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ESTIMATED THERMODYNAMIC FUNCTIONS FOR SOME CHLORINATED BENZENES, PHENOLS AND DIOXINS

WALTER M. SHAUB

Chemical Kinetics Division, National Bureau of Standards, Washington, DC 20234 (U.S.A.)

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ABSTRACT

Procedures for estimating the values of gas phase thermodynamic functions for a large number of chlorinated benzenes, phenols and dioxins (dibenzo-*p*-dioxins) have been developed from estimated values of molecular parameters. Structurally similar model compounds were used to make frequency assignments and, when available, interatomic distances were taken from the literature. Symmetry numbers were assigned based upon known structures.

INTRODUCTION

Equilibrium thermodynamic characterizations of the combustion properties of fuel–air mixtures are often utilized by scientists and engineers to gain some initial insight about the likely behavior of systems under various conditions which are representative of problems of practical interest. Considerable attention has been directed recently towards developing an understanding of the behavior of hazardous waste materials during the process of incineration. Some concern exists at to the destruction efficiency for chlorinated hazardous waste materials such as 2, 3, 7, 8-tetrachlorodibenzo-*p*-dioxin (an extremely toxic substance), which has been reported to have been found at parts per trillion levels in effluents from municipal incinerators [2,3]. As substances such as dioxins, dibenzofurans and related compounds present a potential danger to human health, it is highly desirable to develop a rational base of thermodynamic and kinetic information which will permit scientists and engineers to properly evaluate and determine the conditions under which hazardous waste materials may be efficiently and safely incinerated. In addition, this work responds to a congressional mandate for the National Bureau of Standards to develop such data, as directed under Section 5002 of the Resource Conservation Recovery Act of 1976 (RCRA) and through support from the NBS Office of Recycled Materials and the DOE Office of Energy for Municipal Waste.

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At the present time, a number of sophisticated computer programs have been developed, the NASA–LEWIS equilibrium computer program being a good example [1] of what is generally available for performing equilibrium characterizations. Regardless of what conditions and geometries are initially specified, virtually all of these programs require that thermodynamic functions for all chemical species should be specified. Characteristically, this has been done by way of auxilliary input files in which thermodynamic data are cast into the form of a high-order polynomial representation from which the value of a particular thermodynamic function at any given temperature (within the range of the polynomial formulation) can be recovered [1,4–6]. Specifications of thermodynamic functions are available [1,4–9] for a large number of inorganic and organic molecules. Most commonly, these specifications are for compounds as they exist in the gas phase, although there are a number of exceptions, particularly in the case of stable inorganic molecules. There is, however, a sparsity of thermodynamic information for a very large number of compounds, including many of recent interest such as the dioxins [10,11].

In this paper, I address this problem area in an attempt to generate some interim thermodynamic functions for the chlorinated compounds mentioned above. In principle, the thermodynamic functions can be determined from a knowledge of the molecular parameters which characterize these molecules [5,9]. In a previous paper [12], I have discussed methods for estimating the gas phase heat of formation for these compounds. If the heat capacity and entropy of these compounds were known as a function of temperature, it would then be possible to develop tabulations of the corresponding thermodynamic functions, as in the JANAF tables [7]. In order to specify the heat capacity and entropy of any molecule, one must have knowledge of various molecular parameters, including the product of the principal moments of inertia, the vibrational frequencies, molecular weight and symmetry number. Other parameters are sometimes needed (e.g. in the case of hindered rotation) and must also be specified as required. The procedure for utilizing these molecular parameters in the calculation of thermodynamic functions is detailed, for example, in Benson's monograph [9] and is illustrated briefly in the Appendix. Unfortunately, in the case of some phenols and dioxins there is very little information available in the literature regarding values for those molecular parameters, with the exception of some interatomic distance data, useful in determining the principal moments of inertia [13–18]. It is necessary, therefore, to estimate values of molecular parameters, particularly vibrational frequencies, using model compounds. If this is done with reasonable care, the errors in the thermodynamic entropy and heat capacity functions may be kept small. Benson [9] and others [21,22] have discussed the extent of the errors to be expected. In general, uncertainties are not so severe as to preclude the use of the thermodynamic data generated in this way (to be described below) for equilibrium thermodynamic studies of many interesting systems.

The tables of JANAF type data which accompany this paper are to be regarded strictly as estimates to which further refinements can be made as needed. As presented here, these estimates are adequate for determining whether or not thermodynamic equilibrium controls the destruction of chlorinated organic compounds at elevated temperatures. Use of these tables, however, for other purposes should be made with caution due to the limited availability of reliable experimental data for chlorinated organic compounds.

MOMENTS OF INERTIA DETERMINATIONS

Calculation of the principal moments of inertia is, in principle, straightforward once all bond angles and interatomic distances have been specified [24]. In the case of chlorinated benzenes, a planar hexagonal structure may be reasonably assumed in which all bond angles are 120° and C–C, C–H and C–Cl bond distances are about 1.40, 1.08 and 1.70 Å, respectively [16–20,23]. There are some variations reported in the literature, but they are not substantial to the extent that one would expect significant errors in the moments of inertia calculations in the sense of how these values impact upon thermodynamic function evaluations. In the case of the chlorinated phenols, the $\mathrm{C}\overset{\mathrm{O}}{\diagup\,\diagdown}\mathrm{H}$ bond angle is assumed to be 135° with the hydroxyl group hydrogen atom assumed to lie in the plane of the benzene ring. This is not the actual case, but the mass of the hydrogen atom is small and therefore this approximation, as discussed above, should also not lead to substantial errors in calculating thermodynamic functions. The C–O and O–H bond distances in the phenols are about 1.38 and 1.02 Å, respectively [13,17,18,20]. Comments regarding C–C and C–H bond distances apply as before. All other bond angles are about 120°. Bond angles and interatomic distances have been reported for a few chlorinated dioxins [14,15]. In terms of the determination of the thermodynamic functions for these compounds, a planar structure may be reasonably assumed as an approximation in which all bond angles are taken to be 120° and the C–C, C–O, C–H and C–Cl bond distances are taken as 1.40. 1.40, 1.08 and 1.734 Å, respectively. In Table 1, I present the moments of inertia which have been calculated, using the above data, for several chlorinated benzenes, phenols and dioxins.

FREQUENCY ASSIGNMENTS

Vibrational frequency assignments for the chlorinated benzenes have been reported in the literature [23,25–30]. These assignments can be utilized as described below for making estimations of frequency assignments in chlorinated phenols and dioxins. In the case of chlorinated phenols, it is useful to start with the chlorinated benzenes in making frequency assignments. By way of an example, consider the changes in frequencies one should make in going from 1, 2, 4-trichlorobenzene to 2, 4, 5-trichlorophenol. Basically, there will be two types of change: (i) three additional frequencies must be accounted for due to the extra atom in the phenol and (ii) several frequencies must be adjusted. In Table 2, I show the reported vibrational frequencies for benzene [31] and phenol [32] hierarchically arranged in order of decreasing frequencies. As an approximation, it is seen from Table 2 that, in going from benzene to phenol, one can start with the frequencies reported for benzene and then (i) drop $\nu = 3069$ cm^{-1}, (ii) add $\nu = 3656$, 403, 309 and 225 cm^{-1} and (iii) where differences in ν of $\gtrsim \pm 10\%$ are noted in going from benzene to phenol, the corresponding frequencies in the set specified for benzene should be adjusted accordingly (e.g. the frequencies in benzene of 1038, 975, 606 and 410 cm^{-1} should be adjusted by +10.8, −9.4, −13.2 and +22.7% respectively.) The resulting adjustments in the original set of frequencies reported for benzene now approximate the reported frequency set for phenol [32] to the extent that use of this 'adjusted' benzene set in computing

TABLE 1

Computed moments of inertia

Molecule	$I_x I_y I_z$ (g cm^2)^3
Dibenzo-*p*-dioxin	2.30×10^{-111}
1,2,3-Trichlorobenzene	8.40×10^{-112}
2,4,5-Trichlorophenol	2.49×10^{-111}
1-Chlorodibenzo-*p*-dioxin	7.61×10^{-111}
2-Chlorodibenzo-*p*-dioxin	5.80×10^{-111}
Octachlorodibenzo-*p*-dioxin	3.92×10^{-109}
2,3,7,8-Tetrachlorodibenzo-*p*-dioxin	8.46×10^{-110}
2,3-Dichlorophenol	4.74×10^{-112}
2,4-Dichlorophenol	6.68×10^{-112}
2,5-Dichlorophenol	5.95×10^{-112}
3,4-Dichlorophenol	5.88×10^{-112}
Anthracene	2.51×10^{-111}

TABLE 2

Frequencies (cm^{-1}) reported for benzene [31] and phenol [32]

Benzene	Phenol	Benzene	Phenol
	3656	1038	1070
3068		1010	1025
3063	3087	995	999
3063	3070	992	973
3062	3063	975	958
3047	3049	975	881
3047	3027	849	823
1596	1610	849	817
1596	1603	703	751
1486	1501	673	686
1486	1472	606	619
1326	1343	606	526
1310	1277	410	503
1178	1261	410	409
1178	1176		403
1150	1168		309
1038	1150		225

thermodynamic functions for phenol will lead to values very close to those reported in the literature [8,32]. In the case of going from 1, 2, 4-trichlorobenzene to 2, 4, 5-trichlorophenol, the procedure is exactly analogous. The frequencies reported for 1, 2, 4-trichlorobenzene [25] are used as a model starting set. Any one of the three frequencies corresponding to a C–H stretch may be dropped (e.g. 3094 cm^{-1}) and replaced with the O–H stretching frequency taken as 3656 cm^{-1}. Following the previous prescription given above, one then also adds $\nu = 403$, 309 and 221 cm^{-1}. Finally, it is necessary to examine the frequencies reported for 1, 2, 4-trichlorobenzene, choose the frequencies in this set which are closest in value to those in benzene which were adjusted, and to make the same adjustments ($\pm$%) here also. This procedure may be used in estimating frequencies for any other chlorinated phenol in an exactly analogous manner by starting with the appropriate chlorinated benzene frequency set as an initial model. Since the torsional frequency for the OH group in phenol is low [32], it should not make much difference whether or not OH is treated as a free rotor in the calculation of the thermodynamic functions for the chlorinated phenols, particularly since there are already present many low frequencies due to chlorine atom substitution. Similar remarks apply to effects due to possible hydrogen bonding when the Cl atom is *ortho* to the OH group.

In the case of chlorinated dioxins, it is useful to make adjustments in two steps. The first step is to start with anthracene as a model compound and to determine what frequency adjustments should be made in going from the frequency set chosen for anthracene to the frequency set to be developed for dioxin (dibenzo-*p*-dioxin). A complete set of vibrational frequencies can be assigned for anthracene by using the non-planar vibrational frequencies reported by Evans and Scully [33] together with the frequencies reported for the planar vibrational frequencies by Neto et al. [34] or Cyvin and Cyvin [35]. The frequencies are reported in Table 3. As an initial check on the validity of this combined set of vibrational frequencies for anthracene, the gas phase entropy for anthracene at 298 K was computed. The principal moments of inertia were determined assuming a planar geometry, with C–C and C–H bond distances of 1.40 and 1.08 Å assumed, respectively, and with all bond angles set equal to 120°. D_{2h} symmetry was assumed, corresponding to a symmetry number, $\sigma = 4$. The resulting value computed for the gas phase entropy at 298 K, using the combined frequencies of Evans and Scully [33] and Neto et al. [34], was $S^{\circ}_{298,g} = 92.246$ e.u. This is to be compared with values reported in the literature of 92.0 e.u. [36], 94.4 e.u. [36], 95.3 e.u. [37], 93.8 e.u. [37] and 92.5 e.u. [38]. Agreement is seen to be quite good. Thus the assigned set of frequencies for anthracene seems reasonable, as used for calculation of thermodynamic functions. Note that in going from benzene to cyclohexane, which has no aromatic character, the frequencies (in cm^{-1}) generally decrease, on the average, by about 30–40% [31]. As one proceeds structurally from anthracene to dioxin, there is a loss of some aromatic character due to replacement of two CH groups in the apex positions of the central ring with oxygen atoms. A considerable amount of double bond character is retained in the central ring, however, due to the two adjacent outer aromatic rings. Thus the lowering of frequencies (in cm^{-1}) in this case is not expected to be as pronounced as in the case of going from benzene to cyclohexane. An estimate of about a 15% lowering is probably reasonable. The adjustments in frequencies in going from anthracene to dioxin can now be estimated as follows. There are 66 vibrational modes in anthracene and 60 in dioxin. This decrease is due to replacement of two CH groups with two O atoms and can be accounted for by dropping out six frequencies: two due to in-plane C–H stretching vibrations (e.g. 3055, 3048 cm^{-1}), two due to in-plane C–H bending vibrations (e.g. numerically those at about 1165 and 1125 cm^{-1}), and two due to out-of-plane C–H bending vibrations (e.g. numerically those at about 886 and 907 cm^{-1}). Due to the loss of aromatic character in the central ring, assume

(i) Of the 21 ring deformations (10 are in plane), about one third of the associated frequencies are lowered (in cm^{-1}), as an estimate, corresponding approximately to an adjustment of 3 in-plane ring deformations and 4

TABLE 3

Frequencies (cm^{-1}) reported for anthracene [33,34] and dibenzo-*p*-dioxin (ungrouped and grouped)

Anthracene		Dibenzo-*p*-dioxin		
		Ungrouped		Grouped [a]
3100	886	3100	745	3056 (8)
3088	871	3088	739	1493 (11)
3079	860	3079	652	1226 (8)
3067	826	3063	651	992 (7)
3055	810	3049	603	904.5 (2)
3049	754	3041	601	865.5 (2)
3048	745	3022	601	826
3041	739	3006	552	810
3022	652	1631	524	749.5 (2)
3006	651	1620	512	736
1631	617	1596	444	652
1620	603	1561	400	651
1596	602	1533	369	603
1561	552	1460	325	601 (2)
1533	522	1460	273	552
1481	475	1448	244	524
1462	466	1384	235	512
1448	400	1384	137	444
1403	383	1346	96	400
1398	369	1316		369
1385	321	1274		325
1346	244	1264		273
1316	235	1261		244
1274	137	1188		235
1264	96	1188		137
1261		1169		96
1188		1150		
1169		1100		
1165		1007		
1150		999		
1125		979		
1100		960		
1007		957		
999		936		
979		909		
960		900		
957		871		
936		860		
909		826		
907		810		
900		754		

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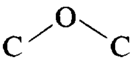
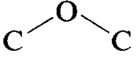
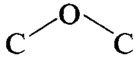
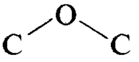
[a] Numbers in parentheses are degeneracies.

out-of-plane ring deformations. Two of these adjusted out-of-plane ring deformations may be thought of approximately as  $\mathrm{C}\overset{\mathrm{O}}{\diagup\diagdown}\mathrm{C}$ out-of-plane ring deformations. Choosing furan as a model [39], these frequencies numerically have values of about 601 cm^{-1}. Operationally then, as an estimate, two anthracene out-of-plane ring deformations (e.g. numerically those at about 475 and 466 cm^{-1}) are to be replaced with  $\mathrm{C}\overset{\mathrm{O}}{\diagup\diagdown}\mathrm{C}$ out-of-plane deformations at about 601 cm^{-1} and the remaining two anthracene out-of-plane ring deformations (e.g. numerically those at about 383 and 321 cm^{-1}) as well as three anthracene in-plane ring deformations (e.g. numerically those at about 522, 602 and 617 cm^{-1}) should be lowered by ~15% as follows from the discussion above.

(ii) Of the 15 in-plane ring stretches, again, about one third of the associated frequencies are to be lowered. Four of these stretches may be associated with in-plane symmetric and anti-symmetric  $\mathrm{C}\overset{\mathrm{O}}{\diagup\diagdown}\mathrm{C}$ ring stretches, which, again using furan as a model [39], numerically have values of about 1384, 1384, 1460 and 1460 cm^{-1}. Operationally, as an estimate, four anthracene in-plane ring stretches at about 1385, 1403, 1462 and 1481 cm^{-1} are replaced with the above  $\mathrm{C}\overset{\mathrm{O}}{\diagup\diagdown}\mathrm{C}$ ring stretching frequencies and one anthracene in-plane ring stretch, numerically about 1398 cm^{-1} should be reduced by about 15%.

Frequency adjustments in going from anthracene to dioxin, as discussed above, are summarized in Table 3. These frequencies for dioxin, by the nature of the way in which they have been chosen, are to be regarded in the sense of estimates. However, it should be noted that a requirement of knowing exactly what the true frequencies for dioxin in fact are, is not necessary. This is because, except for the very lowest frequencies, a good deal of uncertainty is acceptable due to the way in which these frequencies are used in developing thermodynamic functions [9]. I will, in fact, show shortly by way of dioxin as an example that the effect of using an average frequency for several groups of frequencies in computing values for thermodynamic functions is acceptable.

As I have mentioned previously, in making estimates of frequency assignments for chlorinated dioxins, it is useful to make adjustments in two steps. The first step, described above, has been to adjust frequencies in going from anthracene as a model, to dioxin (dibenzo-*p*-dioxin). The second step is to make adjustments in frequencies associated with dioxin due to chlorination. As in the case of going from chlorinated benzenes to chlorinated phenols, a useful approach is to choose a useful model and to then hierarchically order and identify required adjustments. If one examines the possible chlorinated dioxins, it is to be noted that the degree of substitution on either aromatic ring in the dioxin molecule is analogous to the degree of ring substitution in the mono-, *ortho*-, *meta*-, *para*-, 1, 2, 3-, 1, 2, 4- and 1, 2, 3, 4-chlorine substituted benzenes for which frequency assignments have been made [23,25–30] and are reported in Table 4. Thus, it is useful to use these frequency assignments for the chlorinated benzenes as models for estimating the required asjustments in the chlorine-substituted dioxins. The procedure for utilizing the frequency assignments for the chlorine-substituted benzenes

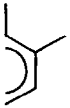
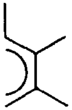
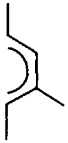
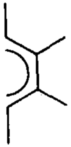
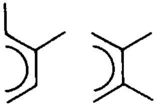
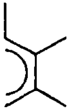
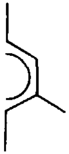
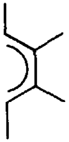
TABLE 4

Frequencies (cm^{-1}) reported [21,23–29] for some chlorinated benzene molecules

Benzene	Mono-	1,2-	1,3-	1,4-	1,2,3-	1,2,4-	1,2,3,4-
3068	3085	3072	3095	3090	3072	3094	3085
3063	3084	3072	3074	3090	3072	3088	3071
3063	3066	3072	3071	3070	3060	3086	1560
3062	3064	3072	3071	3065	1566	1571	1557
3047	3063	1576	1580	1574	1566	1562	1428
3047	1598	1575	1578	1574	1436	1461	1368
1596	1585	1468	1464	1475	1416	1377	1247
1596	1480	1438	1411	1394	1260	1267	1175
1486	1447	1276	1330	1290	1192	1245	1168
1486	1325	1252	1258	1221	1161	1156	1130
1326	1271	1162	1161	1169	1156	1132	1075
1310	1174	1129	1124	1107	1087	1096	940
1178	1157	1122	1079	1096	1049	1036	834
1178	1085	1041	1068	1090	963	942	808
1150	1068	1038	1000	1015	896	869	775
1038	1023	975	966	951	791	817	706
1038	1002	940	891	934	773	811	607
1010	985	855	869	819	737	688	557
995	965	748	784	815	697	679	530
992	902	740	775	747	524	576	515
975	830	695	674	687	513	551	482
975	740	660	663	626	500	459	356
849	703	504	531	550	492	435	332
849	682	480	430	485	400	398	307
703	613	435	428	407	352	328	241
673	467	428	399	350	243	308	223
606	418	334	366	328	212	211	209
606	400	240	212	298	212	197	209
410	297	203	198	226	212	183	111
410	196	154	176	115	98	115	94

TABLE 5

Hierarchical ordering of frequencies (cm^{-1}) to be used in estimating assignments of chlorinated dioxin frequencies [a]

Benzene analogues							
							
Chlorinated dioxin analogues							
							
3063							
3062	3066						
3047	3064	3072	3071	3070			
3047	3063	3072	3071	3065	3060	3086	
1596	1598	1576	1580	1574	1566	1571	1560
1596	1585	1575	1578	1574	1566	1562	1557
1486	1480	1468	1464	1475	1436	1461	1428
1486	1447	1438	1411	1394	1416	1377	1368
1326	1325	1276	1330	1290	1260	1267	1247
1310	1272	1252	1258	1221	1196	1245	1175
1178	1174	1162	1161	1169	1161	1156	1168

1178	1157	1130	1124	1107	1156	1132	808(−31.4)
1150	1084	1129	891(−22.5)	1096	791(−31.2)	817(−29.0)	775(−32.6)
1010	1068	855(−15.3)	869(−14.0)	819(−18.9)	773(−23.5)	811(−19.7)	706(−30.1)
995	902	748(−24.8)	784(−21.2)	815(−18.1)	737(−25.9)	688(−30.1)	607(−39.0)
992	830(−16.3)	740(−25.4)	775(−21.9)	747(−24.7)	697(−29.7)	679(−31.6)	557(−43.9)
849	740(−12.8)	695(−18.1)	674(−20.6)	687(−19.1)	524(−38.3)	576(−32.2)	530(−37.6)
849	703(−17.2)	660(−22.3)	663(−21.9)	626(−26.3)	513(−39.6)	551(−35.1)	515(−39.3)
703	682	504(−28.3)	531(−24.5)	550(−21.8)	500(−28.9)	459(−34.7)	482(−31.4)
673	613	480(−28.7)	430(−36.1)	485(−27.9)	492(−26.9)	435(−35.4)	356(−47.1)
606	467(−22.9)	435(−28.2)	428(−29.4)	407(−32.8)	400(−34.0)	398(−34.3)	332(−45.2)
606	418(−31.0)	428(−29.4)	399(−34.2)	350(−42.2)	352(−41.9)	328(−45.9)	307(−49.3)
410	400	334(−18.5)	366(−10.7)	328(−20.0)	243(−40.7)	308(−24.9)	241(−41.2)
410	297(−27.6)	240(−41.5)	212(−48.3)	298(−27.3)	212(−48.3)	211(−48.5)	223(−45.6)
	196	203	198	226	212	197	209
		154	176	115	212	183	209
					98	115	111
							94

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[a] Values in parentheses indicate % change relative to unchlorinated species.

is as follows. Since there are only at most four substitution positions in either aromatic ring in dioxin, one first drops out of the frequency assignments reported for benzene [31] and the chlorinated benzenes [23,25–30] six frequencies associated with C–H stretches (2 in-plane) and bends (2 in-plane and 2 out-of-plane). Examination of Table 5 will show what frequencies estimated to approximate numerically those vibrations discussed above have been dropped out. Next, the remaining frequencies are hierarchically ordered

TABLE 6

Frequency adjustments (cm^{-1}) between dibenzo-*p*-dioxin and 2,3,7,8-tetrachlorodibenzo-*p*-dioxin

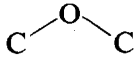
Dibenzo-*p*-dioxin		2,3,7,8-Tetrachlorodibenzo-*p*-dioxin [a]		
3100	979	3100	(731)	[203]
3088	960		(831)	[203]
3079	957		(716)	[154]
3063	936		(698)	[154]
3049	909		909	
3041	900	3041	900	
3022	871	3022	(713)	
3006	860	3006	(652)	
1631	826	1631	(695)	
1620	810	1620	(629)	
1596	754	1596	754	
1561	745	1561	(531)	
1533	739	1533	(530)	
1460	652	1460	(468)	
1460	651	1460	(464)	
1448	603	1448	(426)	
1384	601	1384	601	
1384	601	1384	601	
1346	552	1346	(370)	
1316	524	1316	(396)	
1274	512	1274	(362)	
1273	444	1264	(259)	
1261	400	1261	(326)	
1183	369	1188	(301)	
1169	325	1169	(190)	
1158	273	1158	273	
1150	244	1150	244	
1093	235	1100	235	
1007	137	(853)	137	
999	96	(751)	96	

[a] Values in parentheses are adjusted frequencies. Values in square brackets are added frequencies.

in decreasing frequencies (in cm^{-1}) for all the chlorinated benzenes and benzene, and columns corresponding to each chlorinated benzene are positionally ordered so that adjacent horizontal rows correspond to frequencies of approximately equal numerical value. From this hierarchical ordering, it is easy to see what frequencies drop out, are added, or are changed due to increasing chlorine substitution. As in the case of phenols, the adjustments to dioxin frequencies should then include the following operational procedures.

(a) For any specified chlorinated dioxin, drop out, as required from the list of frequencies reported for dioxins in Table 3, those frequencies approximately numerically equal in value to those dropped out in going from benzene to the analogous chlorinated benzene structure as indicated in Table 5.

(b) Perform the same operation in terms of those frequencies to be added.

(c) Analogous to those frequencies which change by more than about ±10% in going from benzene to a chlorinated benzene, make the same % adjustment in going from dioxin to a chlorinated dioxin, choosing those frequencies for dioxin which are closest in value to the analogous frequencies in benzene with the exception of those at 601, 1384 and 1460, associated with  $\mathrm{C{-}O{-}C}$ motions. Frequencies which change by more than ±10% in going from benzene to a chlorinated benzene have been identified in Table 5.

As an example of the application of this operational procedure, consider the molecule 2, 3, 7, 8-tetrachlorodibenzo-*p*-dioxin. Each of the aromatic rings contains *ortho*-substituted chlorine atoms. The analogue model is therefore *ortho-* chlorobenzene. Using Table 5, the dioxin frequencies which may be dropped, for example, are 3049, 3063, 3079, and 3088 cm^{-1}. Frequencies to be added are 154, 154, 203 and 203 cm^{-1}. As per operational step (c), above, several frequencies for dioxin are adjusted as described, and these adjustments are summarized in Table 6. Frequency assignments for all other chlorinated dioxins are to be made in the same manner.

SYMMETRY NUMBERS

Assignment of symmetry numbers is relatively straightforward by simple inspection of individual chlorinated benzene, phenol, and dioxin molecules. Some brief comments are in order. I have assumed, for the purpose of symmetry assignments, that all the molecules have a planar geometry. In the case of phenols, I have assumed that the OH group is a free rotor in terms of symmetry assignments. There is at least some *X*-ray diffraction data [13–20] from which one might conclude that, particularly in the case of heavily

TABLE 7

Input data used for generation of JANAF type tables[a]

Molecule	ΔH_f°(g,298)[b] (kcal $mole^{-1}$)	M.W. (a.m.u.)	σ
Dibenzo-*p*-dioxin	−15.0	184.184	4
1,2,3-Trichlorobenzene	2.18	181.45	2
1-Chlorodibenzo-*p*-dioxin	−22.24	219.6	1
2-Chlorodibenzo-*p*-dioxin	−32.96	219.6	1
Octachlorodibenzo-*p*-dioxin	−98.36	459.744	4
2,3,7,8-Tetrachlorodibenzo-*p*-dioxin	−82.5	297.84	4
2,3-Dichlorophenol	−40.17	162.9976	1
2,4-Dichlorophenol	−39.47	162.9976	1
2,5-Dichlorophenol	−41.72	162.9976	1
3,4-Dichlorophenol	−46.47	162.9976	1
Anthracene	55.2	178.22	4

[a] See Table 1 for moments of inertia.

[b] Heats of formation are estimated as described in ref. 12. However, for consistency, all secondary interaction effects have been determined here from benzene as a starting point. Therefore the σ_{12}(I) and σ_{12}(II) effects as used here in this paper are assigned the values 2.04 and 6.42 kcal $mole^{-1}$, respectively.

ν (cm^{-1})								
See Table 3								
See ref. 21								
3100	3088	3079	3049	3048	3022	3006	1631	1620
1596	1561	1533	1460	1460	1448	1384	1384	1346
1316	1274	1264	1261	1188	1188	1169	1150	1100
1007	979	960	957	936	909	900	871	836
810	754	745	739	721	720	652	601	601
552	524	512	446	444	416	369	325	290
273	244	235	196	137	96			
Same as 1-chlorodibenzo-*p*-dioxin								
1631	1620	1596	1561	1533	1460	1460	1448	1384
1384	1346	1316	1274	1264	1261	936	909	900
815	793	788	775	769	754	706	609	601
601	586	549	544	537	537	507	501	492
447	394	344	330	302	273	265	259	244
242	235	235	217	209	209	209	209	176
137	111	111	96	94	94			
3100	3041	3022	3006	1631	1620	1596	1561	1533
1460	1460	1448	1384	1384	1346	1316	1273	1264
1261	1188	1169	1158	1150	1100	909	900	853
813	754	751	731	720	713	698	695	652
629	601	601	531	530	468	464	426	396
370	362	326	301	273	259	244	235	203
203	190	154	154	137	96			
3656	3072	3072	3072	1576	1575	1468	1438	1276
1252	1162	1150	1129	1122	1041	940	881	855
748	740	695	573	525	504	480	435	403
334	309	241	225	203	154			
3656	3074	3071	3071	1580	1578	1464	1411	1330
1258	1183	1161	1124	1079	1000	891	875	869
784	775	674	575	531	490	430	428	403
366	309	225	212	198	176			
3656	3090	3070	3065	1574	1574	1475	1394	1290
1221	1169	1125	1107	1096	1090	934	862	819
815	747	687	550	543	499	485	403	350
328	309	298	226	225	115			
Same as 2,3-dichlorophenol								
See Table 3								

TABLE 8A

JANAF type table for 2,4,6-trichlorophenol based on frequencies taken from refs. 25 and 41

2,4,6-Trichlorophenol $C_6H_3OCl_3$ (Ideal Gas State) M.W. 197.44

T (K)	C°_p (cal mole^{-1} K^{-1})	S°_T (cal mole^{-1} K^{-1})	$-(G^\circ_T - H^\circ_0)/T$ (cal mole^{-1} K^{-1})	$H^\circ_T - H^\circ_0$ (kcal mole^{-1})	ΔH°_f (kcal mole^{-1})	ΔG°_f (kcal mole^{-1})	log K_p
200	26.95	80.96	65.02	3.19	−33.91	−21.01	23.961
298	35.41	93.36	72.35	6.26	−34.28	−14.60	11.375
300	35.55	93.58	72.48	6.33	−34.29	−14.47	11.210
400	42.61	104.81	79.19	10.25	−34.50	−7.82	4.777
500	48.28	114.95	85.34	14.80	−34.54	−1.15	0.904
600	52.70	124.16	91.05	19.86	−34.48	5.53	−1.678
700	56.12	132.55	96.39	25.31	−34.33	12.18	−3.516
800	58.79	140.22	101.40	31.06	−34.11	18.81	−4.888
900	60.91	147.28	106.11	37.05	−33.87	25.42	−5.948
1000	62.62	153.79	110.56	43.23	−33.56	31.99	−6.789
1100	64.01	159.82	114.76	49.56	−33.21	38.52	−7.470
1200	65.16	165.44	118.76	56.02	−32.83	45.02	−8.031
1300	66.12	170.70	122.55	62.59	−32.46	51.50	−8.502
1400	66.93	175.63	126.17	69.24	−32.10	57.95	−8.900
1500	67.63	180.27	129.62	75.97	−31.74	64.36	−9.241

chlorinated molecules, there might be some instances in which adjacent Cl atoms lie slightly above and below the aromatic rings by perhaps a few degrees. At the present time, I have ignored these cases as have Stull et al. [8] and Scherer and Evans [23] in the case of hexachlorobenzene.

THERMODYNAMIC FUNCTIONS, GAS PHASE

As mentioned previously, once the gas phase heat of formation, symmetry number(s), frequency assignments and principal moments of inertia have been specified, determination of thermodynamic functions, such as those presented in the JANAF tables [7], is straightforward [9]. On the following pages are presented, in JANAF type format, thermodynamic data for several chlorinated benzenes, phenols and dioxins. Anthracene has also been analyzed and JANAF type data are presented. In the case of unchlorinated dioxin, two JANAF type tables are presented labeled 'ungrouped' and 'grouped' corresponding to calculations in which all the assigned frequencies have been utilized in the former case and in which frequencies have been grouped in the later case. These two tables serve to illustrate the relative insensitivity of the computed thermodynamic functions towards the choice of assigned frequencies. In Tables 9A–9L, frequency grouping was also employed.

On initial revision, various adjustments to the thermodynamic functions reported in the JANAF type tables accompanying this manuscript were made by hand based upon helpful advice regarding some frequency assignments received by the author from Dr. Stanley Abramowitz who has been kind enough to take the time to review extensively the recent literature concerning frequency assignments associated with phenol, anthracene and chlorinated benzenes [40]. The frequencies he has recommended have been utilized in this report as indicated above to construct sets of frequencies for the other compounds, as I have discussed. The reader is cautioned not to think of these constructed sets in the sense of spectroscopic frequency assignments such as would result, for example from an analysis such as that performed by Cyvin and Cyvin [35]. One should not expect to search optically via infrared or Raman techniques, for example, for the dibenzo-*p*-dioxin frequencies based upon the assignments presented in Table 6. The estimation procedure developed here is intended only to permit one to construct a set of estimated frequencies which, *as a group*, numerically reproduce values for thermodynamic functions that would have been obtained had a true set of spectroscopic frequency assignments been available. The extent to which the reproduction of thermodynamic functions is realized by the methods outlined in this paper is illustrated in Tables 8A and 8B for

TABLE 8B

JANAF type table for 2,4,6-trichlorophenol based on frequencies taken from ref. 42

2,4,6-Trichlorophenol $C_6H_3OCl_3$ (Ideal Gas State) M.W. 197.44

T (K)	C_p° (cal mole^{-1} K^{-1})	S_T° (cal mole^{-1} K^{-1})	$-(G_T^\circ - H_0^\circ)/T$ (cal mole^{-1} K^{-1})	$H_T^\circ - H_0^\circ$ (kcal mole^{-1})	ΔH_f° (kcal mole^{-1})	ΔG_f° (kcal mole^{-1})	log K_p
200	27.27	81.44	65.26	3.24	−33.95	−21.15	24.108
298	35.84	93.99	72.70	6.35	−34.29	−14.79	11.513
300	35.98	94.21	72.83	6.41	−34.29	−14.66	11.348
400	42.95	105.55	79.62	10.37	−34.46	−8.08	4.918
500	48.39	115.75	85.84	14.95	−34.48	−1.49	1.051
600	52.56	124.96	91.61	20.01	−34.42	5.11	−1.526
700	55.78	133.31	96.98	25.43	−34.30	11.69	−3.362
800	58.32	140.93	102.00	31.14	−34.12	18.25	−4.732
900	60.37	147.92	106.72	37.08	−33.93	24.78	−5.793
1000	62.03	154.37	111.17	43.21	−33.67	31.29	−6.636
1100	63.42	160.35	115.37	49.48	−33.37	37.77	−7.320
1200	64.58	165.92	119.35	55.88	−33.05	44.22	−7.884
1300	65.56	171.13	123.14	62.39	−32.75	50.65	−8.359
1400	66.40	176.02	126.74	68.99	−32.44	57.05	−8.761
1500	67.12	180.63	130.18	75.67	−32.13	63.43	−9.106

TABLE 9A

JANAF type table for dibenzo-*p*-dioxin (all frequencies)

Dibenzo-*p*-dioxin $C_{12}H_8O_2$ (Ideal Gas State) M.W. 184.184 (all frequencies)

T (K)	C_p° (cal mole^{-1} K^{-1})	S_T° (cal mole^{-1} K^{-1})	$-(G_T^\circ - H_0^\circ)/T$ (cal mole^{-1} K^{-1})	$H_T^\circ - H_0^\circ$ (kcal mole^{-1})	ΔH_f° (kcal mole^{-1})	ΔG_f° (kcal mole^{-1})	log K_p
298	42.13	92.68	70.75	6.51	−14.97	14.13	−10.363
300	42.41	92.94	70.89	6.59	−15.00	14.30	−10.417
400	56.54	107.10	78.05	11.55	−16.51	24.30	−13.277
500	68.18	120.95	85.12	17.81	−17.62	34.65	−15.145
600	77.45	134.31	92.26	25.11	−18.42	45.18	−16.456
700	84.79	146.83	99.14	33.24	−18.98	55.83	−17.430
800	90.71	158.55	105.89	42.03	−19.35	66.53	−18.175
900	95.55	169.53	112.25	51.36	−19.56	77.27	−18.763
1000	99.55	179.80	118.47	61.11	−19.56	88.03	−19.238
1100	102.88	189.46	124.46	71.23	−19.44	98.77	−19.623
1200	105.70	198.53	130.24	81.66	−19.21	109.49	−19.940
1300	108.08	207.06	135.89	92.35	−18.96	120.20	−20.207
1400	110.12	215.09	141.16	103.26	−18.68	130.90	−20.434
1500	111.87	222.84	146.33	114.36	−18.36	141.56	−20.625

TABLE 9B

JANAF type table for dibenzo-*p*-dioxin (grouped frequencies)

Dibenzo-*p*-dioxin $C_{12}H_8O_2$ (Ideal Gas State) M.W. 184.184 (grouped frequencies)

T (K)	C_p° (cal mole^{-1} K^{-1})	S_T° (cal mole^{-1} K^{-1})	$-(G_T^\circ - H_0^\circ)/T$ (cal mole^{-1} K^{-1})	$H_T^\circ - H_0^\circ$ (kcal mole^{-1})	ΔH_f° (kcal mole^{-1})	ΔG_f° (kcal mole^{-1})	log K_p
298	42.03	92.64	70.74	6.50	−14.97	14.13	−10.363
300	42.31	92.90	70.88	6.58	−15.00	14.32	−10.432
400	56.43	107.03	78.03	11.53	−16.52	24.32	−13.288
500	68.10	120.85	85.08	17.78	−17.64	34.68	−15.158
600	77.40	134.21	92.22	25.07	−18.45	45.22	−16.471
700	84.81	146.72	99.08	33.20	−19.01	55.88	−17.446
800	90.70	158.43	105.83	41.99	−19.38	66.59	−18.191
900	95.55	169.41	112.18	51.31	−19.59	77.34	−18.780
1000	99.54	179.69	118.40	61.06	−19.60	88.11	−19.256
1100	102.89	189.34	124.39	71.19	−19.47	98.86	−19.641
1200	105.71	198.41	130.16	81.62	−19.24	109.60	−19.960
1300	108.09	206.95	135.81	92.31	−18.99	120.32	−20.227
1400	110.13	214.93	141.08	103.22	−18.71	131.03	−20.454
1500	111.88	222.73	146.25	114.32	−18.40	141.70	−20.645

TABLE 9C

JANAF type table for anthracene

Anthracene $C_{14}H_{10}$ (Ideal Gas State) M.W. 178.22

T (K)	C_p° (cal mole^{-1} K^{-1})	S_T° (cal mole^{-1} K^{-1})	$-(G_T^\circ - H_0^\circ)/T$ (cal mole^{-1} K^{-1})	$H_T^\circ - H_0^\circ$ (kcal mole^{-1})	ΔH_f° (kcal mole^{-1})	ΔG_f° (kcal mole^{-1})	log K_p
298	43.13	92.38	70.38	6.49	55.24	79.95	−58.633
300	43.33	92.64	70.52	6.57	55.20	80.11	−58.359
400	58.85	107.26	78.12	11.70	53.37	88.66	−48.451
500	71.75	121.83	85.02	18.25	51.96	97.70	−42.695
600	82.06	135.85	92.28	25.95	50.88	106.94	−38.952
700	92.27	149.16	99.59	34.58	50.07	116.35	−36.319
800	96.91	161.68	106.37	43.95	49.47	125.84	−34.372
900	102.38	173.43	113.23	53.92	49.05	135.41	−32.881
1000	166.93	184.46	119.78	64.39	48.86	145.01	−31.691
1100	110.75	194.84	126.10	75.27	48.82	154.61	−30.717
1200	113.99	204.62	132.22	86.51	48.90	164.21	−29.906
1300	116.74	213.85	138.12	98.05	49.01	173.82	−29.221
1400	119.08	222.55	143.72	109.84	49.16	183.42	−28.632
1500	121.11	230.82	149.23	121.85	49.33	193.00	−28.119

TABLE 9D

JANAF type table for 1,2,3-trichlorobenzene

1,2,3-Trichlorobenzene $C_6H_3Cl_3$ (Ideal Gas State) M.W. 181.4497

T (K)	C_p° (cal mole^{-1} K^{-1})	S_T° (cal mole^{-1} K^{-1})	$-(G_T^\circ - H_0^\circ)/T$ (cal mole^{-1} K^{-1})	$H_T^\circ - H_0^\circ$ (kcal mole^{-1})	ΔH_f° (kcal mole^{-1})	ΔG_f° (kcal mole^{-1})	log K_p
298	30.77	88.67	70.09	5.53	2.19	16.06	−11.778
300	30.90	88.86	70.21	5.59	2.18	16.14	−11.758
400	37.58	98.67	76.11	9.03	1.84	20.85	−11.392
500	42.88	107.62	81.54	13.06	1.64	25.62	−11.198
600	46.98	115.85	86.59	17.56	1.53	30.42	−11.080
700	50.17	123.31	91.31	22.43	1.48	35.24	−11.002
800	52.69	130.15	95.65	27.58	1.50	40.05	−10.941
900	54.73	136.51	99.94	32.95	1.53	44.88	−10.898
1000	56.39	142.39	103.90	38.51	1.63	49.69	−10.859
1100	57.77	147.84	107.65	44.22	1.78	54.48	−10.824
1200	58.92	152.91	111.21	50.05	1.96	59.26	−10.792
1300	59.90	157.65	114.60	56.00	2.13	64.02	−10.762
1400	60.72	162.10	117.84	62.03	2.30	68.78	−10.737
1500	61.43	166.29	120.84	68.14	2.48	73.50	−10.709

TABLE 9E

JANAF type table for 2,3-dichlorophenol

2,3-Dichlorophenol $C_6H_4OCl_2$ (Ideal Gas State) M.W. 162.9976

T (K)	C_p° (cal mole^{-1} K^{-1})	S_T° (cal mole^{-1} K^{-1})	$-(G_T^\circ - H_0^\circ)/T$ (cal mole^{-1} K^{-1})	$H_T^\circ - H_0^\circ$ (kcal mole^{-1})	ΔH_f° (kcal mole^{-1})	ΔG_f° (kcal mole^{-1})	log K_p
298	32.03	88.03	69.68	5.46	−40.16	−21.97	17.953
300	32.18	88.23	69.79	5.52	−40.17	−21.85	17.746
400	40.16	98.57	75.59	9.12	−40.67	−15.69	9.944
500	45.23	108.00	80.99	13.36	−40.97	−9.43	5.219
600	49.76	116.74	86.17	18.12	−41.14	−3.12	2.051
700	53.16	124.67	91.05	23.26	−41.21	3.22	−0.222
800	55.95	131.95	95.66	28.72	−41.20	9.55	−1.923
900	58.21	138.57	99.92	34.43	−41.15	15.88	−3.247
1000	60.08	144.70	103.96	40.34	−41.01	22.19	−4.301
1100	61.66	150.59	107.99	46.43	−40.81	28.50	−5.164
1200	62.98	156.10	111.84	52.66	−40.58	34.79	−5.879
1300	64.11	161.22	115.41	59.01	−40.35	41.06	−6.481
1400	65.08	166.06	118.92	65.47	−40.11	47.32	−6.995
1500	65.92	170.62	122.19	72.02	−39.86	53.54	−7.435

TABLE 9F

JANAF type table for 2,4-dichlorophenol

2,4-Dichlorophenol $C_6H_4OCl_2$ (Ideal Gas State) M.W. 162.9976

T (K)	C_p° (cal mole^{-1} K^{-1})	S_T° (cal mole^{-1} K^{-1})	$-(G_T^\circ - H_0^\circ)/T$ (cal mole^{-1} K^{-1})	$H_T^\circ - H_0^\circ$ (kcal mole^{-1})	ΔH_f° (kcal mole^{-1})	ΔG_f° (kcal mole^{-1})	log K_p
298	32.05	88.41	70.01	5.48	−39.46	−21.38	17.520
300	32.20	88.61	70.13	5.54	−39.47	−21.26	17.316
400	39.51	98.94	75.94	9.13	−39.97	−15.14	9.643
500	45.16	108.36	81.35	13.37	−40.28	−8.92	4.996
600	49.68	117.09	86.52	18.12	−40.46	−2.64	1.876
700	53.09	125.00	91.40	23.26	−40.54	3.66	−0.359
800	55.89	132.27	96.01	28.71	−40.55	9.96	−2.035
900	58.15	138.88	100.27	34.41	−40.49	16.25	−3.336
1000	60.03	145.01	104.30	40.32	−40.35	22.54	−4.377
1100	61.61	150.89	108.33	46.40	−40.17	28.82	−5.227
1200	62.94	156.40	112.17	52.63	−39.94	35.08	−5.932
1300	64.08	161.51	115.74	58.98	−39.71	41.32	−6.524
1400	65.04	166.35	119.25	65.43	−39.47	47.55	−7.031
1500	65.89	170.90	122.51	71.98	−39.23	53.74	−7.464

TABLE 9G

JANAF type table for 2,5-dichlorophenol

2,5-Dichlorophenol $C_6H_4OCl_2$ (Ideal Gas State) M.W. 162.9976

T (K)	C_p° (cal mole^{-1} K^{-1})	S_T° (cal mole^{-1} K^{-1})	$-(G_T^\circ - H_0^\circ)/T$ (cal mole^{-1} K^{-1})	$H_T^\circ - H_0^\circ$ (kcal mole^{-1})	ΔH_f° (kcal mole^{-1})	ΔG_f° (kcal mole^{-1})	log K_p
298	32.07	88.42	70.02	5.48	−41.71	−23.63	19.170
300	32.22	88.62	70.13	5.54	−41.72	−23.51	18.955
400	39.57	98.96	75.94	9.12	−42.22	−17.39	10.873
500	45.23	108.39	81.36	13.35	−42.52	−11.17	5.979
600	49.76	117.13	86.54	18.10	−42.69	−4.9	2.699
700	53.16	125.05	91.42	23.24	−42.76	1.40	0.347
800	55.95	132.33	96.03	28.70	−42.75	7.69	−1.415
900	58.21	138.95	100.30	34.41	−42.70	13.98	−2.785
1000	60.08	145.08	104.33	40.32	−42.56	20.25	−3.877
1100	61.65	150.97	108.37	46.41	−42.37	26.53	−4.772
1200	62.97	156.48	112.21	52.64	−42.14	32.78	−5.513
1300	64.11	161.60	115.78	58.99	−41.91	39.01	−6.136
1400	65.07	166.43	119.30	65.45	−41.67	45.23	−6.669
1500	65.91	170.99	122.56	72.00	−41.42	51.42	−7.126

TABLE 9H

JANAF type table for 3,4-dichlorophenol

3,4-Dichlorophenol $C_6H_4OCl_2$ (Ideal Gas State) M.W. 162.9976

T (K)	C_p° (cal mole^{-1} K^{-1})	S_T° (cal mole^{-1} K^{-1})	$-(G_T^\circ - H_0^\circ)/T$ (cal mole^{-1} K^{-1})	$H_T^\circ - H_0^\circ$ (kcal mole^{-1})	ΔH_f° (kcal mole^{-1})	ΔG_f° (kcal mole^{-1})	$\log K_p$
298	32.03	88.25	69.89	5.46	−46.46	−28.33	20.776
300	32.18	88.44	70.00	5.52	−46.47	−28.21	20.550
400	40.16	98.78	75.80	9.12	−46.97	−22.07	12.058
500	45.23	108.21	81.21	13.36	−47.27	−15.84	6.923
600	49.76	116.95	86.38	18.12	−47.45	−9.54	3.475
700	53.16	124.87	91.26	23.26	−47.52	−3.23	1.008
800	55.95	132.15	95.87	28.72	−47.50	3.08	−0.841
900	58.21	138.77	100.13	34.43	−47.45	9.39	−2.280
1000	60.08	144.90	104.17	40.34	−47.31	15.68	−3.427
1100	61.66	150.79	108.20	46.43	−47.12	21.97	−4.365
1200	62.98	156.30	112.04	52.66	−46.89	28.24	−5.143
1300	64.11	161.42	115.61	59.01	−46.66	34.49	−5.798
1400	65.08	166.25	119.13	65.47	−46.42	40.73	−6.358
1500	65.92	170.81	122.39	72.02	−46.17	46.94	−6.839

TABLE 9I

JANAF type for 1-chlorodibenzo-*p*-dioxin

1-Chlorodibenzo-*p*-dioxin $C_{12}H_7O_2Cl$ (Ideal Gas State) M.W. 219.6

T (K)	C_p° (cal mole^{-1} K^{-1})	S_T° (cal mole^{-1} K^{-1})	$-(G_T^\circ - H_0^\circ)/T$ (cal mole^{-1} K^{-1})	$H_T^\circ - H_0^\circ$ (kcal mole^{-1})	ΔH_f° (kcal mole^{-1})	ΔG_f° (kcal mole^{-1})	log K_p
298	45.65	100.60	76.94	7.03	−32.43	−2.31	2.031
300	45.92	100.88	77.08	7.16	−32.46	−2.11	1.872
400	59.76	115.99	84.54	12.46	−33.74	8.16	−4.207
500	71.14	130.60	92.42	19.03	−34.64	18.72	−7.981
600	80.14	144.38	99.81	26.61	−35.26	29.45	−10.559
700	87.26	157.34	107.06	34.99	−35.66	40.26	−12.426
800	92.96	169.41	113.95	44.01	−35.88	51.12	−13.837
900	97.60	180.67	120.68	53.55	−35.97	61.99	−14.938
1000	101.40	191.19	127.15	63.50	−35.87	72.86	−15.820
1100	104.56	201.01	133.37	73.79	−35.66	83.70	−16.536
1200	107.22	210.20	139.24	84.38	−35.35	94.52	−17.128
1300	109.46	218.81	145.07	95.21	−35.04	105.33	−17.627
1400	111.36	226.92	150.60	106.25	−34.70	116.11	−18.051
1500	113.00	234.68	155.91	117.47	−34.35	126.85	−18.412

TABLE 9J

JANAF type table for 2-chlorodibenzo-*p*-dioxin

2-Chlorodibenzo-*p*-dioxin $C_{12}H_7O_2Cl$ (Ideal Gas State) M.W. 219.6

T (K)	C_p° (cal mole^{-1} K^{-1})	S_T° (cal mole^{-1} K^{-1})	$-(G_T^\circ - H_0^\circ)/T$ (cal mole^{-1} K^{-1})	$H_T^\circ - H_0^\circ$ (kcal mole^{-1})	ΔH_f° (kcal mole^{-1})	ΔG_f° (kcal mole^{-1})	log K_p
298	45.65	100.33	76.67	7.03	−22.67	7.45	−5.464
300	45.92	100.61	76.81	7.16	−22.70	7.66	−5.580
400	59.76	115.72	84.27	12.46	−23.95	18.03	−9.849
500	71.14	130.33	92.15	19.03	−24.83	28.61	−12.505
600	80.14	144.11	99.54	26.61	−25.43	39.37	−14.340
700	87.26	157.07	106.79	34.99	−25.82	50.21	−15.676
800	92.92	169.14	113.68	44.01	−26.03	61.09	−16.687
900	97.60	180.40	120.41	53.55	−26.11	71.99	−17.479
1000	101.40	190.92	126.88	63.50	−26.01	82.89	−18.112
1100	104.56	200.74	133.09	73.79	−25.80	93.76	−18.625
1200	107.22	209.93	139.07	84.38	−25.49	104.61	−19.048
1300	109.46	218.54	144.80	95.21	−25.18	115.44	−19.404
1400	111.36	226.65	150.33	106.25	−24.84	126.25	−19.705
1500	113.00	234.41	155.64	117.47	−24.49	137.01	−19.960

TABLE 9K

JANAF type table for 2,3,7,8-tetrachlorodibenzo-*p*-dioxin

2,3,7,8-Tetrachlorodibenzo-*p*-dioxin $C_{12}H_4O_2Cl_4$ (Ideal Gas State) M.W. 297.84

T (K)	C_p° (cal mole^{-1} K^{-1})	S_T° (cal mole^{-1} K^{-1})	$-(G_T^\circ - H_0^\circ)/T$ (cal mole^{-1} K^{-1})	$H_T^\circ - H_0^\circ$ (kcal mole^{-1})	ΔH_f° (kcal mole^{-1})	ΔG_f° (kcal mole^{-1})	log K_p
298	56.79	114.26	83.22	9.27	−82.49	−46.65	34.212
300	56.96	114.61	83.41	9.37	−82.50	−46.41	33.809
400	70.03	132.84	93.23	15.77	−82.90	−34.34	18.762
500	80.46	149.67	102.60	23.32	−83.03	−22.21	9.708
600	88.58	165.05	111.46	31.82	−83.01	−10.07	3.668
700	94.92	179.21	119.94	41.00	−82.86	2.06	−0.643
800	99.90	192.23	128.07	50.75	−82.59	14.17	−3.871
900	103.87	204.24	135.78	60.94	−82.29	26.24	−6.372
1000	107.08	215.37	143.11	71.49	−81.85	38.28	−8.366
1100	109.70	225.69	150.07	82.33	−81.35	50.25	−9.984
1200	111.87	235.32	156.71	93.41	−80.80	62.19	−11.326
1300	113.67	244.33	163.05	104.69	−80.27	74.09	−12.455
1400	115.19	252.80	169.10	116.13	−79.75	85.94	−13.416
1500	116.48	260.78	174.89	127.72	−79.24	97.74	−14.240

TABLE 9L

JANAF type table for octachlorodibenzo-*p*-dioxin

Octachlorodibenzo-*p*-dioxin $C_{12}O_2Cl_8$ (Ideal Gas State) M.W. 459.744

T (K)	C_p° (cal mole^{-1} K^{-1})	S_T° (cal mole^{-1} K^{-1})	$-(G_T^\circ - H_0^\circ)/T$ (cal mole^{-1} K^{-1})	$H_T^\circ - H_0^\circ$ (kcal mole^{-1})	ΔH_f° (kcal mole^{-1})	ΔG_f° (kcal mole^{-1})	log K_p
298	70.97	136.73	95.78	12.23	−98.37	−56.07	42.470
300	71.23	137.17	96.04	12.36	−98.36	−55.79	41.982
400	83.53	159.40	108.87	20.14	−97.63	−41.74	23.810
500	92.86	179.14	120.63	29.01	−96.79	−27.90	12.999
600	99.92	196.65	131.67	38.67	−95.91	−14.22	5.850
700	105.23	212.51	141.91	48.94	−95.03	−0.68	0.787
800	109.25	226.85	151.45	59.69	−94.12	12.72	−2.972
900	112.34	239.93	160.36	70.77	−93.31	26.03	−5.874
1000	114.74	251.92	168.92	82.13	−92.42	39.23	−8.171
1100	116.63	262.94	176.89	93.70	−92.03	52.35	−10.035
1200	118.13	273.16	184.41	105.44	−90.64	65.39	−11.574
1300	119.34	282.63	191.53	117.31	−89.84	78.36	−12.864
1400	120.33	291.47	198.29	129.29	−89.08	91.27	−13.960
1500	121.15	299.76	204.73	141.37	−88.34	104.11	−14.900

the molecule 2, 4, 6-trichlorophenol. In Table 8A, values for the thermodynamic functions have been presented which were based upon an estimated set of frequencies. The set was constructed starting with the assignments of Scherer et al. [25] for 1, 3, 5-trichlorobenzene as a model. Correction from a chlorinated benzene to a chlorinated phenol was made via the method outlined in this report and utilizing the frequencies as assigned by Green [41]. These thermodynamic functions in Table 8A are to be compared with those presented in Table 8B in which a complete frequency assignment for 2, 4, 6-trichlorophenol, as reported by Faniran and Shurvell [42], has been utilized. The agreement is quite reasonable and the estimated functions as reported in Table 8A are clearly adequate for the purpose of modeling the fate of complex organic compounds at thermodynamic equilibrium at high temperatures, e.g. combustion processes associated with thermal incineration. Further refinements in the estimated thermodynamic functions are always desirable. For example, as regards frequency assignments for phenol, the work of Kudchadker et al. [38] is more desirable [40] than that of Green [41]. A complete set of spectroscopic frequencies for unsubstituted dibenzo-*p*-dioxin has not yet been reported, but would certainly be useful for the purpose of further refining estimates for chlorinated dioxins. In a later publication, JANAF type tables for many more compounds will be presented including thermodynamic data for all of the chlorinated dioxins, dibenzofurans, biphenyls and biphenyl ethers. In Table 7, I present a summary of the data used in constructing the JANAF type tables.

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APPENDIX

The following is a brief outline of the formalism by which spectroscopic data are utilized to develop basic thermodynamic information. Moments of inertia calculations, as mentioned previously, require only a specification of the masses and the (x, y, z) position coordinates for each atom in a molecule relative to a fixed cartesian axis system. Then, for example

$$I_{xx} = \sum_i m_i\left(y_i^2 + z_i^2\right) \tag{1}$$

$$I_{yz} = \sum_i m_i y_i z_i \tag{2}$$

and so forth for the other seven inertia elements. The principal axis moments of inertia (Ix, Iy, Iz) are then determined by a suitable transformation to diagonalize the moment of inertia matrix developed from the above calculations.

Simple statistical mechanics [9] can then be used to calculate the (non-linear molecule) entropy and heat capacity terms

$$S^\circ_{\mathrm{tr}} = R[(3/2)\ln M + (5/2)\ln T] - 2.315 \tag{3}$$

$$S^\circ_{\mathrm{e}} = 0,\ \text{usually} \tag{4}$$

$$S^\circ_{\mathrm{rot}} = R[(1/2)\ln(IxIyIz) + (3/2)\ln T] - \ln \sigma \tag{5}$$

$$S^\circ_{\mathrm{vib}} = \sum_i R\left[\frac{u_i}{\mathrm{e}^{u_i} - 1} - \ln(1 - \mathrm{e}^{-u_i})\right] \tag{6}$$

$$u_i = hcw_i/kT \tag{7}$$

$$S^\circ = S^\circ_{\mathrm{tr}} + S^\circ_{\mathrm{e}} + S^\circ_{\mathrm{rot}} + S^\circ_{\mathrm{vib}}$$

$$C^\circ_{\mathrm{tr}} = (3/2)R \tag{8}$$

$$C^\circ_{\mathrm{e}} = 0,\ \text{usually} \tag{9}$$

$$C^\circ_{\mathrm{rot}} = (3/2)R \tag{10}$$

$$C^\circ_{\mathrm{vib}} = \sum_i R\frac{u_i^2\,\mathrm{e}^{u_i}}{(\mathrm{e}^{u_i} - 1)^2} \tag{11}$$

$$C^\circ_{\mathrm{p}} = C^\circ_{\mathrm{v}} + R \tag{12}$$

$$C^\circ_{\mathrm{v}} = C^\circ_{\mathrm{tr}} + C^\circ_{\mathrm{e}} + C^\circ_{\mathrm{rot}} + C^\circ_{\mathrm{vib}} \tag{13}$$

The symbols used above are explained below. It should be noted that if the molecule has internal free or hindered rotation, other additional, but still simple, calculations are required in computing both the entropy and the heat capacity of the molecule. The reader is referred to refs. 7 and 9 for more detail. Once the temperature dependence of the entropy and heat capacity terms have been computed, it is a straightforward matter to determine the values for the thermodynamic functions that are presented in the JANAF tables [7] if the enthalpy of formation is also known.

NOTATION

I_{xx}, I_{yz}, etc.	non-diagonalized moment of inertia matrix elements
m_i	mass of ith atom in the molecule
S°_{tr}	translational entropy term
S°_{e}	electronic entropy term
S°_{rot}	rotational entropy term
S°_{vib}	vibrational entropy term
C°_{tr}	translational heat capacity term
C°_{e}	electronic heat capacity term
C°_{vib}	vibrational heat capacity term
C°_{rot}	rotational heat capacity term
R	universal gas constant
M	molecule molecular weight
T	temperature
Ix, Iy, Iz	principal axis moments of inertia
σ	symmetry number of molecule
h	Planck's constant
c	speed of light constant
w_i	ith vibrational frequency of molecule
k	Boltzmann's constant
S°	total entropy
C°_{p}	total heat capacity at constant pressure
C°_{v}	total heat capacity at constant volume