

Thermodynamic properties of gas phase species of importance to ozone depletion

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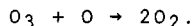
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Abstract

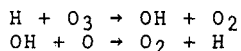
Thermodynamic and spectroscopic data have been evaluated for several chlorine-oxygen gas phase species of interest in the study of ozone depletion models. The evaluated data have been used to compute JANAF Thermochemical Tables for these species. The data will be discussed and applied to several proposed models for ozone depletion. The recent catalytic cycle involving ozone loss by ClO and Cl₂O₂ in the Antarctic stratosphere is discussed.

INTRODUCTION

Pollution of the atmosphere has become a problem of international concern. Problems which face society include ozone depletion, carbon dioxide buildup, and acid rain. The greenhouse effect is due to approximately 50% CO₂ buildup and 50% due to Freons, CH₄, N₂O and O₃. The role thermodynamics can play in assessing these atmospheric phenomena is discussed. The temperature range of interest varies from approximately 190K, in the polar regions to 300K. Particular attention is given to some problems in ozone depletion. There are several chemical cycles that can lead to ozone depletion in the stratosphere (ref.1). The chemical kinetics, thermodynamics and photochemical data for use in stratospheric modelling is evaluated and updated frequently (ref. 2). Cycles to be considered involve nitrogen oxides, hydroxyl radicals, oxygen (¹D) atoms, halogen atoms and organic species. All of these cycles have the net effect of transforming ozone to oxygen according to the reaction,



In order for this thermodynamically favorable process to occur radicals, including nitrogen oxides, have to be available. An example of the processes is



These radicals, which for the purpose of this discussion include nitrogen oxides, are either present via photolysis or their precursors are introduced into the atmosphere by man. An understanding of the equilibrium conditions of the atmosphere is an important beginning to the modelling of the atmosphere disturbed by turbulence, photolytic processes and introduction of pollutants from a variety of sources.

The work described in this paper involves those species of possible importance to the cycles implicated in the removal of ozone by chlorine atoms and chlorine oxygen radicals. These molecular species include ClO, ClOO, OClO, ClClO, ClOCl, Cl₂O₂, Cl₂O₃, and NO₃. Nitrogen trioxide has been included because it is involved in a reaction to provide a potential reservoir, HCl, for Cl atoms (and ClO_x species which are formed by reaction of oxygen moieties with Cl atoms), according to the equilibrium,

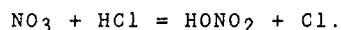


Table 2. Thermodynamic Functions and Formation Properties, $T_r = 298.15$ K

T/K	C_p°	$S^\circ - [G^\circ - H^\circ(T_r)]/T$		$H^\circ - H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	logK
		$\text{Jmol}^{-1}\text{K}^{-1}$					
ClO(g)							
0	0	0	∞	-9.5303	101.03	101.03	0
25	29.102	148.177	500.386	-8.8052	101.03	100.85	-210.71
100	30.872	188.998	254.833	-6.5833	101.07	100.29	-52.38
298.15	34.457	224.960	224.960	0	101.63	98.40	-17.24
350	34.894	230.519	225.381	1.7981	101.77	97.82	-14.60
OC1O(g)							
0	0	0	∞	-10.7957	99.48	99.48	0
25	33.258	170.305	568.877	-9.9643	99.22	101.15	-209.25
100	33.812	216.509	291.123	-7.4614	98.45	103.58	-54.11
298.15	41.953	256.838	256.838	0	97.00	114.84	-20.12
350	44.103	263.735	257.358	2.2319	96.81	117.96	-17.61
ClOO(g)							
0	0	0	∞	-11.6102	91.66	91.66	0
25	33.257	178.433	609.589	-11.7788	91.41	92.13	-192.50
100	35.207	224.950	307.446	-8.2496	90.66	94.95	-49.60
298.15	46.118	269.320	269.321	0	90.00	104.12	-18.14
350	47.517	276.827	269.888	2.4286	90.07	106.58	-15.91
ClOCl(g)							
0	0	0	∞	-11.7134	82.81	82.81	0
25	33.258	180.285	615.564	-10.8820	82.55	83.42	-174.30
100	35.535	227.016	310.283	-8.3367	81.82	86.69	-45.28
298.15	47.909	271.718	271.718	0	81.00	97.08	-17.01
350	49.952	279.566	272.310	2.5394	80.99	99.88	-14.91
ClClO(g)							
0	0	0	∞	-12.2223	71.30	71.30	0
25	33.259	183.918	639.561	-11.3911	71.04	71.82	-150.07
100	37.726	231.479	319.298	-8.7819	70.38	74.79	-39.07
298.15	48.840	278.803	278.803	0	70.00	83.97	-14.71
350	50.370	286.757	279.405	2.5734	70.03	86.40	-12.89
ClOOC1(g)							
0	0	0	∞	-14.4095	13.65	136.45	0
25	33.555	193.022	736.106	-13.5771	13.58	138.05	-288.45
100	42.140	244.048	351.477	-10.7429	13.43	146.13	-76.33
298.15	64.702	300.983	300.983	0	13.30	170.94	-29.95
350	68.330	311.653	301.787	3.4531	13.31	177.53	-26.49
Cl₂O₃(g)							
0	0	0	∞	-17.4381	14.18	141.77	0
25	34.171	197.727	861.839	-16.6028	14.08	144.55	-302.03
100	52.188	254.579	388.264	-13.3684	13.86	158.01	-82.53
298.15	79.209	325.620	325.620	0	13.70	198.17	-34.72
350	83.566	338.670	326.603	4.2234	13.71	208.80	-31.16
NO₃(g)							
0	0	0	∞	-12.0980	69.66	69.66	0
25	33.257	165.147	615.811	-11.2666	69.05	71.40	-149.19
100	35.816	211.835	299.069	-8.7234	67.23	80.03	-41.80
298.15	51.264	258.400	258.400	0	64.40	107.67	-18.86
350	54.530	266.877	259.038	2.7437	64.09	115.22	-17.20

Table 3. Selected Thermodynamic Properties at 298.15K and Their Estimated Uncertainties

Species	Enthalpy of Formation $\Delta_f H^\circ(298.15K)$ kJ mol ⁻¹	Entropy $S^\circ(298.15K)$ J mol ⁻¹ K ⁻¹	Gibbs Energy of Form. $\Delta_f G^\circ(298.15)$ kJ mol ⁻¹
ClO	101.63 ± 0.1	224.96 ± 1.0	98.40 ± 0.31
OC10 O	97 ± 8	256.84 ± 0.1	114.84 ± 8.00
ClOO	90 ± 5	269.32 ± 2.0	104.12 ± 5.00
ClOCl	82.8 ± 2	271.72 ± 1.5	97.08 ± 2.05
ClClO	70 ± 30	278.80 ± 2.0	83.97 ± 30.0
ClOOC1	133 ± 8	300.98 ± 5.0	170.94 ± 8.09
Cl ₂ O ₃	137 ± 13	325.62 ± 5.0	198.17 ± 13.09
NO ₃	64.4 ± 2.0	258.40 ± 1.0	107.67 ± 2.02

Table 4. JANAF Thermochemical Table Text for (ClO)₂

CHLORINE MONOXIDE DIMER (ClO)₂ IDEAL GAS M_r = 102.9042 g mol⁻¹

$S^\circ(298.15 K) = 300.98 \pm 5 \text{ J mol}^{-1} \text{ K}^{-1}$ $\Delta_f H^\circ(0 K) = 136 \pm 8 \text{ kJ mol}^{-1}$
 $\Delta_f H^\circ(298.15 K) = 133 \pm 8 \text{ kJ mol}^{-1}$

Vibrational Frequencies (cm⁻¹) and Degeneracies

765 (1) 649.9 (1)
 647.6 (1) [440] (1)
 [320] (1) 127 (1)

Ground State Quantum Weight = [1]

Point Group: C_s

Moments of Inertia (gmcm²)

Bond angle ClOO = 110.07 ± 0.1°

I_A = 6.4209415 x 10⁻³⁹

Dihedral angle = 81.03 ± 0.8°

I_B = 35.306628 x 10⁻³⁹

Bond Distances: Cl-O = 1.7044 ± .001Å

I_C = 39.722506 x 10⁻³⁹

O-O = 1.4259 ± .0021Å

I_AI_BI_C = 9005.163437 x 10⁻¹¹⁷ gm³cm⁶

Enthalpy of formation

The enthalpy of formation has been obtained from kinetic and equilibrium measurements of the rate of self reaction of ClO and the decomposition of the dimer to form the monomer unit. The results of these studies, as summarized by Cox and Hayman (1, this table) indicate the dimer is bound by 17 kcal mol⁻¹ relative to the monomeric ClO. The $\Delta_r H$ and $\Delta_r S$, as determined by a lnK vs 1/T plot in the temperature range of 203-300 K, of the reaction 2ClO → (ClO)₂ are -72.5 ± 3.0 kJ mol⁻¹ and -144 ± 11 J mol⁻¹ K⁻¹ respectively (1, this table). In this study optical cross sections of the chlorine oxide species were used to determine the equilibrium constants as a function of temperature, from which the thermodynamic properties of the reaction of ClO to form (ClO)₂ were determined. These results are in agreement with previous results within combined experimental errors for the enthalpy of this reaction (2, this table). The cross sections measured by Cox and Hayman (1, this table) are in agreement with recent results of Burkholder, et. al. (3, this table) who measured the ultraviolet cross sections between 210 and 410 nm for (ClO)₂. (These authors (3, this table) also measured the infrared spectrum of (ClO)₂ and Cl₂O₃ in the region of 500 to 2000 cm⁻¹ using a Fourier transform infrared spectrometer.) Using the enthalpy of reaction given by Cox and Hayman (1, this table) and the dissociation energy of ClO as determined by Coxon and Ramsay (4, this table), and the $^2\Pi_{1/2} - ^2\Pi_{3/2}$ splitting A = 318 cm⁻¹ (4, this table) gives the value of 133 kJ mol⁻¹ at 298.15 K for the enthalpy of formation of (ClO)₂ with an estimated uncertainty of 8 kJ mol⁻¹.

Heat capacity and entropy

The microwave spectrum of Cl₂O₂ has been obtained by Birk et. al. (5, this table). The observed microwave spectrum is in substantial agreement with the earlier theoretical calculations which give estimates of both the vibrational frequencies and molecular dimensions of the ClO dimer (6, this table). The molecular dimensions were used to compute the inertial parameters for the normally occurring isotopic species. The computed entropy for the (ClO)₂ species at 298.15 K is 300.98 Jmol⁻¹K⁻¹. The experimental entropy for the dimerization of ClO combined with the standard entropy of ClO gives an S°(298.15 K) of 305.92 ± 11 Jmol⁻¹K⁻¹. The experimental entropy of (ClO)₂ is in good agreement with the calculated value. The major uncertainty in the computed entropy arises from the estimated frequencies 320 and 440 cm⁻¹.

Lowering these estimated frequencies to 250 and 350 cm^{-1} increases the computed S° (298.15 K) by 3.18 $\text{Jmol}^{-1}\text{K}^{-1}$. This would decrease the calculated $\Delta_{\text{r}}S$, for the dimerization of ClO from -149 to -146 $\text{Jmol}^{-1}\text{K}^{-1}$ compared to the measured $\Delta_{\text{r}}S$, $-144 \pm 11 \text{ Jmol}^{-1}\text{K}^{-1}$ (1). The calculated value of the $S^\circ(298.15)$ is chosen for these tables.

The vibrational spectrum of this species in the infrared region of 500 to 2000 cm^{-1} has been observed by Burkholder, et. al. (3, this table). They observed three features that they could assign to $(\text{ClO})_2$ at 750, 653 and 560 cm^{-1} . The two higher frequency absorptions correspond to the 750, 649, and 647 cm^{-1} found by Cheng and Lee (7, this table) in the matrix isolated infrared spectra of the products of the reactions described below. These workers observed the three stretching modes by trapping the molecules formed, in a discharge system, by the reactions: $\text{Cl} + \text{O}_3$, $\text{Cl} + \text{OCIO}$, $\text{O} + \text{OCIO}$, $\text{Cl} + \text{ClOCl}$, and $\text{O} + \text{ClOCl}$ in an argon matrix at 12 K. They obtained the Cl-O, (649.9 and 647.6 cm^{-1}) and O-O (752.6 cm^{-1}) stretching fundamentals, which have appropriate ^{35}Cl - ^{37}Cl isotope shifts. The torsional mode, 127 cm^{-1} , estimated from the microwave measurements (5, this table) is in excellent agreement with the 119 cm^{-1} obtained in the quantum mechanical calculation (6, this table). The bending modes, 320 and 440 cm^{-1} , are obtained from the quantum mechanical calculation (6, this table).

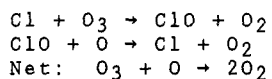
Others have studied the infrared spectrum of the self reaction of ClO by reacting Cl with O_3 , Cl_2O , or OCIO in a flow system (8, this table). These workers observed the Cl-O and O-O stretching modes in addition to absorptions in the 1000 to 1250 cm^{-1} region, which they ascribed to $(\text{ClO})_2$. Later workers, including Burkholder, et. al. (3, this table) and Cheng and Lee (7, this table) supported by quantum mechanical calculations of the frequencies of the $-\text{ClO}_2$ moiety (6, this table), suggest these bands are due to Cl_2O_3 produced by the termolecular reaction of OCIO with ClO. Other workers who studied the infrared spectrum formed by reacting $\text{Cl} + \text{O}_3$ in a matrix have given other absorptions which are probably due to other chlorine oxygen species (9-12, this table).

REFERENCES

1. R.A. Cox and G.D. Hayman, Nature **332**, 796 (1988)
2. N. Basco and J.E. Hunt, Int. J. Chem. Kinetics **11**, 649 (1979)
3. J.B. Burkholder, J.J. Orlando and C.J. Howard, J. Phys. Chem. **94**, 687 (1990)
4. J.A. Coxon and D.A. Ramsay, Can. J. Phys. **54**, 1034 (1976)
5. M. Birk, R.R. Friedl, E.A. Cohen, H.M. Pickett and S.P. Sander, J. Chem. Phys. **91**, 6588 (1989)
6. M.P. McGrath, K.C. Glemitschaw, F.S. Rowland and W.J. Hehre, Geophys. Res. Lett. **15**, 883 (1988)
7. B.M. Cheng and Y.P. Lee, J. Chem. Phys. **90**, 5930 (1989)
8. L.T. Molina and M.J. Molina, J. Phys. Chem. **91**, 433 (1987)
9. M.M. Rockkind and G.C. Pimentel, J. Chem. Phys. **46**, 4481 (1967)
10. W. G. Alcock and G.C. Pimentel, J. Chem. Phys. **48**, 2373 (1968)
11. L. Andrews and J.I. Raymond, J. Chem. Phys. **55**, 3087 (1971)
12. F.K. Chi and L. Andrews, J. Phys. Chem. **77**, 3062 (1973)

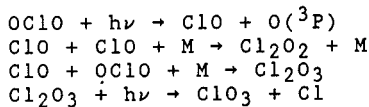
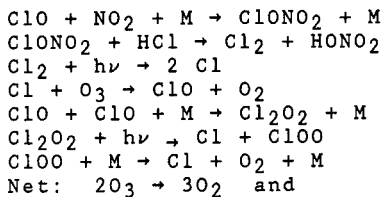
REACTION CYCLES CONTRIBUTING TO OZONE DEPLETION

There are several cycles involving chlorine atoms and chlorine oxygen species that can contribute to ozone depletion. These cycles all require chlorine atoms which can be formed either through photolytic or chemical processes. The process, which is thought to be principally responsible for ozone depletion in the stratosphere is,

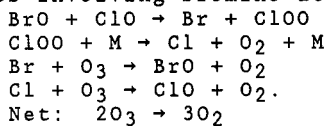


In polar regions, where the temperatures are low, the light flux in the spring and summer high, heterogeneous reactions occurring on polar stratospheric clouds are important (ref. 6, 7). These reactions often involve the reservoir molecules ClONO_2 and HCl which are converted to active Cl species. These reaction can provide large concentrations of ClO and OCIO , other processes involving higher chlorine oxides can also be important.

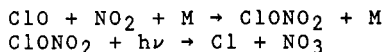
Included in these processes are,



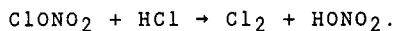
The Cl_2O_3 formed can either be photolyzed to give Cl_2O_2 which in turn is photolyzed to give Cl atoms and ClOO. Another pathway can yield higher order chlorine oxides, such as Cl_2O_4 , Cl_2O_6 and Cl_2O_7 which are formed by the reactions of ClO_3 with itself, ClO or O_3 (ref. 8). These species can then act as a sink for the simpler chlorine oxide molecules. There are also processes involving bromine atoms and bromine oxides such as,



Cycles can also involve nitrogen oxides and halogen atoms. A sink for chlorine atoms is provided by,



The NO_3 formed can be photolyzed to NO_2 ($\approx 90\%$) or NO ($\approx 10\%$), react with OH to form HONO_2 or combine with NO_2 to form N_2O_5 . These species can also enter into cycles, the net effect of which is to remove ozone catalytically from the atmosphere. Chlorine nitrate, ClONO_2 , can also react heterogeneously with HCl according to the reaction,



This heterogeneous reaction may be particularly important in polar atmospheres where it can combine with the other heterogeneous reactions involving the heavier chlorine oxide molecules.

APPLICATION OF THERMODYNAMIC DATA

As one can see from the previous discussions ozone is depleted catalytically by the presence of radicals such as halogen atoms, nitrogen oxides, hydroxyl radicals, or reactions of these radicals with stable species. In many of these cases the reactions are driven by photolytic processes to form the atom or radical. As such, light flux at a particular wavelength, J_λ , optical cross sections (or extinction coefficients), σ_λ , and the quantum yield, ϕ_λ , have to be considered according to the equation as part of the equilibrium model of the atmosphere

$$\text{Rate of Dissociation} = J_\lambda \times \sigma_\lambda \times \phi_\lambda$$

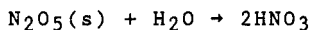
The rate of dissociation refers to the chemical dissociation of molecular species into radicals. The determination of these quantities for molecules implicated in ozone depletion is very important in the understanding of the "equilibrium" atmosphere. Traditional calorimetric measurements to determine enthalpies of reactions, entropies, and equilibrium constants are important to generate reliable estimates of the concentrations in the undisturbed atmosphere. Of special importance are the thermodynamic properties of potential sink molecules for the halogen atoms and halogen oxides and those molecules that react to form these molecules. These species include ClONO_2 , NO_3 , NO_2 , HCl, BrONO_2 , HOCl, ClO_2 , N_2O_5 . Often, as for example the case of N_2O_5 , these thermodynamic data are also important because they are essential for the determination of the thermodynamic properties of other species such as NO_3 .

The importance of accurate and precise thermochemical data for the formation properties, in the case of NO_3 , has already been alluded to earlier (ref. 3,

4). In these studies the equilibrium

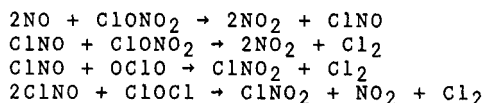


was studied as a function of temperature in the range of 211-273 K. This study which yielded precise values for $\Delta_r H^\circ$ and $\Delta_r S$, is in agreement with the previous studies of this equilibrium. The $\Delta_f G^\circ$ and $\Delta_f H^\circ$ of $\text{N}_2\text{O}_5(\text{s})$ was determined by solution calorimetric studies of the reaction,



The formation properties of $\text{N}_2\text{O}_5(\text{g})$ were determined by measurement of the vapor pressure in the temperature range of 211-273 K.

Among the other molecules of interest for which the $\Delta_f H^\circ$ have been determined using conventional calorimetric methods are ClONO_2 , ClOCl and OClo . Alqasmi, Knauth and Rohlack (ref. 9) have determined the formation properties of these molecules by determining the enthalpies of the reactions



CONCLUSIONS

The accurate and precise determination of the enthalpies of formation and Gibbs energy of formation and entropies of molecular and atomic species implicated in ozone depletion is important to the determination of concentration of molecules in the stratosphere. Usually the uncertainties in the enthalpy of formation is the principal cause in the uncertainty in the Gibbs Energy of formation. In the case of radicals accurate photoionization measurements coupled with an understanding of the channels of dissociation offers the most promising route to an accurate enthalpy of formation. The entropy of these molecules is most accurately determined by detailed molecular spectroscopic observations of their electronic, vibrational and rotational spectra followed by a statistical mechanical calculation. The advent of diode lasers and high resolution Fourier Transform infrared and microwave spectroscopic techniques have made the observation of radicals more feasible. In this connection it should be noted that much of the vibrational and rotational spectroscopic data used in this study for ClO , NO_3 , Cl_2O_2 , OClo , were obtained using these techniques.

There are several molecules which may be important in stratospheric ozone depletion, for which accurate $\Delta_f H^\circ$ are not available. They include ClONO , BrONO , BrONO_2 , and HOCl . Knowledge of Henry Law Constants, solubilities and some $\Delta_f H^\circ$ of condensed phase species are also of interest, particularly in the polar atmosphere where heterogeneous reactions are thought to be responsible for ozone depletion in the spring and summer.

Acknowledgements

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REFERENCES

1. R. Atkinson, D.L. Baulch, R.A. Cox, R.F. Hampson, Jr., J.A. Kerr, and J. Troe, Planet. Space. Sci., **37**, 1605, 1989.
2. W.B. DeMore, D.M. Golden, M.J. Molina, R.F. Hampson, M.J. Kurylo, C.J. Howard, A.R. Ravishankara, Chemical Kinetics and Photochemical Data for Use in Stratosphere Modeling, JPL Publication 90-1, 1990.
3. C.A. Cantrell, J.A. Davidson, A.H. McDaniel, R.E. Shetter, and J.G. Calvert, J. Chem. Phys., **88**, 4997 (1988).
4. A.H. McDaniel, J.A. Davidson, C.A. Cantrell, R.E. Shetter, and J.G. Calvert, J. Phys. Chem., **92**, 4172 (1988).
5. M.W. Chase, Jr., C.A. Davies, J.R. Downey, Jr., D.J. Fruip, R.A. McDonald, and A.N. Syverud, JANAF Thermochemical Tables, Third Edition, J. Phys. Chem. Ref. Data, **14**, Supp. 1 (1985).
6. R.A. Cox and G.D. Hayman, Nature, **332**, 796 (1988).
7. S.P. Sander, R.R. Friedl, and Y.L. Yung, Science, **245**, 1095 (1989).
8. G.D. Hayman and R.A. Cox, Chem Phys. Lett., **155**, 1, (1989).
9. R. Alqasmi, H.-D. Knauth, and D. Rohlack, Ber. Bunsenges. Phys. Chem. **82**, 217 (1978).

ERRATA

Report entitled 'Atomic Weights of the Elements 1989' published in Vol. 63, No. 7 (1991), pp. 975-990

p.980 (Table 2)	Atomic Weight of Sulfur	:	<u>for</u>	35.066(6)	<u>read</u>	32.066(6)
p.989	Reference 24	:	<u>for</u>	Vol.69	<u>read</u>	Vol. 62
p.990	Reference 67	:	<u>for</u>	Howkins	<u>read</u>	Hawkins

Report entitled 'Isotopic Composition of the Elements 1989' published in Vol. 63, No. 7 (1991), pp. 991-1002

p.995	Atomic no. 22, Ti-49	:	<u>Transfer</u>	5.5(1)	<u>from</u>	under column 7	<u>to</u>	under column 9
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Paper entitled 'Thermodynamic Properties of gas phase species of importance to ozone depletion' by S. Abramowitz and M.W. Chase Jr., published in Vol. 63, No. 10(1991), pp. 1449-1454

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IDEAL GAS THERMODYNAMIC TABLES

The importance of accurate and precise thermodynamic values is illustrated by the fact that a recent lowering of the $\Delta_f H^\circ(298.15\text{K})$ of NO_3 by 8.7 kJ mol^{-1} changes the equilibrium constant of this reaction by a factor of 33, from 0.0127 to 0.00042 (ref. 3, 4).

The construction of thermodynamic tables for gas phase species requires a knowledge of the spectroscopic constants of the molecule including electronic energy levels and degeneracies, vibrational frequencies and rotational constants, in the ground vibrational state. These data are either obtained from direct spectroscopic measurements or from theory or by analogy with other similar chemical compounds. In addition $\Delta_f H^\circ$, the enthalpy of formation, is required. These data, for the species of interest, often come from spectroscopic measurements or gas phase kinetics and equilibrium measurements involving chemical reactions. In some cases theoretical quantum mechanical calculations are used, particularly for those species in which low lying electronic states are expected.

Table 1 contains the spectroscopic constants for several chlorine oxides and nitrogen trioxide used in the calculation of thermal functions and formation properties for the ground and in some cases excited electronic states. Thermodynamic functions and formation properties at several temperatures are given in Table 2. These tables were calculated using the formalism described in the third edition of the JANAF Thermochemical Tables (ref. 5). Briefly, for polyatomic species the harmonic oscillator rigid rotor model was utilized. Excited electronic states, where known, were included together with the spectroscopic constants for those states. The anharmonic oscillator non-rigid rotor model presented in the JANAF Thermochemical Tables was used for ClO . Excited electronic states were included. The ground state for ClO , which has a splitting of 318 cm^{-1} , was included as two states, in order to give a more accurate thermal functions at the low temperatures of primary interest in atmospheric phenomena. Table 3 gives $\Delta_f H^\circ(298.15\text{K})$, $S^\circ(298.15\text{K})$ and $\Delta_f G^\circ(298.15)$ together with their estimated uncertainties. These uncertainties are propagated throughout the temperature range of computation of thermal functions. Finally a sample of the text for a JANAF Table is given in Table 4. Note that JANAF Thermochemical Tables for the species studied at some selected temperatures are given in Table 2.

Table 1. Spectroscopic Constants

Species	Vibrational Frequencies cm^{-1}	Bond Distance, Å and Angles
ClO^a	854.9	1.56893
OClO^a	945.6, 447.7, 1110.1	Cl-O: 1.471, O-Cl-O: 117.6°
ClO_2	1143, 373, 407	Cl-O: [1.83], O-O: [1.23] O-O-Cl: $[110]^\circ$
ClOCl	638, 298, 678	Cl-O: 1.9679, Cl-O-Cl: 110.9°
ClClO	961.8, 239.4, 375.1	Cl-O: [1.587], Cl-Cl: [2.268] Cl-Cl-O: $[120]^\circ$
$(\text{ClO})_2$	765, 647.6, 649.9, [440], [320], 127	Cl-O: 1.7044, O-O: 1.4259 Cl-O-O: 110.1° , dihedral angle: 81.0°
Cl_2O_3	1225, 1057, 740, 560, [490] [200], [190], [190], [100]	Cl-O ₂ : [1.47], ClO-ClO ₂ : [1.9], Cl-OClo ₂ : $[1.7]^\circ$, Cl-O: $[116.7]^\circ$ dihedral angle: $[70]^\circ$
NO_3^a	1050, 762.2, 1492.4 ^b , 360 ^b	N-O: 1.2397, O-N-O: 120°

Quantities in brackets are estimated.

^a Spectroscopic constants of excited electronic states were included in calculations

^b Doubly degenerate

Note: This page should have been printed as the second page of the article 'Thermodynamic properties of gas phase species of importance to ozone depletion' by S. Abramowitz and M.W. Chase Jr., published in October 1991 issue of this journal, Vol. 63, No. 10, pp. 1449-1454. It is numbered 1450A, is printed on one-side and should be inserted between pages 1450 and 1451, particularly in the bound volume. Its omission from the article is regrettable; the reasons are mysteriously not apparent; an apology to readers and librarians.