00	117.09	145.81	103.57	78.54
23.00	.66	-40.77	-73.42	-85.73
24.00	-66.57	-20.42	43.98	84.83
25.00	99.11	78.38	65.02	12.61
26.00	-40.81	-101.68	-154.77	-176.74
27.00	-158.42	-118.32	-13.88	118.81
28.00	154.44	203.13	148.10	48.79
29.00	42.72	-11.92	-45.47	-95.52
30.00	-121.20	-81.87	-24.33	16.87
31.00	39.66	59.08	90.81	68.79
32.00	23.94	0	0	0

EXPERIMENTAL INTENSITY CURVES FOR ALUMINUM BROMIDE DIMER
CURVE 1 (2-68-2)

	0.00	0.25	0.50	0.75
2.00	12.45	3.69	-31.33	-57.82
3.00	-36.93	36.35	123.79	172.77
4.00	109.30	-65.64	-219.16	-220.70
5.00	-82.60	81.27	156.89	113.13
6.00	-10.30	-82.27	-16.78	126.80
7.00	137.82	-37.53	-236.27	-310.53
8.00	-226.62	11.23	281.03	367.53
9.00	204.92	-45.66	-176.74	-159.22
10.00	-70.84	-10.22	-22.21	-119.36
11.00	-140.90	-25.80	174.45	292.72
12.00	240.75	40.52	-147.85	-216.06
13.00	-168.80			

CURVE 2 (2-68-4)

	0.00	0.25	0.50	0.75
2.00	2.93	3.79	-9.18	-20.34
3.00	-12.87	13.36	45.65	65.41
4.00	41.10	-29.61	-93.54	-92.41
5.00	-35.17	30.63	57.49	37.82
6.00	-8.70	-34.33	-5.52	44.27
7.00	46.65	-10.84	-77.92	-102.64
8.00	-71.27	10.60	93.66	127.05
9.00	72.41	-4.98	-48.22	-45.79
10.00	-18.75	-4.13	-2.69	-41.96
11.00	-57.81	-12.25	49.04	91.46
12.00	69.58	15.24	-37.12	-55.90
13.00	-52.18			

CURVE 3 (2-68-5)

	0.00	0.25	0.50	0.75
2.00	2.54	2.63	-10.64	-21.77
3.00	-11.69	15.95	50.52	70.12
4.00	44.25	-31.11	-98.94	-96.92
5.00	-32.65	40.19	72.29	53.96
6.00	7.32	-24.22	3.90	53.44
7.00	50.23	-10.97	-88.23	-114.53
8.00	-82.73	4.14	96.08	125.19
9.00	70.65	-16.19	-65.54	-63.48
10.00	-28.76	-9.42	-17.83	-51.29
11.00	-69.01	-20.46	47.97	85.32
12.00	63.30	17.26	-41.31	-73.14
13.00	-64.03			

CURVE 4 (2-76-4)

	0.00	0.25	0.50	0.75
6.00	88.62	30.68	-82.93	8.58
7.00	45.30	-6.68	-103.93	-148.29
8.00	-105.96	12.51	136.87	175.15
9.00	114.21	1.74	-62.90	-56.92
10.00	-31.77	-3.31	-12.90	-65.16
11.00	-70.64	-14.83	61.98	111.89
12.00	83.18	18.36	-57.44	-97.75
13.00	-83.32	-24.74	14.30	21.14
14.00	1.12	-11.06	3.87	44.60
15.00	56.60	53.03	8.23	-35.27
16.00	-64.55	-48.07	-12.58	-0.06
17.00	20.95	9.46	18.65	27.65
18.00	32.06	45.82	18.89	-28.85
19.00	-46.33	-73.31	-56.44	-7.48
20.00	20.66	44.55	56.89	14.20
21.00	25.62	19.00	-29.41	-43.41
22.00	-22.43	-40.61	-27.93	.93
23.00	27.43	42.36	53.59	42.49
24.00	25.05	-2.36	-23.95	-27.44
25.00	-63.30	-39.83	-25.59	4.59
26.00	45.32	27.52	20.50	17.43
27.00	-14.93	-2.82	-23.48	19.38
28.00	34.76	-21.66	35.42	31.67
29.00	23.07	21.58	3.19	-29.91
30.00	-55.42	-29.43	-12.79	2.08
31.00	17.58	5.36	13.36	

CURVE 5 (2-76-3)

	0.00	0.25	0.50	0.75
6.00	39.23	-36.42	-13.22	35.46
7.00	42.95	-1.81	-64.55	-94.41
8.00	-69.45	2.72	79.31	103.96
9.00	59.87	-2.91	-45.32	-38.25
10.00	-15.44	6.30	-3.68	-39.52
11.00	-45.92	-19.73	33.63	70.34
12.00	55.98	13.45	-32.44	-58.78
13.00	-41.59	-11.02	13.32	18.54
14.00	-4.30	-9.97	2.22	27.06
15.00	41.22	38.23	9.61	-32.78
16.00	-43.63	-35.16	-7.67	-2.04
17.00	9.23	3.29	4.94	12.70
18.00	27.78	26.15	14.72	-8.67
19.00	-36.16	-30.62	-28.06	-9.47
20.00	.30	22.20	30.74	29.25
21.00	17.82	-2.37	-7.75	-33.58
22.00	-13.94	-17.97	-18.34	-6.57
23.00	14.42	27.62	20.45	33.77
24.00	10.09	1.93	-10.08	-17.79
25.00	-24.63	-21.26	-8.25	-10.70
26.00	22.45	23.95	31.22	1.22
27.00	-8.60	10.46	-17.35	-8.14
28.00	-4.33	38.92	5.25	7.07
29.00	15.95	-2.79	10.73	-10.90
30.00	-27.52	-34.35	-3.92	5.82
31.00	3.46	-16.45	-2.73	

CURVE 6 (2-76-2)

	0.00	0.25	0.50	0.75
6.00	-32.98	-3.87	7.00	51.54
7.00	56.69	6.26	-69.89	-109.71
8.00	-87.09	-4.13	84.62	112.90
9.00	63.88	-10.42	-52.92	-49.42
10.00	-10.75	8.71	-0.93	-34.57
11.00	-59.24	-23.76	43.01	83.36
12.00	73.59	26.12	-30.83	-70.36
13.00	-56.42	-9.12	34.12	18.27
14.00	-9.49	-18.28	-7.97	14.66
15.00	42.34	41.04	5.11	-31.00
16.00	-46.63	-46.43	-15.51	11.96
17.00	18.76	5.81	-0.85	9.66
18.00	28.05	42.79	29.25	4.83
19.00	-34.96	-45.86	-29.75	-14.40
20.00	20.47	38.69	16.01	20.26
21.00	8.54	-12.96	-11.95	-39.79
22.00	-38.29	-33.67	-12.04	5.06
23.00	19.10	43.93	55.99	22.53
24.00	16.27	-8.12	-33.60	-28.65
25.00	-16.29	-17.97	-17.18	8.00
26.00	24.27	28.25	35.98	17.62
27.00	25.84	-34.93	-18.64	-11.25
28.00	-0.94	31.98	-0.09	16.33
29.00	4.40	9.59	12.94	-8.05
30.00	-35.16	-11.83	-18.92	-5.25
31.00	-35.18	-36.12	-24.57	

EXPERIMENTAL INTENSITY CURVES FOR ALUMINUM IODIDE
CURVE 1 (2-88-1)

	0.00	0.25	0.50	0.75
1.00	-0.18	-0.73	-0.90	-0.18
2.00	.04	-2.32	-4.71	-2.07
3.00	5.99	15.05	15.57	2.26
4.00	-15.99	-22.47	-12.37	5.73
5.00	12.18	4.21	-6.75	-6.78
6.00	6.96	19.23	10.87	-12.03
7.00	-27.86	-22.71	-0.80	24.16
8.00	29.54	16.59	-1.56	-8.30
9.00	-1.96	3.26	-0.70	-11.25
10.00	-13.73	-9.48	5.99	17.28
11.00	12.66	-2.05	-15.09	-14.33
12.00	-6.37	-0.77	2.94	4.39
13.00	7.61			

CURVE 2 (2-88-2)

	0.00	0.25	0.50	0.75
1.00	.01	-1.04	-1.19	-0.31
2.00	.09	-2.39	-4.95	-2.17
3.00	6.46	16.00	16.79	2.78
4.00	-16.79	-23.42	-13.01	6.90
5.00	13.05	4.70	-7.55	-7.47
6.00	7.46	20.56	10.72	-13.71
7.00	-30.42	-26.11	-2.01	25.18
8.00	32.11	17.46	-1.78	-9.88
9.00	-1.29	2.34	-0.50	-11.25
10.00	-16.66	-9.19	6.73	19.62
11.00	13.38	-1.78	-12.42	-17.09
12.00	-9.99	.39	5.23	8.81

CURVE 3 (2-88-3)

	0.00	0.25	0.50	0.75
1.00	.09	-1.27	-1.77	-0.67
2.00	-0.27	-4.28	-8.43	-3.51
3.00	10.66	24.86	25.74	4.99
4.00	-24.64	-35.31	-17.26	10.27
5.00	18.72	7.48	-8.95	-10.62
6.00	9.09	25.96	13.74	-18.74
7.00	-43.59	-36.13	-1.66	35.44
8.00	44.32	23.38	-4.67	-14.54
9.00	-5.09	4.04	-2.89	-17.17
10.00	-23.13	-12.85	11.54	30.52
11.00	24.91	2.55	-14.97	-21.49
12.00	-13.86	-1.86	1.99	8.46

CURVE 4 (2-83-4)

	0.00	0.25	0.50	0.75
1.00	-0.05	-0.61	-0.84	-0.20
2.00	.00	-2.48	-4.69	-2.01
3.00	5.71	13.48	13.62	2.50
4.00	-13.38	-19.42	-9.01	6.19
5.00	10.35	3.55	-5.57	-6.77
6.00	4.93	14.82	7.79	-10.58
7.00	-22.40	-19.75	.85	19.47
8.00	24.48	11.75	-1.23	-8.95
9.00	-4.05	1.02	.33	-7.56
10.00	-10.84	-6.52	7.19	13.41
11.00	9.96	.70	-10.24	-12.77
12.00	-7.33	-0.77	2.68	7.37

CURVE 5 (2-88-5)

	0.00	0.25	0.50	0.75
1.00	-0.06	-0.67	-0.94	-0.16
2.00	-0.16	-2.68	-5.12	-2.14
3.00	6.45	15.07	14.98	1.82
4.00	-15.21	-21.85	-10.15	6.98
5.00	12.04	5.07	-5.17	-5.76
6.00	5.59	17.34	8.60	-12.17
7.00	-27.42	-22.24	-2.05	21.93
8.00	27.29	12.81	-3.86	-8.49
9.00	-1.89	2.46	.12	-9.85
10.00	-12.92	-8.61	7.85	15.97
11.00	12.51	.58	-8.41	-13.37
12.00	-6.74	-2.93	4.06	4.95

CURVE 6 (2-89-3)

	0.00	0.25	0.50	0.75
7.00	-52.13	-44.89	-5.88	35.31
8.00	56.78	34.36	-4.13	-28.26
9.00	-22.01	-4.97	2.85	-12.30
10.00	-20.63	-11.29	16.92	35.01
11.00	30.16	2.94	-17.07	-25.44
12.00	-10.01	-2.50	2.72	5.44
13.00	-3.58	8.12	14.83	17.97
14.00	3.09	-11.89	-14.56	-19.65
15.00	-5.73	2.87	-1.60	10.61
16.00	7.89	1.23	2.32	9.09
17.00	-4.63	-6.54	-8.47	-7.39
18.00	10.25	11.38	2.47	5.70
19.00	8.22	-5.06	-12.76	-3.42
20.00	-0.13	-5.94	-8.69	5.72
21.00	-16.41	-3.72	9.17	-9.03
22.00	2.77	4.05	-2.19	6.33
23.00	-3.41	-6.08	12.22	2.94
24.00	2.12	10.68	8.57	8.31
25.00	14.70	12.49	7.86	-13.01
26.00	11.58	-22.87	-13.72	-11.71
27.00	-2.86	-3.56	-9.72	14.60
28.00	-18.06	3.25	4.61	11.07
29.00	-25.68	14.25	-6.59	7.91
30.00	8.92			

CURVE 7 (2-89-4)

	0.00	0.25	0.50	0.75
7.00	-123.26	-114.16	-16.42	98.52
8.00	139.01	79.02	-19.83	-63.58
9.00	-45.15	18.19	9.38	-31.41
10.00	-56.19	-28.75	32.62	90.15
11.00	73.44	7.24	-63.12	-73.25
12.00	-42.66	-10.86	.62	-11.70
13.00	-13.84	8.91	40.43	36.28
14.00	15.27	-31.73	-47.74	-40.76
15.00	-23.74	15.23	18.65	32.51
16.00	30.14	14.06	25.83	.15
17.00	-27.97	-10.51	-31.95	-14.25
18.00	9.65	24.75	28.82	7.66
19.00	26.55	10.77	24.31	-3.91
20.00	9.64	13.97	1.41	13.62
21.00	14.57	-0.03	17.29	-3.67
22.00	-24.27	8.13	-9.07	-2.74
23.00	-5.19	-13.60	16.30	.43
24.00	4.50	-3.47	-0.83	-1.49
25.00	-21.59	-24.45	-23.53	-34.88
26.00	-20.71	8.91	-34.69	-6.07
27.00	-9.28	11.19	-56.25	16.19
28.00	1.62	30.13	9.87	-26.79
29.00	11.14	-18.22	53.95	53.19
30.00	-12.73			

CURVE 8 (2-89-5)

	0.00	0.25	0.50	0.75
7.00	-153.41	-151.26	-34.15	111.53
8.00	184.60	98.86	-18.20	-83.90
9.00	-68.09	7.23	6.56	-38.17
10.00	-63.72	-33.18	45.40	119.93
11.00	100.34	19.62	-70.71	-75.39
12.00	-50.03	-0.82	3.34	-8.88
13.00	-9.22	14.60	36.78	59.72
14.00	32.12	-28.61	-34.92	-30.46
15.00	-13.42	16.88	39.33	41.27
16.00	31.75	3.36	3.29	18.71
17.00	-24.05	-46.36	-55.71	-19.87
18.00	-13.35	2.92	41.97	7.38
19.00	5.43	10.78	-7.64	-13.29
20.00	-13.95	-29.61	-61.75	-35.83
21.00	1.91	8.68	4.57	-3.13
22.00	14.81	6.71	11.98	20.84
23.00	.32	23.02	1.92	26.01
24.00	11.31	5.64	5.40	-23.81
25.00	-13.69	-27.94	-10.25	15.42
26.00	22.69	20.47	25.02	19.07
27.00	-1.21	-6.74	-11.99	-28.67
28.00	32.03	33.90	22.93	-5.83
29.00	-28.99	5.68	11.19	-10.14
30.00	-53.99			

EXPERIMENTAL INTENSITY CURVES FOR GALLIUM CHLORIDE
CURVE 1 (2-87-6)

	0.00	0.25	0.50	0.75
1.00	2.35	-1.84	-6.29	-14.07
2.00	-16.89	-19.47	-27.32	-28.84
3.00	-9.98	34.70	87.65	134.86
4.00	144.86	75.84	-68.73	-208.68
5.00	-247.03	-171.61	-38.13	88.98
6.00	152.10	150.27	116.17	94.16
7.00	75.91	11.77	-99.28	-193.30
8.00	-217.12	-169.19	-69.34	64.34
9.00	184.72	233.29	184.44	97.67
10.00	17.79	-57.65	-97.11	-120.80
11.00	-148.48	-157.60	-118.64	-10.39
12.00	120.03	205.27	195.61	105.42
13.00	12.86			

CURVE 2 (2-87-7)

	0.00	0.25	0.50	0.75
1.00	2.17	-1.27	-6.70	-11.66
2.00	-14.09	-16.77	-23.28	-24.10
3.00	-7.59	28.52	74.12	111.24
4.00	119.43	63.16	-57.18	-170.11
5.00	-202.94	-142.55	-29.70	68.77
6.00	122.11	122.22	95.20	78.72
7.00	61.55	9.66	-77.81	-156.04
8.00	-174.71	-135.36	-54.08	50.92
9.00	145.39	184.47	146.48	76.41
10.00	12.05	-40.15	-76.82	-93.56
11.00	-115.81	-125.13	-88.58	-18.62
12.00	84.85	167.03	158.10	92.22
13.00	7.99			

CURVE 3 (2-87-8)

	0.00	0.25	0.50	0.75
1.00	1.63	-1.00	-4.97	-8.49
2.00	-10.01	-11.61	-16.41	-17.27
3.00	-5.79	21.13	52.12	78.97
4.00	85.76	45.16	-39.23	-123.08
5.00	-145.78	-99.88	-21.54	49.81
6.00	86.75	87.34	67.23	54.04
7.00	44.49	6.54	-58.28	-110.81
8.00	-123.73	-94.99	-37.61	40.78
9.00	104.99	130.73	103.68	56.75
10.00	8.77	-32.96	-53.88	-73.20
11.00	-87.47	-89.87	-66.16	-1.40
12.00	67.89	116.66	111.39	62.64
13.00	6.68			

CURVE 4 (2-87-9)

	0.00	0.25	0.50	0.75
1.00	.95	-0.74	-3.17	-5.41
2.00	-6.56	-7.52	-10.79	-11.33
3.00	-3.64	13.77	33.89	51.46
4.00	56.14	28.92	-26.26	-79.28
5.00	-94.26	-65.05	-14.10	33.18
6.00	56.75	55.89	43.81	36.85
7.00	27.82	3.97	-39.24	-73.91
8.00	-81.76	-63.28	-25.99	25.66
9.00	70.59	87.90	73.05	38.66
10.00	6.67	-20.00	-34.46	-49.46
11.00	-60.93	-62.96	-45.22	-1.48
12.00	47.24	76.81	71.46	43.13
13.00	6.29			

CURVE 5 (2-87-10)

	0.00	0.25	0.50	0.75
1.00	1.39	-1.08	-3.59	-5.87
2.00	-6.98	-7.98	-11.33	-11.75
3.00	-3.66	14.32	35.94	54.81
4.00	59.86	31.31	-28.16	-84.18
5.00	-99.51	-69.13	-15.21	33.96
6.00	59.88	58.48	46.35	37.79
7.00	31.10	3.65	-40.33	-77.82
8.00	-85.55	-66.25	-26.27	26.12
9.00	74.31	91.15	76.11	40.93
10.00	7.80	-20.69	-37.92	-52.14
11.00	-62.03	-64.70	-49.16	-0.40
12.00	48.55	79.21	75.95	44.22
13.00	7.27			

CURVE 6 (2-87-1)

	0.00	0.25	0.50	0.75
7.00	197.85	39.52	-210.08	-418.02
8.00	-482.25	-366.42	-137.60	112.28
9.00	351.15	454.27	375.55	224.80
10.00	27.82	-92.82	-174.98	-246.49
11.00	-278.51	-305.24	-208.19	-19.53
12.00	209.12	349.82	351.84	245.50
13.00	7.74	-138.67	-202.58	-158.73
14.00	-101.47	-78.24	-83.19	-99.18
15.00	-77.22	28.68	154.28	301.74
16.00	298.63	185.38	26.81	-142.03
17.00	-247.45	-282.26	-209.34	-105.53
18.00	25.42	83.25	162.11	207.01
19.00	212.07	203.57	63.76	-76.78
20.00	-200.32	-289.03	-309.10	-205.44
21.00	-94.99	95.33	253.00	330.05
22.00	321.19	226.46	45.45	-90.96
23.00	-253.05	-334.52	-308.81	-268.90
24.00	-59.17	80.69	261.72	340.55
25.00	306.17	246.72	42.32	-79.79
26.00	-200.39	-328.60	-306.66	-141.76
27.00	-2.45	105.85	277.89	262.49
28.00	202.10	106.31	-59.90	-174.02
29.00	-204.50	-257.05	-185.82	-79.07
30.00	36.18	127.93	252.25	251.91

CURVE 7 (2-87-4)

	0.00	0.25	0.50	0.75
7.00	124.03	39.40	-148.07	-284.07
8.00	-321.31	-248.26	-100.25	75.36
9.00	248.49	307.21	260.45	143.09
10.00	19.47	-70.84	-132.91	-170.60
11.00	-201.65	-214.00	-153.11	2.11
12.00	176.78	273.20	252.63	125.55
13.00	8.39	-91.22	-130.09	-118.54
14.00	-66.82	-36.82	-50.76	-87.96
15.00	-41.79	6.71	114.50	198.14
16.00	192.21	129.64	-8.36	-97.92
17.00	-189.49	-180.15	-151.27	-64.44
18.00	8.83	43.39	109.55	169.27
19.00	173.67	135.70	77.25	-43.07
20.00	-110.42	-172.78	-205.96	-200.41
21.00	-79.90	47.75	165.18	238.88
22.00	198.27	126.99	20.67	-97.52
23.00	-176.32	-229.40	-203.18	-106.98
24.00	-22.48	124.30	207.96	254.98
25.00	186.63	103.75	-10.32	-75.96
26.00	-170.28	-204.72	-211.96	-122.74
27.00	-12.20	101.67	171.61	213.52
28.00	157.08	81.90	-39.34	-132.14
29.00	-148.59	-135.71	-71.79	-42.44
30.00	-60.27	94.74	102.04	175.73

CURVE 8 (2-87-5)

	0.00	0.25	0.50	0.75
7.00	139.91	31.42	-161.14	-312.38
8.00	-352.16	-279.44	-99.24	85.34
9.00	273.63	331.78	281.70	153.02
10.00	30.32	-67.79	-134.71	-202.85
11.00	-238.76	-241.37	-167.05	-22.20
12.00	187.39	298.98	318.23	162.47
13.00	18.70	-112.71	-157.02	-137.93
14.00	-63.37	-61.56	-54.23	-70.28
15.00	-34.70	36.04	127.85	200.46
16.00	202.59	139.98	-11.75	-126.72
17.00	-204.03	-201.02	-160.41	-86.74
18.00	.70	73.51	130.80	123.61
19.00	183.15	125.48	106.03	-18.17
20.00	-147.67	-217.76	-251.57	-179.26
21.00	-54.12	77.97	183.47	297.37
22.00	210.13	179.03	38.10	-95.65
23.00	-170.03	-282.49	-233.58	-155.49
24.00	-19.12	132.12	169.06	235.76
25.00	224.10	141.51	2.39	-147.48
26.00	-173.92	-277.02	-190.56	-90.65
27.00	-24.10	114.93	225.89	219.00
28.00	186.85	92.55	15.39	-143.53
29.00	-165.30	-195.71	-174.24	-48.86
30.00	-2.58	173.85	103.34	167.58

EXPERIMENTAL INTENSITY CURVES FOR GALLIUM BROMIDE
AT 163 DEG. C
CURVE 1 (2-97-2)

	0.00	0.25	0.50	0.75
2.00	-8.81	-16.93	-33.57	-30.92
3.00	8.17	75.15	139.51	153.69
4.00	70.04	-93.80	-225.68	-227.94
5.00	-113.37	29.07	113.57	119.88
6.00	79.92	77.29	136.31	140.34
7.00	4.70	-208.16	-364.28	-348.14
8.00	-179.84	115.34	367.74	427.31
9.00	273.93	84.69	-58.69	-92.92
10.00	-132.39	-196.18	-284.09	-303.00
11.00	-151.00	127.24	356.71	421.45
12.00	259.29	52.04	-130.18	-180.86

CURVE 2 (2-97-3)

	0.00	0.25	0.50	0.75
2.00	-12.59	-19.81	-35.27	-31.34
3.00	10.41	85.12	155.61	172.61
4.00	73.21	-103.95	-248.06	-251.00
5.00	-128.10	28.38	122.09	127.50
6.00	89.59	91.08	155.39	163.08
7.00	5.43	-239.58	-419.91	-411.50
8.00	-199.00	148.05	432.40	468.33
9.00	326.52	92.16	-52.49	-105.92
10.00	-144.13	-221.04	-321.64	-347.68
11.00	-195.37	107.80	386.06	479.66
12.00	342.96	85.47	-126.23	-244.84

CURVE 3 (2-97-4)

	0.00	0.25	0.50	0.75
2.00	-15.02	-23.56	-43.56	-38.93
3.00	12.62	102.78	190.70	217.27
4.00	89.38	-132.12	-312.00	-315.43
5.00	-159.67	40.41	163.38	165.24
6.00	114.25	113.43	195.35	203.01
7.00	3.80	-304.49	-523.14	-510.95
8.00	-240.16	172.22	524.98	602.60
9.00	383.31	96.63	-79.05	-126.50
10.00	-169.36	-273.14	-354.49	-410.73
11.00	-244.74	134.76	482.35	585.21
12.00	406.48	52.11	-158.71	-262.46

CURVE 4 (2-97-5)

	0.00	0.25	0.50	0.75
2.00	-8.32	-15.32	-29.19	-26.76
3.00	7.20	66.13	120.22	132.50
4.00	59.66	-77.11	-189.51	-189.75
5.00	-95.14	23.79	94.97	98.19
6.00	65.38	66.20	106.50	111.37
7.00	5.43	-177.68	-306.05	-305.68
8.00	-158.18	89.30	311.11	341.15
9.00	233.95	78.51	-38.90	-66.41
10.00	-80.96	-147.67	-206.27	-229.07
11.00	-130.15	98.92	298.60	331.25
12.00	184.63	7.90	-137.57	-207.83
13.00	-177.49	-75.98		

CURVE 5 (2-96-3)

	0.00	0.25	0.50	0.75
8.00	-52.44	22.01	89.40	106.48
9.00	74.44	30.30	.92	-14.37
10.00	-30.38	-56.11	-83.44	-85.99
11.00	-48.62	20.55	90.17	115.92
12.00	89.35	38.20	-25.89	-54.08
13.00	-69.36	-65.69	-46.52	-31.91
14.00	-9.51	31.55	79.77	87.49
15.00	85.70	33.97	-20.05	-80.67
16.00	-97.10	-82.67	-46.22	-17.51
17.00	38.14	68.60	84.76	82.90
18.00	48.35	1.55	-49.88	-91.75
19.00	-96.66	-83.36	-25.95	29.82
20.00	75.41	104.95	86.18	63.17
21.00	5.15	-48.87	-72.64	-105.17
22.00	-73.70	-34.89	8.88	48.22
23.00	85.08	85.99	56.47	22.55
24.00	-25.90	-61.95	-82.44	-86.12
25.00	-26.01	.56	51.96	68.93
26.00	72.39	63.65	13.74	-27.70
27.00	-73.53	-63.36	-70.37	-43.24
28.00	-8.00	50.66	85.67	65.60
29.00	68.00	7.83	-0.06	-61.94
30.00	-86.48	-61.48	-30.32	-3.54
31.00	30.48			

CURVE 6 (2-96-4)

	0.00	0.25	0.50	0.75
8.00	-167.83	70.60	263.58	321.34
9.00	197.18	55.24	-43.52	-87.66
10.00	-92.82	-150.65	-203.71	-206.98
11.00	-106.88	86.48	273.66	328.62
12.00	235.66	66.31	-86.80	-184.29
13.00	-195.97	-135.68	-105.57	-65.85
14.00	-18.31	74.49	154.32	221.95
15.00	203.08	76.55	-59.93	-184.52
16.00	-222.62	-215.62	-121.57	-11.91
17.00	80.55	180.03	204.08	209.28
18.00	145.07	-0.75	-109.06	-226.27
19.00	-243.25	-204.71	-73.64	40.23
20.00	167.71	244.42	254.00	137.54
21.00	53.26	-96.16	-160.50	-253.22
22.00	-227.45	-115.70	-3.60	152.49
23.00	197.60	218.29	182.24	47.35
24.00	-69.69	-187.86	-249.56	-186.12
25.00	-130.71	.48	114.02	220.82
26.00	204.61	222.87	61.87	-32.06
27.00	-151.30	-206.94	-138.89	-131.28
28.00	-75.98	141.49	146.65	155.98
29.00	89.76	41.36	26.60	-137.56
30.00	-171.09	-142.43	-50.65	-7.47
31.00	32.28			

CURVE 7 (2-96-5)

	0.00	0.25	0.50	0.75
8.00	-109.44	49.96	172.31	206.31
9.00	133.55	52.88	-15.67	-42.80
10.00	-55.38	-100.72	-144.32	-142.37
11.00	-85.00	43.78	166.79	215.59
12.00	162.52	41.51	-59.40	-104.55
13.00	-131.53	-98.04	-79.23	-52.48
14.00	-7.77	57.93	123.37	161.12
15.00	150.97	71.19	-36.65	-134.45
16.00	-155.25	-145.69	-74.16	-13.33
17.00	49.74	94.60	142.49	128.69
18.00	72.80	-13.14	-71.35	-151.27
19.00	-182.89	-138.56	-56.69	59.82
20.00	125.88	166.69	148.79	146.30
21.00	41.52	-28.15	-149.40	-181.04
22.00	-160.89	-107.50	28.27	121.13
23.00	150.62	155.69	114.95	30.66
24.00	-79.30	-116.37	-127.93	-158.51
25.00	-135.93	25.30	68.83	140.30
26.00	168.66	127.71	37.61	-27.84
27.00	-92.03	-170.71	-127.46	-58.25
28.00	-18.02	64.52	123.68	134.89
29.00	99.76	64.59	-22.23	-87.33
30.00	-120.40	-137.57	-91.58	-26.07
31.00	87.68			

EXPERIMENTAL INTENSITY CURVES FOR GALLIUM BROMIDE
AT 192 DEG. C
CURVE 1 (2-119-7)

	0.00	0.25	0.50	0.75
2.00	-2.93	-9.87	-21.12	-20.08
3.00	.37	40.01	76.33	84.62
4.00	39.65	-44.36	-113.14	-115.78
5.00	-60.11	6.40	43.60	45.98
6.00	39.17	54.11	84.62	85.02
7.00	18.59	-98.98	-188.99	-193.51
8.00	-110.58	33.19	157.04	199.14
9.00	155.85	80.63	16.23	-15.21
10.00	-52.18	-116.07	-164.96	-184.97
11.00	-115.16	29.37	168.48	239.76
12.00	184.97	81.64	-36.21	-111.35

CURVE 2 (2-119-8)

	0.00	0.25	0.50	0.75
2.00	-5.66	-13.32	-25.70	-24.21
3.00	3.31	52.43	97.46	105.92
4.00	48.36	-58.05	-141.41	-145.91
5.00	-76.85	6.58	53.66	57.66
6.00	50.26	68.84	110.25	113.73
7.00	21.37	-130.35	-248.14	-259.13
8.00	-149.83	42.74	221.44	272.92
9.00	206.60	102.52	25.45	-23.52
10.00	-67.30	-150.54	-232.74	-247.59
11.00	-144.55	38.07	234.91	301.96
12.00	249.56	101.05	-47.52	-141.45

CURVE 3 (2-119-9)

	0.00	0.25	0.50	0.75
2.00	-0.99	-7.84	-18.65	-19.67
3.00	-1.73	33.84	67.02	74.40
4.00	33.92	-39.36	-99.00	-100.12
5.00	-50.82	7.04	38.77	40.41
6.00	36.51	47.16	74.91	74.44
7.00	14.36	-85.73	-165.06	-167.24
8.00	-91.10	29.03	131.91	165.18
9.00	126.37	60.67	12.70	-11.65
10.00	-42.81	-89.05	-134.83	-141.17
11.00	-84.65	25.35	135.53	186.11
12.00	140.55	59.82	-26.35	-82.60

CURVE 4 (2-119-10)

	0.00	0.25	0.50	0.75
2.00	-0.75	-7.49	-18.49	-19.95
3.00	-2.18	33.06	66.10	74.63
4.00	35.28	-38.89	-99.18	-101.63
5.00	-52.03	6.79	39.41	41.55
6.00	35.03	46.19	74.88	76.74
7.00	19.24	-82.25	-160.08	-169.34
8.00	-93.05	27.79	131.70	161.79
9.00	120.42	58.27	10.30	-16.74
10.00	-41.84	-82.25	-135.06	-144.15
11.00	-85.89	37.74	143.24	184.25
12.00	134.41	62.04	-31.42	-82.77

CURVE 5 (2-119-1)

	0.00	0.25	0.50	0.75
8.00	-275.11	55.19	328.78	415.02
9.00	287.11	140.69	21.03	-53.48
10.00	-102.15	-227.44	-349.17	-362.34
11.00	-210.43	84.57	362.48	501.63
12.00	402.02	161.00	-81.60	-254.75
13.00	-300.95	-289.23	-225.07	-161.46
14.00	-29.02	144.90	341.38	422.57
15.00	365.18	159.31	-127.94	-340.17
16.00	-421.78	-362.71	-185.33	-32.08
17.00	151.86	298.92	367.95	321.15
18.00	188.74	-18.00	-228.70	-368.32
19.00	-409.96	-306.71	-112.38	141.35
20.00	326.77	387.31	342.67	221.51
21.00	4.34	-157.01	-309.84	-369.57
22.00	-320.55	-153.80	65.86	255.62
23.00	368.24	340.30	264.69	82.55
24.00	-135.24	-248.77	-400.69	-351.49
25.00	-199.04	6.12	154.13	298.82
26.00	319.63	225.97	106.58	-37.72
27.00	-230.35	-317.01	-262.07	-121.98
28.00	-10.70	193.34	234.23	300.78
29.00	208.00	73.29	-61.36	-212.67
30.00	-302.00	-264.48	-144.68	-10.22
31.00	147.30			

CURVE 6 (2-119-4)

	0.00	0.25	0.50	0.75
8.00	-226.32	46.65	280.33	332.43
9.00	247.35	121.84	25.96	-38.33
10.00	-105.86	-213.47	-301.12	-307.27
11.00	-158.54	99.69	341.19	427.03
12.00	331.66	135.95	-81.70	-220.24
13.00	-277.59	-254.23	-196.50	-131.45
14.00	-10.09	127.44	282.89	359.04
15.00	290.87	96.56	-100.51	-290.66
16.00	-342.34	-301.99	-164.09	-11.17
17.00	141.09	257.86	314.78	286.34
18.00	167.92	-13.91	-183.29	-336.96
19.00	-352.74	-250.36	-75.80	108.38
20.00	278.46	335.31	292.27	205.99
21.00	17.30	-159.35	-284.40	-325.04
22.00	-262.21	-142.70	38.83	216.71
23.00	276.84	268.53	180.22	26.39
24.00	-148.36	-218.79	-260.02	-241.18
25.00	-103.69	41.06	160.22	280.12
26.00	285.45	210.22	68.39	-93.66
27.00	-213.82	-279.83	-264.16	-165.86
28.00	8.04	155.03	232.31	232.24
29.00	169.41	92.30	-30.45	-209.78
30.00	-212.45	-221.90	-107.94	3.12
31.00	86.10			

CURVE 7 (2-119-5)

	0.00	0.25	0.50	0.75
8.00	-346.07	69.32	420.45	516.71
9.00	374.92	164.50	8.33	-80.07
10.00	-142.14	-305.49	-460.42	-434.35
11.00	-251.13	147.14	501.22	663.08
12.00	523.34	203.84	-127.93	-358.50
13.00	-423.42	-375.66	-309.58	-200.42
14.00	-18.36	187.83	453.66	553.56
15.00	464.71	164.69	-188.27	-452.45
16.00	-522.40	-447.39	-241.21	-3.64
17.00	175.89	357.70	464.41	425.71
18.00	228.58	-5.72	-255.20	-433.82
19.00	-496.04	-359.66	-104.64	157.86
20.00	399.77	425.28	442.98	242.97
21.00	-5.44	-205.98	-427.18	-492.38
22.00	-325.45	-181.86	53.84	360.79
23.00	374.65	450.52	303.30	6.89
24.00	-175.76	-365.22	-409.44	-318.82
25.00	-194.93	7.65	277.47	371.45
26.00	388.80	293.09	121.34	-145.58
27.00	-316.64	-364.20	-291.88	-168.59
28.00	-35.79	194.56	271.85	321.08
29.00	233.59	152.24	-48.22	-245.88
30.00	-315.72	-344.26	-165.63	-16.06
31.00	148.38			

EXPERIMENTAL INTENSITY CURVES FOR GALLIUM BROMIDE
AT 226 DEG. C
CURVE 1 (2-111-1)

	0.00	0.25	0.50	0.75
2.00	-3.71	-11.07	-21.23	-21.55
3.00	-1.37	39.35	78.11	82.85
4.00	36.76	-39.95	-98.73	-103.16
5.00	-61.11	-12.02	17.02	25.45
6.00	38.11	72.00	113.33	112.16
7.00	39.01	-87.64	-197.54	-223.18
8.00	-141.00	-1.08	129.66	191.25
9.00	175.93	121.04	65.68	19.75
10.00	-45.63	-128.55	-208.62	-222.26
11.00	-147.64	4.07	171.00	264.77
12.00	236.54	126.67	6.14	-98.22

CURVE 2 (2-111-2)

	0.00	0.25	0.50	0.75
2.00	-2.63	-8.71	-17.47	-18.20
3.00	-2.22	31.68	63.73	69.11
4.00	31.93	-31.44	-81.45	-86.61
5.00	-54.64	-10.72	13.89	20.28
6.00	33.42	60.92	93.86	95.75
7.00	36.07	-66.55	-157.56	-182.93
8.00	-122.49	-6.72	102.67	151.53
9.00	142.86	98.85	53.03	14.88
10.00	-34.14	-106.96	-170.15	-184.44
11.00	-116.97	15.55	143.83	215.32
12.00	192.18	101.21	-5.32	-74.99

CURVE 3 (2-111-3)

	0.00	0.25	0.50	0.75
2.00	-4.35	-12.31	-23.03	-23.13
3.00	-1.56	44.44	85.20	89.50
4.00	39.28	-44.03	-107.40	-112.28
5.00	-67.86	-13.11	19.36	28.72
6.00	41.53	77.13	122.19	121.95
7.00	42.88	-93.32	-211.93	-239.85
8.00	-158.19	-4.31	143.59	213.45
9.00	191.41	133.11	70.84	23.45
10.00	-52.00	-149.23	-236.36	-251.16
11.00	-166.99	16.82	193.80	299.50
12.00	266.90	146.26	-1.18	-113.34

CURVE 4 (2-111-4)

	0.00	0.25	0.50	0.75
2.00	-2.15	-8.54	-17.28	-18.37
3.00	-2.79	31.38	62.69	67.46
4.00	31.20	-30.27	-79.68	-84.86
5.00	-50.16	-9.72	13.24	19.79
6.00	28.22	59.78	91.92	92.80
7.00	35.44	-66.43	-159.98	-182.35
8.00	-113.40	.83	104.24	147.88
9.00	131.97	91.30	50.92	14.80
10.00	-32.65	-95.40	-154.94	-171.85
11.00	-115.43	7.54	129.20	201.35
12.00	180.84	98.39	-2.03	-67.88

CURVE 5 (2-112-2)

	0.00	0.25	0.50	0.75
8.00	-411.14	2.29	346.83	446.88
9.00	397.88	244.50	103.45	28.49
10.00	-130.31	-316.50	-491.84	-531.39
11.00	-301.47	114.31	511.89	684.09
12.00	632.53	325.66	-31.35	-377.55
13.00	-510.23	-498.37	-422.74	-270.74
14.00	-87.94	203.36	477.97	625.64
15.00	518.14	233.12	-172.05	-504.19
16.00	-608.93	-551.82	-254.54	-1.23
17.00	316.85	505.63	640.32	525.10
18.00	302.62	16.80	-377.01	-618.34
19.00	-680.82	-487.27	-171.56	196.28
20.00	471.98	592.47	494.09	265.74
21.00	-24.83	-271.10	-511.37	-600.25
22.00	-427.48	-215.55	127.14	346.16
23.00	584.43	538.09	402.73	91.70
24.00	-148.43	-416.69	-547.93	-465.72
25.00	-227.44	19.60	255.82	438.16
26.00	423.36	343.77	163.32	-54.73
27.00	-287.15	-418.44	-414.18	-290.25
28.00	-47.35	194.32	205.78	423.39
29.00	280.06	228.56	-41.71	-264.37
30.00	-310.56	-320.33	-222.85	-114.22
31.00	133.04			

CURVE 6 (2-112-4)

	0.00	0.25	0.50	0.75
8.00	-457.09	-22.16	363.54	532.69
9.00	458.06	318.83	125.32	19.49
10.00	-144.37	-349.22	-559.82	-604.13
11.00	-359.82	79.17	534.23	741.62
12.00	667.53	350.35	-20.08	-337.40
13.00	-533.33	-535.25	-456.84	-312.80
14.00	-31.71	279.00	552.63	646.63
15.00	586.80	262.70	-196.05	-531.39
16.00	-683.01	-635.83	-350.60	-87.04
17.00	307.65	563.83	654.88	604.14
18.00	361.43	47.14	-431.64	-663.38
19.00	-713.37	-526.67	-204.22	181.94
20.00	513.68	614.55	594.20	409.11
21.00	27.10	-301.75	-575.94	-636.40
22.00	-523.14	-280.14	78.53	434.51
23.00	680.88	654.54	362.66	104.02
24.00	-210.30	-437.90	-537.40	-517.25
25.00	-306.22	-18.77	289.33	482.44
26.00	520.66	344.57	78.46	-154.73
27.00	-320.32	-475.14	-353.30	-220.43
28.00	.20	252.63	316.76	323.42
29.00	315.88	244.76	-26.85	-173.86
30.00	-396.68	-481.66	-322.78	-170.05
31.00	282.50			

CURVE 7 (2-112-5)

	0.00	0.25	0.50	0.75
8.00	-387.18	-26.88	308.59	455.35
9.00	376.82	266.44	127.06	10.66
10.00	-109.38	-332.42	-509.42	-521.67
11.00	-303.36	72.30	454.46	655.40
12.00	572.63	305.07	-35.73	-290.84
13.00	-444.89	-468.23	-371.87	-239.28
14.00	-50.27	231.90	518.03	588.28
15.00	494.39	191.98	-155.11	-470.90
16.00	-565.04	-505.89	-299.78	-36.02
17.00	207.93	434.94	468.67	473.58
18.00	255.85	-40.03	-301.11	-480.61
19.00	-561.01	-382.52	-129.42	148.81
20.00	422.09	482.13	451.63	289.18
21.00	33.00	-239.42	-401.09	-482.18
22.00	-395.40	-177.01	90.42	358.89
23.00	466.73	465.28	334.18	47.75
24.00	-164.13	-373.36	-474.87	-388.78
25.00	-227.09	-5.08	153.86	354.84
26.00	360.46	251.07	132.99	-131.70
27.00	-199.54	-303.88	-251.71	-163.16
28.00	-28.07	210.53	285.74	293.83
29.00	266.67	133.97	-55.69	-264.27
30.00	-337.88	-334.85	-251.72	-2.44
31.00	149.12			

EXPERIMENTAL INTENSITY CURVES FOR DINITROGEN TETROXIDE -
NITROGEN DIOXIDE AT 104 DEG. C. CURVE 1 (2-143-9)

	0.00	0.25	0.50	0.75
1.00	.55	2.28	4.11	5.39
2.00	5.11	2.69	-1.09	-5.82
3.00	-12.44	-19.23	-27.68	-37.09
4.00	-47.19	-56.74	-61.70	-57.84
5.00	-43.43	-18.15	17.35	55.76
6.00	93.03	117.56	129.05	122.12
7.00	97.30	62.17	23.74	-19.21
8.00	-49.12	-74.25	-86.54	-88.01
9.00	-87.01	-81.47	-76.60	-72.52
10.00	-64.67	-50.78	-26.11	5.00
11.00	47.81	88.18	124.69	151.16
12.00	149.53	132.76	97.37	43.47

CURVE 2 (2-143-10)

	0.00	0.25	0.50	0.75
1.00	.78	2.23	4.27	5.90
2.00	5.49	3.05	-1.09	-6.41
3.00	-13.44	-20.92	-29.80	-39.81
4.00	-50.64	-60.82	-67.19	-62.23
5.00	-47.17	-19.67	17.40	60.41
6.00	99.61	127.64	139.57	131.86
7.00	107.27	68.60	23.44	-20.03
8.00	-54.74	-80.31	-91.41	-95.41
9.00	-93.51	-89.24	-84.90	-78.67
10.00	-71.49	-53.84	-26.68	8.12
11.00	51.30	98.77	133.25	159.18
12.00	160.62	144.77	105.01	47.55

CURVE 3 (2-142-6)

	0.00	0.25	0.50	0.75
8.00	-34.58	-50.13	-57.57	-59.59
9.00	-58.22	-53.58	-53.06	-48.37
10.00	-46.31	-38.25	-23.00	1.02
11.00	29.48	60.71	90.62	107.24
12.00	107.93	99.91	72.31	35.68
13.00	-3.27	-40.55	-64.40	-86.09
14.00	-92.46	-88.81	-75.91	-58.15
15.00	-43.48	-24.33	-12.16	3.62
16.00	12.25	29.80	50.63	64.94
17.00	82.14	89.77	83.58	79.99
18.00	63.96	27.07	-13.34	-49.38
19.00	-69.80	-95.70	-100.51	-93.02
20.00	-74.32	-49.88	-23.99	-6.39
21.00	12.54	27.94	37.88	42.62
22.00	47.85	59.61	63.48	59.03
23.00	59.30	41.17	37.90	4.37
24.00	-24.03	-48.65	-71.59	-85.36
25.00	-80.48	-69.84	-57.43	-30.50
26.00	-9.85	16.70	29.10	51.75
27.00	55.61	54.10	47.56	51.62
28.00	47.66	33.68	25.17	8.56
29.00	10.52	-17.82	-33.31	-65.09
30.00	-78.62			

CURVE 4 (2-142-8)

	0.00	0.25	0.50	0.75
8.00	-49.73	-62.47	-72.96	-75.64
9.00	-77.17	-72.36	-69.27	-70.12
10.00	-59.83	-51.33	-29.37	4.06
11.00	41.32	78.35	116.56	142.10
12.00	145.69	131.00	92.38	46.85
13.00	-5.70	-51.01	-90.26	-113.21
14.00	-121.93	-116.24	-97.13	-75.03
15.00	-52.69	-32.60	-15.83	3.45
16.00	22.00	49.05	59.31	81.60
17.00	104.07	116.02	115.78	96.78
18.00	72.75	32.85	-12.94	-60.92
19.00	-94.90	-123.96	-129.55	-118.89
20.00	-100.75	-65.98	-36.84	-2.20
21.00	21.38	36.70	54.85	68.07
22.00	69.70	72.13	77.62	80.56
23.00	71.77	56.64	34.40	3.20
24.00	-34.36	-64.23	-92.88	-110.80
25.00	-105.03	-94.92	-68.99	-40.75
26.00	-5.27	14.52	45.52	66.42
27.00	66.51	76.41	74.28	57.69
28.00	61.36	50.12	30.65	20.99
29.00	-0.99	-29.56	-44.90	-75.50
30.00	-104.70			

EXPERIMENTAL INTENSITY CURVES FOR DINITROGEN TETROXIDE -
NITROGEN DIOXIDE AT 25 DEG. C. CURVE 1 (2-143-6)

	0.00	0.25	0.50	0.75
2.00	2.81	1.91	-0.23	-3.25
3.00	-8.23	-13.91	-21.51	-30.27
4.00	-40.57	-50.09	-54.91	-52.69
5.00	-40.66	-17.60	14.60	51.04
6.00	81.70	101.07	107.27	97.52
7.00	78.00	51.56	19.70	-11.43
8.00	-35.87	-55.76	-67.90	-74.99
9.00	-74.13	-69.67	-65.87	-59.68
10.00	-53.22	-41.25	-21.38	4.05
11.00	35.42	68.35	94.73	114.43
12.00	116.07	107.06	81.50	48.85
13.00	9.63			

CURVE 2 (2-143-7)

	0.00	0.25	0.50	0.75
2.00	3.32	2.29	-0.04	-3.92
3.00	-9.90	-17.08	-26.40	-37.74
4.00	-50.47	-62.06	-69.37	-66.05
5.00	-51.50	-21.40	19.47	63.14
6.00	100.00	125.38	131.97	122.67
7.00	98.67	66.51	26.88	-13.13
8.00	-45.48	-70.77	-87.81	-92.45
9.00	-92.44	-89.14	-82.13	-74.45
10.00	-66.18	-50.99	-26.60	5.89
11.00	46.07	86.14	118.82	140.38
12.00	141.73	133.21	101.93	64.62

CURVE 3 (2-142-9)

	0.00	0.25	0.50	0.75
8.00	-31.92	-53.91	-71.14	-77.77
9.00	-82.67	-76.55	-72.42	-68.75
10.00	-58.60	-49.25	-26.00	7.88
11.00	42.28	79.44	110.88	131.04
12.00	132.84	116.59	89.19	41.71
13.00	-2.52	-48.73	-82.81	-100.99
14.00	-108.50	-106.16	-89.65	-69.90
15.00	-46.48	-27.47	-13.65	1.55
16.00	18.61	28.05	51.54	71.11
17.00	89.79	95.87	100.57	89.63
18.00	68.48	34.78	-6.57	-49.58
19.00	-78.88	-103.50	-112.14	-100.74
20.00	-73.95	-55.38	-26.27	-2.73
21.00	22.06	32.33	42.83	49.45
22.00	57.50	59.39	69.30	65.45
23.00	52.65	51.15	27.40	1.91
24.00	-29.50	-55.86	-81.88	-94.57
25.00	-99.52	-89.20	-66.67	-37.17
26.00	-2.58	21.47	45.75	52.00
27.00	63.32	66.33	67.06	59.34
28.00	53.17	47.98	30.12	10.56
29.00	-13.65	-19.37	-35.42	-66.48
30.00	-62.94	-78.32	-64.92	-56.63
31.00	-37.65			

CURVE 4 (2-142-11)

	0.00	0.25	0.50	0.75
8.00	-36.36	-59.29	-76.22	-90.70
9.00	-89.60	-89.34	-82.15	-76.09
10.00	-65.52	-51.79	-26.32	8.22
11.00	50.02	91.22	119.50	142.23
12.00	147.80	129.66	94.79	47.71
13.00	-2.85	-51.33	-89.07	-113.33
14.00	-119.86	-116.11	-98.00	-75.92
15.00	-54.43	-36.19	-18.47	1.00
16.00	16.10	33.47	57.12	80.25
17.00	101.30	112.50	117.17	103.14
18.00	69.94	32.29	-10.11	-59.03
19.00	-93.05	-111.83	-116.37	-115.01
20.00	-97.41	-63.79	-32.26	.12
21.00	22.06	35.88	41.00	64.36
22.00	77.74	79.71	82.87	79.47
23.00	73.20	58.75	37.50	-6.78
24.00	-44.09	-65.56	-86.91	-104.16
25.00	-112.73	-87.86	-81.95	-46.02
26.00	-23.04	11.34	32.24	51.05
27.00	60.21	77.47	64.27	48.57
28.00	50.16	53.14	43.50	30.44
29.00	15.41	-12.44	-25.67	-40.29
30.00	-65.90	-76.59	-79.83	-79.19
31.00	-75.48			

EXPERIMENTAL INTENSITY CURVES FOR DINITROGEN TETROXIDE -
NITROGEN DIOXIDE AT 2 DEG. C. CURVE 1 (2-143-4)

	0.00	0.25	0.50	0.75
2.00	1.34	.67	-0.20	-1.88
3.00	-5.66	-11.22	-20.33	-32.20
4.00	-46.32	-59.34	-67.23	-60.79
5.00	-41.81	-6.69	30.88	67.35
6.00	89.72	95.83	90.45	78.56
7.00	67.64	54.94	36.87	17.19
8.00	-12.13	-42.73	-70.75	-86.20
9.00	-91.09	-89.36	-82.83	-73.80
10.00	-63.13	-47.77	-22.23	9.35
11.00	46.73	80.88	105.76	117.02
12.00	118.50	110.29	87.18	60.01

CURVE 2 (2-143-5)

	0.00	0.25	0.50	0.75
2.00	2.05	.86	-0.47	-2.80
3.00	-7.62	-14.60	-26.14	-40.53
4.00	-58.48	-74.64	-83.35	-76.82
5.00	-49.27	-8.47	40.70	83.13
6.00	111.44	119.69	112.26	97.21
7.00	82.48	69.40	50.26	22.11
8.00	-13.16	-51.78	-86.82	-107.13
9.00	-115.70	-112.82	-104.59	-93.42
10.00	-82.42	-62.25	-28.86	13.17
11.00	62.23	102.84	131.29	148.08
12.00	148.18	138.41	108.47	79.62

CURVE 3 (2-142-4)

	0.00	0.25	0.50	0.75
8.00	-10.24	-41.76	-69.81	-89.65
9.00	-95.37	-93.12	-85.87	-74.80
10.00	-65.69	-48.71	-26.85	8.27
11.00	46.83	82.14	106.94	120.05
12.00	125.33	114.98	95.07	60.99
13.00	20.19	-24.32	-72.83	-106.70
14.00	-120.76	-119.52	-101.30	-75.43
15.00	-47.21	-27.12	-9.96	.19
16.00	13.41	31.35	50.04	73.12
17.00	87.04	99.53	103.78	94.15
18.00	76.55	45.81	7.46	-44.63
19.00	-90.33	-121.56	-137.21	-128.67
20.00	-96.97	-62.12	-30.02	-1.13
21.00	23.17	37.79	47.68	54.06
22.00	69.96	86.83	81.89	95.29
23.00	78.46	67.88	48.10	15.75
24.00	-29.55	-70.21	-100.16	-117.34
25.00	-121.76	-112.84	-86.04	-43.09
26.00	-15.44	17.90	39.32	49.61
27.00	59.14	63.14	67.94	59.95
28.00	63.20	52.01	36.02	20.53
29.00	4.60	-3.32	-34.98	-57.18
30.00	-62.75	-72.48	-72.82	-62.67
31.00	-28.54	-7.15	-57.14	

CURVE 4 (2-142-5)

	0.00	0.25	0.50	0.75
8.00	-6.12	-41.71	-83.54	-111.40
9.00	-122.91	-115.63	-103.67	-95.94
10.00	-79.19	-62.00	-28.22	18.10
11.00	63.51	104.71	137.75	153.82
12.00	154.61	141.56	110.24	70.29
13.00	20.93	-36.63	-84.80	-127.64
14.00	-149.42	-147.48	-121.36	-94.76
15.00	-60.69	-31.17	-20.88	-1.90
16.00	14.07	33.41	58.51	75.84
17.00	102.30	108.63	117.05	109.64
18.00	91.11	57.53	15.30	-38.80
19.00	-96.19	-132.26	-146.59	-139.56
20.00	-111.10	-70.34	-26.28	4.93
21.00	24.29	42.79	55.30	64.81
22.00	80.02	79.31	94.98	91.21
23.00	85.34	68.39	40.35	8.83
24.00	-31.22	-82.66	-124.06	-128.56
25.00	-140.24	-124.01	-86.15	-45.74
26.00	-10.80	20.73	47.27	60.52
27.00	68.45	76.35	78.07	79.30
28.00	69.01	55.18	52.58	32.83
29.00	6.70	-10.39	-38.74	-66.33
30.00	-84.86	-88.77	-88.67	-81.56
31.00	-69.95	-29.54	-5.28	

EXPERIMENTAL INTENSITY CURVES FOR DINITROGEN TETROXIDE -
NITROGEN DIOXIDE AT -25 DEG. C. CURVE 1 (2-143-1)

	0.00	0.25	0.50	0.75
2.00	-0.82	-0.90	-0.16	.87
3.00	-1.72	-7.37	-19.07	-35.10
4.00	-56.03	-74.75	-84.51	-76.63
5.00	-46.53	1.65	53.63	93.21
6.00	108.14	100.86	80.34	62.00
7.00	54.33	57.61	58.78	46.59
8.00	14.52	-32.34	-77.51	-108.04
9.00	-120.69	-116.60	-104.51	-92.19
10.00	-74.99	-53.04	-20.33	21.84
11.00	65.19	102.91	123.09	128.69
12.00	126.46	115.44	97.94	70.63

CURVE 2 (2-143-2)

	0.00	0.25	0.50	0.75
2.00	-0.75	-1.22	-0.26	.61
3.00	-2.41	-9.88	-24.88	-45.25
4.00	-71.83	-95.62	-108.24	-96.79
5.00	-58.74	1.62	68.87	118.72
6.00	139.03	129.24	103.19	77.98
7.00	68.54	72.95	75.17	59.98
8.00	20.47	-38.57	-97.27	-138.94
9.00	-155.88	-151.09	-136.88	-118.17
10.00	-96.78	-67.92	-24.30	28.89
11.00	83.46	134.19	156.34	165.63
12.00	159.04	148.30	126.46	93.65

CURVE 3 (2-142-1)

	0.00	0.25	0.50	0.75
8.00	15.77	-36.43	-89.41	-130.06
9.00	-147.41	-138.43	-123.53	-108.03
10.00	-90.07	-61.99	-22.95	27.07
11.00	78.19	120.46	147.12	154.80
12.00	153.47	137.37	117.13	82.86
13.00	35.01	-25.96	-92.37	-152.91
14.00	-181.29	-173.08	-139.43	-95.29
15.00	-54.42	-22.94	-4.72	1.52
16.00	19.11	45.11	64.94	94.82
17.00	106.56	118.21	131.31	130.85
18.00	118.94	84.43	24.61	-41.86
19.00	-112.67	-168.78	-190.29	-181.61
20.00	-139.20	-88.51	-34.45	4.35
21.00	29.79	41.64	58.76	67.29
22.00	82.72	102.32	106.70	105.48
23.00	98.29	94.53	59.32	23.09
24.00	-38.64	-83.54	-134.92	-150.24
25.00	-163.40	-142.53	-105.12	-46.75
26.00	-8.52	24.84	44.24	56.59
27.00	79.42	92.40	88.84	87.27
28.00	79.05	79.90	64.55	40.52
29.00	14.98	-6.95	-45.13	-85.33
30.00	-112.04	-128.61	-103.12	-90.52
31.00	-67.56	-40.93		

CURVE 4 (2-142-2)

	0.00	0.25	0.50	0.75
8.00	14.84	-36.28	-94.08	-140.38
9.00	-157.93	-149.48	-134.21	-118.83
10.00	-93.57	-70.25	-31.47	28.80
11.00	82.08	133.13	154.63	168.73
12.00	164.18	149.55	131.59	95.62
13.00	44.11	-25.19	-103.13	-158.59
14.00	-193.89	-188.14	-150.12	-106.49
15.00	-62.92	-32.15	-8.17	2.37
16.00	22.62	40.88	76.16	104.19
17.00	123.09	134.73	145.23	141.93
18.00	126.14	90.84	36.32	-50.47
19.00	-131.46	-193.63	-213.14	-196.84
20.00	-157.04	-96.20	-42.41	-3.46
21.00	26.65	47.97	66.94	73.19
22.00	92.09	103.61	118.26	107.89
23.00	105.92	92.87	73.01	32.69
24.00	-19.33	-77.78	-130.22	-161.28
25.00	-166.84	-147.26	-106.77	-49.37
26.00	-13.86	24.96	43.39	74.57
27.00	86.68	82.40	88.52	85.98
28.00	79.93	72.05	57.43	49.40
29.00	5.86	-17.12	-41.80	-85.82
30.00	-118.32	-133.77	-117.76	-102.89
31.00	-61.54	-33.74		

EXPERIMENTAL INTENSITY CURVES FOR DINITROGEN TETROXIDE -
NITROGEN DIOXIDE AT -35 DEG. C. CURVE 1 (2-148-8)

	0.00	0.25	0.50	0.75
2.00	-0.55	-1.38	-0.46	.89
3.00	-2.00	-9.74	-26.16	-48.95
4.00	-77.44	-103.77	-117.20	-103.65
5.00	-61.90	5.92	76.77	128.26
6.00	146.73	131.45	99.88	73.33
7.00	66.88	77.34	86.69	72.59
8.00	33.65	-31.03	-97.22	-146.71
9.00	-164.84	-161.13	-147.24	-126.91
10.00	-104.96	-76.51	-32.38	26.87
11.00	86.50	134.37	161.75	169.51
12.00	160.31	153.59	140.30	

CURVE 2 (2-148-9)

	0.00	0.25	0.50	0.75
2.00	-0.41	-1.44	-0.89	.81
3.00	-2.16	-9.20	-24.29	-47.70
4.00	-76.05	-103.02	-116.88	-105.17
5.00	-60.87	5.88	72.74	127.57
6.00	146.90	132.80	103.06	72.07
7.00	67.28	75.17	87.33	69.62
8.00	26.97	-30.45	-103.19	-143.24
9.00	-165.49	-157.97	-140.16	-125.24
10.00	-100.02	-71.50	-31.71	27.28
11.00	83.37	133.43	158.61	168.63
12.00	159.34	146.14	124.59	117.17

CURVE 3 (2-149-8)

	0.00	0.25	0.50	0.75
8.00	7.16	-26.24	-77.52	-127.97
9.00	-152.99	-150.19	-135.92	-120.14
10.00	-101.87	-74.46	-33.97	24.54
11.00	78.76	125.42	154.21	163.71
12.00	159.22	148.96	129.31	93.63
13.00	46.86	-20.73	-91.79	-149.92
14.00	-184.47	-178.08	-146.42	-101.03
15.00	-62.29	-29.21	-16.27	2.56
16.00	14.82	35.79	58.11	83.91
17.00	106.68	123.17	126.22	135.20
18.00	122.08	91.73	41.58	-33.52
19.00	-104.82	-156.09	-191.53	-179.75
20.00	-143.19	-90.04	-39.67	.34
21.00	32.67	48.99	53.67	68.19
22.00	77.00	90.95	103.13	106.77
23.00	96.99	85.11	60.85	27.75
24.00	-17.39	-80.79	-128.95	-163.80
25.00	-159.50	-143.37	-109.67	-60.50
26.00	-20.01	27.59	43.62	60.95
27.00	86.74	81.44	90.89	87.56
28.00	83.82	79.71	59.78	38.41
29.00	16.08	.14	-14.99	-72.11
30.00	-112.59	-110.10	-113.85	-104.07

CURVE 4 (2-149-9)

	0.00	0.25	0.50	0.75
8.00	14.06	-20.41	-49.70	-71.92
9.00	-79.79	-75.68	-69.33	-59.33
10.00	-50.54	-39.42	-19.09	10.45
11.00	36.56	60.71	77.32	86.68
12.00	86.93	80.07	71.33	50.23
13.00	25.79	-6.06	-44.44	-75.78
14.00	-95.14	-88.13	-76.94	-53.09
15.00	-32.77	-17.82	-7.99	2.35
16.00	3.78	15.33	30.38	47.68
17.00	50.95	57.70	69.86	69.29
18.00	65.70	48.07	21.39	-17.46
19.00	-63.49	-92.79	-107.24	-96.13
20.00	-79.12	-53.92	-19.94	2.63
21.00	15.14	26.30	32.96	32.71
22.00	41.37	53.53	59.51	62.08
23.00	58.11	54.24	43.96	22.18
24.00	-9.75	-38.24	-65.05	-85.56
25.00	-87.91	-76.74	-64.68	-28.67
26.00	8.92	14.53	23.10	21.78
27.00	26.93	41.33	39.95	34.44
28.00	34.12	43.78	34.38	24.00
29.00	21.53	-4.12	-22.81	-45.10
30.00	-52.28	-51.26	-58.61	-46.58

EXPERIMENTAL INTENSITY CURVES FOR DINITROGEN TETROXIDE-
NITROGEN DIOXIDE AT -12 DEG. C (SAMPLE BATH AT -26 DEG. C)
CURVE 1 (2-148-4)

	0.00	0.25	0.50	0.75
2.00	.15	-1.91	-1.26	.13
3.00	-3.41	-13.70	-34.18	-64.16
4.00	-101.14	-134.85	-151.01	-134.80
5.00	-78.82	9.40	98.89	161.51
6.00	185.87	171.56	136.44	106.12
7.00	95.91	104.86	112.47	91.90
8.00	34.64	-46.48	-131.65	-192.03
9.00	-218.06	-211.77	-193.28	-168.81
10.00	-139.09	-96.68	-41.68	35.58
11.00	111.70	180.17	216.56	228.41
12.00	222.18	214.44		

CURVE 2 (2-148-5)

	0.00	0.25	0.50	0.75
2.00	.10	-1.47	-1.00	.11
3.00	-3.59	-12.60	-30.60	-55.90
4.00	-38.29	-117.21	-131.74	-117.04
5.00	-69.66	4.94	84.08	141.35
6.00	163.35	153.06	123.30	95.61
7.00	85.40	91.44	94.09	78.59
8.00	29.52	-44.46	-115.03	-165.04
9.00	-189.59	-183.81	-169.30	-147.07
10.00	-122.25	-87.53	-36.91	27.06
11.00	98.09	159.55	188.00	203.94
12.00	193.96	189.32		

CURVE 3 (2-149-6)

	0.00	0.25	0.50	0.75
8.00	8.31	-58.72	-126.20	-173.05
9.00	-230.15	-194.41	-176.93	-154.41
10.00	-127.66	-98.11	-41.31	24.53
11.00	96.35	157.12	202.80	223.28
12.00	225.12	214.65	177.89	127.37
13.00	55.94	-34.94	-130.03	-203.23
14.00	-248.83	-245.65	-204.13	-143.44
15.00	-87.92	-48.86	-20.38	2.61
16.00	21.92	57.66	95.73	130.33
17.00	150.64	177.60	199.18	192.93
18.00	170.23	125.40	49.99	-47.68
19.00	-157.42	-244.59	-279.26	-269.36
20.00	-215.43	-146.67	-62.39	-1.26
21.00	40.30	69.74	95.54	110.26
22.00	124.07	141.27	157.88	150.72
23.00	143.98	142.22	82.48	39.57
24.00	-46.59	-119.74	-187.42	-237.15
25.00	-240.20	-212.76	-168.79	-98.15
26.00	-25.72	30.66	73.84	106.10
27.00	119.83	127.96	141.86	138.43
28.00	120.55	125.29	96.87	82.91
29.00	36.80	.30	-83.76	-121.84
30.00	-153.93	-197.18	-182.32	

CURVE 4 (2-149-7)

	0.00	0.25	0.50	0.75
8.00	10.30	-60.49	-126.48	-173.96
9.00	-194.55	-188.16	-172.98	-155.02
10.00	-126.64	-97.23	-43.16	23.91
11.00	95.50	159.02	202.07	221.80
12.00	222.81	206.84	173.94	125.10
13.00	51.97	-36.30	-130.11	-207.44
14.00	-249.31	-240.99	-200.98	-142.71
15.00	-87.12	-41.91	-12.96	6.96
16.00	29.30	61.65	102.88	133.85
17.00	165.21	190.50	198.22	196.51
18.00	171.60	119.39	43.04	-66.45
19.00	-170.92	-250.38	-288.84	-272.38
20.00	-220.02	-141.68	-68.62	-12.33
21.00	37.89	65.39	86.25	102.40
22.00	116.40	141.32	152.34	154.36
23.00	154.51	140.51	105.60	47.05
24.00	-28.84	-111.04	-191.31	-234.03
25.00	-238.47	-210.25	-150.83	-82.18
26.00	-13.64	47.02	82.38	110.63
27.00	125.75	129.80	133.17	106.68
28.00	110.69	95.05	79.35	52.48
29.00	15.44	-14.40	-65.16	-118.25
30.00	-145.88	-167.22	-162.95	

EXPERIMENTAL INTENSITY CURVES FOR DINITROGEN TETROXIDE-
 NITROGEN DIOXIDE AT -12 DEG. C (SAMPLE BATH AT -36 DEG. C)
 CURVE 1 (2-148-6)

	0.00	0.25	0.50	0.75
2.00	.67	-1.54	-1.43	-0.88
3.00	-5.54	-15.65	-36.10	-65.31
4.00	-101.99	-134.95	-151.82	-135.50
5.00	-79.33	5.91	96.12	161.30
6.00	188.70	173.87	149.86	120.42
7.00	107.09	108.12	104.47	82.99
8.00	26.66	-57.14	-140.70	-198.58
9.00	-220.07	-211.94	-198.12	-170.62
10.00	-142.21	-95.78	-37.00	38.62
11.00	122.67	191.04	223.22	236.19
12.00	229.50	216.94		

CURVE 2 (2-148-7)

	0.00	0.25	0.50	0.75
2.00	-0.14	-1.02	-0.55	.11
3.00	-3.72	-12.11	-28.23	-51.17
4.00	-79.96	-105.26	-118.14	-105.19
5.00	-64.33	1.53	72.73	127.80
6.00	150.81	145.25	121.01	95.32
7.00	82.74	84.11	78.70	58.73
8.00	14.89	-49.87	-112.61	-153.26
9.00	-163.37	-161.75	-147.45	-129.28
10.00	-106.66	-76.16	-29.26	29.01
11.00	90.21	145.23	175.04	187.04
12.00	177.14	167.60	145.25	

CURVE 3 (2-149-3)

	0.00	0.25	0.50	0.75
8.00	2.53	-68.72	-127.27	-173.20
9.00	-197.11	-197.33	-179.20	-158.58
10.00	-134.67	-96.07	-40.75	23.64
11.00	103.67	167.55	211.78	234.57
12.00	231.05	215.42	181.45	129.09
13.00	49.89	-42.09	-138.42	-214.63
14.00	-257.01	-252.17	-208.26	-152.58
15.00	-94.13	-45.62	-12.24	4.55
16.00	38.04	70.15	104.25	138.66
17.00	172.86	195.15	205.48	193.70
18.00	174.86	113.34	34.88	-73.35
19.00	-167.30	-246.30	-283.30	-273.48
20.00	-226.32	-155.53	-83.85	-8.54
21.00	36.61	76.13	91.14	121.98
22.00	142.34	157.35	170.68	166.44
23.00	163.69	133.23	85.30	8.64
24.00	-57.83	-143.30	-207.99	-245.10
25.00	-238.44	-203.07	-143.84	-71.01
26.00	2.35	47.66	78.94	133.71
27.00	133.23	141.07	153.75	123.90
28.00	126.47	102.10	71.04	29.55
29.00	26.30	-21.50	-103.22	-144.09
30.00	-184.50	-178.34	-145.88	

CURVE 4 (2-149-2)

	0.00	0.25	0.50	0.75
8.00	-19.76	-69.53	-141.36	-206.08
9.00	-238.01	-240.01	-219.08	-189.57
10.00	-156.05	-121.77	-60.05	26.65
11.00	124.92	206.94	261.32	273.46
12.00	272.31	257.93	221.13	161.71
13.00	74.40	-33.50	-160.52	-259.63
14.00	-318.22	-307.65	-257.34	-182.93
15.00	-109.45	-56.69	-23.25	-1.70
16.00	23.69	68.19	114.30	166.23
17.00	202.13	231.38	248.32	248.08
18.00	227.46	166.42	69.31	-76.99
19.00	-196.60	-300.68	-349.80	-331.54
20.00	-276.31	-177.08	-68.45	-4.44
21.00	59.43	103.17	114.17	134.63
22.00	145.31	156.21	165.07	174.00
23.00	185.36	164.19	124.85	61.66
24.00	-39.73	-144.77	-228.72	-296.57
25.00	-320.91	-299.02	-218.28	-120.01
26.00	-26.05	55.73	112.11	145.67
27.00	158.22	169.32	167.61	175.34
28.00	162.24	144.45	122.79	87.32
29.00	39.06	-12.48	-93.26	-153.58
30.00	-207.41	-228.37	-233.67	-222.89

EXPERIMENTAL INTENSITY CURVES FOR DINITROGEN TETROXIDE-
NITROGEN DIOXIDE AT -12 DEG. C (SAMPLE BATH AT -44 DEG. C)
CURVE 1 (2-148-2)

	0.00	0.25	0.50	0.75
2.00	.62	.16	-0.04	-0.70
3.00	-4.04	-9.58	-19.26	-32.23
4.00	-48.43	-62.62	-70.46	-65.36
5.00	-43.81	-4.46	41.12	78.40
6.00	97.29	94.82	80.50	64.20
7.00	55.46	51.43	45.55	29.74
8.00	-1.01	-37.93	-71.80	-91.92
9.00	-98.53	-95.15	-84.63	-75.09
10.00	-61.57	-44.01	-17.66	15.60
11.00	51.09	83.49	102.86	111.32
12.00	109.96	104.26	88.44	

CURVE 2 (2-148-3)

	0.00	0.25	0.50	0.75
2.00	.66	.21	-0.23	-0.66
3.00	-4.03	-9.88	-19.65	-32.65
4.00	-48.93	-63.41	-72.13	-66.20
5.00	-44.59	-4.01	41.31	78.91
6.00	97.22	96.58	81.52	65.64
7.00	58.22	54.06	47.72	30.04
8.00	-0.53	-40.68	-72.96	-94.87
9.00	-100.96	-95.86	-86.35	-77.11
10.00	-62.62	-44.39	-18.13	15.76
11.00	53.31	85.92	103.81	114.32
12.00	111.47	105.41	89.86	

CURVE 3 (2-149-4)

	0.00	0.25	0.50	0.75
8.00	-18.25	-55.46	-88.52	-130.83
9.00	-150.33	-139.52	-128.45	-113.37
10.00	-92.37	-70.12	-29.46	23.05
11.00	77.08	122.32	157.37	168.67
12.00	171.50	153.61	118.90	86.59
13.00	24.97	-45.80	-100.96	-154.04
14.00	-177.80	-167.14	-131.75	-102.97
15.00	-65.43	-28.74	-14.22	6.93
16.00	18.49	48.26	79.53	89.88
17.00	117.55	125.18	132.47	135.15
18.00	110.77	73.58	17.30	-56.71
19.00	-114.17	-161.50	-183.51	-171.19
20.00	-131.25	-86.42	-32.72	10.19
21.00	28.10	47.78	60.79	70.23
22.00	79.77	99.60	113.26	110.27
23.00	101.38	88.08	60.23	16.92
24.00	-36.33	-88.52	-139.40	-176.00
25.00	-168.01	-158.74	-114.03	-65.15
26.00	-25.92	24.06	54.78	32.76
27.00	106.41	92.46	97.50	94.98
28.00	82.38	71.96	51.26	31.66
29.00	15.47	.41	-33.89	-63.77
30.00	-93.30	-103.69	-120.38	-87.11
31.00	-89.19			

CURVE 4 (2-149-5)

	0.00	0.25	0.50	0.75
8.00	25.33	-56.61	-94.79	-117.55
9.00	-124.76	-116.29	-107.63	-92.71
10.00	-74.82	-53.88	-19.61	26.17
11.00	67.39	105.63	134.25	143.56
12.00	135.29	124.16	105.14	71.55
13.00	25.90	-25.49	-79.57	-117.59
14.00	-139.04	-133.44	-111.73	-80.09
15.00	-53.33	-30.40	-14.92	-3.26
16.00	9.35	31.50	50.24	71.24
17.00	89.60	99.65	106.90	105.03
18.00	92.81	51.93	6.30	-50.38
19.00	-99.21	-130.64	-155.62	-146.76
20.00	-112.39	-73.30	-33.55	-6.83
21.00	14.61	34.57	44.52	59.73
22.00	74.64	90.61	99.47	97.44
23.00	84.33	84.01	64.29	23.17
24.00	-4.99	-47.67	-100.89	-117.02
25.00	-117.95	-105.11	-82.50	-37.56
26.00	-2.92	28.38	33.83	48.31
27.00	52.19	60.04	48.81	65.33
28.00	53.65	44.53	28.74	6.07
29.00	-15.17	-18.27	-41.11	-69.22
30.00	-84.24	-88.69	-69.65	-48.19
31.00	-12.53			