

THERMODYNAMIC FUNCTIONS FOR HALOGENATED BENZENES

by

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## ABSTRACT

The availability of molecular structural and spectrographic data has enabled the calculation of the ideal gas thermodynamic functions  $C_p^\circ$ ,  $S^\circ$ ,  $(H^\circ - H_0^\circ)/T$ ,  $-(F^\circ - H_0^\circ)/T$  for thirty eight halogenated benzenes. The thermodynamic functions are given for temperatures between  $273.15^\circ$  K. and  $1500^\circ$  K., at one atmosphere.

The contribution of the anharmonicity effect to the thermodynamic properties is discussed. Additionally, a method is described for making real gas corrections to the ideal gas thermodynamic functions, however, only over a limited range of pressure and temperature (15 atm. to 0.25 atm.,  $273.15^\circ$  K. to  $1000^\circ$  K.). This method, based on the Berthelot equation of state, requires the critical temperature and pressure, which are summarized in this work for several of the halogenated benzenes. As an example of the method, the real gas thermodynamic functions for fluorobenzene are shown, at pressures between 10 atm. and 0.25 atm. Finally the thermal stability of the halogenated benzenes is discussed and the temperatures over which the ideal gas thermodynamic functions are applicable are indicated.

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## CHAPTER I

## INTRODUCTION

The aim of this work was to calculate the thermodynamic functions,  $C_p^{\circ}$ ,  $S^{\circ}$ ,  $(H^{\circ}-H_0^{\circ})/T$ ,  $-(F^{\circ}-H_0^{\circ})/T$  of the halogenated benzenes from  $273.15^{\circ}$  K. to  $1500^{\circ}$  K., using the methods of statistical thermodynamics and available spectroscopic and molecular structural data. The compounds investigated included mono- to hexahalobenzenes and some unsymmetrical dihalobenzenes. To do this, a survey was made of the methods of calculation of the thermodynamic functions from molecular data and the problems associated with these calculations. The accuracy and scope of this work is bound by its purpose - to present a set of calculated thermodynamic function tables for use in chemical engineering problems.

At present, the most commonly industrially used halobenzenes are the chlorobenzenes. Chlorobenzene is the starting point for the production of DDT. Shreve (114) gives the annual production in the United States as 537 million lb. (1964). Aniline is produced industrially from chlorobenzene by treatment with ammonia at  $480^{\circ}$  K. under pressure, using a copper catalyst (114). Phenol is produced in a catalytic vapor phase reaction at  $700^{\circ}$  K. (114) by the action of steam on chlorobenzene. The chlorobenzene for this process is also made in the vapor phase at  $500^{\circ}$  K. by contacting HCl and air with benzene vapor (114). Chlorobenzene has many other indust-

rial uses (11) such as in solvents, dye intermediates, etc. Hexachlorobenzene is hydrolysed by alkali to give pentachlorophenol, which is used to treat lumber to prevent blueing and mildew (91). Ortho-dichlorobenzene is used as a solvent and the para isomer (moth repellent) is used to protect fruit trees from the peach borer. Annual U.S. production of paradichlorobenzene was 30,000 tons in 1953 (91).

Recently the fluoro- substituted benzenes have attained more industrial and theoretical importance (27,80,107). The perfluorinated aromatics are among the stablest organic compounds known (53); a perfluoropolyphenyl polymer derivative has been shown to be very thermally stable (76). The starting point for these substances is hexa- or pentafluorobenzene. High temperature lubricants have also been made from fluorinated benzenes (107). Pummer and Wall expect that "as better methods for industrial synthesis are developed, the fluorobenzenes will find new and useful applications" (107).

In view of the increasing industrial importance of vapor phase reactions and the significance of the compounds mentioned above, as fungicides, pesticides and especially reagents, it was felt that a systematic presentation of thermodynamic functions for the halobenzenes would be useful. Up to the present these functions have only been calculated for the monohalobenzenes, the difluoro- and dichlorobenzenes and hexafluorobenzene (14,64,81,61,77).

In assessing any proposed process involving a vapor

phase reaction it is essential to know the heat capacities involved as well as the possible equilibrium compositions. This entails a calculation of the standard free energy of reaction  $\Delta F^\circ/T$  at the reaction temperature. This value can easily be found if the free energy function  $-(F^\circ - H^\circ_0)/T$  is known from statistical mechanical (or other) calculations. The heat of formation  $\Delta H^\circ_f$  can also be found, usually from heat of combustion data. Similarly, the standard heat of reaction  $\Delta H^\circ_T$  can be computed if the enthalpy function  $(H^\circ - H^\circ_0)/T$ , and  $\Delta H^\circ_f$ , are known. The methods for these calculations are given in thermodynamics textbooks (83,84).

An example of the use of tabulations such as those mentioned is the determination of the isomeric equilibrium of ortho-, meta- and para-difluorobenzene. Green, Kynaston and Paisley (54), who have calculated the thermodynamic functions of these compounds, also listed the equilibrium compositions of the three isomers at temperatures between  $273.15^\circ$  K. and  $1500^\circ$  K.

There are several experimental sources of thermodynamic data. Calorimetry can be used to determine heat capacities (vapor flow calorimetry) and heats of combustion (bomb calorimetry). The best calorimetric results are considered by Green (4) to be accurate to about  $\pm 0.02\%$ , while Whiffen (58) states experimental error may be as large as  $\pm 3\%$ . For the determination of entropies, and thus free energies, the so called "third law calculations" must be made.

These consist of integration under the heat capacity curve from  $0^{\circ}$  K. to the temperature desired, including the entropy changes associated with the phase transitions:

$$S_{T_f} = \int_0^{T_1} (C_p/t) dt + \frac{\Delta H_1}{T_1} + \int_{T_1}^{T_2} (C_p/t) dt + \dots + \frac{\Delta H_i}{T_i} + \int_{T_i}^{T_f} (C_p/t) dt$$

where  $S_{T_f}$  is the entropy at temperature  $T_f$  and  $C_p$  is the heat capacity at temperature  $t$ . The  $T_i$  are the temperatures of the phase changes and the  $\Delta H_i$  the enthalpy changes (latent heats). It is not possible to determine experimentally the heat capacity right to  $0^{\circ}$  K., and usually a Debye function (84) is used to describe part of the first integral in Equation 1.

As well as by direct "third law" measurements, the thermodynamic functions can be computed from experimental molecular structural and spectrographic data. When the problem of molecular motion and attractive and repulsive forces can be solved by quantum mechanics, then both vibrational (spectrographic) and structural data will be calculated, rather than experimentally determined.

From the structural information the moments of inertia of a molecule may be calculated to determine the rotational contribution to the thermodynamic functions. The assignment of the fundamental normal vibrations of the molecule enables the computation of the vibrational contribution, using the harmonic-oscillator rigid-rotator approximation. If the molecule has a group of atoms which undergoes "internal rotation", then the contribution of this motion to the thermo-

dynamic functions can be found with a knowledge of the type and size of the barrier to internal rotation or by isomerization energy data in the cases where rotational isomers are known. If semi-empirical anharmonicity corrections are not used, the error ascribed to the results of this work, using these methods, is between  $\pm 0.5\%$  and  $\pm 1.5\%$  of the thermodynamic functions, depending on the accuracy of the input data. These error limits refer to the temperature range where experimental data is usually available (viz.  $< 500^\circ \text{K.}$ ). For the purposes of engineering calculations these limits of error are reasonable and are more accurate than other predictive methods (2,83,102).

For practical use, real gas corrections to the ideal gas thermodynamic functions may be required. In Chapter III an equation of state (Berthelot) is proposed for these corrections, but is of use over a limited range of temperature and pressure only.

The above methods are thought to be the best way to determine the thermodynamic functions of the halogenated benzenes. Methods have been developed for correlations of existing data and for group contribution techniques and generalized vibrational contributions (2,83,102) but it is thought that these methods will be less accurate than the statistical thermodynamic approach.

CHAPTER IITHEORYA. The Simple Case

It has been shown (see for example Herzberg, ref.85) that the macroscopic thermodynamic functions  $C_p^o$ ,  $S^o$ ,  $(H^o-H_o^o)/T$ , and  $-(F^o-H_o^o)/T$  can be calculated from the properties of the molecules of the gas. This forms a part of statistical thermodynamics which relates statistical mechanics to the thermodynamics as used by the engineer.

The first assumption made to derive the formulae for the thermodynamic functions is that the gases involved are ideal (signified in the nomenclature above by a "o" superscript). This assumption is necessary since statistical mechanics considers each molecule as an independent entity, subject only to its own internal energy. In a real gas the molecules interact with or exert forces on one another. Presently, these interactions can not be described quantitatively for polyatomic molecules.

The Maxwell-Boltzman distribution law gives the partition function of the (molal) gas system,  $Q$ , which is proportional to the total number of molecules  $N$ . If it is assumed that for a system in equilibrium there are a certain number of molecules  $N_n$  in an energy state  $\epsilon_n$  and a degeneracy  $g_n$ , then it may be written that  $N_n$  is proportional to  $g_n \exp(-\epsilon_n/kT)$  (85, 94). The total partition function is the sum over all the states:

$$Q = \sum g_n \exp(-\epsilon_n/kT) \quad (2)$$

The ideal gas thermodynamic function can be related to this partition function (84,85,94): if the partition function of the gas can be quantitatively expressed, so can the thermodynamic functions.

The total energy  $\epsilon_n$  of the molecules in state  $n$  can be described as the sum of the translational and internal energies  $\epsilon_n = \epsilon_t + \epsilon_{int}$ . Because these energies are additive the total partition function describing the energy distribution can be separated into the product of translational and internal partition functions.

$$Q = Q_t * Q_{int} \quad (3)$$

In the simple cases the "internal" partition function,  $Q_{int}$ , can be separated again into the product of contributions due to the vibrational, rotational and excited electronic degrees of freedom of the molecule.

The vibrational partition function (84,85,86,87) can be evaluated from the fundamental vibrational frequencies of the molecule. The molecule's atoms may be thought of as point masses attached to springs which follow Hooke's law, in which the restoring force on the mass is proportional to the distance of the mass from the equilibrium position, forming a system of harmonic oscillators. In the energized molecule, these point masses vibrate in a complicated manner. If the harmonic oscillator assumption is valid, the atomic

motions can be resolved into normal vibrations, all orthogonal to each other. Some of the thirty normal vibrations for fluorobenzene are shown in Figure 1 (58).

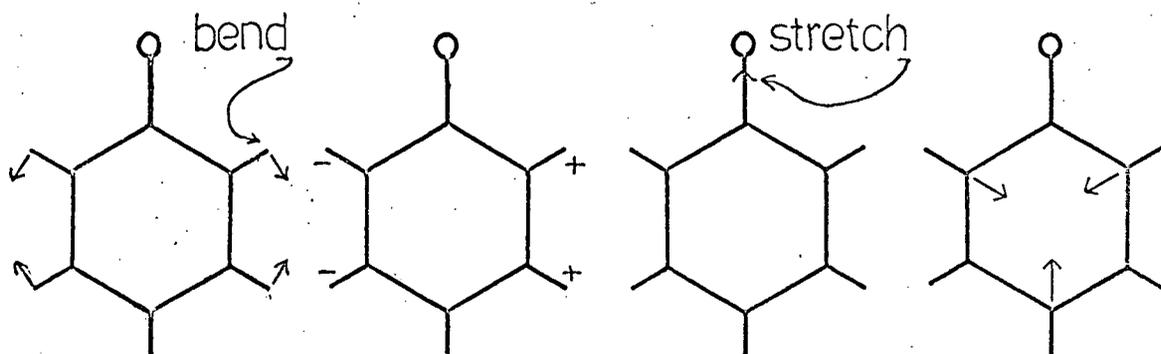


Figure 1: Some Normal Vibrations of Fluorobenzene

Two classes of molecular vibrations are apparent: stretching along the axis of a bond, and deformation, in which the position of the bond changes with respect to the original axis. These vibrations occur at certain characteristic frequencies for each different molecule. When infra-red light of the same frequency is incident on the molecule, energy is absorbed and therefore the amplitude of the vibration is increased. For an observable absorption of infra-red energy, a given frequency of vibration must cause a change in the dipole moment of the molecule (85). Herzberg (85), Wilson, Decius and Cross (88) and Wu (89) have given vibrational selection rules to determine which normal coordinate vibrations are observable by the infra-red absorption method.

It has been shown that (85,94) a molecule with  $n$  atoms has  $3n$  degrees of freedom: three of these describe the translational motion of the molecule and three describe the position of the center of gravity; the remaining  $3n - 6$  independent degrees of freedom describe the fundamental vibrational modes. Thus for a benzene type molecule there are thirty fundamental vibrations. As indicated above not all of these  $3n - 6$  modes are infra-red active. Other methods than direct infra-red observations must be used to measure these vibrations. In several cases those frequencies that are inactive in the infra-red are active in the Raman spectrum (101), which measures the scattering of incident infra-red radiation, rather than the absorption. Also non-fundamental absorption bands may occur in both infra-red and Raman spectra, because of the presence of harmonic overtone frequencies (in reduced intensity). These may occur at twice or three times the wave number, as combination bands of the sum of two frequencies and as difference bands (the difference of two frequencies). These additional bands often enable the assignment of non-active bands, especially in the low frequencies (lower than  $400 \text{ cm}^{-1}$ ), where direct infra-red or Raman data is often lacking. Due to symmetry it may happen that two or more of the fundamental vibrations have the same frequency, in which case that frequency is said to be degenerate.

To assist in the assignment of a new compound often a "normal coordinate analysis" is performed. This is a mathe-

mathematical solution to the many-body problem of the molecule, using the harmonic oscillator approximation. The atoms are assigned an equilibrium distance from each other. The force acting on an atom is described by the product of its distance from equilibrium and a force constant characteristic of the two atoms under consideration. If the masses of the atoms (assumed point masses) are known and the harmonic oscillator approximation is valid, the frequencies of the vibrations of the atoms (resolved into the normal directions) can be calculated. A normal coordinate analysis has been done for the chlorobenzenes by Scherer and his coworkers (63). The weakness of these calculations as an "a priori" method of predicting frequencies is that the force constants have to be taken from other, similar molecules, whose normal coordinate analysis has been shown to give frequencies close to the observed fundamental vibrations. The force constants between the same atoms in different molecules vary, because of their differing environments. For very similar molecules, however, such as the chlorobenzenes, it is reasonable to assume that there will be little difference in the force constants (63).

The derivation of the rotation partition function  $Q_r$  (84,85,86,87) uses several assumptions, given below. For rigid molecules, such as the halogenated benzenes, these assumptions are very good. The maximum error in the thermodynamic functions caused by their use is given by Herzberg as 0.3% (85). The most important assumption is that the molecule

is rigid and does not change dimensions (see Part C of this chapter). The derivation neglects any vibrational cross product terms in the rotational partition function. The partition function  $Q_r$  is derived for spherical top molecules (85). However it may also be used for the symmetric and asymmetric top molecules which appear in this work (85).

The molecular shape factor  $\sigma$  appears in the rotational partition function. It is the number of identical positions in which the molecule can be replaced by rotations about the center of gravity. It accounts for the "influence of the identity of the nuclei" and reduces the partition function to account for rotational degeneracy (85,90). The molecular symmetry number  $\sigma$  does not take into account that the identical nuclei may not have zero spin. That is, it is assumed that all the rotational levels have the same weight in the sum of rotational states. Usually the nuclear spin can be neglected in calculations, since for all molecules except hydrogen at low temperatures (85), it has no detectable effect on the thermodynamic functions. In these calculations of the thermodynamic functions of the halogenated benzenes the nuclear spin may be safely neglected.

For most molecules at low temperatures the electronic state is a single quantum level (which is assigned as the zero state). In this case the electrons of the molecule are paired to give zero electronic spin and zero orbital angular momentum. Thus the electronic partition function is

1 and there is no electronic contribution to the thermodynamic functions. At higher temperatures the higher electronic states may become filled, but Pitzer and Brewer (84) have shown that for most di- and polyatomic molecules (except  $O_2$ ,  $NO_2$ ,  $NO$ ) the electronic partition function may be taken as unity to about  $2000^\circ K$ . It is not expected that electronic effects will be important in the range of temperatures used in this work (see Chapter IV).

The equations relating the partition function and the thermodynamic properties, heat capacity, free energy and entropy are given in the literature (84,85,86,87). Using the restrictions mentioned above, quantitative expressions for the contributions of the translational, rotational and vibrational degrees of freedom can be derived, and the thermodynamic functions can be calculated. The enthalpy function  $(H^\circ - H^\circ_0)/T$  may be found from the difference\*

$$(H^\circ - H^\circ_0)/T = S^\circ + (F^\circ - H^\circ_0)/T \quad (4)$$

Table I shows the derived formulae for the ideal gas thermodynamic functions, according to the theory above. The nomenclature for these formulae is found in Appendix A.

---

\* Note that  $H^\circ_0$  is the zero point ( $0^\circ K$ .) enthalpy which is equivalent to the zero point internal energy  $U^\circ_0$  (or  $E^\circ_0$ , as is sometimes found in the literature). The free energy and enthalpy functions may in some cases be based on  $298^\circ K$ . rather than  $0^\circ K$ . The conversion of  $-(F^\circ - H^\circ_0)/T$  to  $-(F^\circ - H^\circ_{298})/T$  is easily done (84), by the formula

$$(F^\circ - H^\circ_{298})/T = (F^\circ - H^\circ_0)/T - (H^\circ_{298} - H^\circ_0)/T.$$

TABLE I

Contributions of the Separate Degrees of Freedom\* to the Thermodynamic Functions

degree of freedom	heat capacity $C_p^0$	free energy $-(F^0 - H_0^0)T$	entropy $S^0$
translation	$5 R / 2$	$R (3/2 \ln M + 5/2 \ln T) - 7.283$	$R (3/2 \ln M + 5/2 \ln T) - 2.315$
rotation	$3 R / 2$	$R(1/2 \ln I_{ABC} \times 10^{117} + 3/2 \ln T - \ln \sigma) - 3.014$	$R(1/2 \ln I_{ABC} \times 10^{117} + 3/2 \ln T - \ln \sigma) - 0.033$
vibration	$R \left[ \frac{u^2 e^u}{(e^u - 1)^2} \right]$	$- R \ln (1 - e^{-u})$	$R \left[ \frac{u}{(e^u - 1)} - \ln (1 - e^{-u}) \right]$
units	cal/gmole °K.	cal/gmole °K.	E. U.

where  $u = h c \nu / k T$

see Appendix A for a list of nomenclature used

These formulae have been programmed in FORTRAN IV  
see Appendix B and C for these computer programs

\* To obtain the total ideal gas thermodynamic function  
the contribution of each degree of freedom is summed.

## B. Calculation of the Moments of Inertia

It is seen that the formulae for the rotational contributions to the entropy and free energy, given in Table I, include the product of the principal moments of inertia,  $I_{ABC}$ . This product is the value of the determinant:

$$I_{ABC} = \begin{vmatrix} I_{xx} & -I_{xy} & -I_{xz} \\ -I_{xy} & I_{yy} & -I_{yz} \\ -I_{xz} & -I_{yz} & I_{zz} \end{vmatrix} \quad (5)$$

If the origin of Cartesian coordinates is at the center of gravity of the molecule, then the diagonal elements have the form

$$I_{xx} = \sum m_i (y_i^2 + z_i^2) \quad (6a)$$

and the off-diagonal elements have the form

$$I_{xy} = \sum m_i x_i y_i \quad (6b)$$

Godnev (87) states, "To determine the main central moments of inertia, it is very important to determine the position of the center of inertia". This has led previous calculators of moments of inertia for molecules (73,74) to adjust all their coordinates to the center of gravity. This is not necessary. Any origin of coordinates can be used providing that, by the theorem of Parallel Axes (85), a modification to the elements of the determinant in Equation 5 is made. Then the diagonal elements become

$$I_{xx} = \sum m_i (y_i^2 + z_i^2) - \frac{1}{M} \left( \sum m_i y_i \right)^2 - \frac{1}{M} \left( \sum m_i z_i \right)^2 \quad (7a)$$

and the off-diagonal elements are modified to have the form

$$I_{xy} = \sum m_i x_i y_i - \frac{1}{M} \left( \sum m_i x_i \right) \left( \sum m_i y_i \right) \quad (7b)$$

where the nomenclature is as in Appendix A.

In the simple case, where the rigid rotator, harmonic oscillator approximation is used, only the product  $I_{ABC}$  is needed. In other cases however it is necessary to find the individual principal moments of inertia  $I_A$ ,  $I_B$  and  $I_C$ . These moments are used in calculations involving internal rotations and may be used as a check on microwave structural data, which usually gives the rotational constants directly.\*

It is possible by a rotation and translation of axes to make all the cross product terms ( $I_{ab}$  etc.) zero in the determinant  $I_{ABC}$ . In this case the determinant will be

$$I_{ABC} = \begin{vmatrix} I_{xx} & 0 & 0 \\ 0 & I_{yy} & 0 \\ 0 & 0 & I_{zz} \end{vmatrix} \quad (8)$$

where  $I_{xx} = I_A$ ,  $I_{yy} = I_B$  and  $I_{zz} = I_C$ , the principal moments of inertia. After this rotation (and translation if the original center of coordinates was not the center of gravity) the principal axes A, B and C, corresponding to  $I_A$ ,  $I_B$  and  $I_C$ , will be those which have the greatest symmetry with respect to the atoms of the molecule.

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\* The rotational constants may be converted to moments of inertia by  $A = h / (8 \pi^2 I_A)$ , or, when A is in Mc/sec,  $I_A = 5.05531 \times 10^5 / A$ .

A molecule of 1-2-4-5-tetrachlorobenzene is shown in Figure 2 with its origin of coordinates and axes X Y and Z. The axes for which the molecule has the greatest symmetry are A B and C, through the center of gravity, as in Figure 2. In fact, the molecule is symmetric about each of these principal axes. The A and B axes have resulted from a translation and rotation of the old X and Y axes. Since the molecule is planar the Z or C coordinates remain unchanged.

Mathematically this rotation and translation is done by solving for the eigenvalues of the determinant  $I_{ABC}$ , such that

$$\begin{vmatrix} I_{xx}-\lambda & I_{xy} & I_{xz} \\ I_{xy} & I_{yy}-\lambda & I_{yz} \\ I_{xz} & I_{yz} & I_{zz}-\lambda \end{vmatrix} = 0 \quad (9)$$

The roots of Equation 9 are  $\lambda = I_a$ ,  $\lambda = I_B$ ,  $\lambda = I_C$ . The determinant in Equation 9 yields a cubic equation in  $\lambda$  and is solved by Newton-Raphson iteration, which has been done by Cross (73) and Bryce (74). This solution is a result of the Cayley-Hamilton theorem which states (95) that if A is a square matrix (and similar to a diagonal matrix), with characteristic polynomial  $f(\lambda)$ , then  $f(A) = 0$ . In this case the matrix of Equation 5 is similar to the matrix of Equation 8, which is a diagonal matrix.

Alternatively any one of the methods for finding symmetric matrix eigenvalues may be used. These methods are

in general faster and more widely applicable. It was found in this work that the iterative method does not converge if a molecule has high symmetry (e.g. benzene, hexahalobenzenes), in which case identical eigenvalues appear, which cannot be handled by iteration.\* In this work, Householder's method was used to find a 'tri-diagonal matrix' (96,97) and Sturm sequencing (96,97) was used to isolate the individual moments of inertia (eigenvalues).\*\* The mathematical inaccuracy of this method (96,97) is expected to be less than the inaccuracy caused by the uncertainties in the bond lengths and angles. The accuracy of the iterative method is considered to be good, where it converges.

To calculate the terms of the determinant, the atomic weight  $m_i$  of each atom and its coordinates  $x_i$ ,  $y_i$  and  $z_i$  with respect to some axis are needed. In this work, on the halogenated benzenes, the center of coordinates was taken as one of the carbon atoms in the benzene ring. The bond distances and angles were used to calculate the coordinates from this origin. Figure 2 shows a molecule typical of those described in this work: 1-2-4-5- (sym) tetrachlorobenzene.

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\* This is not as severe a drawback as it may seem, since the axes of symmetry are obvious in this case and can be chosen "by hand" giving directly the determinant with cross terms ( $I_{xy}$  etc.) as zero.

\*\* See Appendix B for a description of the computer program which finds the principal moments of inertia by Householder's method and Sturm sequencing. See Appendix C for a copy of the program.

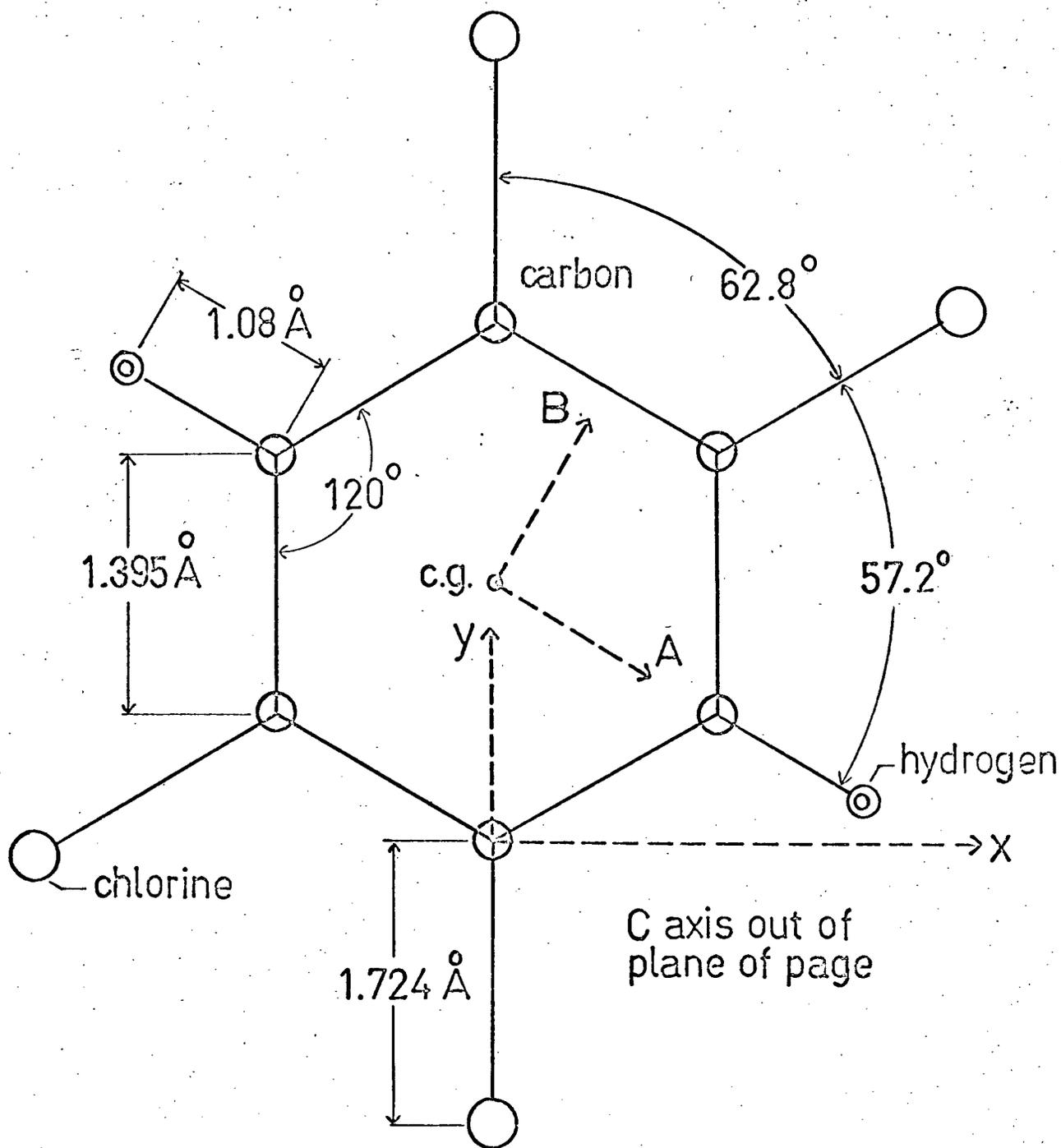


Figure 2 : 1-2-4-5- Tetrachlorobenzene Molecule  
( not to scale )

For this case structural data was taken from the vapor electron-diffraction experiments of Strand (66).

The bond lengths and angles used in this work are generally obtained by one of two techniques. Vapor electron-diffraction measurements (such as those mentioned above) are often used. The information is also found by microwave spectroscopy (for example, Rosenthal and Dailey, ref. 1), which usually also gives the rotational constants A, B and C. The "Tables of Interatomic Distances" by Sutton (80) are often useful, although more recent data may be available in the literature. It should be noted for what aggregate state the structural data has been found, since bond lengths may change with changes of state. Both electron-diffraction and microwave measurements may be made on compounds in the vapor state, although it is more common to find electron-diffraction data on vapors.

In several cases in this work (see Chapter V) experimentally determined structural data was unavailable. In these cases the structure was assigned using data on similar compounds whose structure was known. Other methods that may help in the determination of moments of inertia are ultra-violet spectroscopy and X-ray diffraction techniques.

### C. Anharmonicity Corrections

The use of the assumptions of the previous section gives rise to differences between the third law (experimentally observed) functions and the calculated functions. This difference is generally ascribed to "anharmonicity". Strictly, anharmonicity refers to deviations from harmonic (Hooke's law) vibration in the molecule. If, for example, the force  $F$  on an atom is given by

$$F = k_1 x + k_2 x^2 + \dots \quad (10)$$

where  $x$  is the displacement of the atom from its equilibrium position and the  $k_i$  are force constants describing the atoms' interactions, anharmonic vibrations result. The anharmonic motion of a diatomic molecule can be mathematically described but this becomes exceedingly complicated for polyatomic molecules. When force is not proportional to displacement the Lissajous (85) motion that results cannot be separated into normal vibrations. Then the total energy is no longer the sum of independent (even though anharmonic, as in the diatomic case) vibrations. Thus the concept of individual fundamental frequencies cannot be used for polyatomic molecules, if the effect of anharmonicity is large. Aston and Fritz (86) show results for HCN and the anharmonicity contributions for diatomic molecules are shown by Pitzer and Brewer (84).

If a rigorous development is followed (85), the vibrational-rotational interaction terms must be included in the partition function. This interaction is caused by the

vibrations changing the size and shape of the molecule, altering  $I_{ABC}$ , which figures in the rotational partition function. An interaction between vibrational and rotational energies results in each level of the vibrational partition function having a term expressing the contribution to that level from each rotational level. When there are a large number of rotational levels and thirty vibrational levels (as there are in the halogenated benzenes) this becomes mathematically complicated.

A related effect which changes the rotational partition function is rotational stretching of the molecule. At high temperatures the molecule rotates faster and the centrifugal force tends to increase the moments of inertia. This can be treated for simple molecules (86) but again is too complicated for quantitative expression for polyatomic molecules. It is possible that this effect could be allowed for by making microwave or electron-diffraction measurements on a compound at a series of temperatures and obtaining the dependance of  $I_{ABC}$  on the temperature. This empirical result could then be incorporated into the formulae in Table I.

Occasionally included under the heading of "anharmonicity" may be the contribution of the higher electronic states. As has already been mentioned (84) this is not important for most molecules under  $2000^{\circ}$  K. and even for inorganic molecules such as  $N_2O$ ,  $O_2$  etc., for which the electronic states are important (84), Herzberg (85) has shown

that this effect is only apparent above about 1000° K.

Pennington and Kobe (14) have calculated approximations to a generalized partition function to account for the contribution of anharmonicity, vibrational-rotational interaction and centrifugal distortion. The calculation depends on a knowledge of constants derived from spectroscopy (14), which are not available for complicated molecules. These authors (14) have calculated the anharmonicity contributions for nitrous oxide, considering only the first order terms of the anharmonic potential function. In order to apply the work of Pennington and Kobe to polyatomic molecules McCullough, Finke and their coworkers (16) have given a semi-empirical expression to account for anharmonicity. They have given the following formulae for the total contributions of "anharmonicity" to the thermodynamic functions.

$$C_{\text{anh}}^{\circ} = Z \left\{ \frac{C^{\circ}}{R} \left( \frac{3C^{\circ}}{Rw} \right) - \left( 1 + \frac{2}{w} \right) \left( \frac{H^{\circ} - H_0^{\circ}}{RT} \right) \right\}$$

$$S_{\text{anh}}^{\circ} = Z (C^{\circ}/Rw) (H^{\circ} - H_0^{\circ}/RT) \quad (11)$$

$$\frac{H^{\circ} - H_0^{\circ}}{T_{\text{anh}}} = \frac{Z}{2w} \left( \frac{H^{\circ} - H_0^{\circ}}{RT} \right) \left( \frac{2C^{\circ}}{R} - \frac{H^{\circ} - H_0^{\circ}}{RT} \right)$$

where  $w = h c \nu^* / k T$  and the values  $C^{\circ}/R$  and  $(H^{\circ} - H_0^{\circ})/R T$  are those for anharmonic oscillator of frequency  $\nu^*$ . The parameters  $Z$  and  $\nu^*$  are adjustable so that the observed "anharmonicity" may be accounted for. There is danger, however, in putting too much reliance in formulae of this sort,

since the "calculated results" can be made to fit the experimental data by a simple adjustment of the anharmonicity parameters  $Z$  and  $\gamma^*$ . It may be that an observed difference in experimental and calculated properties is due to an incorrect vibrational assignment, use of liquid state frequencies (see Chapter V), incorrect structural data or incorrect internal rotational data (if any). Scott and McCullough and their coworkers have used Equations 10 in calculations of the thermodynamic functions of benzenethiol (15), benzotrifluoride (8), toluene (9) and 4-fluorotoluene (69), 1-2-difluorobenzene (41) and fluorobenzene (11). The anharmonicity contribution is less than 2 % of  $C_p^\circ$  and  $S^\circ$  at  $1500^\circ$  K. for most of these compounds (for fluorobenzene, in this work, less than 1 %). The experimental data which has been used to determine the constants  $Z$  and does not go to higher temperatures than  $500^\circ$  K. Thus it is difficult to assess whether this 2 % contribution actually brings the calculated thermodynamic functions nearer their true values. At temperatures below  $500^\circ$  K. the anharmonicity contributions are within the experimental error, which may vary, up to 3 % (58). It is not expected that the halogenated benzenes will show more anharmonicity than the more loosely connected toluene derivatives, such as those mentioned above.

#### D. Internal Rotation

In the development outlined in Part A of this chapter, it is assumed that the molecules are rigid and that the groups of atoms do not rotate about their bond axes. This is the situation in the case of the halogenated benzenes, which are rigidly bonded. In some molecules however, internal rotations of groups of atoms may appear. For example in ethane-type molecules there is a rotation about the C-C bond. In general this rotation is not free, because of steric and electric effects and the nature of the axial bond itself.

If there is an internal rotational degree of freedom and the potential barrier to rotation is very high, then a vibration (usually  $< 200 \text{ cm}^{-1}$ ) will be caused by the torsional oscillation (6), and the contribution to the thermodynamic functions of this highly hindered rotation may be calculated as a vibrational contribution of the frequency of the torsional oscillation.

In other cases Pitzer's and Gwinn's method (76) may be used: Pitzer's method of treating internal rotations (76, 77, 78, 84, 85, 90, 102) assumes that a potential barrier to free rotation exists, which may be described as a function of the angle of rotation by

$$V = \frac{1}{2} V_0 (1 - \cos n' \phi) \quad (12)$$

where  $V$  is the potential barrier,  $\phi$  is the angle of rotation and  $n'$  is the number of equivalent positions in one revolution.

Pitzer (76.) has given the partition function for free rotation,  $Q_f$ , and has calculated tables which give the contribution of the internal rotation to the ideal gas thermodynamic functions for symmetric top molecules. These contributions are expressed as functions of  $V / R T$  and  $1 / Q_f$ . The value of  $Q_f$  is given by Equation 13 (84,85):

$$Q_f = \frac{1}{n} \left\{ \frac{8 \pi^3 I_r}{h^2} \frac{k T}{k T} \right\}^{1/2} \quad (13)$$

The reduced moment of inertia  $I_r$ , which appears in Eqn. 13 (84,85) is

$$I_r = I \left\{ 1 - \sum_{i=A}^C (\alpha_i^2 I / I_i) \right\} \quad (14)$$

where  $I$  is the moment of inertia of the rotating top,  $I_i$  is the principal moment of inertia of the molecule and  $\alpha_i$  is the direction cosine between the axis of rotation and the  $i^{\text{th}}$  principal axis with  $i = A, B, C$ . A computer program has been written by Cross (73) and modified by the author, to calculate the reduced moment of inertia and the directional cosines. This program is described in Appendix B.

A method of treating internal rotations by assuming a mixture of isomers has been proposed by Lielmezs and Bondi (6,99). For example, Butler and Lielmezs have calculated the thermodynamic functions of 1-1-2-2-tetrabromo-ethane by this method (100). The thermodynamic functions of each isomer are calculated and then the properties of the mixture of the two isomers are computed. This

method requires vibrational frequency assignments and structural data for both isomers and the isomerization energy. The Lielmezs-Bondi method has been successfully used for several compounds (2,3,6,100,103,104).

In this brief mention of the internal rotational problem, an outline of two useful methods has been given, in order to show what data is required for the calculations of the contributions to the thermodynamic functions. A summary of all the data required follows in the next section.

### E. Data Required to Calculate Thermodynamic Functions

Table II, below, summarizes the data which must be available in order to calculate the ideal gas thermodynamic functions  $C_p^\circ$ ,  $S^\circ$ ,  $(H^\circ - H_0^\circ)/T$ , and  $-(F^\circ - H_0^\circ)/T$  for polyatomic molecules, according to the methods given in this chapter. The table is divided into three sections: first, the data required for the harmonic oscillator, rigid rotator calculations; second, the data required if corrections are to be made for anharmonicity, using Eqns. 11 (method of McCullough, Scott et al.); third, the data for internal rotational calculations (Pitzer-Gwinn method and Lielmezs-Bondi method).

Computer programs to do the calculations with the data in Table II are contained in Appendix C, and explained in detail in Appendix B. The calculation of the thermodynamic functions of the halogenated benzenes, which forms the substance of this work, was done on the University of British Columbia IBM 7040 computer, with these programs, which are written in Fortran IV.

Table II: Data Required for Ideal Gas Thermodynamic Function Calculations

	DATA	USED TO FIND	WHERE USUALLY FOUND
simple case:	fundamental vibrational frequencies ( $3n-6$ )	vibrational contribution to thermodynamic functions	infra-red and Raman spectra normal coordinate analysis
rigid rotator harmonic oscill- ator approx.	molecular symmetry group	molecular symmetry number	as above or by inspection
	molecular weight	translational contribution to the thermodynamic functions	
	bond lengths and angles of molecule (molecular structure)	coordinates of atoms of molecule and thus $I_{ABC}$	electron-diffraction microwave, X-ray spectra
anharmonicity corrections	experimental third law data to empirically determine the anharmonicity contribution	$\nu^*$ and $Z$ (see Equations 11)	calorimetry
internal rotations Pitzer- Gwinn (76)	height of potential barrier $V_0$ and number of equivalent positions in $360^\circ$ , $n$	(see Equations 12)	microwave spectra infra-red spectra others - see ref. 79
	bond lengths and angles of molecule (molecular structure)	reduced moment of inertia $I_r$	electron-diffraction microwave, X-ray spectra
internal rotations Lielmezs- Bondi (99)	"simple case" data (above) for each isomer of compound		
	isomerization energy of the isomers	used in isomer mixture calculations	sound absorption microwave, infra-red, and Raman spectra electron-diffraction electric dipole moment

## CHAPTER III

## REAL GAS CORRECTIONS

A. The Equation of State

The results of the thermodynamic function calculations in which the ideal gas assumption is used need some modification in order to obtain the properties of a real gas. It is well known that at high pressures and low temperatures intermolecular force effects may contribute greatly to deviations from the ideal gas law where  $P V = R T$ , for one mole of gas. Vukalovich and Novikov (28) in an excellent paper on the Thermodynamic Properties of Imperfect Gases have surveyed how and why "real gas" effects occur. It is found (28) that the molecules of a gas associate into groups of two, three or more molecules. The principal reason for this is a Van der Waals type (28) interaction of molecules of the gas. It can now easily be seen why the ideal gas thermodynamic functions do not describe the real gas. The formulae for the ideal gas are derived by methods of statistical thermodynamics, considering individual particles. On association, the number of effective particles changes, and the rotational degrees of freedom of each individual molecule in an associated group are reduced (28), which tends to reduce the entropy. At 1 atm. and at the temperatures considered in this work ( $273.15^{\circ}$  to  $1500^{\circ}$  K.) real gas corrections are small (see for example, refs. 11,50). In design problems, however, pressures greater than one atmosphere may occur, and in this case real gas effects may be important.

Relations between the thermodynamic properties and the P-V-T properties of fluids, which enable these corrections, have been developed (23,83,84,90,87,85,102).

The text books and other literature give various equations of state, which generally fall into two categories. The virial equation of state, first used to fit experimental data by Kammerlingh Onnes, expresses deviation from ideal behaviour as a power series in P or 1/V. In this work Equation 15 will be used as the virial equation of state.

$$P V = R T + B P + C P^2 + \dots \quad (15)$$

At reasonably low pressures the higher terms drop out and only the second virial coefficient need be considered (83,84,90,102). For example Lewis and Randall (84) show for nitrogen at 273° K., that the use of the second virial coefficient alone is an excellent approximation up to 10 atm., while in error about 1.5 % at 100 atm. The method of virial coefficients has a theoretical background, which considers the intermolecular forces, and which has been well described by Hirschfelder, Curtiss and Bird (90). Unfortunately these methods cannot be used for the halogenated benzenes since there is little or no data on intermolecular potentials, such as the Lennard-Jones or Stockmayer potentials (102). Experimental data on the P-V-T properties of gases is usually presented (11,41,50) using the virial equation.

The second type of equation used is the various forms of the corresponding states equation, such as those of

Van der Waals, Dieterici, Berthelot, Benedict, Rubin and Webb, Beattie and Bridgeman and many others. (83,84,90,102). These equations attempt to describe the P-V-T behavior over as large a fluid range as possible. In this thesis it appeared that instead of the virial expansion an appropriate corresponding states equation could be used. A two constant equation was required, for two reasons. Firstly, the evaluation of constants for multiple constant equations, such as the Beattie Bridgeman equation, requires several parameters (84,102) which are not available for the halogenated benzenes. Secondly, thermodynamic calculations which use real gas corrections are usually of the once-only type: such calculations occur in the design of proposed processes. This type of correction must be done "by hand", and since computers are almost essential in the more complicated equations, simplicity is important.

The simple two constant equations were tested to see which would best fit the available P-V-T data for the halogenated benzenes. The Van der Waals, Dieterici and Berthelot equations have two constants, which can be expressed as functions of the critical temperature  $T_c$  ( $^{\circ}$  K.) and the critical pressure  $P_c$  (atm.) (102). The second virial coefficient B is expressed in terms of these functions in Equations 16, 17, 18 (83,84,90,102). This enables a comparison between the experimental virial coefficient B and that calculated from the equations of state.

Van der Waals:

$$B = b - a/RT \quad \text{where} \quad \begin{cases} a/R = 27 R T_c^2 / 64 P_c \\ b = R T_c / 8 P_c \end{cases} \quad (16)$$

Dieterici:

$$B = b - a/RT \quad \text{where} \quad \begin{cases} a/R = 16 R T_c^2 / 29.85 P_c \\ b = 4 R T_c / 29.85 P_c \end{cases} \quad (17)$$

Berthelot:

$$B = \frac{9}{128} \frac{R T_c}{P_c} \left( 1 - 6 (T_c/T)^2 \right) \quad (18)$$

These expressions for B (Equations 16, 17, 18) may be used in the virial equation

$$P V = R T + B P \quad (19)$$

where the gas constant  $R = 82.06 \text{ cc atm} / ^\circ\text{K. gmole}$  and the other quantities are in compatible units.\*

Experimental data for the coefficient B was available for fluorobenzene (11), 1-2-difluorobenzene (41) and hexafluorobenzene (50). In each case B was determined from heat of vaporization and vapor pressure measurements.

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\* Note that although the virial equation of Counsell, Green, Hales and Martin is expanded in terms of P (50) and the equation used by Scott and his coworkers (11,41) is expanded in terms of V, the values of B are identical (84).

Unfortunately no critical data for 1-2- difluorobenzene was found so no comparison could be made for this compound. The critical data used in Equations 16, 17, 18 was taken from Counsell, Green, Hales and Martin (50) for hexafluorobenzene; for fluorobenzene the critical data given by Reid and Sherwood (102) was used. The experimental determination of Counsell and his coworkers of the second virial coefficient of hexafluorobenzene was fitted by the equation (50)

$$B = -477 - 15.78 \exp(1470 / T) \quad (315^{\circ} - 353^{\circ} \text{ K.})$$

and for fluorobenzene Scott and his coworkers have found (11)

$$B = 212 - 158.6 \exp(750 / T) \quad (318^{\circ} - 500^{\circ} \text{ K.})$$

Patrick and Prosser (5) have also experimentally determined some values of the second virial coefficient from vapor pressure and heat of vaporization data for these compounds.

The values of B calculated by the equation of state (Equations 16, 17, 18) and the experimental data cited above are shown in Table 3, for selected temperatures.

For hexafluorobenzene Counsell's values (50) are considerably higher than those of Patrick and Prosser (5). For fluorobenzene both workers' experimental data is about the same. The equation of state values ( $B_{\text{calc}}$ ) are generally lower than the experimental values. The best fit is that of the Berthelot equation, which agrees well with all the

experimental data except that of Counsell and his coworkers.\*

TABLE III

Second Virial Coefficient (cc/gmole) for Fluorobenzene and Hexafluorobenzene

Hexafluorobenzene					
Temp. (° K.)	B <sub>expt</sub> Counsell	B <sub>expt</sub> Patrick	B <sub>calc</sub> Waals	B <sub>calc</sub> Dieterici	B <sub>calc</sub> Berthelot
298.2	-2664	-1540	-775	-1044	-1518
320.0	-2033		-711	-974	-1306
353.5	-1489	-1090	-678	-854	-1054
Fluorobenzene					
Temp. (° K.)	B <sub>expt</sub> Scott	B <sub>expt</sub> Patrick	B <sub>calc</sub> Waals	B <sub>calc</sub> Dieterici	B <sub>calc</sub> Berthelot
318.4	-1460		-637	-842	-1272
357.9	-1077	-1070	-553	-735	-992
382.4	-916		-509	-678	-861

Patrick and Prosser (5) in their paper have also stated that the Berthelot equation compares very satisfactorily with experimental measurements on hexafluoro-, pentafluoro-, fluoro-benzene and benzene itself. This is also borne out by Table III.

No specific information on the maximum pressure at which the Berthelot equation is accurate could be found, except

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\* See the paragraph on hexafluorobenzene in Chapter V, which gives a discussion of the reliability of these experimental results, which may be in error since  $(\partial S / \partial T)$  increases with T rather than decreasing as would be expected from the general theory.

that it is good for moderate pressures. (83,84,90). In view of the data on nitrogen (84) given above and the data on similar gases given by Guggenheim (20) it might be thought that the Berthelot equation would be reasonably accurate ( $\pm 2\%$ ) up to, say, 100 atm. However the critical point of the halobenzenes (see Table IV) is typically at  $500^{\circ} - 700^{\circ}$  K., 30 - 40 atm. The Berthelot equation of state is not expected to be accurate in the vicinity of the critical point (90). Thus it is felt that the most that can be said about the upper limit of applicability for pressure is that the Berthelot equation should be a good approximation up to 15 atm. The lower limit of applicability for pressure should be less than 0.25 atm., since experimental data for fluorobenzene (11) and hexafluorobenzene (50) show that this equation is good at that pressure.

In the absence of sufficient critical point and vapor pressure data to test the other members of the halogenated benzenes, and on the basis of the above evidence, it is assumed that the Berthelot equation describes the P-V-T properties of these compounds reasonably well, within the stated ranges of applicability.

## B. The Thermodynamic Functions for Real Gases

We have seen that the P-V-T behavior can be expressed functionally by the equation of state. The differences between the ideal gas thermodynamic functions (where the state equation is  $P V = R T$ ) and the real functions (where at moderate pressures,  $P V = R T + B P$ ) can be derived (83,94,90,102) from Equations 20, which relate P-V-T properties to the thermodynamic functions.

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T \left(\frac{\partial V}{\partial T}\right)_P \quad \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \quad (20)$$

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \quad \left(\frac{\partial C_p}{\partial P}\right)_T = -T \left(\frac{\partial^2 V}{\partial T^2}\right)_P$$

If the virial equation of state is used, it has been shown that (84) the difference (departure) in enthalpy at a temperature T is

$$(H-H^{\circ})_T = \left(B - T \frac{dB}{dT}\right) P + \left(C - T \frac{dC}{dT}\right) \frac{P^2}{2} + \dots \quad (21)$$

to obtain the heat capacity correction the enthalpy contribution is differentiated (84) to give Equation 22

$$(C_p - C_p^{\circ})_T = -T \left( \frac{d^2 B}{dT^2} P + \frac{d^2 C}{dT^2} \frac{P^2}{2} + \dots \right) \quad (22)$$

The correction for the entropy departure is

$$(S^{\circ} - S)_T = R \ln P + \left(\frac{dB}{dT}\right) P + \left(\frac{dC}{dT}\right) \frac{P^2}{2} + \dots \quad (23)$$

The ideal gas state is defined as being at "zero pressure",

but  $\lim_{P \rightarrow 0} S = \infty$ . In order that a finite entropy may be tabulated  $S^0$  is defined as being the ideal gas entropy at one atmosphere. The term  $R \ln P$  in Equation 23 accounts for the difference in pressure between zero and one atmospheres (84). The free energy function departure may be found by the difference in Equation 4. When the third virial coefficient is zero (as for moderate pressures it may be assumed to be), the terms in  $C$  in Equation 21, 22 and 23 drop out.

Since the second virial coefficient may be expressed in terms of the corresponding states equations, the "ideal - real" thermodynamic function difference may also be expressed in terms of the critical constants (and the other parameters of the more complicated equations of state). Godnev has derived the results for the Berthelot equation (87). Equations 24, 25 and 26 are used in this work.\*

$$(H-H^0)_T = \frac{9}{128} \frac{R T}{P_C} \left\{ 1 - 18 \frac{T_C^2}{T} P \right\} \quad (24)$$

$$(C_p - C_p^0) = \frac{81}{32} \frac{R T_C^3}{P_C T^3} P \quad (25)$$

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\* Godnev (87) and Reid and Sherwood (102) have also given methods for the calculation of the thermodynamic functions of liquids and solids from the ideal gas properties.

$$(S^{\circ}-S)_T^{**} = \frac{27}{32} \frac{R T_c^3 P}{P_c T^3} + R \ln P \quad (26)$$

Similar formulae to the above may be derived for other equations of state using Equation 20.

The use of the Berthelot equation in this work has been generally justified in Part A of this chapter; its use over the temperature range  $T/T_c = 0.3$  to  $T/T_c = 2$  has also been justified by Hirschfelder, Curtiss and Bird (90). The critical temperatures of the halogenated benzenes (see Table IV) fall in the range  $500^{\circ}$  to  $800^{\circ}$  K. Depending on  $T_c$ , the tables of ideal gas thermodynamic functions in Appendix D can be corrected by this equation at least up to  $1000^{\circ}$  K.

Another possible method of making real gas corrections is the use of generalized thermodynamic function departure tables (87,102). The maximum inaccuracy of this method is given (84) as 15 %. However, at the present time there is not sufficient data available for this method to be effectively used.

These methods for real gas corrections require either experimental data for  $B$  as a function of temperature,

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\*\* The  $R \ln P$  term is not given in Godnev's formulae. However in the notation used in this work  $S^{\circ}$  is the ideal gas entropy at 1 atm. The  $R \ln P$  is a correction that must be made to obtain the ideal gas entropy at pressure  $P$ , before the non-ideality correction (the first term in Equation 26) is applied. Some texts (85) include it in the formulae given in Table I in this thesis.

or critical data. The available critical data for the halogenated benzenes is shown in Table IV. Where there is no critical data available, the critical constants may be evaluated approximately by the methods given in the literature (83,84,90,92,102).

TABLE IV

## Critical Data for the Halogenated Benzenes

compound	$T_c$ (° K.)	$P_c$ (atm.)	$V_c$ (cc/gmole)	Ref.
benzene	562.1	48.6	260	102
fluorobenzene	560.1	44.6	271	102
chlorobenzene	632.4	44.6	308	102
bromobenzene	670.2	44.6	324	102
iodobenzene	721	44.6	351	102
1-2- dichlorobenzene	697.3	40.5	368	7
1-3- dichlorobenzene	684.0	38.3	359	7
1-4- dichlorobenzene	684.8	38.6	372	7
1-2-4- trichlorobenzene	735.0	39.4	385	7
hexafluorobenzene	516.7	32.6	385	50
chloropentafluorobenzene	571.0	31.8		52
bromopentafluorobenzene	(601)	(30)		52
pentafluorobenzene	532.0	34.7		52

A computer program (see Appendix B) has been written to calculate real gas thermodynamic functions by correcting the ideal gas thermodynamic functions with Equations 24, 25 and 26. In Appendix E the real gas thermodynamic functions of fluorobenzene are tabulated at several pressures between 0.25 atm. and 10.0 atm. These results are those of Table D-1 (a recalculation of the work of Scott et al.) (11), corrected using the Berthelot equation of state. The heat capacities  $C_p$ , fit the experimental data of Scott and his coworkers over

its range of applicability. The deviation between the two values ranges from - 0.28 % at 500.20° K. and 0.25 atm., to - 1.90 % at 389.20° K. and 2.0 atm. The deviation in the real vapor entropy of fluorobenzene varies from + 0.03 % at 382.20° K. and at 2.0 atm. to a deviation of - 0.14 % at 318.40° K. at 0.25 atm. The experimental entropy accuracy is stated (11) to be about  $\pm 0.20$  %.

As has been mentioned, at 1 atm. the real gas effects are small, since there are few intermolecular force effects. As the temperature increases, the thermodynamic functions for the real gas approach those for the ideal gas more closely. For fluorobenzene at 1 atm. (Tables D-1 and E-4) the real gas contributions to the entropy are 0.25 E.U. and 0.01 E.U. at 298.15 K. and 1000° K., at 1 atm. The contributions to the heat capacity are 0.75 cal/gmole ° K. and 0.02 cal/gmole ° K. at 298.15° and 1000° K. respectively.

The real gas correction method, using the Berthelot equation of state, for which a computer program was written by the author, gives accurate results over the range where experimental data is available. For the purposes of engineering calculations it should give sufficiently accurate results for all the halogenated benzenes, between 273° K. and 1000° K. and at pressures between 0.25 and 15 atmospheres.

## CHAPTER IV

## THE THERMODYNAMIC FUNCTIONS AT HIGH TEMPERATURES

In the next chapter (Chapter V), a description of the calculation of the ideal gas thermodynamic functions of the halogenated benzenes is given for temperatures up to  $1500^{\circ}$  K. It is doubtful that these properties will have any physical significance for most of these compounds at this temperature. The question of the applicability of the high temperature thermodynamic properties cannot be answered without experimental study of the thermal structural stability of these compounds at elevated temperatures. The available data on this subject is given below.

Johns, McElhill and Smith (53) have shown that hexafluorobenzene, which is an exceptionally stable compound, shows no signs of decomposition at temperatures as high as  $920^{\circ}$  K. Pummer and Wall (107) stated that at  $1070^{\circ}$  K. hexafluorobenzene changes to yield per-fluorodiphenyl. Benzene decomposes at the rate of 1 mole % per hour at  $870^{\circ}$  K. (53) and hexachlorobenzene at the same rate at  $790^{\circ}$  K. (53). According to Johns et al. (53), the partially halogenated benzenes, which comprise the majority of compounds found in this thesis, are not as stable as benzene. On the other hand, Cullis and Priddy (108) find that chlorobenzene and dichlorobenzene start to decompose at  $930^{\circ}$  K. and  $920^{\circ}$  K. respectively. These temperatures are affected by the methods and apparatus of the experiment (53), but do indicate the general range where

thermal decomposition may be expected.

The products of the halobenzene decomposition probably depend not only on the environment but on the state of the compound (53): the ratio of hydrogen to alkyl fragments in toluene decomposition is higher in the vapor phase than in the liquid (53). The decomposition products of the halogenated benzenes are likely to contain alkyl fragments, solid residues (108), hydrogen halides, halogenated alkyl fragments, molecular hydrogen and halogens; at higher temperatures (above  $1000^{\circ}$  K.) atomic halogens and hydrogen and free radicals are expected; at still higher temperatures, outside the range of this work, ionic phenomena become predominant.

If a reaction is of short duration, the thermodynamic function tables given in Appendix D may be valid at temperatures higher than those above; if short reaction times are involved few decomposition products will be evolved. If, however, mixtures of several components are present, due to thermal breakdown, the properties must be calculated using the methods for mixtures given in the literature (90,102,109,110, 111,112).

For temperatures above  $1000^{\circ}$  K., several methods of calculating thermodynamic functions and chemical equilibria for mixtures of gases have been proposed (109,110,111,112). For the system carbon-nitrogen, a statistical thermodynamic approach, using the partition function and including the electronic states which are relevant for atoms and ions at high temperatures, has

been shown by Kwang-Tien Shih and his coworkers (109). Woolley (111) has applied ionic solution theory to the high temperature gases. Brinkley (110) calculated the equilibrium compositions and thermodynamic properties of multi-constituent systems. For  $N_2-O_2-A$  mixtures, Shipley (112) has developed computer programs for the thermodynamic properties for temperatures up to  $50,000^\circ K$ . However, the above methods can only be used for simple gas mixtures, where the dissociation products are known. For the halogenated benzenes, where the high temperature products are unknown and may vary considerably, these methods can not be used.

At high temperatures the effect of the third virial coefficient becomes felt (90,112) due to the energy becoming sufficiently high for three- particle collisions to have a noticeable effect on the P-V-T properties (90). Indeed, if a gas is at a high enough temperature to be ionized, the virial equation of state may diverge (113). Shipley (112) lists the real gas correction equations, which include the third virial coefficients and their temperature derivatives, and their range of application.

As data concerning the decomposition products and temperatures was not available for the halogenated benzenes, and as the available methods (109,110,111,112) were not sufficiently general to treat high temperature polyatomic molecules, no calculations could be made for the complex halogenated benzene decomposition equilibrium. It appears that the

halogenated benzenes probably start to decompose at about 800° K., 1 atm. Practically, this is not a problem, since no processes are apparent which use temperatures above 800° K., since decomposition of the compounds would tend to defeat the purpose of any synthesis.

## CHAPTER V

## DISCUSSION OF THE CALCULATIONS

A. General Discussion

In this chapter the sources of the data for the calculations of the ideal gas thermodynamic functions will be given, with the additional information on how the computations were made. An attempt will be made to give an indication of the reliability of the results (for a discussion of errors, see Part B of this chapter). Each page of the Appendix D contains the ideal gas thermodynamic functions for one of the halogenated benzenes. Those with normal boiling points below  $400^{\circ}$  K. are given over a temperature range of  $273.15^{\circ}$  to  $1400^{\circ}$  K. and those with boiling points above  $400^{\circ}$  K. are given between  $298.15^{\circ}$  and  $1500^{\circ}$  K. The fundamental frequencies ( $\text{cm}^{-1}$ ) used in the vibrational partition function calculation are shown, as are the principal moments of inertia  $I_A$ ,  $I_B$ ,  $I_C$  ( $\text{amu } \text{A}^2$ ), the molecular symmetry number  $\sigma$  and the molecular weight (g/gmole). A list of references used in the calculations is given. The tables of thermodynamic functions are numbered consecutively from Table D-1 to Table D-38.

The Monohalobenzenes

The ideal gas thermodynamic functions for fluorobenzene, chlorobenzene, bromobenzene and iodobenzene have been calculated by other workers (11,38,58). In this work some new structural data was available, making a recalculation worthwhile. The data of Scott and his coworkers (11,35) for

fluorobenzene was used, with the exception of the microwave structural data of Bak, Christensen, Hansen-Nygaard, and Tannenbaum (12). The anharmonicity corrections of McCullough, Scott et al. were also employed in this calculation. The results are similar to those of Scott and his coworkers and for discussion of their agreement with the experimental data one may refer to the original work (11).

The data of Whiffen (58) was used to calculate the thermodynamic functions for chlorobenzene, bromobenzene and iodobenzene. The results (Tables D-2, D-3 and D-4) agree with Whiffen's work (58). The principal moments of inertia used for bromobenzene were taken from the microwave measurements of Rosenthal and Dailey (1). These workers give the moments of inertia for isotopes  $C_6H_5^{79}Br$  and  $C_6H_5^{81}Br$ . The average molecular weight of bromine is 79.909 g/gmole. The average moments of inertia were calculated by interpolation between the moments of the two isotopes. It is considered that this is accurate since the difference is only  $1.2392 \times 10^{-113} g^3 cm^6$  versus  $1.2628 \times 10^{-113} g^3 cm^6$ . For iodobenzene the vapor microwave structural data of Johansson, Oldenberg and Selen (42) were used. All other data, including the frequency assignments, on the monohalobenzenes, and comparison with experimental work, is given by Whiffen (58).

#### The Polyfluorobenzenes

The thermodynamic functions for the difluorobenzenes have been calculated by other workers (41,54) but are

again included to complete the series. Scott and his group (41) have made experimental measurements and calculations of the properties of 1-2- (ortho) difluorobenzene. The calculations in this work were made using the data of Scott and his coworkers (41) which includes the semi-empirical anharmonicity correction (Equations 11). The resulting thermodynamic functions (Table D-5) for 1-2- difluorobenzene are identical with Scott's figures at low temperatures but at high temperatures ( $> 1000^{\circ}$  K.) are somewhat lower: the entropy at  $1000^{\circ}$  K.,  $S_{1000}^{\circ}$ , in this work is 0.12 % lower than in the original work.\* It is assumed that this difference is due to slightly different calculation methods. In Table V the values of  $C_p^{\circ}$  and  $S^{\circ}$  calculated in this thesis (see Table D-5) are compared with selected values found by calorimetry reported by Scott and his group (41).

Green, Kynaston and Paisley (54) have calculated the thermodynamic functions for the difluorobenzenes. For the ortho isomer the product of principal moments of inertia according to Green is  $6.414 \times 10^{-113} \text{ g}^3 \text{ cm}^6$  versus  $6.113 \times 10^{-113} \text{ g}^3 \text{ cm}^6$  given by Scott and his coworkers. Scott's  $I_{ABC}$  agreed with that calculated by this author using the bond lengths and angles given by Sutton (80). Green, Kynaston and Paisley use the vapor state frequencies, while Scott et al. use those for the liquid state. These factors account for the

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\* This may also be noticed in the thermodynamic functions of fluorobenzene (Table D-1)

Table V: Heat Capacity and Entropy of 1-2- (ortho) difluorobenzene

Temp. ( $^{\circ}$ K.)	$C_p^{\circ}$ (cal/gmole $^{\circ}$ K.)		$S^{\circ}$ (E.U.)	
	this work	exptl. ref. 41	this work	exptl. ref. 41
326.90			79.39	79.38
345.61			80.96	80.94
355.20	29.68	29.69		
367.07			82.75	82.71
418.20	33.90	33.93		
459.20	36.36	36.41		
500.20	38.60	38.66		

minor differences in the thermodynamic functions reported in the two papers.\* In this work the frequencies of Scott (41) are used.

The calculations for the 1-3- (meta) difluorobenzene (Table D-6) have been made using the vapor state vibrational frequency data of Ferguson, Collins, Nielsen and Smith (34), as corrected by Green, Kynaston and Paisley (54). A few frequencies were not available in the vapor state, in which case the liquid state frequencies were used.

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\* It may be noted that the work of Scott et al. agrees more closely with the experimental data because of the use of the anharmonicity correction (Equations 10), the parameters of which can be chosen so that a defect between the calculated and "third law" properties can be accounted for.

Green, Kynaston and Paisley have reported that the structural data for 1-3- difluorobenzene given by Sutton in his Tables of Interatomic Distances (80) gives a product of moments of inertia of  $I_{ABC} = 7.255 \times 10^{-113} \text{ g}^3 \text{ cm}^6$ . This work using the same structural data has found a product  $I_{ABC} = 7.4137 \times 10^{-113} \text{ g}^3 \text{ cm}^6$ . It is felt that a calculation error was made in the other work. The molecular symmetry number for the  $C_{2v}$  symmetry group (34) is  $\sigma = 2$ , in accordance with Herzberg (85). The results of this author's calculations of the thermodynamic functions are very close to those obtained by Green et al. (54). It is expected that these values will be accurate, since vapor state frequencies were used and the structure of this compound (and thus  $I_{ABC}$ ) is well known (80).

The vibrational frequencies for 1-4- (para) difluorobenzene (see Table D-7) are those of Ferguson, Hudson, Nielsen and Smith (32), as corrected by Stojoljkovic and Whiffen (25). The only major difference between this assignment and that of Green, Kynaston and Paisley is the assignment of  $163 \text{ cm}^{-1}$  to a  $b_{2u}$  fundamental frequency, whereas previously it was assigned as  $186 \text{ cm}^{-1}$  (see also ref. 47). This corresponds to a difference of about  $0.03 \text{ cal/gmole } ^\circ\text{K}$ . in  $C_p^\circ$  and about  $0.22 \text{ E.U.}$  in  $S^\circ$  at  $273.15^\circ \text{ K}$ . As the temperature increases, the heat capacity difference becomes even smaller and the entropy difference remains about the same. The structural data for 1-4- difluorobenzene was taken from Sutton (80). The product of the moments of inertia calculated in

this work,  $6.3464 \times 10^{-113} \text{ g}^3 \text{ cm}^6$  is close to that given by Green, Kynaston and Paisley, which is  $6.364 \times 10^{-113} \text{ g}^3 \text{ cm}^6$ . This molecule belongs to the  $V_h$  symmetry group (32) which corresponds to  $\sigma = 4$  (85). Again, the results are close to those calculated by Green, Kynaston and Paisley (54). Unfortunately no experimental data is available, but the accuracy of these thermodynamic functions is about the same as for the meta isomer.

For 1-3-5- trifluorobenzene, the vapor state fundamental frequencies of Nielsen, Liang and Smith (22), corrected by the work of Ferguson (46) and Scherer, Evans and Muelder (55) were used to calculate the vibrational contributions.\* The molecular symmetry group is  $D_{3h}$  (46) giving  $\sigma = 6$ . There was no available structural data, so planar bond distances were assumed, by analogy with the other halogenated benzenes. This is justified since it has been fairly conclusively shown that the halogenated benzenes are planar molecules, within the precision of present measurements (46, 65, 66, 67, 103). For 1-3-5- trifluorobenzene all bond angles are  $120^\circ$ : it is not expected that there is repulsion of fluorine atoms and resultant distortion of bond angles (which may be apparent (80) in ortho bonds) since these bonds are not adjacent on the carbon ring. The C-F bond distance was assumed to be  $1.30 \text{ \AA}$ , as in meta- and para-difluorobenzene (80).\*\*

\* See also Steele (51) and Nonnenmacher (61) for vibrational data.

\*\* It is found that if the atoms of the molecule are crowded, as in ortho compounds, the C-F bond is stretched to  $1.35 \text{ \AA}$  (41). In hexafluorobenzene the bond is stretched to  $1.327 \text{ \AA}$  (50, 75).

The C-C bond distance is assumed to be 1.397 Å, which is the most common distance in the halogenated benzenes (12,50,66,67,75). The most common distance for the C-H bond, 1.08 Å, is also used. The moments of inertia were calculated with these distances, using the computer program described in Appendix B of this thesis. The accuracy of the results is expected to be good (see Part B of this chapter), since the frequencies used were determined for the vapor state, provided there are no errors in assignments.

The only available vibrational assignment for 1-2-4- trifluorobenzene is the work of Ferguson, Hudson, Nielsen and Smith (36) who obtained liquid infra-red and Raman spectra. Vapor-liquid frequency shifts may cause errors in the calculated thermodynamic functions, but it is assumed that they are small (Part B, this chapter). Again, it was assumed that the molecule is planar and that the bond angles are 120°. The ortho fluorines are thought to be connected to the ring by bonds of the same type as found in ortho-difluorobenzene (i.e. C-F = 1.35 Å) and the "4 position" fluorine atom is bonded by C-F = 1.30 Å, as in the other difluorobenzenes (80). As before, C-H = 1.08 Å and C-C = 1.397 Å. The molecule is of the C<sub>s</sub> symmetry group (36) which gives  $\sigma = 1$ . These data were used to calculate the thermodynamic functions in Table D-9. Errors may be caused by the liquid state frequencies (36) but the results are probably within  $\pm 1\%$  of the thermodynamic functions for the ideal gas.

Steele (51) has assigned the fundamental frequencies for two of the tetrafluorobenzenes. Where possible the data given by Steele in his paper have been modified in this work to fit his infra-red vapor observations, rather than the liquid frequencies presented in his tables.

Steele has not assigned the  $a_1$  frequency corresponding to  $1157 \text{ cm}^{-1}$  in  $\text{C}_6\text{F}_6$  or the  $b_1$  frequency corresponding to  $215 \text{ cm}^{-1}$  in  $\text{C}_6\text{F}_6$ . However, these frequencies are assigned in this work by analogy with the other fluoro substituted benzenes, as shown by Steele in his paper (51). The required  $a_1$  frequency is between  $1245 \text{ cm}^{-1}$  and  $1157 \text{ cm}^{-1}$ . This frequency is arbitrarily assigned as  $1200 \text{ cm}^{-1}$ . An error of  $\pm 40 \text{ cm}^{-1}$  in this figure would change  $C_p^\circ$  by less than  $0.02 \text{ cal/gmole } ^\circ\text{K.}$  and  $S^\circ$  by  $0.01 \text{ E.U.}$  at  $273.15^\circ \text{ K.}$ ; at  $1000^\circ \text{ K.}$  the changes would be less than  $0.03 \text{ cal/gmole } ^\circ\text{K.}$  and  $0.05 \text{ E.U.}$  respectively. The unassigned  $b_1$  frequency is between  $249 \text{ cm}^{-1}$  and  $215 \text{ cm}^{-1}$  (51). Since the effect of the low frequency vapor-liquid shift (72) should be counteracted if possible, the frequency assigned in this work was  $220 \text{ cm}^{-1}$ . (Vapor state frequencies were not available below  $440 \text{ cm}^{-1}$ .) The symmetry group of this molecule is  $\text{C}_{2v}$  (51), giving  $\sigma = 2$ .

No published data for the structure of the tetrafluorobenzenes could be found. Following the previous discussion the molecules were assumed to be planar with all bond

angles  $120^\circ$ . \* By analogy with the chlorobenzenes it was assumed that the bond lengths would be approximately the same as for the tetra- and hexa- compounds. Thus the C-F bond distance of  $1.327 \text{ \AA}$  found in hexafluorobenzene (50,75) was the distance for the tetrafluorobenzenes also. The other bond distances used were C-C =  $1.394 \text{ \AA}$  (50,67,75) and C-H =  $1.08 \text{ \AA}$ . as in the other halogenated benzenes.

The fundamental vibrational assignment for 1-2-4-5-tetrafluorobenzene has been made by Ferguson, Hudson, Nielsen and Smith (33). Later, several changes have been proposed by Steele and Whiffen (31), which are adopted in this work. Wherever possible the vapor state frequencies have been used. Again, two frequencies are unassigned in the most recent work (31): these are assigned by analogy with the known vibrational frequencies of the same mode.

The first unknown frequency is an X (X = F,Cl,Br,I) sensitive  $a_1$  fundamental vibration. In Figure 3, it is seen that the frequencies of this mode are linearly decreasing over the series ortho-, meta-, para-tetrafluorobenzene. In this nomograph, the fundamental frequency corresponding to  $443 \text{ cm}^{-1}$  in  $C_6F_6$  is plotted against the increasing sequence of isomers 1-2-4-5- (para), 1-2-3-5- (meta) and 1-2-3-4- (ortho), giving a straight line. The desired  $a_1$  frequency corresponds to the

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\* The validity of the assumption of  $120^\circ$  bond angles is discussed below, in the paragraphs on the dibromobenzenes.

315  $\text{cm}^{-1}$  vibration for  $\text{C}_6\text{F}_6$ . These frequencies for the 1-2-3-5- and 1-2-3-4- isomers are 445  $\text{cm}^{-1}$  and 460  $\text{cm}^{-1}$  respectively.

In Figure 3 the straight line between the points given by these two known frequencies is extrapolated to predict the desired  $a_1$  frequency for the 1-2-4-5- isomer as  $\sim 420 \text{ cm}^{-1}$ .\*

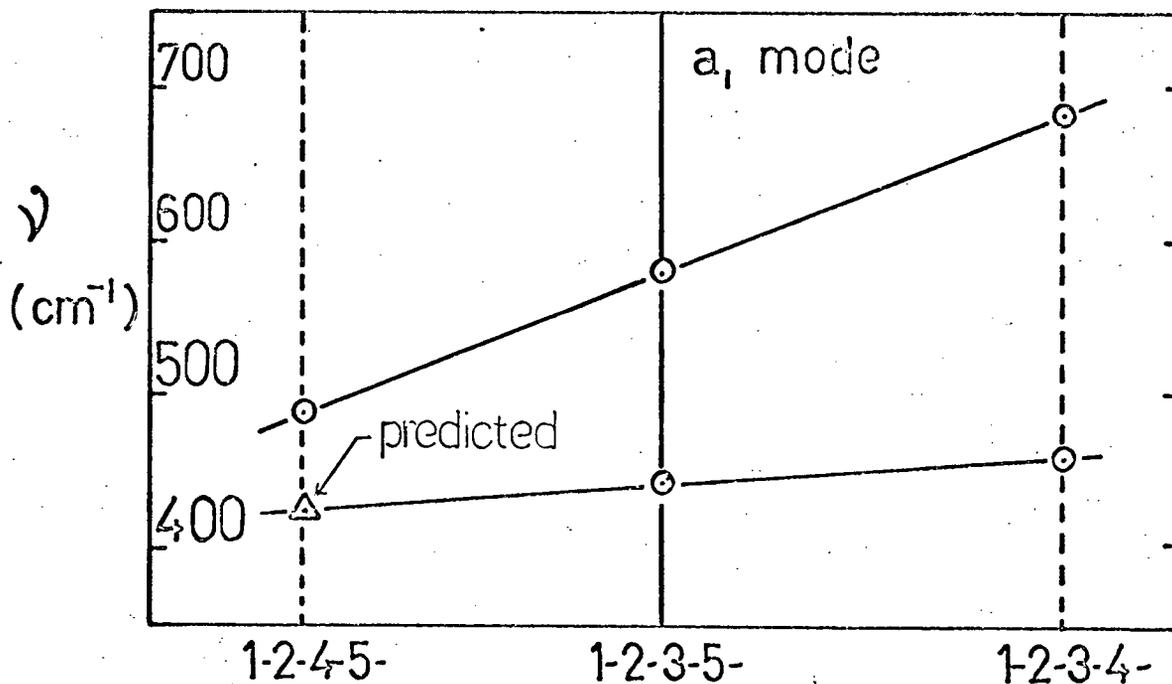


Figure 3: Nomograph to predict the unknown frequency for 1-2-4-5- tetrafluorobenzene, by analogy with similar frequencies of same mode.

\* This is a reasonable value if compared with the values of the same fundamental frequency for similar molecules  $\text{C}_6\text{HF}_5$ ,  $\text{C}_6\text{DF}_5$ ,  $\text{C}_6\text{F}_6$  as shown by Steele (31).

The other previously unassigned vibrational frequency was approximated, by the same method, as  $270 \text{ cm}^{-1}$ .

The moments of inertia of this molecule were calculated using the data presented above, for the tetrafluorobenzenes. The molecule has symmetry group  $V_h$  (31) which corresponds to a symmetry number  $\sigma = 4$ . The thermodynamic functions for 1-2-4-5- tetrafluorobenzene (Table D-11) may have a relatively large error, since at least four of the low frequencies ( $420, 270, 140$  and  $240 \text{ cm}^{-1}$ ) used in the vibrational contribution calculation are of doubtful accuracy (31). These frequencies include those assigned above in this work, for which there is no direct experimental evidence. It is still expected, however, that the entropy  $S^\circ$  is within  $\pm 1.5 \%$  of the experimental "third law" values.

Steele (51) has assigned most of the fundamental vapor phase frequencies of 1-2-3-4- tetrafluorobenzene. However, only one of the five  $a_2$  vibrations has been assigned by Steele. The remaining four have been assigned in this work, by analogy with the change in frequency of the highest (already assigned)  $a_2$  vibration, over the series o-  $C_6H_4D_2$ , 1-2-3-4-  $C_6F_4H_2$  and  $C_6F_6$ , which is also used for comparative purposes by Steele (51). The nomograph in Figure 4 is used to predict these frequencies. In Figure 4 the y-axis is frequency, the left hand vertical line (dashed line) represents the frequencies of o-  $C_6H_4D_2$ , the right hand line (dashed line) represents the frequencies of  $C_6F_6$ . Steele's experimentally observed  $a_2$

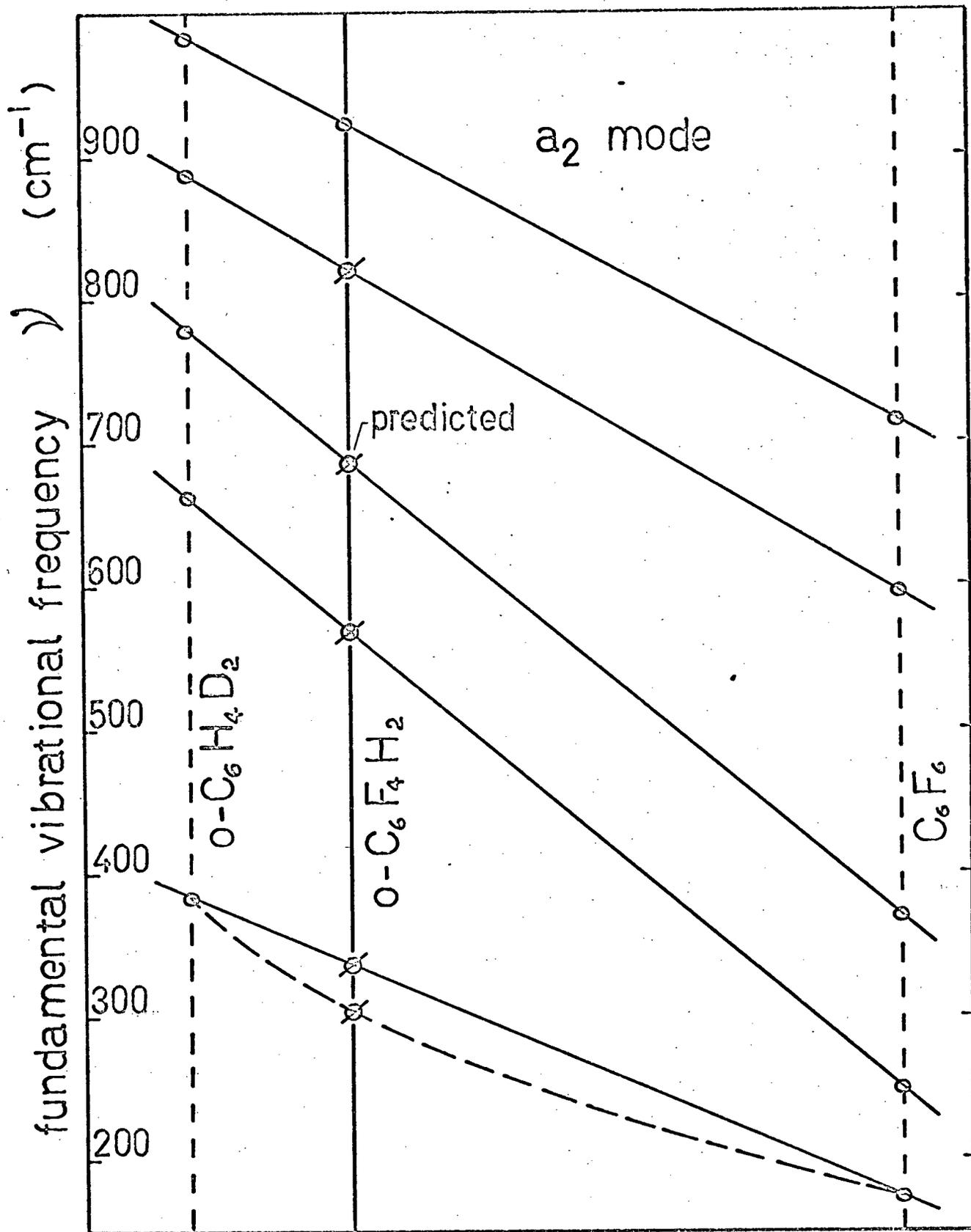


Figure 4 : Assignment of  $o\text{-C}_6\text{F}_4\text{H}_2$  Frequencies

frequencies are  $982\text{ cm}^{-1}$  and  $714\text{ cm}^{-1}$  respectively. The corresponding frequency for 1-2-3-4- tetrafluorobenzene is  $922\text{ cm}^{-1}$  (51). A vertical line (continuous line) was drawn on Figure 4 so that these three frequencies would form the uppermost straight line on the plot. It was then assumed that the other frequencies would follow a similar pattern: a line could be drawn between the two known frequencies, to cross the 1-2-3-4- tetrafluorobenzene line and thus indicate its approximate frequency. The three  $a_2$  vibrational frequencies predicted by Figure 4 were  $820\text{ cm}^{-1}$ ,  $685\text{ cm}^{-1}$  and  $570\text{ cm}^{-1}$ . The lowest frequency, corresponding to  $175\text{ cm}^{-1}$  in  $\text{C}_6\text{F}_6$ , was predicted by the above method as  $335\text{ cm}^{-1}$  but was assigned as  $305\text{ cm}^{-1}$  since it was observed that the lower frequencies ( $500\text{ cm}^{-1}$ ) for 1-2-3-4- tetrafluorobenzene were relatively closer to those of  $\text{C}_6\text{F}_6$  than the higher frequencies. The structural data (as shown above) for the tetrafluorobenzenes was used to calculate the moments of inertia. The molecular symmetry number of this molecule is  $\sigma = 2$ , from the  $\text{C}_{2v}$  symmetry group (51). The frequencies assigned by the above method are only approximate and there is possible a large margin of error in each frequency. The overall error produced in the thermodynamic functions for 1-2-3-4- tetrafluorobenzene should not be greater than  $\pm 1.5\%$ .

Pentafluorobenzene fundamental vibrations have been assigned by Steele and Whiffen (31) and Long and Steele (48) have performed a normal coordinate analysis. Where available, the vapor state frequencies were used in the calculations.

Steele and Whiffen do not assign the highest  $a_2$  vibration but, following similar compounds  $C_6H_2F_4$ ,  $C_6DF_5$  and  $C_6F_6$ , suggest that it is  $600\text{ cm}^{-1}$ . In the  $b_1$  mode there are two unassigned frequencies. That corresponding to  $249\text{ cm}^{-1}$  in hexafluorobenzene is assigned as  $300\text{ cm}^{-1}$ , following the recommendation of Steele and Whiffen that it must be lower than  $350\text{ cm}^{-1}$  and higher than the corresponding  $C_6F_6$  frequency. Using similar reasoning the lowest  $a_2$  frequency corresponding to  $175\text{ cm}^{-1}$  in  $C_6F_6$  is assigned as  $200\text{ cm}^{-1}$ . The structural data for pentafluorobenzene is the same as for hexafluorobenzene (see below) with  $C-H = 1.08\text{ \AA}$ . The  $C_{2v}$  symmetry group predicts  $\sigma = 2$  for this molecule. The accuracy of the thermodynamic functions (Table D-13) can not be put at less than  $\pm 1.5\%$  due to the uncertainty of the low frequency fundamental vibrations assigned in this work.

The ideal gas thermodynamic functions for hexafluorobenzene (Table D-14) have been calculated from spectroscopic and third law data by Counsell, Green, Hales and Martin (50). These workers have revised the vibrational frequency assignments made by Steele and Whiffen (39). The major difference is in the assignment of the lowest  $e_{2u}$  mode (doubly degenerate) frequency to  $125\text{ cm}^{-1}$  as opposed to the Steele and Whiffen value of  $175\text{ cm}^{-1}$ . This has been justified by Counsell and his coworkers (50) by the fact that this frequency brings the calculated and observed entropies into satisfactory agreement over a  $30\text{ K.}^\circ$  experimental range, from  $290^\circ\text{ K.}$  to  $320^\circ\text{ K.}$ ,

and by its agreement with the normal coordinate analysis calculated values of  $121 \text{ cm}^{-1}$  (39) and  $119 \text{ cm}^{-1}$  (61). The same structural data (75) was used in this work as was used by Counsell et al: C-C =  $1.394 \text{ \AA}$ , C-F =  $1.327 \text{ \AA}$ , in a planar molecule having bond angles of  $120^\circ$ . In this work, however, the calculated  $I_{ABC} = 10.9007 \times 10^{-112} \text{ g}^3 \text{ cm}^6$ . An error is suspected in the value of  $I_{ABC} = 8.870 \times 10^{-112} \text{ G}^3 \text{ cm}^6$ , reported by Counsell, Green, Hales and Martin. If the proposed larger value of the product of the principal moments of inertia is used, it is found that the lowest  $e_{2u}$  mode frequency to give the best fit to the experimental  $S^\circ$  is  $133 \text{ cm}^{-1}$ , not  $125 \text{ cm}^{-1}$  as was reported by Counsell and his associates (50). Until experimental work is done in the low frequency infra-red region for hexafluorobenzene vapor, the assignment of the lowest frequency is a matter of arbitrary choice: in this work it was assigned as  $133 \text{ cm}^{-1}$ . This frequency, with the higher value of  $I_{ABC}$ , gives a slightly better fit to the experimental  $C_p^\circ$  (50) over the entire experimental range, from  $290^\circ$  to  $320^\circ \text{ K}$ . The fit to the experimental  $S^\circ$  is about the same of that of Counsell et al., but slightly better at low temperatures and slightly poorer at high temperatures in the experimental range.

Figure 5 shows the curve for  $S^\circ$  at one atmosphere calculated in this work (continuous line), that calculated by Counsell et al. (dashed line) and that experimentally determined using the third law of thermodynamics by Counsell et al. (heavy line). It is suggested that there is an error in the

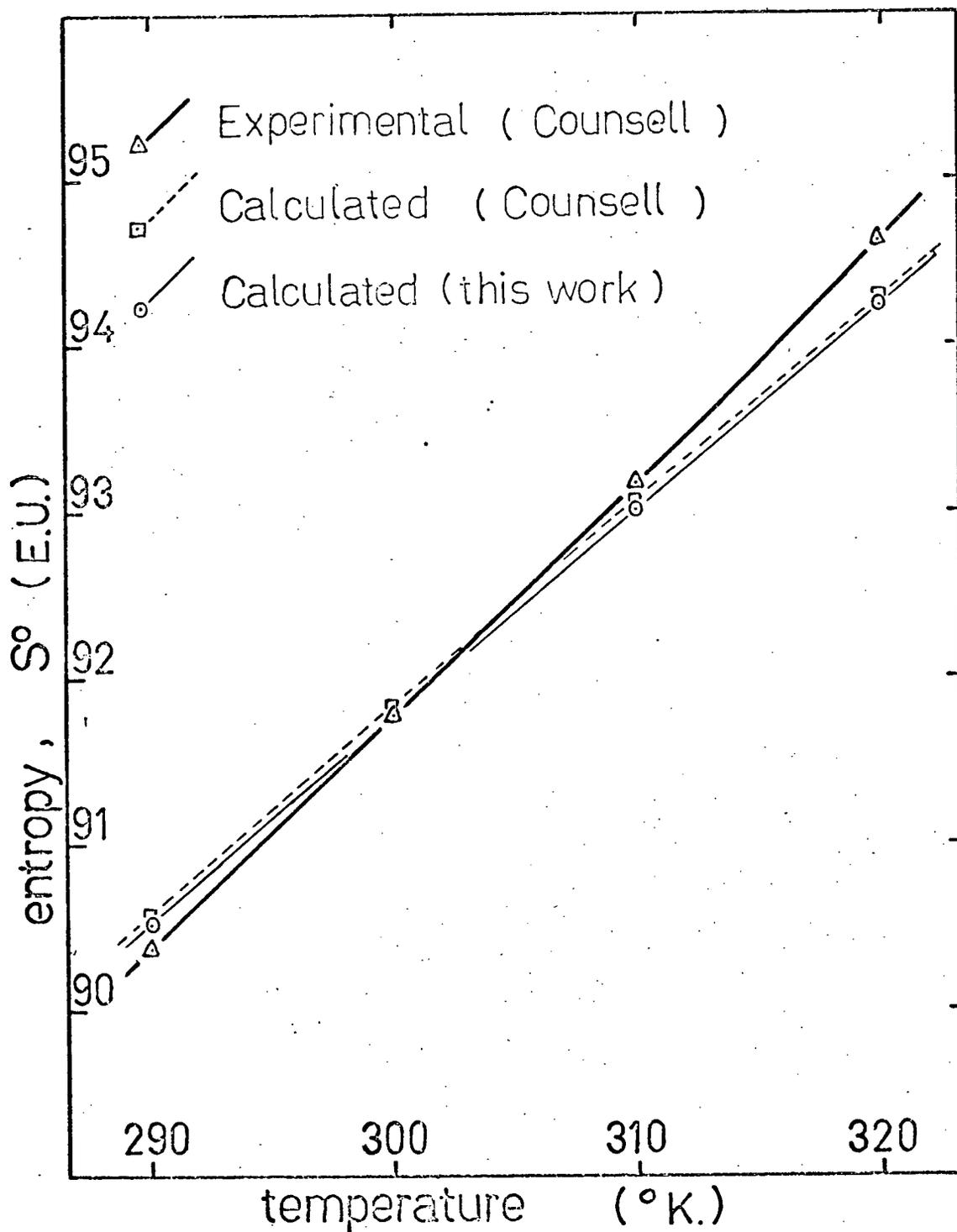


Figure 5:  $S^\circ$  for Hexafluorobenzene

experimental work, making  $S^{\circ}$  too large at the higher temperatures. This is supported by the fact that for the experimental results (50),  $(\partial S / \partial T)_p$  is increasing with temperature rather than decreasing, as would be expected from the general theory and from experimental results for other compounds. It is also unlikely, with the fundamental frequencies and structure of hexafluorobenzene as well known and as accurate as they are, that there should be such a large difference between the calculated and the "third law" values as is shown in Figure 5.

Thermodynamic functions have been calculated for chloro-, bromo- and iodo-pentafluorobenzene (Tables D-15, D-16, D-17) using the liquid state fundamental frequencies assigned by Hyams, Lippincott and Bailey (59), who improved on the work of Long and Steele (48,49). For these compounds there are two unassigned fundamental frequencies, an  $a_2$  and a  $b_1$  mode. Following the suggestion of Hyams, Lippincott and Bailey, the highest  $a_2$  frequency was assigned as  $600 \text{ cm}^{-1}$  for all three compounds, since the  $a_2$  frequencies are not X-sensitive (59). The  $b_1$  frequency, which is also X-insensitive, was assigned as  $550 \text{ cm}^{-1}$  since it should be about  $50 \text{ cm}^{-1}$  lower than the corresponding  $\text{C}_6\text{H}_6$  value (69). The bond distances and angles used for these compounds were those occurring in hexafluorobenzene. The C-Cl distance used,  $1.717 \text{ \AA}$ , was that found in hexachlorobenzene (66) and the C-Br =  $1.879 \text{ \AA}$  was taken from Strand's (67) data for hexabromobenzene. The only information found on C-I bonds was for iodobenzene (42), where C-I =  $2.08 \text{ \AA}$ . It is probable that due to crowding of

the halogen atoms this distance is increased in  $C_6F_5I$ , but there is no data to verify this. Analogously to the other halogen substituted benzenes,  $2.10 \text{ \AA}$  was chosen as a reasonable carbon-iodine bond length. All these molecules belong to the  $C_{2v}$  symmetry group (59), giving a molecular symmetry number of  $\sigma = 2$ . The use of liquid state frequencies puts an accuracy of  $\pm 1\%$  on the thermodynamic functions for chloro- and bromopentafluorobenzene. In view of the uncertainty in the structure of iodo-pentafluorobenzene,  $\pm 1.5\%$  is a reasonable limit of error for this compound.

#### The Unsymmetrical Dihalobenzenes

Nielsen's group have measured and assigned the spectra (17,57,104) of the 1-2-, 1-3-, 1-4- isomers of chlorofluorobenzene (Tables D-18, D-19, D-20). All the fundamental vibrations except the low frequencies are for the vapor state. The symmetry numbers of these molecules are 1, 1, and 2 respectively. The only published data for these compounds is the vapor microwave measurement of Rachman (43) for the 1-3-isomer. The moments of inertia given in Rachman's paper are used in this work. In the ortho (1-2-) isomer it was assumed that some bond stretching takes place, due to crowding of the atoms. The bond distances were assumed to be as follows:  $C-F = 1.33 \text{ \AA}$ ,  $C-Cl = 1.71 \text{ \AA}$ ,  $C-C = 1.397 \text{ \AA}$  and  $C-H = 1.08 \text{ \AA}$ , where all the angles are  $120^\circ$  in a planar configuration. To calculate the principal moments of inertia for para (1-4-) chlorofluorobenzene, bond distances similar to those observed

by Rachman for the meta isomer (43) were assumed, since in general meta and para halobenzenes have similar bond lengths: the C-C and C-H bonds were as above for the ortho isomer, the C-Cl = 1.699 Å and C-F = 1.329 Å, again in a planar molecule. Of these three structures that of the meta isomer is the most reliable, and the assumed ortho structure the most doubtful, as it is difficult to predict what effect crowding of the two halogen atoms has on the molecular structure. All the vibrational data is considered reliable (17,57,104), providing there are no large vapor-liquid shifts in the low frequencies. An accuracy of  $\pm 1.5\%$  is estimated for the thermodynamic functions of 1-2- chlorofluorobenzene: the others should be accurate to within  $\pm 1\%$ .

In the calculations for the ortho compounds bromo-fluoro-, fluoroiodo- and bromochlorobenzene (Tables D-21, D-22, D-23) the vibrational assignments of Krishnamachari (71) are used. These liquid film measurements are assigned by analogy with similar substituted benzenes, using infra-red vapor phase contours, Raman lines and the relative intensities of the spectra. No indication of the possible accuracy of these assignments is given and since there are no vapor phase frequencies shown it is difficult to assess what may be the vapor-liquid shift. Published structural information was lacking for these compounds, so bond lengths were assumed analogously to the other disubstituted benzenes. As with other compounds the C-C bond was taken as 1.397 Å and C-H = 1.08 Å. All the

molecules were assumed to be planar and to have bond angles of  $120^\circ$ . The ortho C-F distance, like that for 1-2-difluorobenzene (80) was  $1.35 \text{ \AA}$ ; the C-Cl distance like that for 1-2-dichlorobenzene (see below) was  $1.71 \text{ \AA}$ ; similarly C-Br was chosen as  $1.883 \text{ \AA}$  (67). The C-I distance for these ortho compounds was assumed to be  $2.10 \text{ \AA}$ , using the same reasoning as stated for iodo-pentafluorobenzene (see above). For all these compounds the molecular symmetry number is one. It is expected that the maximum errors will be less than 2 % of the thermodynamic functions.

#### The Polychlorobenzenes

In a major work, Scherer and Evans (62) have assigned the fundamental vibrational frequencies of sixteen chlorobenzenes and have presented normal coordinate analyses for these compounds (63,105), and have surveyed the existing literature on the chlorobenzenes (62). This thesis uses the liquid state frequencies of Scherer and Evans. The symmetry number is determined (85) from the symmetry group of the molecule, which is given with the frequency assignments.

Godnev and Sverdlin (39) have calculated the thermodynamic functions for the dichlorobenzenes, but they are recalculated here using the more recent vibrational data referred to above. For 1-2-difluorobenzene the C-Cl distance is  $1.71 \text{ \AA}$  (39), for the 1-3- and 1-4- isomers C-Cl =  $1.69 \text{ \AA}$  (39). The products of moments of inertia calculated by the program described in Appendix B agree with those calculated by Godnev

and Sverdlin (39). The molecular symmetry number  $\sigma$  is 2, 2 and 4 for the ortho, meta and para forms respectively. The thermodynamic functions (Tables D-24, D-25, D-26) also agree with those calculated by Godnev and Sverdlin (39), except for the case of the entropy of 1-4-dichlorobenzene, where this work finds an entropy about 0.5 E.U. higher. The heat capacity calculated in this work is slightly lower than that of Godnev and Sverdlin (by 0.04 cal/gmole  $^{\circ}$ K.). But  $I_{ABC}$  in this work is  $2.5591 \times 10^{-112} \text{ g}^3 \text{ cm}^6$  versus  $2.5942 \times 10^{-112} \text{ g}^3 \text{ cm}^6$  in the other paper, so Godnev's rotational contribution to entropy is the larger. The reason for Godnev's calculated entropy being smaller than  $S^{\circ}$  in this work is that this work uses lower "low frequencies" ( $125 \text{ cm}^{-1}$  and  $226 \text{ cm}^{-1}$  versus  $200 \text{ cm}^{-1}$  and  $240 \text{ cm}^{-1}$ ), a shift which causes a large change in the entropy but has little effect on the heat capacity (93). These thermodynamic functions (Table D-26) should be accurate since the data used is well established (21,24,25,39,62,68,70.)

Scherer, Evans, Muelder and Overend (82) have given the vibrational assignment of 1-3-5-trichlorobenzene. Three of the frequencies used in the assignment ( $a_2$  mode) are the calculated (normal coordinate) values and are of very limited reliability. The bond lengths used were as in meta- and para-dichlorobenzene. The thermodynamic functions (Table D-27) are considered accurate to  $\pm 1.5 \%$ .

For 1-2-3- and 1-2-4-trichlorobenzene Scherer's and Evan's (62) vibrational frequency data was used. The bond

lengths are as in ortho-dichlorobenzene for adjacent C-Cl bonds, other bond lengths being the same as those given above. The estimated limit of error for the thermodynamic functions (Tables D-28, D-29) is  $\pm 1.5$  %.

For 1-2-4-5- tetrachlorobenzene the vapor electron-diffraction data of Strand and Cox (66) gives C-C = 1.395 Å, C-Cl = 1.724 Å, and C-H = 1.08 Å, where the radial angle between the C-Cl bonds is  $62.8^\circ$ , as opposed to the symmetric  $60^\circ$ . Experimental data for the other tetrachlorobenzene isomers was lacking, so C-C and C-H bond distances as in the 1-2-4-5- isomer were assumed. Since the C-Cl bonds in the 1-2-3-4- form are closer than in the 1-2-4-5- isomer, it is expected that the C-Cl distance will be closer to that of hexachlorobenzene. C-Cl = 1.721 Å was chosen. It is also expected that the two outer C-Cl bonds will be at a greater radial angle than  $60^\circ$ , but this has been neglected in the calculation of the moments of inertia, since it has been shown that angular changes such as this have a negligible effect on the  $I_{ABC}$  (see 1-2- dibromobenzene, below). Again, based on the work of Strand and Cox (67) the bond distances chosen for 1-2-3-5- tetrachlorobenzene were 1.722 Å for the 1, 2 and 3 chlorine atoms and 1.725 Å for the 5 position chlorine atom. The thermodynamic data for the tetrachlorobenzenes (Tables D-30 D-31, D-32) are expected to be accurate for the 1-2-4-5- isomer and accurate to within  $\pm 1$  % for the other isomers.

For pentachlorobenzene (Table D-33) a selection of bond lengths intermediate between those of tetrachloro- and hexachlorobenzene (66) was used: C-C = 1.40 Å, C-Cl = 1.72 Å, C-H = 1.08 Å. It was assumed all bond angles were 120° and that the molecule is planar. Scherer's and Evan's liquid state frequencies (62) were employed. For hexachlorobenzene, the structural data used to calculate  $I_{ABC}$  was taken from the paper of Strand and Cox (66). The accuracy of the results of the calculations is estimated as  $\pm 1\%$ .

### The Polybromobenzenes

Shurvell, Dulaurens and Pesteil (56) have assigned the liquid state frequencies of the dibromobenzenes to their normal modes and shown the molecular symmetry group. For 1-2-dibromobenzene Strand (67) gives the structural data as follows: C-C = 1.402 Å, C-Br = 1.883 Å and the radial angle between the C-Br bonds as 63.6°. Using this data the  $I_{ABC}$  was calculated to be  $12.555 \times 10^{-112} \text{ g}^3 \text{ cm}^6$ . To determine the effect of neglecting the distortion of the structure due to the repulsion of the bromine atoms, the  $I_{ABC}$  was also calculated using a radial angle of 60° between the bonds. This gave  $I_{ABC} = 12.562 \times 10^{-112} \text{ g}^3 \text{ cm}^6$ . The difference between these two values of  $I_{ABC}$  is small enough for it to have a negligible effect on the thermodynamic functions. This approximation was also used in other compounds whose thermodynamic functions have been calculated in this thesis, which probably have steric repulsion, but where experimental data is not available.

For 1-4- dibromobenzene however, the data of Shurvell, Dulaurens and Pesteil does not give the two lowest frequencies. A more recent work by Griffiths and Thompson (68) gives these frequencies as  $103 \text{ cm}^{-1}$  ( $b_{3u}$ ) and  $173 \text{ cm}^{-1}$  ( $b_{2u}$ ). Unfortunately these values are for solid solutions of 1-4- dibromobenzene and there may be an appreciable frequency shift between these and the needed vapor state vibrational frequencies. The structural data (gaseous electron-diffraction) of Bastiansen and Hassel (70) and Strand (67) enabled the calculation of the principal moments of inertia.

Since the bond lengths in ortho and para-dibromobenzene are the same (67,70), it was assumed that they would be unchanged in the meta isomer. Thus  $\text{C-C} = 1.402 \text{ \AA}$ , and  $\text{C-Br} = 1.883 \text{ \AA}$  were used to calculate  $I_{ABC}$ . The vibrational frequencies of Shurvell and his coworkers (56) were employed. For ortho- and meta-dibromobenzene the accuracy of the results in Tables D-35, D-36 is estimated to be  $\pm 1 \%$ ; for the para isomer however, due to the use of two solid state frequencies, an accuracy of only  $\pm 1.5 \%$  can be ascribed to the thermodynamic functions (Table D-37).

The vibrational assignment of Scherer, Evans and Muelder (55) was used for 1-3-5- tribromobenzene (see also ref. 64). This assignment agrees well with the fundamental frequencies given by Nonnenmacher and Mecke (61). For the three  $a_1$  frequencies not reported in the above papers the best normal coordinate calculation results (55) were assigned. To

calculate the principal moments of inertia the C-Br distance was assumed to be 1.88 Å (55). This value is intermediate between the bond distances in di- and hexabromobenzene (67,70). The C-C and C-H bond lengths were those found in dibromobenzene (67). Again it is assumed that the atoms are coplanar and the bond angles are  $120^\circ$ . The accuracy of the results (Table D-38) is estimated to be greater than  $\pm 1.5\%$ .

## B. Discussion of Errors

In the calculation of the ideal gas thermodynamic functions for the halogenated benzenes, the results of which are contained in Appendix D, there may arise three types of errors. These errors may cause deviations between the calculated properties and the "accurate" properties experimentally determined by calorimetry and the third law of thermodynamics.

The first type of error is due to the lack of validity of the basic assumptions in the derivation of the formulae in Table I. This has already been discussed in Part C of Chapter II under the heading "anharmonicity". These effects are very small at temperatures below, say,  $500^{\circ}$  K., which is the region in which experimental data is usually available. As has already been mentioned, the contributions of the anharmonic partition function at higher temperatures may be larger (14), such as 2 % at  $1000^{\circ}$  K. The error limits which have been ascribed to the thermodynamic functions in Part A of this chapter do not include the contribution of anharmonicity. These error limits, which are all less than 2 %, estimate the third type of error, which is explained below. Since the anharmonicity effect is generally felt little below  $500^{\circ}$  K., these error limits may be taken as the possible error of the thermodynamic functions in the experimental data range, that is to say, below  $500^{\circ}$  K.

The second type of error may be called the "mathematical error". Again, these errors are small compared to the

third type, and they should contribute very little to the thermodynamic functions. This type includes round-off error generated in the computer calculations of vibrational contributions and in the moments of inertia.

The most important type of error, and the most likely in the results in this thesis, is due to errors in the molecular and structural data needed to calculate the thermodynamic functions. (For a summary of the data required, see Table II.) There are experimental and perhaps theoretical errors found in the estimates of the fundamental vibrational frequencies, the bond lengths and angles of the molecule.

In the compounds for which there is direct experimental structural data for the molecule, the accuracy of the bond lengths is usually within  $\pm 0.01 \text{ \AA}$  (12,66,67), although for some of the results in Tables of Interatomic Distances, edited by Sutton (80),  $\pm 0.05 \text{ \AA}$  is reported. For the compounds whose bond lengths have been predicted in this thesis, by analogy with known bond distances, the errors should not be much greater than  $\pm 0.05 \text{ \AA}$  also. In most cases the data is sufficient to make accurate predictions: for example, the structure of pentachlorobenzene can quite reasonably be predicted if tetrachloro- and hexachlorobenzene structures (67) are known. Errors in the bond lengths should not greatly change the calculated thermodynamic properties.\*

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\* The effect of angular distortions has already been indicated to be negligible, by the calculation reported for 1-2- dibromobenzene, in Part A of this chapter.

An error of 10 % in  $I_{ABC}$  in 1-2- difluorobenzene changes the entropy  $S^\circ$  by  $\pm 0.09$  E.U., or about  $\pm 0.12$  % at  $298.15^\circ$  K. and  $\pm 0.07$  % at  $1000^\circ$  K. Errors larger than 10 % in  $I_{ABC}$  are very unlikely.

The errors in the frequency assignments may be of two kinds. First the errors due to the use of liquid state frequencies instead of those for the vapor state; second errors due to incorrect assignments. The second kind of error is unlikely in most assignments, since the approximate location of the fundamental frequencies is generally known, by analogies with similar compounds and by normal coordinate analysis results. Most authors (such as Scherer, ref. 62) also give the assignment of the combination bands observed in the spectra, in order to verify the fundamental frequency assignments. Regarding the first type of error, Fateley, Matsubara and Witkowski (72) have investigated low frequency vapor-liquid shifts for halogenated toluenes and other aromatic compounds. They conclude that for most compounds the frequency shift from liquid to vapor decreases the frequency ( $\text{cm}^{-1}$ ) for vibrations below  $700 \text{ cm}^{-1}$  and increases the frequency above this. By this author's observation the higher frequency shifts, when they occur at all, are usually less than  $+5 \text{ cm}^{-1}$  above  $700 \text{ cm}^{-1}$ . This would have very little effect on the high frequency contribution to the vibrational partition function. On the other hand, the low frequency shifts may be as large as  $10-20 \text{ cm}^{-1}$  (72), which would cause a noticeable change in the thermodynamic functions, since the low frequencies contribute

more than the higher frequencies (93).

The percentage errors ascribed to the thermodynamic functions in Part A of this chapter are a somewhat subjective estimate, since it is impossible to say without experimental measurements, if an appreciable vapor-liquid frequency shift takes place in any given compound (9,72). Where no numerical estimate has been given in Part A, or the results are referred to as "accurate", the expected possible error is less than  $\pm 0.5$  % of the thermodynamic functions in the region where experimental data is usually available ( $500^{\circ}\text{K}.$ ): this classification is given if vapor state frequencies are available and the structure is based on known data. Where the assignment of frequencies is considered reliable, but where liquid state frequencies only are available, the error is estimated as  $\pm 1$  %. Half of this error ( $\pm 0.5$  %) corresponds to a possible vapor-liquid shift of  $10\text{ cm}^{-1}$  in six frequencies spaced evenly between  $110\text{ cm}^{-1}$  and  $700\text{ cm}^{-1}$ . Usually, in the halogenated benzenes, there are about six to ten frequencies below  $700\text{ cm}^{-1}$ , but is not expected that they all have vapor-liquid shifts (72). If low frequencies are assigned, in this work, by methods of analogy with other compounds or other frequencies of the same mode (see Figures 3,4) or the structure is doubtful,  $\pm 1.5$  % is assigned as the error limit. This corresponds to a possible error of  $20\text{ cm}^{-1}$  in six frequencies below  $700\text{ cm}^{-1}$ . In the case of calculations using liquid state frequencies it is probable that the assigned errors will

take their positive values rather than the negative: since the low liquid frequencies will be too high, the entropy and the heat capacity will tend to be too low.

It is again mentioned that these error limits do not include the effects of anharmonicity, which may contribute 2 % at 1000° K., but are small at lower temperatures. In several cases, the results in Appendices D and E contain more significant figures than is warranted by their accuracy. This has been done to maintain internal consistency in the tables.

## CHAPTER VI

## CONCLUSION AND RECOMMENDATIONS FOR FURTHER STUDY

A. Conclusion

In this thesis the thermodynamic functions of 38 halogenated benzenes have been calculated, by statistical methods. The "halogenated benzene" series in this work does not include the more highly substituted bromo- and iodo-benzenes, but does include some of the unsymmetrical dihalobenzenes. However, it is felt that most of the industrially important and potentially important halobenzenes are included. The error in the calculated thermodynamic functions is, below 500° K., less than  $\pm 2\%$ , and between 500° and 1000° K., a possible maximum additional error of  $\pm 2\%$  may be caused in the thermodynamic properties by the so-called "anharmonicity". Above about 1000° K. the results cannot be used with certainty, since decomposition of the compounds takes place, and this process can not be quantitatively treated. Both these errors tend to take their negative values, that is, the thermodynamic functions tend to be too small rather than too large.

A comparison of the experimental virial coefficient data for two of the halogenated benzenes with that predicted by the Berthelot equation of state was made. Real gas correction equations derived from this equation of state were shown. These corrections may be used for the compounds in this thesis over a limited range of temperature and pressure (273° K. to 1000° K. and 0.25 atm. to 15 atm.). Their accuracy is expected

to be sufficient for engineering calculations occurring in processes involving these compounds.

## B. Recommendations for Further Study

(1) There remain many of the halogenated benzenes for which thermodynamic functions have not been calculated, indeed not all of which have even been synthesized. Whenever spectroscopic and molecular structural data become available for any of these that may be industrially important, the appropriate calculations may be made.

(2) The results of this thesis may provide correlations of the contributions to the thermodynamic functions of the distinguishing elements of the compounds. Thus the effect of the number and type of halogen atoms and their respective positions on the ring (whether ortho, meta, 1-3-5-, 1-2-3- &c) could be investigated. A short example of the possibilities for this type of study is given below.

In this work the thermodynamic functions for 1-2-3-trifluorobenzene have not been calculated, because data was not available. However the entropy of 1-2-3- trifluorobenzene can be predicted by analogy with other trihalobenzenes. The nomograph in Figure 6 predicts the entropy of this compound by a method similar to that used for predicting frequencies in Figure 4. It is found that the entropy at 298.15° K. of the trichlorobenzenes increases through the isomeric series 1-3-5-, 1-2-3-, 1-2-4-. The vertical lines in the nomograph are arranged so that the entropy of the trichlorobenzenes will increase linearly. The known values of  $S^{\circ}$  of 1-3-5- and 1-2-4- trifluorobenzene are plotted on their respective (dashed)

lines. The straight line joining these points crosses the vertical 1-2-3- isomer line, indicating the desired entropy, 81.0 E.U. This correlation assumes that the entropy of the isomers of trichlorobenzene and trifluorobenzene increases in a similar way through the series 1-3-5-, 1-2-3-, 1-2-4-. This type of nomograph might be drawn for entropies at other temperatures, and for other thermodynamic functions.

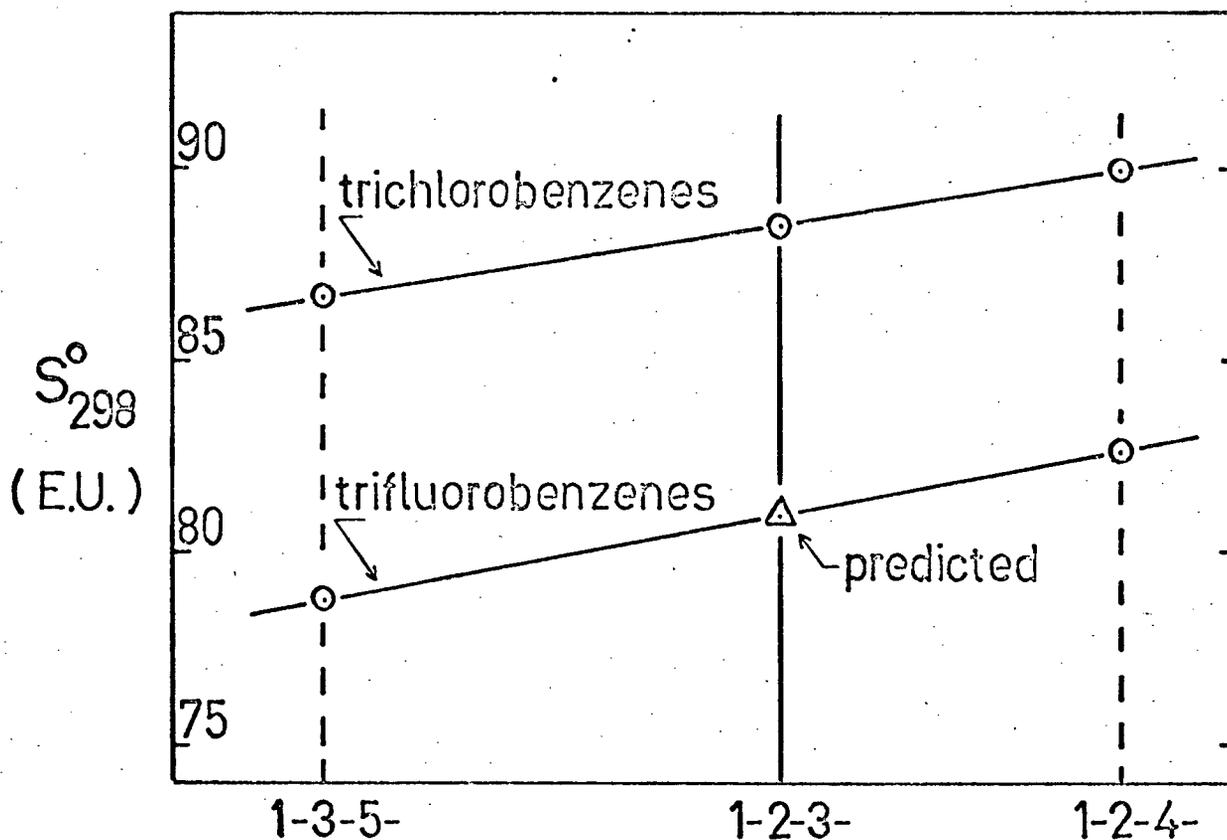


Figure 6: Prediction of  $S_{298}^{\circ}$  for 123 Trifluorobenzene

Other regularities in isomeric series of the halogenated benzenes may appear, and may help in production of a generalized group contribution method for the halobenzenes, more accurate than existing methods (83).

(3) A real gas correction method should be developed, to be useful at pressures higher than the upper limit of pressure (15 atm.) in this work. This would require experimental P-V-T measurements over the range of temperature and pressure chosen, and choice (or development) of a suitable equation of state for the halogenated benzenes. The ideal gas thermodynamic functions computed in this thesis would then be useful in high pressure industrial processes.

(4) Although the calculation of high temperature thermodynamic properties is of great importance in some industrial processes, it is not at present thought to be important for the halogenated benzenes. The halobenzenes are mainly used for synthesis of more complex aromatics. At temperatures where the halogenated benzenes become thermally unstable, they lose their aromatic character, which is necessary in the synthesis of higher aromatic compounds. It is suggested that more work be done to determine the temperatures at which the compounds start to decompose, at various pressures. It is not deemed necessary to analyse the high temperature decomposition equilibrium with a view to calculating the thermodynamic properties for this equilibrium, at least while there are no processes in which these temperatures are likely.

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APPENDIX A

Nomenclature

- $\alpha_i$  = directional cosine between axis of rotation and the  $i^{\text{th}}$  principal axis, where  $i = A, B, C$
- $B$  = second virial coefficient (cc/gmole)
- $C$  = third virial coefficient (cc/gmole-atm.)
- $C_p^{\circ}$  = ideal gas heat capacity at constant pressure (cal/gmole  $^{\circ}\text{K}.$ )
- $c$  = speed of light in vacuum ( $2.99793 \times 10^{10}$  cm/sec)
- $-(F^{\circ} - H^{\circ})/T$  = ideal gas free energy function (cal/gmole  $^{\circ}\text{K}.$ )
- $H_f^{\circ}$  = heat of formation (cal/gmole)
- $H_T^{\circ}$  = standard heat of reaction (cal/gmole)
- $(H^{\circ} - H^{\circ}_0)/T$  = ideal gas enthalpy function (cal/gmole  $^{\circ}\text{K}.$ )
- $h$  = Planck constant ( $6.6256 \times 10^{-27}$  erg. sec)
- $I$  = moment of inertia of rotating top in a molecule with internal rotation ( $\text{g cm}^2$  or  $\text{amu } \text{Å}^2$ )
- $I_r$  = reduced moment of inertia ( $\text{g cm}^2$  or  $\text{amu } \text{Å}^2$ )
- $I_{ij}$  = element of "moment of inertia" determinant ( $\text{amu } \text{Å}^2$ ), where  $i, j = x, y, z$
- $I_A$  }  
 $I_B$  } = principal moment of inertia ( $\text{g cm}^2$  or  $\text{amu } \text{Å}^2$ )  
 $I_C$  }
- $I_{ABC}$  = product of principal moments of inertia ( $\text{g}^3 \text{cm}^6$  or  $\text{amu}^3 \text{Å}^6$ )
- $k$  = Boltzmann constant ( $1.38054 \times 10^{10}$  erg/ $^{\circ}\text{K}.$ )

- $\lambda$  = eigenvalue of "moment of inertia" determinant  
 $M$  = molecular weight (g/gmole)  
 $m_i$  = atomic mass of the  $i^{\text{th}}$  atom in a molecule (amu)  
 $n'$  = number of equivalent positions in one revolution of a group of atoms with internal rotation (rotating top)  
 $n$  = number of atoms in molecule  
 $P$  = pressure (atm.)  
 $P_c$  = critical pressure (atm.)  
 $Q_t$  = translational partition function  
 $Q_r$  = rotational partition function  
 $Q_v$  = vibrational partition function  
 $Q_{\text{int}}$  = "internal energy" partition function  
 $Q_f$  = free internal rotation partition function  
 $R$  = gas constant (82.06 cc atm./gmole  $^{\circ}\text{K}.$ )  
 $S^{\circ}$  = ideal gas entropy (E.U.)  
 $\sigma$  = molecular symmetry number  
 $T$  = temperature ( $^{\circ}\text{K}.$ )  
 $T_c$  = critical temperature ( $^{\circ}\text{K}.$ )  
 $\nu$  = fundamental vibrational frequency ( $\text{cm}^{-1}$ )  
 $\nu^*$  = adjustable "anharmonicity parameter, Equations 11 ( $\text{cm}^{-1}$ )

$V$  = Pitzer's (76) "potential barrier to internal rotation"  
(cal/gmole)

$V_0$  = Pitzer's (76) "maximum height of potential barrier"  
(cal/gmole)

$V$  = volume (cc)

$V_c$  = critical volume (cc)

$x_i$  }  
 $y_i$  } = coordinates of the  $i^{\text{th}}$  atom of a molecule ( $\text{\AA}$ )  
 $z_i$  }

$Z$  = adjustable "anharmonicity" parameter, Equations 11  
(cal/gmole  $^{\circ}\text{K.}$ )

## APPENDIX B

Description of FORTRAN IV Programs for IBM 7040  
Computer used in this Thesis

## 1. Program for Calculation of Ideal Gas Thermodynamic Functions

Program No. 1 (THERMO) in Appendix C evaluates the thermodynamic functions using the equations in Table I, Chapter II. It also has built into the anharmonicity correction equations of McCullough, Scott et al. (16) (Equations 10). The values of the fundamental constants are taken from the compilation of Cohen and Dumond (10). A sample of the format of the input data can be found immediately following the program itself in Appendix C. Examples of the output of the program may be found in Appendix D. The units of the thermodynamic functions that the program calculates are cal., ° K. and g.mole.

The nomenclature in this program follows that of Appendix A as much as possible, but significant differences will be mentioned in the instruction for the use of the program, on the following page (Table B-1).

It is possible to get either paper-printed output or card-punched output from this program, by defining MOUT as the number of the appropriate output unit (for the UBC IBM 7040, 6 gives paper output and 7 gives punched card output). MOUT is defined directly in the Program.

The first data card must always be a card which specifies the number of sets of data that the program is required to process. If the last card in a data set is left blank the anharmonicity correction equations will be omitted from the calculation.

TABLE B-1

## Input Data Cards for THERMO

card	variable	definition and explanation	format	column
0	NDATA	number of data sets following	I5	1-5
1	NF	number of frequencies	I5	1-5
	NT	number of temperatures	I5	6-10
	SPOT	name of compound	6A6	12-47
2	IA	$I_A$ ( $\text{amu } \text{Å}^2$ )	F10.3	1-10
	IB	$I_B$ ( $\text{amu } \text{Å}^2$ )	F10.3	11-20
	IC	$I_C$ ( $\text{amu } \text{Å}^2$ )	F10.3	21-30
	M	molecular weight (g/gmole)	F10.3	31-40
	SIG	symmetry number $\sigma$	F10.3	41-50
3	V(I)	reads NF frequencies ( $\text{cm}^{-1}$ ) 14 on each card	14 F5.0	
.				
.				
.	T(I)	reads NT temperatures ( $^{\circ}\text{K.}$ ) at which the thermodynamic functions are required, 7 on each card	7 F10.5	
.				
.				
last card	Z	anharmonicity constant Z ( $\text{cal/gmole } ^{\circ}\text{K.}$ )	F10.3	1-10
	VV	anharmonicity constant $\gamma^*$ ( $\text{cm}^{-1}$ )	F10.3	11-20

2. Program for Calculation of Real Gas Thermodynamic Functions

This program is basically the same as Program No.1. The ideal gas thermodynamic functions are calculated in the main program, but before they are printed a call is made on subroutine REALGA. This subroutine makes the real gas corrections to the thermodynamic functions, using the Berthelot equation of state (as shown in Chapter III).

These corrections require the pressure (PR) and the critical temperature and pressure (TC,PC). The input data cards for this program are identical to those of Program No.1, except that card 2 contains the critical temperature ( $^{\circ}$  K.) in columns 51-60 and the critical pressure (atm.) in columns 61-70. Card 3 contains the pressure (atm.) at which the properties are desired, in columns 1-10. The other cards follow as described in Table B-1. Samples of the output of this program may be found in Appendix E.

As above, the first card after the \$ENTRY card must always specify the number of data sets (NDATA) that the program is required to process.

### 3. Program for Calculation of Principal Moments of Inertia

This program was originally written by Cross (73), but has been changed in this thesis, and uses a more efficient method of solving Equation 9 in Chapter II. Where Cross used a Newton-Raphson iterative technique, this program used library subroutine MLEW (98) for the solution. Using the coordinates  $x_i$ ,  $y_i$  and  $z_i$  with respect to an arbitrary origin and the mass  $m_i$  of atom "i", the program calculates the elements of the matrix in Equation 5, by the formulae in Equation 7 (Part B, Chapter II). The value of this determinant (ABClI) is computed and printed in the output. The center of gravity corrections (the coordinates of the center of gravity) are also calculated and printed, with the molecular weight, obtained by summing the

atomic masses  $m_i$ .

When the elements of the determinant  $I_{ABC}$  have been found, the eigenvalues (Principal moments of inertia) are computed by subroutine MLEW. The principal moments of inertia ( $X_1, X_2, X_3$ ) are printed in two systems of units,  $\text{amu } \text{Å}^2$  and in  $\text{g cm}^2$ , and the respective products  $I_{ABC}$  ( $ABC2I, ABC3I$ ) in  $\text{amu}^3 \text{Å}^6$  and  $\text{g}^3 \text{cm}^6$ . These values of  $I_{ABC}$  should agree with the value found at the beginning of the program by multiplying out the terms of the determinant.

The instruction for use of Program 3 is found in Table B-2. This program will continue to solve sets of data until it finds a blank card after the last set of data cards.

A copy of Program 3 may be found in Appendix C, followed by a sample of the output that this program generates. This program (MOMENT) may be adapted to calculate the reduced moment of inertia for molecules that have internal rotations. This was done by Cross in the original program (73), and a modified program has been written by this author (106).

TABLE B-2

Input Data Cards for MOMENT

card	variable	definition and explanation	format	column
1	N Q1	number of atoms in molecule name of the molecule	I5 6A6	1-5 7-43
2	A(I,J)	reads $m_1$ (amu), $x_1$ , $y_1$ and $z_1$ (Å)	4F10.5	
3	A(I,J)	reads $m_2$ (amu) $x_2$ , $y_2$ and $z_2$ (Å)	4F10.5	
etc.				

## APPENDIX C

FORTRAN IV Computer Programs for IBM 7040 Computer, used in this Thesis

PROGRAM 1

A Program for Ideal Gas Thermodynamic Functions of Polyatomic Molecules

ISN SOURCE STATEMENT

```

0 # $IBFTC THERMO
# C CALCULATION OF IDEAL GAS THERMODYNAMIC FUNCTIONS
# C FREE ENERGY CALCULATED BY DIFFERENCE
1 # 40 FORMAT (7F10.3)
2 # 41 FORMAT(2I5,6A6)
3 # 42 FORMAT (14F5.0)
4 # 43 FORMAT ( 8X,5F12.2)
5 # 44 FORMAT(1H1/1H-,7X,36HIDEAL GAS THERMODYNAMIC FUNCTIONS OF,
# 1 6A6 /1H-,14X,4HTEMP,9X,2HCP,8X,7H(H-H)/T,5X,
# 2 7H(H-F)/T,8X,1HS/)
6 # 45 FORMAT (/1H-,9X,23HFREQUENCIES USED (1/CM) /)
7 # 46 FORMAT (1H-,9X,21HPRINCIPAL MOMENTS ...,3F10.3/1H0,9X,
# 1 21HSYMMETRY NUMBER .....,F7.0/1H0,9X,
# 2 21HMOLECULAR WEIGHT .....,F10.3/1H0,9X,
# 3 21HREFERENCE(S) ....., / 1H0,9X,
# 4 28HUNITS ARE IN CAL/DEG KELVIN ,
# 5 30HMOLE - PRESSURE ONE ATMOSPHERE, ///1H-,9X,
# 6 21HTABLE NUMBER ..... //)
10 # 47 FORMAT (8X,5F12.0)
# C IF MOUT=6, GET PRINT OUT, IF MOUT=7, GET CARD OUTPUT
11 # MOUT = 6
12 # REAL IA, IB, IC, K, M
13 # DIMENSION V(60),T(40)
14 # DATA C,H,R,K/2.99793E10,6.6256E-27,1.98719,1.38054E-16/
15 # READ (5,41) NDATA
17 # DO 27 IJ=1,NDATA
20 # READ (5,41) NF,NT,SPOT,THE,DOG,WAS,BLACK,WHITE
23 # READ (5,40) IA,IB,IC,M,SIG
24 # READ (5,42) (V(I),I=1,NF)
31 # READ (5,40)(T(I),I=1,NT)
36 # READ (5,40) Z,VV
37 # WRITE (MOUT,44) SPOT,THE,DOG,WAS,BLACK,WHITE
40 # DO 26 JJ=1,NT
41 # P=T(JJ)
42 # D = IA*IB*IC/218.49354167
43 # CV=0.
44 # HV=0.
45 # SV=0.
46 # DO 25 J=1,NF
47 # U = .299793 * 6.6256 * V(J) / (1.38054 * P)
50 # CV=CV+ U**2*EXP(U)/((EXP(U)-1.)**2)
51 # HV=HV+U/(EXP(U)-1.)
52 # 25 SV=SV+U/(EXP(U)-1.)-ALOG(1.-EXP(-U))
54 # CP=R*(4.+CV)
55 # HO=R*(4.+HV)
56 # S=R*(ALOG(P**4*M**1.5*SQRT(D)/SIG)+SV)-2.347
57 # F=S-HO
60 # CPO=CP/R
61 # HOD=HO/R
62 # FO=F/R
63 # SO=S/R
64 # IF (Z.EQ.0.0.AND.VV.EQ.0.0) GO TO 26
# C 'ANHARMONICITY CONTRIBUTIONS' TO THE THERMODYNAMIC
# C FUNCTIONS, TAKEN FROM R-25 ... MCCULLOUGH ET AL.
# C USING FOLLOWING SEMI-EMPIRICAL EQUATIONS. NOTE

```

ISN SOURCE STATEMENT

```
      * C      THE NEW VALUES OF THE FUNCTIONS INCLUDE THE
      * C      ANHARMONICITY CONTRIBUTION.
67 *      UV= H*C*VV/(K*P)
70 *      CA=(UV**2*EXP(UV)/((EXP(UV)-1.)**2))*R
71 *      HA=(UV/(EXP(UV)-1.) )*R
72 *      CP= CP+Z*(CA/R)*((3.*(CA/R)/UV)-(1.+2./UV)*HA/R)
73 *      S= S+(Z/UV)*(CA/R)*(HA/R)
74 *      HO= HO+ (Z/(2.*UV))*(HA/R)*(2.*(CA/R)-(HA/R))
75 *      26  WRITE (MOUT,43) P,CP,HO,F,S
77 *      WRITE (MOUT,45)
100 *      WRITE (MOUT,47) (V(I),I=1,NF)
105 *      27  WRITE (MOUT,46) IA,IB,IC,SIG,M
107 *      STOP
110 *      END
```

NO MESSAGES FOR ABOVE ASSEMBLY

23HRS 34MIN 19.4SEC

## EXAMPLE OF DATA FOR PROGRAM 1

1  
 30 21 1-3- CHLOROFLUORO BENZENE  
 147.575 429.661 577.312 130.550 1.000  
 245. 408. 517. 691. 892.1007.1061.1081.1128.1157.1228.1264.1292.1435.  
 1478.1596.3030.3082.3189. 191. 245. 382. 443. 489. 673. 774. 862. 990.  
 1600.3082.  
 273.150 298.150 300.000 350.000 400.000 450.000 500.000  
 550.000 600.000 650.000 700.000 750.000 800.000 850.000  
 900.000 950.000 1000.000 1100.000 1200.000 1300.000 1400.000  
 0.000 0.000

TIME 23HRS 33MIN 52.3SEC

\$\$

00 AJ092

PROGRAM 2

A Program for Ideal Gas Thermodynamic Functions, Corrected to the Real Gas  
State, using the Berthelot Equation

JOB NUMBER 16086 CATEGORY F USER'S NAME- J BUTLER

JOB START 22HRS 32MIN 36.0SEC V9M011

\$JOB 16086 J BUTLER THDY. PROPS. REAL

\$PAGE 20

\$FORTRAN

\$IBFTC REALO

C CALCULATION OF IDEAL GAS FUNCTIONS, CORRECTED TO THE REAL GAS  
 C FREE ENERGY CALCULATED BY DIFFERENCE

```

1   40  FORMAT (7F10.3)
2   41  FORMAT(2I5,6A6)
3   42  FORMAT (14F5.0)
4   43  FORMAT ( 8X,5F12.2)
5   44  FORMAT(1H1/1H-,7X, 35HREAL GAS THERMODYNAMIC FUNCTIONS OF,
      1  6A6 /1H-,14X,4HTEMP,9X,2HCP,8X,7H(H-H)/T,5X,
      2  7H(H-F)/T,8X,1HS/)
6   45  FORMAT (/1H-,9X,23HFREQUENCIES USED (1/CM) /)
7   46  FORMAT (1H-,9X,21HPRINCIPAL MOMENTS ...,3F10.3/1H0,9X,
      1  21HSYMMETRY NUMBER .....,F7.0/1H0,9X,
      2  21HMOLECULAR WEIGHT .....,F10.3/1H0,9X,
      3  21HPRESSURE (ATM) ....., F9.2/1H0,9X,
      4  21HCRITICAL TEMPERATURE , F9.2/1H0,9X,
      5  21HCRITICAL PRESSURE ...., F9.2/1H-//9X,
      6  21HTABLE NUMBER ..... //)
10  47  FORMAT (8X,5F12.0)
      C  IF MOUT=6, GET PRINT OUT, IF MOUT=7, GET CARD OUTPUT
11      MOUT = 6
12      REAL IA, IB, IC, K, M
13      COMMON R,PC,TC,PR
14      DIMENSION V(60),T(40)
15      DATA C,H,R,K/2.99793E10,6.6256E-27,1.98719,1.38054E-16/
16      READ (5,41) NDATA
17      DO 27 IJ=1,NDATA
20      READ (5,41) NF,NT,SPOT,THE,DOG,WAS,BLACK,WHITE
21      READ (5,40) IA,IB,IC,M,SIG,TC,PC,PR
22      READ (5,42) (V(I),I=1,NF)
23      READ (5,40)(T(I),I=1,NT)
24      READ (5,40) Z,VV
25      WRITE (MOUT,44) SPOT,THE,DOG,WAS,BLACK,WHITE
26      DO 26 JJ=1,NT
27      P=T(JJ)
30      D = IA*IB*IC/218.49354167
31      CV=0.
32      HV=0.
33      SV=0.
34      DO 25 J=1,NF
35      U = .299793 * 6.6256 * V(J) / (1.38054 * P)
36      CV=CV+ U**2*EXP(U)/((EXP(U)-1.)**2)
37      HV=HV+U/(EXP(U)-1.)
40      25 SV=SV+U/(EXP(U)-1.)-ALOG(1.-EXP(-U))
41      CP=R*(4.+CV)
42      HO=R*(4.+HV)
43      S=R*(ALOG(P**4*M**1.5*SQRT(D)/SIG)+SV)-2.347
44      F=S-HO

```

```

45      CPO=CP/R
46      HCO=HO/R
47      FO=F/R
50      SO=S/R
51      IF (Z.EQ.0.0.AND.VV.EQ.0.0) GO TO 26
C      'ANHARMONICITY CONTRIBUTIONS' TO THE THERMODYNAMIC
C      FUNCTIONS, TAKEN FROM R-25 ... MCCULLOUGH ET AL.
C      USING FOLLOWING SEMI-EMPIRICAL EQUATIONS. NOTE
C      THE NEW VALUES OF THE FUNCTIONS INCLUDE THE
C      ANHARMONICITY CONTRIBUTION.
52      UV= H*C*VV/(K*P)
53      CA=(UV**2*EXP(UV)/((EXP(UV)-1.)**2))*R
54      HA=(UV/(EXP(UV)-1.) )*R
55      CP= CP+Z*(CA/R)*((3.*(CA/R)/UV)-(1.+2./UV)*HA/R)
56      S= S+(Z/UV)*(CA/R)*(HA/R)
57      HO= HO+ (Z/(2.*UV))*(HA/R)*(2.*(CA/R)-(HA/R))
60      CALL REALGA (P,CP,HO,F,S)
61      26  WRITE (MOUT,43) P,CP,HO,F,S
62      WRITE (MOUT,45)
63      WRITE (MOUT,47) (V(I),I=1,NF)
64      27  WRITE (MOUT,46) IA,IB,IC,SIG,M,PR,TC,PC
65      STOP
66      END

```

```

67      SUBROUTINE REALGA (T,CP,HO,F,S)
C      REAL GAS CORRECTIONS TO IDEAL GAS THERMODYNAMIC
C      FUNCTIONS, USING BERTHELOT EQUATION OF STATE,
C      APPLICABLE FOR MODERATE PRESSURES ONLY TO THE
C      HALOGENATED BENZENES.
70      COMMON R,PC,TC,PR
71      HO=HO+9.*R*TC*PR*(1.-18.*TC**2/T**2)/(128.*PC*T)
72      CP=CP+91.*R*TC**3*PR/(32.*PC*T**3)
73      S=S-27.*R*TC**3*PR/(32.*PC*T**3)-R*ALOG(PR)
74      F = S-HQ
75      RETURN
76      END

```

```

$ENTRY

```

PROGRAM 3

A Program for Calculation of Principal Moments of Inertia of Molecules

JTLER MOM  
ISN

## FORTRAN SOURCE LIST

## SOURCE STATEMENT

```

0 # $IBFTC MOMENT
# C MOMENTS OF INERTIA CALCULATIONS FOR RIGID MOLECULES
# C WEIGHTS READ AS G/GMOLE INTERATOMIC DISTANCES READ AS ANGSTROMS
# C N = NO. OF ATOMS IN MOLECULE
1 # 10 FORMAT (I5,6A6)
2 # 15 FORMAT (40H AT.WT. X-COORD Y-COORD Z-COORD )
3 # 20 FORMAT (4F10.5)
4 # 25 FORMAT (/ 24H ELEMENTS OF DETERMINANT/ )
5 # 35 FORMAT ( 3(E20.8,5X, E20.8,5X,E20.8/ ))
6 # 45 FORMAT(45H PRODUCT OF PRINCIPAL MOMENTS OF INERTIA = ,E18.6/)
7 # 56 FORMAT (3F10.5,32X,F10.3)
10 # 65 FORMAT(/36H PRINCIPAL MOMENTS OF INERTIA (MLEW) /)
11 # 75 FORMAT(8H IA = ,F10.5,27H X(10**(-39) GRAM-CM SQUARED/6X,2H= ,F11
# 1.4,21H AMU-ANGSTROM SQUARED)
12 # 81 FORMAT (1H1/1H-/ 31H MOMENT OF INERTIA CALCULATIONS,6A6/ )
13 # 83 FORMAT(30H CENTER OF GRAVITY CORRECTIONS,30X,16HMOLECULAR WEIGHT/)
14 # 85 FORMAT(8H0 IB = ,F10.5,27H X(10**(-39) GRAM-CM SQUARED/6X,2H= ,F11
# 1.4,21H AMU-ANGSTROM SQUARED)
15 # 86 FORMAT(45HOPRODUCT OF PRINCIPAL MOMENTS OF INERTIA /F18.4, 28H
# 1 X(10**(-117) GRAM-CM SQUARED ,E18.6,21H AMU-ANGSTROM SQUA
# 1RED)
16 # 95 FORMAT(8H0 IC = ,F10.5,27H X(10**(-39) GRAM-CM SQUARED/6X,2H= ,F11
# 1.4,21H AMU-ANGSTROM SQUARED)
17 # 205 FORMAT (1H1)
20 # DIMENSION A(40,4),ABCI(10),B(3,3),VEC(3,3),EXTRA(3,5)
21 # EQUIVALENCE(B(1,1),G),(B(1,2),R),(B(1,3),S),(B(2,2),H),
# 1 (B(2,3),T),(B(3,3),C), (EXTRA(1,1),X1), (EXTRA(2,1),X2) ,
# 2 (EXTRA(3,1),X3)
22 # 1 READ (5,10) N,Q1,Q2,Q3,Q4,Q5,Q6
24 # IF (N .NE. 0) GO TO 3
27 # WRITE (6,205)
30 # STOP
31 # 3 WRITE (6,81) Q1,Q2,Q3,Q4,Q5,Q6
32 # READ (5,20) ((A(I,J),J=1,4),I=1,N)
# C CARD READS AT. WT., X-COORD, Y-COORD, Z-COORD
43 # WRITE (6,15)
44 # WRITE (6,20) ((A(I,J),J=1,4),I=1,N)
45 # YZSQM=0.0
46 # XZSQM=0.0
47 # XYSQM=0.0
48 # XM=0.0
49 # YM=0.0
50 # ZM=0.0
51 # XYM=0.0
52 # XZM=0.0
53 # YZM=0.0
54 # TMASS = 0.0
55 # DO 2 I=1,N
56 # YZSQM=YZSQM+A(I,1)*(A(I,3)**2+A(I,4)**2)
57 # XZSQM=XZSQM+A(I,1)*(A(I,2)**2+A(I,4)**2)
58 # XYSQM=XYSQM+A(I,1)*(A(I,2)**2+A(I,3)**2)
59 # XM=XM+A(I,1)*A(I,2)
60 # YM=YM+A(I,1)*A(I,3)
61 # ZM=ZM+A(I,1)* A(I,4)
62 # XYM= XYM+A(I,1)*A(I,2)*A(I,3)

```

JTLER MOM

FORTRAN SOURCE LIST MOMENT

ISN

SOURCE STATEMENT

```

77 #      XZM= XZM+A(I,1)*A(I,2)*A(I,4)
100 #     YZM= YZM+A(I,1)*A(I,3)*A(I,4)
101 #     TMASS=TMASS + A(I,1)
102 #     2 CONTINUE
104 #     G=YZSQM-YM**2/TMASS-ZM**2/TMASS
105 #     H=XZSQM-XM**2/TMASS-ZM**2/TMASS
106 #     C=XYSQM-XM**2/TMASS-YM**2/TMASS
107 #     D=XYM-XM*YM/TMASS
110 #     E=XZM-XM*ZM/TMASS
111 #     F=YZM-YM*ZM/TMASS
112 #     R=-D
113 #     S=-E
114 #     T=-F
115 #     ABC1I=G*H*C-G*F*F-C*D*D-2.*D*E*F-H*E*E
116 #     WRITE (6,25)
117 #     WRITE (6,35) G,R,S,R,H,T,S,T,C
120 #     WRITE (6,45) ABC1I
121 #     WRITE (6,83)
122 #     XO=XM/TMASS
123 #     YO=YM/TMASS
124 #     ZO=ZM/TMASS
125 #     WRITE (6,56) XO,YO,ZO,TMASS
126 #     4 CALL MLEW (3,B,VEC,EXTRA)
127 #     AI=X1/6.023
130 #     BI=X2/6.023
131 #     CI=X3/6.023
132 #     WRITE (6,65)
133 #     WRITE (6,75)          AI          ,X1
134 #     WRITE (6,85)        BI          ,X2
135 #     WRITE (6,95)        CI          ,X3
136 #     ABC2I=AI*BI*CI
137 #     ABC3I=X1*X2*X3
140 #     WRITE (6,86) ABC2I ,ABC3I
141 #     GO TO 1
142 #     END

```

NO MESSAGES FOR ABOVE ASSEMBLY

S 32MIN 49.1SEC

MOMENT OF INERTIA CALCULATIONS 1-2- CHLOROFLUORO BENZENE

AT.WT.	X-COORD	Y-COORD	Z-COORD
12.01100	-0.00000	-0.00000	-0.00000
12.01100	-1.20980	0.69850	-0.00000
12.01100	-1.20980	2.09550	-0.00000
12.01100	-0.00000	2.79400	-0.00000
12.01100	1.20980	2.09550	-0.00000
12.01100	1.20980	0.69850	-0.00000
1.00800	-0.00000	-1.08000	-0.00000
1.00800	-2.14510	0.15850	-0.00000
1.00800	-2.14510	2.63550	-0.00000
35.45300	-0.00000	4.50400	-0.00000
18.99800	2.36160	2.76050	-0.00000
1.00800	2.14510	0.15850	-0.00000

ELEMENTS OF DETERMINANT

0.32461208E 03	-0.15216606E 02	-0.00000000E-38
-0.15216606E 02	0.17621898E 03	-0.00000000E-38
-0.00000000E-38	-0.00000000E-38	0.50083106E 03

PRODUCT OF PRINCIPAL MOMENTS OF INERTIA = 0.285330E 08

CENTER OF GRAVITY CORRECTIONS

0.32711 2.41050 -0.00000

MOLECULAR WEIGHT

130.549

PRINCIPAL MOMENTS OF INERTIA (MLEW)

IA = 83.15309 X(10\*\*-39) GRAM-CM SQUARED  
 = 500.8311 AMU-ANGSTROM SQUARED

IB = 54.15181 X(10\*\*-39) GRAM-CM SQUARED  
 = 326.1564 AMU-ANGSTROM SQUARED

IC = 29.00128 X(10\*\*-39) GRAM-CM SQUARED  
 = 174.6747 AMU-ANGSTROM SQUARED

PRODUCT OF PRINCIPAL MOMENTS OF INERTIA  
 130589.5632 X(10\*\*-117) GRAM-CM SQUARED

0.285330E 08 AMU-ANGSTROM SQUARED

## APPENDIX D

Ideal Gas Thermodynamic Functions for the Halogenated Benzenes

## LIST OF COMPOUNDS IN APPENDIX D

D-1	FLUOROBENZENE
D-2	CHLOROBENZENE
D-3	BROMOBENZENE
D-4	IODOBENZENE
D-5	1-2- DIFLUOROBENZENE
D-6	1-3- DIFLUOROBENZENE
D-7	1-4- DIFLUOROBENZENE
D-8	1-3-5- TRIFLUOROBENZENE
D-9	1-2-4- TRIFLUOROBENZENE
D-10	1-2-3-5- TETRAFLUOROBENZENE
D-11	1-2-4-5- TETRAFLUOROBENZENE
D-12	1-2-3-4- TETRAFLUOROBENZENE
D-13	PENTAFLUOROBENZENE
D-14	HEXAFLUOROBENZENE
D-15	CHLOROPENTAFLUOROBENZENE
D-16	BROMOPENTAFLUOROBENZENE
D-17	IODOPENTAFLUOROBENZENE
D-18	1-2- CHLOROFLUOROBENZENE
D-19	1-3- CHLOROFLUOROBENZENE
D-20	1-4- CHLOROFLUOROBENZENE

QD-21	1-2-	BROMOFLUOROBENZENE
D-22	1-2-	FLUOROIODOBENZENE
D-23	1-2-	BROMOCHLOROBENZENE
D-24	1-2-	DICHLOROBENZENE
D-25	1-3-	DICHLOROBENZENE
D-26	1-4-	DICHLOROBENZENE
D-27	1-3-5-	TRICHLOROBENZENE
D-28	1-2-4-	TRICHLOROBENZENE
D-29	1-2-3-	TRICHLOROBENZENE
D-30	1-2-3-5-	TETRACHLOROBENZENE
D-31	1-2-4-5-	TETRACHLOROBENZENE
D-32	1-2-3-4-	TETRACHLOROBENZENE
D-33		PENTACHLOROBENZENE
D-34		HEXACHLOROBENZENE
D-35	1-2-	DIBROMOBENZENE
D-36	1-3-	DIBROMOBENZENE
D-37	1-4-	DIBROMOBENZENE
D-38	1-3-5-	TRIBROMOBENZENE

## IDEAL GAS THERMODYNAMIC FUNCTIONS OF FLUOROBENZENE

TEMP	CP	(H-H)/T	(H-F)/T	S
273.15	20.62	12.18	58.25	70.43
298.15	22.54	12.97	59.35	72.32
300.00	22.69	13.03	59.43	72.46
350.00	26.44	14.68	61.56	76.24
400.00	29.94	16.37	63.63	80.00
450.00	33.11	18.06	65.65	83.72
500.00	35.96	19.71	67.64	87.36
550.00	38.49	21.30	69.59	90.90
600.00	40.75	22.83	71.51	94.35
650.00	42.77	24.29	73.39	97.69
700.00	44.58	25.67	75.24	100.93
750.00	46.21	26.99	77.05	104.06
800.00	47.68	28.24	78.83	107.09
850.00	49.02	29.42	80.57	110.02
900.00	50.25	30.54	82.28	112.86
950.00	51.37	31.61	83.96	115.61
1000.00	52.39	32.62	85.60	118.27
1100.00	54.21	34.51	88.80	123.35
1200.00	55.75	36.21	91.86	128.14
1300.00	57.07	37.77	94.82	132.65
1400.00	58.21	39.19	97.66	136.92

## FREQUENCIES USED (1/CM)

519.	808.	1008.	1022.	1157.
1220.	1499.	1596.	3044.	3067.
3101.	405.	614.	1066.	1157.
1236.	1323.	1460.	1603.	3058.
3091.	405.	826.	970.	242.
500.	685.	754.	894.	997.

PRINCIPAL MOMENTS ... 89.230 196.642 285.949

SYMMETRY NUMBER ..... 2.

MOLECULAR WEIGHT ..... 96.100

REFERENCE(S) ..... 11, 12 35

UNITS ARE IN CAL/DEG KELVIN MOLE - PRESSURE ONE ATMOSPHERE

ANHARMONICITY .....  $Z = 0.154$   $\gamma^* = 550.$

TABLE NUMBER ..... D-1

## IDEAL GAS THERMODYNAMIC FUNCTIONS OF CHLOROBENZENE

TEMP	CP	(H-H)/T	(H-F)/T	S
273.15	21.54	12.90	60.17	73.07
298.15	23.42	13.70	61.33	75.04
300.00	23.56	13.76	61.42	75.18
350.00	27.22	15.43	63.66	79.09
400.00	30.62	17.12	65.83	82.95
450.00	33.71	18.79	67.95	86.74
500.00	36.48	20.42	70.01	90.44
550.00	38.95	22.00	72.03	94.03
600.00	41.14	23.50	74.01	97.52
650.00	43.11	24.94	75.95	100.89
700.00	44.87	26.30	77.85	104.15
750.00	46.45	27.59	79.71	107.30
800.00	47.89	28.82	81.53	110.34
850.00	49.20	29.98	83.31	113.29
900.00	50.39	31.08	85.06	116.13
950.00	51.48	32.12	86.76	118.89
1000.00	52.47	33.12	88.44	121.55
1100.00	54.24	34.96	91.68	126.64
1200.00	55.73	36.63	94.80	131.42
1300.00	57.01	38.15	97.79	135.94
1400.00	58.11	39.54	100.67	140.20

## FREQUENCIES USED (1/CM)

3069.	3050.	3029.	3071.	3052.
1582.	1581.	1478.	1444.	1324.
1267.	1174.	1157.	1068.	1025.
1003.	986.	965.	902.	831.
740.	682.	616.	400.	1084.
701.	417.	297.	467.	196.

PRINCIPAL MOMENTS ... 89.190 320.500 409.800

SYMMETRY NUMBER ..... 2.

MOLECULAR WEIGHT ..... 112.560

REFERENCE(S) ..... 58

UNITS ARE IN CAL/DEG KELVIN MOLE - PRESSURE ONE ATMOSPHERE

TABLE NUMBER ..... D-2

## IDEAL GAS THERMODYNAMIC FUNCTIONS OF BROMOBENZENE

TEMP	CP	(H-H)/T	(H-F)/T	S
273.15	21.98	13.33	62.42	75.75
298.15	23.82	14.13	63.63	77.76
300.00	23.95	14.19	63.71	77.91
350.00	27.54	15.85	66.03	81.87
400.00	30.90	17.52	68.25	85.77
450.00	33.95	19.18	70.41	89.59
500.00	36.69	20.80	72.52	93.31
550.00	39.13	22.35	74.57	96.92
600.00	41.30	23.84	76.58	100.42
650.00	43.25	25.26	78.55	103.81
700.00	44.99	26.61	80.47	107.08
750.00	46.57	27.89	82.35	110.24
800.00	47.99	29.10	84.19	113.29
850.00	49.29	30.25	85.99	116.24
900.00	50.47	31.34	87.75	119.09
950.00	51.55	32.38	89.47	121.85
1000.00	52.54	33.36	91.15	124.52
1100.00	54.29	35.19	94.42	129.61
1200.00	55.78	36.84	97.55	134.40
1300.00	57.06	38.35	100.56	138.91
1400.00	58.15	39.73	103.46	143.18

## FREQUENCIES USED (1/CM)

3067.	3050.	3029.	3069.	3056.
1579.	1578.	1473.	1443.	1321.
1264.	1175.	1159.	1068.	1021.
1001.	989.	963.	904.	832.
736.	681.	615.	409.	1071.
671.	315.	254.	459.	181.

PRINCIPAL MOMENTS ... 89.190 510.492 599.747

SYMMETRY NUMBER ..... 2.

MOLECULAR WEIGHT ..... 157.020

REFERENCE(S) ..... 1, 58

UNITS ARE IN CAL/DEG KELVIN MOLE - PRESSURE ONE ATMOSPHERE

TABLE NUMBER ..... D-3

## IDEAL GAS THERMODYNAMIC FUNCTIONS OF IODOBENZENE

TEMP	CP	(H-H)/T	(H-F)/T	S
273.15	22.28	13.69	64.13	77.82
298.15	24.09	14.49	65.37	79.85
300.00	24.23	14.54	65.46	80.00
350.00	27.78	16.18	67.82	84.01
400.00	31.10	17.84	70.09	87.93
450.00	34.13	19.49	72.29	91.78
500.00	36.85	21.09	74.42	95.52
550.00	39.27	22.64	76.51	99.14
600.00	41.43	24.11	78.54	102.65
650.00	43.36	25.52	80.53	106.05
700.00	45.10	26.86	82.47	109.33
750.00	46.66	28.13	84.36	112.49
800.00	48.08	29.33	86.22	115.55
850.00	49.37	30.47	88.03	118.50
900.00	50.54	31.56	89.80	121.36
950.00	51.62	32.58	91.54	124.12
1000.00	52.61	33.56	93.23	126.80
1100.00	54.35	35.37	96.52	131.89
1200.00	55.83	37.02	99.67	136.69
1300.00	57.10	38.52	102.69	141.21
1400.00	58.19	39.88	105.60	145.48

## FREQUENCIES USED (1/CM)

3067.	3050.	3031.	3064.	3048.
1573.	1573.	1471.	1436.	1320.
1258.	1176.	1156.	1068.	1016.
998.	988.	963.	904.	836.
730.	684.	613.	398.	1060.
654.	266.	220.	449.	166.

PRINCIPAL MOMENTS ... 88.225 673.320 763.527

SYMMETRY NUMBER ..... 2.

MOLECULAR WEIGHT ..... 204.020

REFERENCE(S) ..... 42, 58

UNITS ARE IN CAL/DEG KELVIN MOLE - PRESSURE ONE ATMOSPHERE

TABLE NUMBER ..... D-4

## IDEAL GAS THERMODYNAMIC FUNCTIONS OF 1-2- DIFLUORO BENZENE

TEMP	CP	(H-H)/T	(H-F)/T	S
273.15	23.51	13.87	60.93	74.80
298.15	25.45	14.76	62.19	76.94
300.00	25.59	14.82	62.28	77.10
350.00	29.31	16.63	64.70	81.33
400.00	32.74	18.43	67.04	85.47
450.00	35.83	20.20	69.31	89.51
500.00	38.59	21.90	71.53	93.43
550.00	41.04	23.53	73.69	97.22
600.00	43.22	25.08	75.80	100.89
650.00	45.16	26.55	77.87	104.43
700.00	46.89	27.95	79.88	107.84
750.00	48.45	29.26	81.85	111.13
800.00	49.86	30.51	83.78	114.30
850.00	51.14	31.68	85.66	117.36
900.00	52.30	32.80	87.50	120.32
950.00	53.36	33.85	89.29	123.18
1000.00	54.33	34.85	91.05	125.94
1100.00	56.03	36.70	94.45	131.20
1200.00	57.48	38.37	97.70	136.14
1300.00	58.71	39.89	100.82	140.79
1400.00	59.78	41.28	103.81	145.18

## FREQUENCIES USED (1/CM)

296.	567.	762.	1024.	1155.
1200.	1279.	1518.	1605.	3080.
3080.	436.	548.	855.	1102.
1212.	1252.	1464.	1622.	3080.
3080.	240.	585.	703.	855.
969.	197.	451.	750.	929.

PRINCIPAL MOMENTS ... 155.618 225.363 380.981

SYMMETRY NUMBER ..... 2.

MOLECULAR WEIGHT .... 114.094

REFERENCE(S) ..... 41, 54, 80

UNITS ARE IN CAL/DEG KELVIN MOLE - PRESSURE ONE ATMOSPHERE

ANHARMONICITY .....  $Z = 0.97$   $\gamma^* = 1250.$

TABLE NUMBER ..... D-5

## IDEAL GAS THERMODYNAMIC FUNCTIONS OF 1-3- DIFLUORO BENZENE

TEMP	CP	(H-H)/T	(H-F)/T	S
273.15	23.51	13.62	60.74	74.36
298.15	25.50	14.53	61.97	76.50
300.00	25.64	14.60	62.06	76.66
350.00	29.41	16.45	64.45	80.90
400.00	32.84	18.29	66.77	85.06
450.00	35.92	20.08	69.03	89.11
500.00	38.66	21.80	71.23	93.04
550.00	41.08	23.45	73.39	96.84
600.00	43.22	25.01	75.50	100.50
650.00	45.12	26.48	77.56	104.04
700.00	46.81	27.88	79.57	107.45
750.00	48.33	29.19	81.54	110.73
800.00	49.69	30.43	83.46	113.89
850.00	50.92	31.60	85.34	116.94
900.00	52.04	32.70	87.18	119.88
950.00	53.06	33.75	88.98	122.73
1000.00	53.99	34.74	90.73	125.47
1100.00	55.61	36.56	94.13	130.69
1200.00	56.99	38.21	97.38	135.59
1300.00	58.15	39.70	100.50	140.20
1400.00	59.15	41.05	103.50	144.55

## FREQUENCIES USED (1/CM)

3087.	3096.	3049.	524.	736.
1008.	1068.	1279.	1256.	1449.
599.	879.	251.	3096.	1157.
952.	1120.	459.	1497.	1616.
1604.	514.	1339.	478.	771.
852.	674.	862.	331.	253.

PRINCIPAL MOMENTS ... 134.104 286.907 421.010

SYMMETRY NUMBER ..... 2.

MOLECULAR WEIGHT .... 114.094

REFERENCE(S) ..... 34, 54, 80

UNITS ARE IN CAL/DEG KELVIN MOLE - PRESSURE ONE ATMOSPHERE

TABLE NUMBER ..... D-6

## IDEAL GAS THERMODYNAMIC FUNCTIONS OF 1-4- DIFLUORO BENZENE

TEMP	CP	(H-H)/T	(H-F)/T	S
273.15	23.98	13.77	59.34	73.11
298.15	26.06	14.71	60.59	75.30
300.00	26.21	14.78	60.68	75.46
350.00	30.12	16.70	63.10	79.80
400.00	33.66	18.60	65.45	84.06
450.00	36.79	20.45	67.75	88.20
500.00	39.54	22.23	70.00	92.23
550.00	41.94	23.91	72.20	96.11
600.00	44.06	25.50	74.35	99.85
650.00	45.92	27.00	76.45	103.45
700.00	47.57	28.41	78.50	106.92
750.00	49.05	29.74	80.51	110.25
800.00	50.37	30.99	82.47	113.46
850.00	51.56	32.17	84.38	116.55
900.00	52.64	33.27	86.25	119.53
950.00	53.62	34.32	88.08	122.40
1000.00	54.51	35.31	89.87	125.17
110.00	10.87	8.73	49.67	58.40
1200.00	57.39	38.76	96.62	135.38
1300.00	58.51	40.24	99.78	140.02
1400.00	59.47	41.58	102.81	144.39

## FREQUENCIES USED (1/CM)

3084.	1245.	1617.	859.	840.
451.	800.	3080.	1285.	635.
1142.	507.	692.	887.	375.
935.	370.	3028.	1183.	1511.
737.	1012.	509.	833.	186.
3088.	1437.	1212.	350.	1085.

PRINCIPAL MOMENTS ... 88.932 352.903 441.834

SYMMETRY NUMBER ..... 4.

MOLECULAR WEIGHT ..... 114.094

REFERENCE(S) ..... 25, 32, 47, 54, 80

UNITS ARE IN CAL/DEG KELVIN MOLE - PRESSURE ONE ATMOSPHERE

TABLE NUMBER ..... D-7

## IDEAL GAS THERMODYNAMIC FUNCTIONS OF 1-3-5- TRIFLUORO BENZENE

TEMP	CP	(H-H)/T	(H-F)/T	S
273.15	26.33	15.22	61.13	76.36
298.15	28.33	16.24	62.51	78.75
300.00	28.48	16.31	62.61	78.93
350.00	32.23	18.32	65.28	83.60
400.00	35.61	20.28	67.85	88.13
450.00	38.62	22.15	70.35	92.50
500.00	41.27	23.93	72.78	96.71
550.00	43.60	25.62	75.14	100.76
600.00	45.65	27.20	77.44	104.64
650.00	47.46	28.69	79.67	108.37
700.00	49.06	30.09	81.85	111.94
750.00	50.49	31.41	83.97	115.38
800.00	51.76	32.64	86.04	118.68
850.00	52.91	33.80	88.05	121.85
900.00	53.94	34.89	90.02	124.91
950.00	54.87	35.92	91.93	127.85
1000.00	55.71	36.89	93.80	130.68
1100.00	57.18	38.67	97.40	136.06
1200.00	58.41	40.26	100.83	141.09
1300.00	59.44	41.70	104.11	145.81
1400.00	60.32	43.00	107.25	150.25

## FREQUENCIES USED (1/CM)

578.	1010.	1350.	3080.	253.
595.	847.	326.	505.	995.
1122.	1473.	1618.	3115.	253.
595.	847.	326.	505.	995.
1122.	1473.	1618.	3115.	664.
847.	214.	564.	1294.	1165.

PRINCIPAL MOMENTS ... 286.894 288.038 574.932

SYMMETRY NUMBER ..... 6.

MOLECULAR WEIGHT ..... 132.084

REFERENCE(S) ..... 22, 46, 55

UNITS ARE IN CAL/DEG KELVIN MOLE - PRESSURE ONE ATMOSPHERE

TABLE NUMBER .....

D-8

## IDEAL GAS THERMODYNAMIC FUNCTIONS OF 1-2-4- TRIFLUORO BENZENE

TEMP	CP	(H-H)/T	(H-F)/T	S
273.15	26.79	15.45	64.72	80.18
298.15	28.85	16.49	66.12	82.61
300.00	29.00	16.57	66.22	82.79
350.00	32.82	18.62	68.93	87.55
400.00	36.24	20.61	71.55	92.16
450.00	39.26	22.52	74.09	96.61
500.00	41.91	24.33	76.56	100.89
550.00	44.22	26.03	78.96	104.99
600.00	46.25	27.64	81.29	108.93
650.00	48.02	29.14	83.56	112.70
700.00	49.60	30.54	85.77	116.32
750.00	50.99	31.86	87.93	119.79
800.00	52.23	33.10	90.02	123.12
850.00	53.35	34.26	92.06	126.32
900.00	54.35	35.34	94.05	129.40
950.00	55.25	36.37	95.99	132.36
1000.00	56.08	37.33	97.88	135.22
1100.00	57.50	39.10	101.53	140.63
1200.00	58.69	40.69	105.00	145.69
1300.00	59.70	42.11	108.31	150.43
1400.00	60.55	43.40	111.48	154.88

## FREQUENCIES USED (1/CM)

288.	341.	441.	503.	586.
728.	781.	835.	964.	1098.
1143.	1204.	1250.	1308.	1376.
1441.	1518.	1628.	3062.	3094.
3094.	161.	238.	377.	456.
602.	688.	808.	856.	932.

PRINCIPAL MOMENTS ... 166.027 399.072 565.099

SYMMETRY NUMBER ..... 1.

MOLECULAR WEIGHT ..... 132.084

REFERENCE(S) ..... 36

UNITS ARE IN CAL/DEG KELVIN MOLE - PRESSURE ONE ATMOSPHERE

TABLE NUMBER ..... D-9

## IDEAL GAS THERMODYNAMIC FUNCTIONS OF 1-2-3-5- TETRAFLUORO BENZENE

TEMP	CP	(H-H)/T	(H-F)/T	S
273.15	29.10	17.01	65.64	82.66
298.15	31.08	18.11	67.18	85.29
300.00	31.22	18.19	67.29	85.48
350.00	34.88	20.32	70.26	90.58
400.00	38.16	22.35	73.10	95.45
450.00	41.06	24.27	75.85	100.12
500.00	43.62	26.08	78.50	104.58
550.00	45.87	27.78	81.07	108.84
600.00	47.84	29.37	83.55	112.92
650.00	49.57	30.86	85.96	116.82
700.00	51.10	32.25	88.30	120.55
750.00	52.45	33.55	90.57	124.12
800.00	53.65	34.77	92.78	127.55
850.00	54.72	35.91	94.92	130.83
900.00	55.68	36.99	97.00	133.99
950.00	56.54	37.99	99.03	137.02
1000.00	57.31	38.94	101.00	139.94
1100.00	58.65	40.67	104.80	145.47
1200.00	59.75	42.22	108.40	150.62
1300.00	60.67	43.60	111.84	155.44
1400.00	61.44	44.85	115.11	159.97

## FREQUENCIES USED (1/CM)

3090.	1642.	1531.	1405.	1200.
1130.	1000.	787.	580.	465.
310.	845.	645.	205.	3080.
1642.	1466.	1249.	1179.	1056.
640.	843.	707.	610.	368.
220.	185.	508.	334.	258.

PRINCIPAL MOMENTS ... 290.247 408.629 698.877

SYMMETRY NUMBER ..... 2.

MOLECULAR WEIGHT .... 150.074

REFERENCE(S) ..... 51

UNITS ARE IN CAL/DEG KELVIN MOLE - PRESSURE ONE ATMOSPHERE

TABLE NUMBER ..... D-10

## IDEAL GAS THERMODYNAMIC FUNCTIONS OF 1-2-4-5- TETRAFLUORO BENZENE

TEMP	CP	(H-H)/T	(H-F)/T	S
273.15	29.65	17.37	64.54	81.90
298.15	31.62	18.48	66.11	84.59
300.00	31.76	18.56	66.22	84.78
350.00	35.40	20.71	69.25	89.96
400.00	38.66	22.76	72.15	94.90
450.00	41.55	24.69	74.94	99.63
500.00	44.09	26.50	77.64	104.14
550.00	46.32	28.21	80.24	108.45
600.00	48.27	29.80	82.77	112.56
650.00	49.97	31.29	85.21	116.50
700.00	51.48	32.68	87.58	120.25
750.00	52.80	33.97	89.88	123.85
800.00	53.98	35.19	92.11	127.30
850.00	55.03	36.33	94.28	130.60
900.00	55.97	37.39	96.38	133.78
950.00	56.81	38.39	98.43	136.82
1000.00	57.56	39.33	100.43	139.76
1100.00	58.87	41.05	104.26	145.31
1200.00	59.94	42.58	107.90	150.48
1300.00	60.84	43.95	111.36	155.31
1400.00	61.59	45.19	114.66	159.85

## FREQUENCIES USED (1/CM)

3097.	1335.	1374.	748.	280.
487.	417.	1196.	1643.	635.
1125.	240.	669.	871.	295.
600.	140.	3088.	1222.	1439.
420.	700.	461.	869.	240.
1277.	1534.	853.	270.	1164.

PRINCIPAL MOMENTS ... 223.028 491.971 714.999

SYMMETRY NUMBER ..... 4.

MOLECULAR WEIGHT ..... 150.070

REFERENCE(S) ..... 31, 33

UNITS ARE IN CAL/DEG KELVIN MOLE - PRESSURE ONE ATMOSPHERE

TABLE NUMBER ..... D-11

## IDEAL GAS THERMODYNAMIC FUNCTIONS OF 1-2-3-4- TETRAFLUORO BENZENE

TEMP	CP	(H-H)/T	(H-F)/T	S
273.15	28.48	16.46	64.87	81.33
298.15	30.47	17.55	66.36	83.91
300.00	30.62	17.63	66.47	84.10
350.00	34.30	19.75	69.34	89.10
400.00	37.61	21.78	72.12	93.90
450.00	40.55	23.71	74.79	98.50
500.00	43.14	25.52	77.39	102.91
550.00	45.43	27.23	79.90	107.13
600.00	47.44	28.83	82.34	111.17
650.00	49.21	30.33	84.71	115.04
700.00	50.77	31.74	87.01	118.74
750.00	52.15	33.05	89.24	122.29
800.00	53.37	34.29	91.41	125.70
850.00	54.47	35.44	93.53	128.97
900.00	55.45	36.53	95.58	132.11
950.00	56.33	37.55	97.59	135.13
1000.00	57.12	38.51	99.54	138.04
1100.00	58.48	40.26	103.29	143.55
1200.00	59.61	41.83	106.86	148.69
1300.00	60.55	43.23	110.27	153.50
1400.00	61.34	44.50	113.52	158.02

## FREQUENCIES USED (1/CM)

3090.	1634.	1525.	1331.	1192.
1165.	1050.	682.	460.	325.
268.	3070.	1606.	1517.	1402.
1239.	993.	748.	489.	310.
291.	802.	597.	374.	170.
922.	820.	685.	570.	305.

PRINCIPAL MOMENTS ... 241.875 424.738 666.612

SYMMETRY NUMBER ..... 2.

MOLECULAR WEIGHT ..... 150.074

REFERENCE(S) ..... 51

UNITS ARE IN CAL/DEG KELVIN MOLE - PRESSURE ONE ATMOSPHERE

TABLE NUMBER .....

D-12

## IDEAL GAS THERMODYNAMIC FUNCTIONS OF PENTAFLUORO BENZENE

TEMP	CP	(H-H)/T	(H-F)/T	S
273.15	32.37	18.94	67.77	86.71
298.15	34.29	20.15	69.48	89.63
300.00	34.43	20.24	69.61	89.84
350.00	37.94	22.52	72.90	95.42
400.00	41.05	24.65	76.05	100.69
450.00	43.80	26.62	79.07	105.69
500.00	46.22	28.47	81.97	110.43
550.00	48.34	30.18	84.76	114.94
600.00	50.20	31.77	87.46	119.23
650.00	51.83	33.25	90.06	123.31
700.00	53.26	34.63	92.58	127.21
750.00	54.52	35.92	95.01	130.93
800.00	55.63	37.11	97.37	134.48
850.00	56.61	38.23	99.65	137.88
900.00	57.49	39.28	101.87	141.14
950.00	58.27	40.26	104.02	144.27
1000.00	58.96	41.18	106.10	147.28
1100.00	60.15	42.85	110.11	152.96
1200.00	61.12	44.33	113.90	158.23
1300.00	61.91	45.66	117.50	163.16
1400.00	62.58	46.84	120.93	167.77

## FREQUENCIES USED (1/CM)

3105.	1648.	1514.	1410.	1286.
1075.	718.	578.	470.	325.
272.	600.	391.	171.	838.
697.	556.	300.	217.	200.
1648.	1540.	1268.	1182.	1138.
953.	688.	436.	304.	247.

PRINCIPAL MOMENTS ... 343.112 491.808 834.921

SYMMETRY NUMBER ..... 2.

MOLECULAR WEIGHT ..... 168.064

REFERENCE(S) ..... 31, 48, 75

UNITS ARE IN CAL/DEG KELVIN MOLE - PRESSURE ONE ATMOSPHERE

TABLE NUMBER ..... D-13

## IDEAL GAS THERMODYNAMIC FUNCTIONS OF HEXAFLUORO BENZENE

TEMP	CP	(H-H)/T	(H-F)/T	S
273.15	35.53	21.19	67.16	88.34
298.15	37.40	22.47	69.07	91.54
300.00	37.53	22.56	69.21	91.77
350.00	40.90	24.95	72.87	97.81
400.00	43.86	27.13	76.34	103.47
450.00	46.48	29.14	79.65	108.79
500.00	48.77	30.99	82.82	113.81
550.00	50.79	32.70	85.86	118.56
600.00	52.55	34.28	88.77	123.05
650.00	54.08	35.75	91.57	127.32
700.00	55.42	37.11	94.27	131.38
750.00	56.59	38.37	96.88	135.24
800.00	57.62	39.54	99.39	138.93
850.00	58.52	40.63	101.82	142.45
900.00	59.31	41.65	104.17	145.82
950.00	60.01	42.59	106.45	149.04
1000.00	60.63	43.48	108.66	152.14
1100.00	61.67	45.09	112.88	157.97
1200.00	62.51	46.51	116.86	163.37
1300.00	63.18	47.76	120.64	168.40
1400.00	63.73	48.89	124.22	173.10

## FREQUENCIES USED (1/CM)

1655.	1655.	1530.	1530.	1490.
1323.	1253.	1157.	1157.	1006.
1006.	714.	691.	640.	595.
595.	559.	443.	443.	372.
372.	315.	315.	264.	264.
249.	215.	208.	133.	133.

PRINCIPAL MOMENTS ... 491.971 492.005 983.976

SYMMETRY NUMBER ..... 12.

MOLECULAR WEIGHT ..... 186.054

REFERENCE(S) ..... 39, 50, 75

UNITS ARE IN CAL/DEG KELVIN MOLE - PRESSURE ONE ATMOSPHERE

TABLE NUMBER ..... D-14

## IDEAL GAS THERMODYNAMIC FUNCTIONS OF CHLOROPENTAFLUORO BENZENE

TEMP	CP	(H-H)/T	(H-F)/T	S
273.15	36.53	22.06	72.57	94.63
298.15	38.37	23.35	74.55	97.90
300.00	38.50	23.44	74.70	98.14
350.00	41.80	25.84	78.49	104.33
400.00	44.70	28.02	82.09	110.11
450.00	47.24	30.02	85.51	115.52
500.00	49.47	31.85	88.76	120.62
550.00	51.42	33.54	91.88	125.43
600.00	53.12	35.11	94.87	129.97
650.00	54.61	36.55	97.74	134.29
700.00	55.90	37.89	100.49	138.38
750.00	57.03	39.13	103.15	142.28
800.00	58.02	40.28	105.71	145.99
850.00	58.88	41.35	108.19	149.53
900.00	59.65	42.34	110.58	152.92
950.00	60.32	43.27	112.89	156.17
1000.00	60.91	44.14	115.14	159.27
1100.00	61.92	45.71	119.42	165.13
1200.00	62.71	47.10	123.46	170.55
1300.00	63.36	48.32	127.27	175.60
1400.00	63.89	49.42	130.90	180.31

## FREQUENCIES USED (1/CM)

1643.	1518.	1448.	1300.	1102.
882.	589.	516.	394.	310.
277.	600.	397.	116.	622.
550.	357.	217.	178.	116.
1643.	1518.	1274.	1153.	986.
716.	441.	310.	217.	202.

PRINCIPAL MOMENTS ... 1169.170 677.518 491.650

SYMMETRY NUMBER ..... 2.

MOLECULAR WEIGHT .... 202.509

REFERENCE(S) ..... 48, 49, 59

UNITS ARE IN CAL/DEG KELVIN MOLE - PRESSURE ONE ATMOSPHERE

TABLE NUMBER ..... D-15

## IDEAL GAS THERMODYNAMIC FUNCTIONS OF BROMOPENTAFLUORO BENZENE

TEMP	CP	(H-H)/T	(H-F)/T	S
273.15	37.09	22.74	74.75	97.49
298.15	38.89	24.02	76.80	100.82
300.00	39.02	24.11	76.95	101.06
350.00	42.25	26.48	80.84	107.32
400.00	45.09	28.63	84.52	113.15
450.00	47.59	30.60	88.01	118.61
500.00	49.78	32.41	91.33	123.74
550.00	51.70	34.08	94.50	128.58
600.00	53.37	35.62	97.53	133.15
650.00	54.83	37.04	100.44	137.48
700.00	56.10	38.36	103.23	141.59
750.00	57.21	39.58	105.92	145.50
800.00	58.18	40.71	108.51	149.22
850.00	59.03	41.77	111.01	152.78
900.00	59.78	42.75	113.43	156.17
950.00	60.44	43.66	115.76	159.42
1000.00	61.03	44.51	118.02	162.54
1100.00	62.01	46.06	122.34	168.40
1200.00	62.80	47.43	126.41	173.83
1300.00	63.44	48.63	130.25	178.89
1400.00	63.95	49.71	133.90	183.61

## FREQUENCIES USED (1/CM)

1639.	1515.	1426.	1291.	1093.
834.	583.	496.	360.	280.
239.	600.	378.	114.	618.
550.	350.	217.	156.	114.
1639.	1515.	1268.	1154.	976.
714.	440.	310.	217.	151.

PRINCIPAL MOMENTS ... 1520.720 1029.070 491.650

SYMMETRY NUMBER ..... 2.

MOLECULAR WEIGHT ..... 246.965

REFERENCE(S) ..... 48, 49, 59

UNITS ARE IN CAL/DEG KELVIN MOLE - PRESSURE ONE ATMOSPHERE

TABLE NUMBER ..... D-16

## IDEAL GAS THERMODYNAMIC FUNCTIONS OF IODOPENTAFLUORO BENZENE

TEMP	CP	(H-H)/T	(H-F)/T	S
273.15	37.37	23.13	76.46	99.59
298.15	39.15	24.40	78.54	102.94
300.00	39.28	24.49	78.69	103.19
350.00	42.48	26.84	82.65	109.49
400.00	45.30	28.97	86.37	115.35
450.00	47.77	30.93	89.90	120.83
500.00	49.95	32.72	93.25	125.98
550.00	51.85	34.38	96.45	130.83
600.00	53.51	35.91	99.51	135.41
650.00	54.96	37.32	102.44	139.76
700.00	56.22	38.62	105.25	143.88
750.00	57.32	39.83	107.96	147.79
800.00	58.28	40.96	110.57	151.52
850.00	59.12	42.00	113.08	155.08
900.00	59.87	42.97	115.51	158.48
950.00	60.52	43.88	117.86	161.74
1000.00	61.10	44.73	120.13	164.86
1100.00	62.07	46.26	124.47	170.73
1200.00	62.85	47.61	128.55	176.16
1300.00	63.48	48.81	132.41	181.22
1400.00	64.00	49.88	136.07	185.94

## FREQUENCIES USED (1/CM)

1633.	1507.	1406.	1296.	1083.
805.	581.	489.	349.	278.
204.	600.	381.	110.	600.
550.	349.	217.	133.	114.
1633.	1517.	1263.	1149.	977.
714.	438.	311.	215.	129.

PRINCIPAL MOMENTS ... 1870.300 1378.640 491.650

SYMMETRY NUMBER ..... 2.

MOLECULAR WEIGHT .... 293.960

REFERENCE(S) ..... 48, 49, 59

UNITS ARE IN CAL/DEG KELVIN MOLE - PRESSURE ONE ATMOSPHERE

TABLE NUMBER ..... D-17

## IDEAL GAS THERMODYNAMIC FUNCTIONS OF 1-2- CHLOROFLUORO BENZENE

TEMP	CP	(H-H)/T	(H-F)/T	S
273.15	24.52	14.51	63.99	78.51
298.15	26.46	15.43	65.30	80.74
300.00	26.60	15.50	65.40	80.90
350.00	30.27	17.35	67.93	85.28
400.00	33.61	19.18	70.37	89.54
450.00	36.61	20.95	72.73	93.68
500.00	39.28	22.65	75.02	97.68
550.00	41.63	24.27	77.26	101.53
600.00	43.72	25.81	79.44	105.25
650.00	45.57	27.26	81.56	108.82
700.00	47.22	28.63	83.63	112.26
750.00	48.70	29.92	85.65	115.57
800.00	50.03	31.13	87.62	118.76
850.00	51.23	32.28	89.54	121.83
900.00	52.33	33.36	91.42	124.79
950.00	53.32	34.39	93.25	127.64
1000.00	54.23	35.36	95.04	130.40
1100.00	55.82	37.15	98.50	135.64
1200.00	57.16	38.76	101.80	140.56
1300.00	58.30	40.22	104.96	145.18
1400.00	59.28	41.55	107.99	149.54

## FREQUENCIES USED (1/CM)

231.	375.	497.	552.	684.
826.	1030.	1068.	1130.	1157.
1237.	1264.	1287.	1450.	1481.
1589.	1597.	3025.	3066.	3083.
3155.	167.	269.	443.	535.
703.	750.	795.	850.	935.

PRINCIPAL MOMENTS ... 500.831 326.156 174.675

SYMMETRY NUMBER ..... 1.

MOLECULAR WEIGHT .... 130.550

REFERENCE(S) ..... 57

UNITS ARE IN CAL/DEG KELVIN MOLE - PRESSURE ONE ATMOSPHERE

TABLE NUMBER ..... D-18

## IDEAL GAS THERMODYNAMIC FUNCTIONS OF 1-3- CHLOROFLUORO BENZENE

TEMP	CP	(H-H)/T	(H-F)/T	S
273.15	24.44	14.58	64.22	78.80
298.15	26.30	15.48	65.54	81.02
300.00	26.44	15.55	65.63	81.18
350.00	30.01	17.36	68.16	85.53
400.00	33.31	19.15	70.60	89.75
450.00	36.29	20.89	72.96	93.85
500.00	38.96	22.57	75.25	97.82
550.00	41.33	24.17	77.47	101.64
600.00	43.43	25.69	79.64	105.33
650.00	45.30	27.13	81.76	108.88
700.00	46.97	28.49	83.82	112.30
750.00	48.46	29.77	85.83	115.59
800.00	49.81	30.98	87.79	118.77
850.00	51.03	32.12	89.70	121.82
900.00	52.13	33.21	91.57	124.77
950.00	53.14	34.23	93.39	127.62
1000.00	54.06	35.20	95.17	130.37
1100.00	55.67	36.99	98.61	135.60
1200.00	57.03	38.60	101.90	140.50
1300.00	58.19	40.07	105.05	145.11
1400.00	59.18	41.40	108.07	149.46

## FREQUENCIES USED (1/CM)

245.	408.	517.	691.	892.
1007.	1061.	1081.	1128.	1157.
1228.	1264.	1292.	1435.	1478.
1596.	3030.	3082.	3189.	191.
245.	382.	443.	489.	673.
774.	862.	990.	1600.	3082.

PRINCIPAL MOMENTS ... 147.575 429.661 577.312

SYMMETRY NUMBER ..... 1.

MOLECULAR WEIGHT .... 130.550

REFERENCE(S) ..... 17, 43

UNITS ARE IN CAL/DEG KELVIN MOLE - PRESSURE ONE ATMOSPHERE

TABLE NUMBER ..... D-19

## IDEAL GAS THERMODYNAMIC FUNCTIONS OF 1-4- CHLOROFLUORO BENZENE

TEMP	CP	(H-H)/T	(H-F)/T	S
273.15	23.17	13.33	61.46	74.78
298.15	25.19	14.24	62.66	76.90
300.00	25.34	14.31	62.75	77.06
350.00	29.17	16.16	65.10	81.25
400.00	32.67	18.01	67.37	85.38
450.00	35.80	19.81	69.60	89.42
500.00	38.57	21.56	71.78	93.33
550.00	41.02	23.22	73.91	97.13
600.00	43.18	24.79	76.00	100.79
650.00	45.09	26.28	78.04	104.32
700.00	46.78	27.69	80.04	107.73
750.00	48.30	29.01	82.00	111.01
800.00	49.66	30.26	83.91	114.17
850.00	50.89	31.44	85.78	117.22
900.00	52.01	32.55	87.61	120.16
950.00	53.02	33.60	89.40	123.00
1000.00	53.95	34.60	91.15	125.74
1100.00	55.57	36.43	94.53	130.96
1200.00	56.94	38.08	97.77	135.86
1300.00	58.10	39.58	100.88	140.46
1400.00	59.09	40.94	103.87	144.81

## FREQUENCIES USED (1/CM)

376.	680.	815.	1017.	1096.
1153.	1246.	1490.	1592.	3076.
3184.	336.	419.	630.	1123.
1270.	1287.	1402.	1592.	3101.
3152.	267.	498.	691.	750.
830.	936.	368.	839.	868.

PRINCIPAL MOMENTS ... 620.633 531.762 88.871

SYMMETRY NUMBER ..... 2.

MOLECULAR WEIGHT .... 130.550

REFERENCE(S) ..... 104

UNITS ARE IN CAL/DEG KELVIN MOLE - PRESSURE ONE ATMOSPHERE

TABLE NUMBER ..... D-20

## IDEAL GAS THERMODYNAMIC FUNCTIONS OF 1-2- BROMOFLUOROBENZENE

TEMP	CP	(H-H)/T	(H-F)/T	S
273.15	25.30	15.06	66.23	81.28
298.15	27.28	16.00	67.59	83.59
300.00	27.43	16.07	67.68	83.75
350.00	31.21	17.97	70.30	88.27
400.00	34.68	19.84	72.83	92.67
450.00	37.79	21.67	75.27	96.94
500.00	40.54	23.42	77.64	101.06
550.00	42.97	25.09	79.95	105.04
600.00	45.10	26.67	82.21	108.88
650.00	46.98	28.16	84.40	112.56
700.00	48.64	29.57	86.54	116.10
750.00	50.11	30.89	88.62	119.51
800.00	51.43	32.13	90.66	122.79
850.00	52.61	33.30	92.64	125.94
900.00	53.67	34.40	94.58	128.98
950.00	54.62	35.44	96.46	131.91
1000.00	55.49	36.42	98.31	134.73
1100.00	57.00	38.23	101.87	140.09
1200.00	58.25	39.85	105.26	145.11
1300.00	59.31	41.30	108.51	149.81
1400.00	60.20	42.62	111.62	154.24

## FREQUENCIES USED (1/CM)

157.	189.	262.	298.	437.
471.	530.	546.	653.	695.
751.	791.	821.	850.	937.
1025.	1049.	1115.	1156.	1233.
1261.	1285.	1446.	1479.	1579.
1591.	1020.	3065.	3085.	3174.

PRINCIPAL MOMENTS ... 695.490 512.650 180.840

SYMMETRY NUMBER ..... 1.

MOLECULAR WEIGHT ..... 175.005

REFERENCE(S) ..... 71

UNITS ARE IN CAL/DEG KELVIN MOLE - PRESSURE ONE ATMOSPHERE

TABLE NUMBER ..... D-21

## IDEAL GAS THERMODYNAMIC FUNCTIONS OF 1-2- FLUORO IODOBENZENE

TEMP	CP	(H-H)/T	(H-F)/T	S
273.15	25.32	15.36	67.94	83.30
298.15	27.19	16.28	69.32	85.60
300.00	27.33	16.34	69.42	85.76
350.00	30.90	18.17	72.08	90.25
400.00	34.17	19.97	74.62	94.59
450.00	37.11	21.71	77.08	98.79
500.00	39.72	23.39	79.45	102.84
550.00	42.03	24.98	81.76	106.73
600.00	44.07	26.49	83.99	110.48
650.00	45.89	27.91	86.17	114.08
700.00	47.51	29.25	88.29	117.54
750.00	48.96	30.52	90.35	120.87
800.00	50.26	31.71	92.36	124.07
850.00	51.45	32.84	94.32	127.15
900.00	52.52	33.90	96.22	130.13
950.00	53.50	34.91	98.08	132.99
1000.00	54.39	35.86	99.90	135.76
1100.00	55.96	37.62	103.40	141.02
1200.00	57.28	39.20	106.74	145.95
1300.00	58.41	40.64	109.94	150.58
1400.00	59.37	41.94	113.00	154.94

## FREQUENCIES USED (1/CM)

144.	166.	252.	252.	434.
460.	527.	541.	640.	694.
752.	781.	819.	849.	937.
1020.	1040.	1110.	1156.	1231.
1259.	1279.	1443.	1472.	1581.
1581.	3021.	3072.	3072.	3164.

PRINCIPAL MOMENTS ... 873.570 692.040 181.530

SYMMETRY NUMBER ..... 1.

MOLECULAR WEIGHT ..... 222.000

REFERENCE(S) ..... 71

UNITS ARE IN CAL/DEG KELVIN MOLE - PRESSURE ONE ATMOSPHERE

TABLE NUMBER ..... D-22

## IDEAL GAS THERMODYNAMIC FUNCTIONS OF 1-2- BROMOCHLOROBENZENE

TEMP	CP	(H-H)/T	(H-F)/T	S
273.15	26.97	16.14	67.99	84.14
298.15	28.85	17.13	69.45	86.58
300.00	28.99	17.20	69.56	86.76
350.00	32.51	19.14	72.35	91.50
400.00	35.68	21.01	75.03	96.05
450.00	38.50	22.80	77.61	100.42
500.00	40.99	24.50	80.10	104.60
550.00	43.18	26.10	82.52	108.62
600.00	45.12	27.61	84.85	112.46
650.00	46.84	29.02	87.12	116.14
700.00	48.37	30.35	89.32	119.67
750.00	49.75	31.60	91.45	123.05
800.00	50.99	32.77	93.53	126.30
850.00	52.11	33.88	95.55	129.43
900.00	53.13	34.92	97.52	132.44
950.00	54.06	35.90	99.43	135.33
1000.00	54.91	36.83	101.30	138.13
1100.00	56.41	38.54	104.89	143.43
1200.00	57.67	40.09	108.31	148.40
1300.00	58.75	41.48	111.58	153.06
1400.00	59.68	42.75	114.70	157.45

## FREQUENCIES USED (1/CM)

142.	165.	231.	281.	436.
461.	522.	386.	441.	688.
746.	807.	719.	856.	945.
1036.	1021.	1122.	1161.	645.
1252.	1269.	1434.	1455.	1570.
1570.	2990.	3064.	3064.	3138.

PRINCIPAL MOMENTS ... 808.790 513.500 295.290

SYMMETRY NUMBER ..... 1.

MOLECULAR WEIGHT ..... 191.460

REFERENCE(S) ..... 71

UNITS ARE IN CAL/DEG KELVIN MOLE - PRESSURE ONE ATMOSPHERE

TABLE NUMBER ..... D-23

## IDEAL GAS THERMODYNAMIC FUNCTIONS OF 1-2- DICHLORO BENZENE

TEMP	CP	(H-H)/T	(H-F)/T	S
298.15	27.14	16.07	65.59	81.66
300.00	27.27	16.13	65.69	81.83
350.00	30.86	17.99	68.32	86.30
400.00	34.14	19.80	70.84	90.64
450.00	37.08	21.56	73.27	94.84
500.00	39.70	23.25	75.63	98.88
550.00	42.02	24.85	77.93	102.78
600.00	44.07	26.37	80.15	106.52
650.00	45.89	27.80	82.32	110.12
700.00	47.52	29.15	84.43	113.58
750.00	48.97	30.43	86.49	116.91
800.00	50.28	31.63	88.49	120.12
850.00	51.47	32.76	90.44	123.20
900.00	52.54	33.83	92.34	126.17
950.00	53.52	34.84	94.20	129.04
1000.00	54.42	35.80	96.01	131.81
1100.00	55.99	37.56	99.51	137.07
1200.00	57.31	39.16	102.85	142.00
1300.00	58.44	40.60	106.04	146.63
1400.00	59.40	41.91	109.10	151.00
1500.00	60.23	43.10	112.03	155.13

## FREQUENCIES USED (1/CM)

3070.	1575.	1468.	1276.	1162.
1130.	1041.	660.	480.	203.
3070.	3070.	3070.	1575.	1438.
1252.	1130.	1038.	740.	429.
334.	975.	850.	685.	504.
154.	934.	748.	435.	241.

PRINCIPAL MOMENTS ... 612.330 355.870 256.460

SYMMETRY NUMBER ..... 2.

MOLECULAR WEIGHT ..... 147.004

REFERENCE(S) ..... 39, 65

UNITS ARE IN CAL/DEG KELVIN MOLE - PRESSURE ONE ATMOSPHERE

TABLE NUMBER ..... D-24

## IDEAL GAS THERMODYNAMIC FUNCTIONS OF 1-3- DICHLORO BENZENE

TEMP	CP	(H-H)/T	(H-F)/T	S
298.15	27.21	16.13	65.95	82.07
300.00	27.34	16.20	66.05	82.24
350.00	30.92	18.05	68.68	86.73
400.00	34.20	19.86	71.21	91.08
450.00	37.14	21.62	73.65	95.28
500.00	39.75	23.31	76.02	99.33
550.00	42.06	24.91	78.32	103.23
600.00	44.11	26.43	80.55	106.98
650.00	45.93	27.86	82.72	110.58
700.00	47.55	29.21	84.84	114.04
750.00	49.00	30.48	86.90	117.38
800.00	50.30	31.68	88.90	120.58
850.00	51.48	32.81	90.86	123.67
900.00	52.56	33.88	92.76	126.64
950.00	53.53	34.89	94.62	129.51
1000.00	54.42	35.84	96.44	132.28
1100.00	55.99	37.60	99.94	137.54
1200.00	57.31	39.19	103.28	142.47
1300.00	58.44	40.63	106.47	147.10
1400.00	59.40	41.94	109.53	151.47
1500.00	60.22	43.13	112.47	155.60

## FREQUENCIES USED (1/CM)

3074.	3074.	3074.	1576.	1411.
1124.	1068.	999.	663.	399.
198.	3095.	1576.	1464.	1330.
1258.	1161.	1079.	784.	430.
364.	891.	531.	212.	966.
869.	775.	674.	428.	176.

PRINCIPAL MOMENTS ... 762.070 585.510 176.560

SYMMETRY NUMBER ..... 2.

MOLECULAR WEIGHT ..... 147.004

REFERENCE(S) ..... 39, 62

UNITS ARE IN CAL/DEG KELVIN MOLE - PRESSURE ONE ATMOSPHERE

TABLE NUMBER ..... D-25

## IDEAL GAS THERMODYNAMIC FUNCTIONS OF 1-4- DICHLORO BENZENE

TEMP	CP	(H-H)/T	(H-F)/T	S
298.15	27.22	16.12	64.34	80.46
300.00	27.36	16.19	64.44	80.62
350.00	30.95	18.04	67.07	85.12
400.00	34.24	19.87	69.60	89.47
450.00	37.18	21.63	72.04	93.67
500.00	39.80	23.32	74.41	97.73
550.00	42.12	24.92	76.71	101.63
600.00	44.16	26.44	78.94	105.39
650.00	45.98	27.88	81.12	108.99
700.00	47.59	29.23	83.23	112.46
750.00	49.04	30.50	85.29	115.80
800.00	50.35	31.70	87.30	119.00
850.00	51.53	32.84	89.26	122.09
900.00	52.60	33.90	91.16	125.07
950.00	53.57	34.91	93.02	127.94
1000.00	54.46	35.87	94.84	130.71
1100.00	56.02	37.63	98.34	135.97
1200.00	57.34	39.22	101.69	140.91
1300.00	58.46	40.66	104.88	145.54
1400.00	59.42	41.97	107.94	149.91
1500.00	60.24	43.16	110.88	154.04

## FREQUENCIES USED (1/CM)

3070.	1574.	1169.	1096.	747.
328.	3065.	1574.	1290.	626.
350.	3090.	1477.	1090.	1015.
550.	3090.	1394.	1221.	1107.
226.	815.	934.	687.	298.
951.	407.	819.	485.	125.

PRINCIPAL MOMENTS ... 88.640 751.120 839.770

SYMMETRY NUMBER ..... 4.

MOLECULAR WEIGHT ..... 147.004

REFERENCE(S) ..... 39, 62

UNITS ARE IN CAL/DEG KELVIN MOLE - PRESSURE ONE ATMOSPHERE

TABLE NUMBER ..... D-26

## IDEAL GAS THERMODYNAMIC FUNCTIONS OF 1-3-5- TRICHLORO BENZENE

TEMP	CP	(H-H)/T	(H-F)/T	S
298.15	30.80	18.54	68.10	86.64
300.00	30.93	18.61	68.22	86.83
350.00	34.43	20.62	71.24	91.86
400.00	37.58	22.55	74.12	96.67
450.00	40.38	24.38	76.88	101.26
500.00	42.85	26.11	79.54	105.65
550.00	45.02	27.73	82.11	109.84
600.00	46.94	29.25	84.59	113.84
650.00	48.62	30.68	86.98	117.66
700.00	50.12	32.01	89.31	121.32
750.00	51.45	33.27	91.56	124.82
800.00	52.64	34.44	93.74	128.18
850.00	53.71	35.54	95.87	131.41
900.00	54.67	36.58	97.93	134.51
950.00	55.55	37.55	99.93	137.49
1000.00	56.34	38.47	101.88	140.35
1100.00	57.72	40.16	105.63	145.79
1200.00	58.88	41.68	109.19	150.86
1300.00	59.85	43.04	112.58	155.62
1400.00	60.68	44.27	115.81	160.08
1500.00	61.39	45.39	118.91	164.29

## FREQUENCIES USED (1/CM)

853.	662.	148.	869.	869.
530.	530.	215.	215.	3084.
1149.	997.	379.	1373.	1249.
474.	3089.	3089.	1570.	1570.
1420.	1420.	1098.	1098.	816.
816.	429.	429.	191.	191.

PRINCIPAL MOMENTS ... 1177.600 588.810 588.790

SYMMETRY NUMBER ..... 6.

MOLECULAR WEIGHT ..... 181.449

REFERENCE(S) ..... 82

UNITS ARE IN CAL/DEG KELVIN MOLE - PRESSURE ONE ATMOSPHERE

TABLE NUMBER ..... D-27

## IDEAL GAS THERMODYNAMIC FUNCTIONS OF 1-2-4- TRICHLORO BENZENE

TEMP	CP	(H-H)/T	(H-F)/T	S
298.15	30.88	18.58	71.36	89.94
300.00	31.02	18.66	71.47	90.13
350.00	34.52	20.68	74.50	95.18
400.00	37.68	22.61	77.39	100.00
450.00	40.48	24.44	80.16	104.60
500.00	42.96	26.17	82.82	109.00
550.00	45.13	27.80	85.39	113.19
600.00	47.04	29.32	87.88	117.20
650.00	48.72	30.75	90.28	121.04
700.00	50.21	32.09	92.61	124.70
750.00	51.54	33.34	94.87	128.21
800.00	52.72	34.52	97.06	131.58
850.00	53.79	35.62	99.19	134.81
900.00	54.75	36.66	101.25	137.91
950.00	55.62	37.63	103.26	140.89
1000.00	56.41	38.55	105.21	143.77
1100.00	57.78	40.24	108.97	149.21
1200.00	58.93	41.75	112.54	154.29
1300.00	59.90	43.11	115.93	159.04
1400.00	60.73	44.34	119.17	163.51
1500.00	61.44	45.46	122.27	167.73

## FREQUENCIES USED (1/CM)

3094.	3072.	1570.	1562.	1461.
1371.	1264.	1247.	1156.	1131.
1096.	1036.	816.	677.	575.
459.	398.	328.	211.	197.
942.	869.	811.	688.	550.
435.	305.	183.	117.	3072.

PRINCIPAL MOMENTS ... 1117.970 850.220 267.750

SYMMETRY NUMBER ..... 1.

MOLECULAR WEIGHT ..... 181.449

REFERENCE(S) ..... 62

UNITS ARE IN CAL/DEG KELVIN MOLE - PRESSURE ONE ATMOSPHERE

TABLE NUMBER ..... D-28

## IDEAL GAS THERMODYNAMIC FUNCTIONS OF 1-2-3- TRICHLORO BENZENE

TEMP	CP	(H-H)/T	(H-F)/T	S
298.15	30.77	18.57	69.90	88.47
300.00	30.91	18.64	70.02	88.66
350.00	34.42	20.65	73.04	93.69
400.00	37.59	22.57	75.93	98.50
450.00	40.41	24.40	78.69	103.09
500.00	42.89	26.13	81.35	107.48
550.00	45.07	27.75	83.92	111.67
600.00	46.99	29.28	86.40	115.68
650.00	48.68	30.71	88.80	119.51
700.00	50.18	32.04	91.13	123.17
750.00	51.51	33.30	93.38	126.68
800.00	52.70	34.47	95.57	130.04
850.00	53.77	35.58	97.69	133.27
900.00	54.73	36.62	99.75	136.37
950.00	55.61	37.59	101.76	139.35
1000.00	56.40	38.51	103.71	142.23
1100.00	57.78	40.20	107.46	147.67
1200.00	58.93	41.72	111.03	152.75
1300.00	59.90	43.08	114.42	157.50
1400.00	60.73	44.31	117.66	161.97
1500.00	61.44	45.43	120.76	166.19

## FREQUENCIES USED (1/CM)

3072.	1566.	1416.	1161.	1088.
1050.	738.	516.	352.	212.
3072.	1566.	1436.	1261.	1192.
791.	492.	400.	212.	896.
524.	212.	963.	773.	697.
500.	242.	90.	3060.	1156.

PRINCIPAL MOMENTS ... 929.010 592.080 336.920

SYMMETRY NUMBER ..... 2.

MOLECULAR WEIGHT ..... 181.449

REFERENCE(S) ..... 62

UNITS ARE IN CAL/DEG KELVIN MOLE - PRESSURE ONE ATMOSPHERE

TABLE NUMBER ..... D-29

## IDEAL GAS THERMODYNAMIC FUNCTIONS OF 1-2-3-5- TETRACHLORO BENZENE

TEMP	CP	(H-H)/T	(H-F)/T	S
298.15	34.60	21.20	74.30	95.50
300.00	34.73	21.28	74.43	95.72
350.00	38.15	23.45	77.88	101.33
400.00	41.18	25.49	81.14	106.63
450.00	43.85	27.38	84.26	111.64
500.00	46.18	29.15	87.23	116.38
550.00	48.21	30.79	90.09	120.88
600.00	49.98	32.32	92.84	125.15
650.00	51.53	33.74	95.48	129.22
700.00	52.89	35.06	98.03	133.09
750.00	54.09	36.29	100.49	136.78
800.00	55.16	37.43	102.87	140.30
850.00	56.11	38.51	105.17	143.68
900.00	56.96	39.51	107.40	146.91
950.00	57.72	40.45	109.56	150.01
1000.00	58.40	41.33	111.66	152.99
1100.00	59.59	42.93	115.67	158.61
1200.00	60.56	44.36	119.47	163.84
1300.00	61.38	45.64	123.08	168.72
1400.00	62.07	46.79	126.50	173.29
1500.00	62.65	47.83	129.77	177.60

## FREQUENCIES USED (1/CM)

3075.	1564.	1407.	1170.	1128.
1048.	835.	597.	381.	326.
206.	3076.	1546.	1377.	1250.
1191.	810.	521.	431.	215.
192.	871.	520.	215.	859.
692.	560.	313.	147.	80.

PRINCIPAL MOMENTS ... 1477.170 881.080 596.090

SYMMETRY NUMBER ..... 2.

MOLECULAR WEIGHT ..... 215.894

REFERENCE(S) ..... 62, 66

UNITS ARE IN CAL/DEG KELVIN MOLE - PRESSURE ONE ATMOSPHERE

TABLE NUMBER .....

## IDEAL GAS THERMODYNAMIC FUNCTIONS OF 1-2-4-5- TETRACHLORO BENZENE

TEMP	CP	(H-H)/T	(H-F)/T	S
298.15	34.61	21.18	72.84	94.03
300.00	34.74	21.27	72.98	94.24
350.00	38.17	23.44	76.42	99.86
400.00	41.20	25.48	79.68	105.16
450.00	43.86	27.37	82.79	110.17
500.00	46.19	29.14	85.77	114.91
550.00	48.22	30.79	88.63	119.41
600.00	49.99	32.31	91.37	123.69
650.00	51.53	33.73	94.02	127.75
700.00	52.89	35.06	96.56	131.62
750.00	54.09	36.29	99.02	135.31
800.00	55.16	37.43	101.40	138.84
850.00	56.10	38.50	103.71	142.21
900.00	56.95	39.50	105.94	145.44
950.00	57.71	40.44	108.10	148.54
1000.00	58.40	41.32	110.19	151.52
1100.00	59.58	42.93	114.21	157.14
1200.00	60.56	44.36	118.01	162.37
1300.00	61.38	45.64	121.61	167.25
1400.00	62.06	46.79	125.03	171.82
1500.00	62.65	47.83	128.30	176.13

## FREQUENCIES USED (1/CM)

3070.	1549.	1165.	684.	352.
190.	1566.	1240.	868.	511.
312.	3094.	1327.	1063.	510.
218.	1448.	1226.	1118.	645.
209.	348.	860.	681.	225.
600.	80.	878.	442.	140.

PRINCIPAL MOMENTS ... 1531.970 1088.370 433.600

SYMMETRY NUMBER ..... 4.

MOLECULAR WEIGHT ..... 215.894

REFERENCE(S) ..... 62, 66

UNITS ARE IN CAL/DEG KELVIN MOLE - PRESSURE ONE ATMOSPHERE

TABLE NUMBER ..... D-31

## IDEAL GAS THERMODYNAMIC FUNCTIONS OF 1-2-3-4- TETRACHLORO BENZENE

TEMP	CP	(H-H)/T	(H-F)/T	S
298.15	34.46	21.07	73.84	94.91
300.00	34.59	21.15	73.97	95.12
350.00	38.03	23.32	77.40	100.72
400.00	41.08	25.36	80.65	106.00
450.00	43.76	27.26	83.74	111.00
500.00	46.10	29.03	86.71	115.73
550.00	48.13	30.67	89.55	120.22
600.00	49.91	32.20	92.29	124.49
650.00	51.47	33.63	94.92	128.55
700.00	52.84	34.95	97.46	132.41
750.00	54.05	36.18	99.92	136.10
800.00	55.11	37.34	102.29	139.62
850.00	56.07	38.41	104.58	142.99
900.00	56.92	39.41	106.81	146.22
950.00	57.68	40.36	108.97	149.32
1000.00	58.37	41.24	111.06	152.30
1100.00	59.56	42.85	115.07	157.92
1200.00	60.54	44.29	118.86	163.15
1300.00	61.36	45.57	122.45	168.03
1400.00	62.06	46.72	125.87	172.60
1500.00	62.64	47.77	129.13	176.90

## FREQUENCIES USED (1/CM)

3068.	1557.	1368.	1247.	1175.
1130.	834.	515.	332.	223.
209.	3074.	1557.	1428.	1168.
1075.	775.	607.	482.	356.
209.	940.	706.	530.	307.
808.	557.	240.	116.	89.

PRINCIPAL MOMENTS ... 1367.540 933.790 433.750

SYMMETRY NUMBER ..... 2.

MOLECULAR WEIGHT ..... 215.894

REFERENCE(S) ..... 62

UNITS ARE IN CAL/DEG KELVIN MOLE - PRESSURE ONE ATMOSPHERE

TABLE NUMBER ..... D-32

## IDEAL GAS THERMODYNAMIC FUNCTIONS OF PENTACHLORO BENZENE

TEMP	CP	(H-H)/T	(H-F)/T	S
298.15	38.24	23.74	77.91	101.65
300.00	38.37	23.83	78.06	101.89
350.00	41.71	26.15	81.91	108.06
400.00	44.62	28.28	85.54	113.82
450.00	47.15	30.24	88.99	119.23
500.00	49.34	32.04	92.27	124.31
550.00	51.23	33.70	95.40	129.11
600.00	52.87	35.23	98.40	133.64
650.00	54.29	36.65	101.28	137.93
700.00	55.53	37.95	104.04	141.99
750.00	56.60	39.16	106.70	145.86
800.00	57.55	40.28	109.27	149.55
850.00	58.39	41.32	111.74	153.06
900.00	59.13	42.29	114.13	156.42
950.00	59.78	43.19	116.44	159.64
1000.00	60.37	44.04	118.68	162.72
1100.00	61.36	45.57	122.95	168.52
1200.00	62.17	46.92	126.97	173.89
1300.00	62.84	48.12	130.78	178.90
1400.00	63.39	49.19	134.38	183.58
1500.00	63.86	50.16	137.81	187.97

## FREQUENCIES USED (1/CM)

3065.	1523.	1338.	1198.	1086.
823.	562.	387.	344.	215.
200.	1554.	1399.	1235.	1166.
868.	683.	556.	320.	225.
215.	597.	343.	80.	863.
701.	526.	270.	147.	95.

PRINCIPAL MOMENTS ... 1826.350 1105.960 720.340

SYMMETRY NUMBER ..... 2.

MOLECULAR WEIGHT .... 250.339

REFERENCE(S) ..... 62, 66

UNITS ARE IN CAL/DEG KELVIN MOLE - PRESSURE ONE ATMOSPHERE

TABLE NUMBER ..... D-33

## IDEAL GAS THERMODYNAMIC FUNCTIONS OF HEXACHLORO BENZENE

TEMP	CP	(H-H)/T	(H-F)/T	S
298.15	41.90	26.26	77.88	104.13
300.00	42.03	26.35	78.04	104.39
350.00	45.28	28.83	82.29	111.12
400.00	48.07	31.07	86.29	117.36
450.00	50.47	33.09	90.07	123.16
500.00	52.52	34.94	93.65	128.59
550.00	54.28	36.62	97.06	133.68
600.00	55.78	38.15	100.31	138.47
650.00	57.07	39.56	103.42	142.98
700.00	58.18	40.85	106.40	147.25
750.00	59.13	42.04	109.26	151.30
800.00	59.96	43.13	112.01	155.14
850.00	60.68	44.14	114.66	158.80
900.00	61.31	45.08	117.21	162.29
950.00	61.86	45.95	119.67	165.62
1000.00	62.34	46.76	122.05	168.80
1100.00	63.15	48.21	126.57	174.78
1200.00	63.79	49.48	130.82	180.31
1300.00	64.30	50.61	134.83	185.43
1400.00	64.72	51.60	138.62	190.22
1500.00	65.06	52.49	142.21	194.69

## FREQUENCIES USED (1/CM)

1210.	372.	1108.	369.	630.
1224.	230.	1512.	870.	323.
219.	1350.	699.	218.	340.
594.	80.	1512.	870.	323.
219.	1350.	699.	218.	340.
594.	80.	209.	704.	97.

PRINCIPAL MOMENTS ... 2225.240 1118.180 1107.060

SYMMETRY NUMBER ..... 12.

MOLECULAR WEIGHT ..... 284.784

REFERENCE(S) ..... 62, 66

UNITS ARE IN CAL/DEG KELVIN MOLE - PRESSURE ONE ATMOSPHERE

TABLE NUMBER ..... D-34

## IDEAL GAS THERMODYNAMIC FUNCTIONS OF 1-2- DIBROMO BENZENE

TEMP	CP	(H-H)/T	(H-F)/T	S
298.15	27.99	16.92	69.51	86.43
300.00	28.13	16.99	69.61	86.61
350.00	31.60	18.83	72.37	91.21
400.00	34.79	20.63	75.01	95.64
450.00	37.67	22.37	77.54	99.90
500.00	40.22	24.03	79.98	104.01
550.00	42.48	25.61	82.34	107.95
600.00	44.49	27.10	84.64	111.73
650.00	46.27	28.50	86.86	115.37
700.00	47.86	29.83	89.02	118.85
750.00	49.28	31.08	91.12	122.21
800.00	50.56	32.26	93.17	125.43
850.00	51.72	33.37	95.16	128.53
900.00	52.78	34.42	97.10	131.51
950.00	53.73	35.41	98.98	134.39
1000.00	54.61	36.35	100.82	137.17
1100.00	56.15	38.08	104.37	142.45
1200.00	57.45	39.64	107.75	147.40
1300.00	58.56	41.06	110.98	152.04
1400.00	59.51	42.34	114.07	156.41
1500.00	60.32	43.51	117.03	160.55

## FREQUENCIES USED (1/CM)

3082.	3082.	3062.	3062.	1568.
1560.	1445.	1429.	1267.	1255.
1161.	1108.	1074.	1035.	1013.
983.	943.	852.	748.	703.
660.	643.	531.	434.	374.
316.	257.	220.	200.	134.

PRINCIPAL MOMENTS ... 1031.430 517.480 513.950

SYMMETRY NUMBER ..... 2.

MOLECULAR WEIGHT .... 235.916

REFERENCE(S) ..... 56, 67

UNITS ARE IN CAL/DEG KELVIN MOLE - PRESSURE ONE ATMOSPHERE

TABLE NUMBER ..... D-35

## IDEAL GAS THERMODYNAMIC FUNCTIONS OF 1-3- DIBROMO BENZENE

TEMP	CP	(H-H)/T	(H-F)/T	S
298.15	28.04	17.15	70.54	87.69
300.00	28.17	17.21	70.65	87.86
350.00	31.59	19.03	73.44	92.46
400.00	34.76	20.80	76.09	96.89
450.00	37.61	22.51	78.64	101.15
500.00	40.16	24.15	81.10	105.25
550.00	42.42	25.71	83.48	109.19
600.00	44.42	27.19	85.78	112.96
650.00	46.20	28.58	88.01	116.59
700.00	47.79	29.90	90.18	120.07
750.00	49.22	31.14	92.28	123.42
800.00	50.51	32.31	94.33	126.64
850.00	51.67	33.42	96.32	129.74
900.00	52.73	34.46	98.26	132.72
950.00	53.69	35.45	100.15	135.60
1000.00	54.57	36.38	101.99	138.38
1100.00	56.12	38.11	105.54	143.65
1200.00	57.42	39.66	108.93	148.59
1300.00	58.54	41.07	112.16	153.23
1400.00	59.49	42.36	115.25	157.61
1500.00	60.31	43.53	118.21	161.74

## FREQUENCIES USED (1/CM)

3085.	3070.	3059.	3059.	1573.
1564.	1455.	1410.	1291.	1258.
1162.	1112.	1097.	1067.	1020.
994.	894.	869.	769.	725.
672.	648.	482.	431.	354.
309.	288.	196.	158.	133.

PRINCIPAL MOMENTS ... 1605.030 1374.040 230.990

SYMMETRY NUMBER ..... 2.

MOLECULAR WEIGHT .... 235.916

REFERENCE(S) ..... 56, 67

UNITS ARE IN CAL/DEG KELVIN MOLE - PRESSURE ONE ATMOSPHERE

TABLE NUMBER ..... D-36

## IDEAL GAS THERMODYNAMIC FUNCTIONS OF 1-4- DIBROMO BENZENE

TEMP	CP	(H-H)/T	(H-F)/T	S
298.15	28.94	17.44	68.89	86.33
300.00	29.08	17.51	69.00	86.51
350.00	32.60	19.42	71.84	91.26
400.00	35.78	21.27	74.56	95.83
450.00	38.61	23.04	77.17	100.21
500.00	41.11	24.73	79.68	104.41
550.00	43.30	26.32	82.12	108.43
600.00	45.24	27.81	84.47	112.28
650.00	46.96	29.22	86.75	115.98
700.00	48.49	30.54	88.97	119.51
750.00	49.86	31.79	91.12	122.90
800.00	51.09	32.96	93.21	126.16
850.00	52.21	34.06	95.24	129.29
900.00	53.22	35.09	97.21	132.31
950.00	54.15	36.07	99.14	135.21
1000.00	54.99	37.00	101.01	138.01
1100.00	56.48	38.70	104.62	143.32
1200.00	57.73	40.24	108.05	148.29
1300.00	58.81	41.63	111.33	152.96
1400.00	59.72	42.89	114.46	157.35
1500.00	60.52	44.04	117.46	161.50

## FREQUENCIES USED (1/CM)

3080.	3068.	3068.	3050.	1570.
1570.	1468.	1381.	1251.	1170.
1100.	1067.	1066.	1003.	950.
935.	815.	807.	708.	685.
623.	473.	429.	400.	307.
271.	218.	173.	103.	623.

PRINCIPAL MOMENTS ... 1891.210 1801.690 89.520

SYMMETRY NUMBER ..... 4.

MOLECULAR WEIGHT .... 235.916

REFERENCE(S) ..... 56, 67, 68, 70

UNITS ARE IN CAL/DEG KELVIN MOLE - PRESSURE ONE ATMOSPHERE

TABLE NUMBER ..... D-37

## IDEAL GAS THERMODYNAMIC FUNCTIONS OF 1-3-5- TRIBROMO BENZENE

TEMP	CP	(H-H)/T	(H-F)/T	S
298.15	32.21	20.29	75.01	95.30
300.00	32.34	20.37	75.14	95.50
350.00	35.65	22.32	78.42	100.74
400.00	38.66	24.18	81.53	105.70
450.00	41.34	25.94	84.48	110.41
500.00	43.70	27.60	87.30	114.89
550.00	45.78	29.16	90.00	119.16
600.00	47.62	30.62	92.60	123.22
650.00	49.24	31.99	95.11	127.10
700.00	50.67	33.28	97.52	130.80
750.00	51.95	34.48	99.86	134.34
800.00	53.09	35.61	102.12	137.73
850.00	54.12	36.67	104.31	140.98
900.00	55.05	37.66	106.44	144.10
950.00	55.89	38.60	108.50	147.10
1000.00	56.66	39.48	110.50	149.99
1100.00	57.99	41.11	114.34	155.45
1200.00	59.11	42.56	117.98	160.55
1300.00	60.06	43.87	121.44	165.32
1400.00	60.86	45.06	124.74	169.80
1500.00	61.55	46.14	127.89	174.02

## FREQUENCIES USED (1/CM)

3073.	1115.	985.	241.	1319.
1199.	435.	3090.	1557.	1408.
1099.	742.	348.	118.	870.
509.	193.	3090.	1557.	1408.
1099.	742.	348.	118.	870.
509.	193.	849.	659.	113.

PRINCIPAL MOMENTS ... 2743.070 1371.780 1371.280

SYMMETRY NUMBER ..... 6.

MOLECULAR WEIGHT .... 314.897

REFERENCE(S) ..... 55

UNITS ARE IN CAL/DEG KELVIN MOLE - PRESSURE ONE ATMOSPHERE

TABLE NUMBER ..... D-38

## APPENDIX E

Real Gas Thermodynamic Functions for Fluorobenzene from 0.25 to 10 Atmospheres

E-1	10 atm.
E-2	5 atm.
E-3	2 atm.
E-4	1 atm.
E-5	0.25 atm.

## REAL GAS THERMODYNAMIC FUNCTIONS OF FLUOROBENZENE

TEMP	CP	(H-H)/T	(H-F)/T	S
273.15	30.34	7.38	55.23	62.61
298.15	30.02	9.29	55.96	65.25
300.00	30.03	9.42	56.02	65.44
350.00	31.06	12.42	57.71	70.13
400.00	33.03	14.86	59.53	74.40
450.00	35.29	17.01	61.41	78.42
500.00	37.54	18.95	63.30	82.25
550.00	39.68	20.74	65.19	85.93
600.00	41.67	22.40	67.07	89.47
650.00	43.49	23.95	68.92	92.88
700.00	45.15	25.41	70.75	96.16
750.00	46.68	26.78	72.55	99.33
800.00	48.07	28.06	74.32	102.39
850.00	49.35	29.28	76.06	105.34
900.00	50.52	30.43	77.77	108.20
950.00	51.60	31.51	79.44	110.96
1000.00	52.59	32.54	81.09	113.63

## FREQUENCIES USED (1/CM)

519.	808.	1008.	1022.	1157.
1220.	1499.	1596.	3044.	3067.
3101.	405.	614.	1066.	1157.
1236.	1323.	1460.	1603.	3058.
3091.	405.	826.	970.	242.
500.	685.	754.	894.	997.

PRINCIPAL MOMENTS ...	89.230	196.642	285.949
SYMMETRY NUMBER .....	2.		
MOLECULAR WEIGHT ....	96.100		
PRESSURE (ATM) .....	10.00		
CRITICAL TEMPERATURE	560.10		
CRITICAL PRESSURE ...	44.60		

TABLE NUMBER ..... E-1

## REAL GAS THERMODYNAMIC FUNCTIONS OF FLUOROBENZENE

TEMP	CP	(H-H)/T	(H-F)/T	S
273.15	25.48	9.78	55.83	65.61
298.15	26.28	11.13	56.75	67.88
300.00	26.36	11.22	56.82	68.04
350.00	28.75	13.55	58.73	72.27
400.00	31.48	15.62	60.67	76.29
450.00	34.20	17.53	62.62	80.16
500.00	36.75	19.33	64.57	83.89
550.00	39.09	21.02	66.49	87.51
600.00	41.21	22.62	68.39	91.00
650.00	43.13	24.12	70.26	94.38
700.00	44.86	25.54	72.10	97.64
750.00	46.44	26.88	73.90	100.79
800.00	47.87	28.15	75.68	103.83
850.00	49.18	29.35	77.42	106.77
900.00	50.38	30.49	79.13	109.62
950.00	51.48	31.56	80.81	112.37
1000.00	52.49	32.58	82.46	115.04

## FREQUENCIES USED (1/CM)

519.	808.	1008.	1022.	1157.
1220.	1499.	1596.	3044.	3067.
3101.	405.	614.	1066.	1157.
1236.	1323.	1460.	1603.	3058.
3091.	405.	826.	970.	242.
500.	685.	754.	894.	997.

PRINCIPAL MOMENTS ...	89.230	196.642	285.949
SYMMETRY NUMBER .....	2.		
MOLECULAR WEIGHT .....	96.100		
PRESSURE (ATM) .....	5.00		
CRITICAL TEMPERATURE	560.10		
CRITICAL PRESSURE ...	44.60		

TABLE NUMBER ..... E-2

## REAL GAS THERMODYNAMIC FUNCTIONS OF FLUOROBENZENE

TEMP	CP	(H-H)/T	(H-F)/T	S
273.15	22.56	11.22	57.19	68.41
298.15	24.04	12.23	58.21	70.44
300.00	24.15	12.30	58.29	70.59
350.00	27.36	14.22	60.33	74.56
400.00	30.56	16.07	62.35	78.42
450.00	33.55	17.85	64.35	82.19
500.00	36.28	19.56	66.32	85.87
550.00	38.73	21.19	68.26	89.45
600.00	40.93	22.74	70.17	92.91
650.00	42.91	24.22	72.05	96.27
700.00	44.69	25.62	73.90	99.52
750.00	46.30	26.95	75.71	102.65
800.00	47.76	28.20	77.49	105.69
850.00	49.09	29.39	79.23	108.63
900.00	50.30	30.52	80.95	111.47
950.00	51.41	31.59	82.62	114.22
1000.00	52.43	32.61	84.27	116.88

## FREQUENCIES USED (1/CM)

519.	808.	1008.	1022.	1157.
1220.	1499.	1596.	3044.	3067.
3101.	405.	614.	1066.	1157.
1236.	1323.	1460.	1603.	3058.
3091.	405.	826.	970.	242.
500.	685.	754.	894.	997.

PRINCIPAL MOMENTS ...	89.230	196.642	285.949
SYMMETRY NUMBER .....	2.		
MOLECULAR WEIGHT ....	96.100		
PRESSURE (ATM) .....	2.00		
CRITICAL TEMPERATURE	560.10		
CRITICAL PRESSURE ...	44.60		

TABLE NUMBER ..... E-3

## REAL GAS THERMODYNAMIC FUNCTIONS OF FLUOROBENZENE

TEMP	CP	(H-H)/T	(H-F)/T	S
273.15	21.59	11.70	58.41	70.11
298.15	23.29	12.60	59.47	72.07
300.00	23.42	12.67	59.55	72.22
350.00	26.90	14.45	61.64	76.09
400.00	30.25	16.22	63.68	79.90
450.00	33.33	17.95	65.69	83.64
500.00	36.12	19.63	67.67	87.30
550.00	38.61	21.25	69.62	90.86
600.00	40.84	22.79	71.53	94.32
650.00	42.84	24.25	73.42	97.67
700.00	44.63	25.65	75.27	100.91
750.00	46.25	26.97	77.08	104.05
800.00	47.72	28.22	78.86	107.08
850.00	49.06	29.41	80.61	110.01
900.00	50.27	30.53	82.32	112.85
950.00	51.39	31.60	84.00	115.60
1000.00	52.41	32.62	85.65	118.26

## FREQUENCIES USED (1/CM)

519.	808.	1008.	1022.	1157.
1220.	1499.	1596.	3044.	3067.
3101.	405.	614.	1066.	1157.
1236.	1323.	1460.	1603.	3058.
3091.	405.	826.	970.	242.
500.	685.	754.	894.	997.

PRINCIPAL MOMENTS ...	89.230	196.642	285.949
SYMMETRY NUMBER .....	2.		
MOLECULAR WEIGHT .....	96.100		
PRESSURE (ATM) .....	1.00		
CRITICAL TEMPERATURE	560.10		
CRITICAL PRESSURE ...	44.60		

TABLE NUMBER .....

E-4

## REAL GAS THERMODYNAMIC FUNCTIONS OF FLUOROBENZENE

TEMP	CP	(H-H)/T	(H-F)/T	S
273.15	20.86	12.06	61.05	73.11
298.15	22.73	12.88	62.14	75.01
300.00	22.87	12.94	62.22	75.15
350.00	26.55	14.62	64.34	78.96
400.00	30.01	16.33	66.40	82.73
450.00	33.17	18.03	68.42	86.45
500.00	36.00	19.69	70.41	90.10
550.00	38.52	21.29	72.36	93.65
600.00	40.77	22.82	74.28	97.10
650.00	42.78	24.28	76.16	100.44
700.00	44.59	25.67	78.01	103.68
750.00	46.22	26.98	79.83	106.81
800.00	47.69	28.23	81.61	109.84
850.00	49.03	29.42	83.36	112.78
900.00	50.25	30.54	85.07	115.61
950.00	51.37	31.61	86.75	118.36
1000.00	52.40	32.62	88.40	121.02

## FREQUENCIES USED (1/CM)

519.	808.	1008.	1022.	1157.
1220.	1499.	1596.	3044.	3067.
3101.	405.	614.	1066.	1157.
1236.	1323.	1460.	1603.	3058.
3091.	405.	826.	970.	242.
500.	685.	754.	894.	997.

PRINCIPAL MOMENTS ...	89.230	196.642	285.949
SYMMETRY NUMBER .....	2.		
MOLECULAR WEIGHT .....	96.100		
PRESSURE (ATM) .....	0.25		
CRITICAL TEMPERATURE	560.10		
CRITICAL PRESSURE ...	44.60		

TABLE NUMBER .....

E-5