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An Improved Calculation of the Ideal Gas Thermodynamic Functions of Selected Diatomic Molecules

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An Improved Calculation of the Ideal Gas Thermodynamic Functions of Selected Diatomic Molecules

by

R. C. Feber
C. C. Herrick

ABSTRACT

Ideal gas thermodynamic functions of selected diatomic molecules are calculated to 6000°K at 100° intervals by direct summation over experimental and extrapolated vibrational-rotational levels of electronic states which contribute to the functions at the maximum temperature. The procedure used for the extrapolation of energy levels allows for cutoff of both vibrational and rotational quantum numbers. Thermodynamic functions are tabulated for F_2, Cl_2, Br_2, I_2, HF, HCl, HBr, HI, Li_2, Na_2, K_2, B_2, C_2, and HgH.

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INTRODUCTION

With the growth of interest in high temperature chemistry and technology, there has developed an increasing need for reliable thermodynamic data at elevated temperatures. This paper is concerned with the calculation of the thermodynamic functions of diatomic gases from spectroscopic data using the methods of statistical mechanics. The procedures commonly used to derive the necessary partition functions when high temperature corrections are applied to the harmonic oscillator-rigid rotator treatment involve simplifications and approximations the magnitude of whose effect becomes more uncertain as the temperature increases. It is of interest, therefore, to eliminate the major sources of these uncertainties from the calculations. The earlier approximate procedures were developed largely to reduce the time required for computation with desk calculators. The availability of high speed computers largely eliminates this need. It therefore becomes practicable to evaluate partition functions routinely by a process of direct summation over all vibrational-rotational term values. There still remains the problem of performing a suitable extrapolation of experimentally established term values to energies beyond the observed range. To facilitate such extrapolations, the concept of the effective potential energy of a vibrating-rotating system is used to determine the limiting value of the rotational quantum number, J, as a function of the vibrational quantum number, v, for electronic states of selected diatomic molecules. The Morse, Rydberg, and Hulburt-Hirschfelder potential energy functions for the nonrotating molecule are used to calculate effective potential energies.

When necessary, observed vibrational term values are extrapolated to the dissociation limit with suitable boundary conditions. Ideal gas thermodynamic functions are then determined from partition functions and their derivatives calculated by a process of direct summation over experimental and extrapolated energy levels for those identified (and, in a few cases, predicted) stable electronic states which contribute to the functions to 6000°K. Previous applications of the concept of an effective potential to the calculation of thermodynamic functions of diatomic molecules have been made by Baumann,[4,5] Gurvich and Yungman,[26] Stupochenko et al.,[73] and Woolley, Scott, and Brickwedde.[82]

PRELIMINARIES

The procedure for calculating thermodynamic functions of diatomic gases from partition functions will not be reviewed here. The subject is amply discussed in a variety of places. Likewise, no detailed review will be made of all the methods which have been developed to calculate approximate partition functions for the general diatomic molecule, taking into account the anharmonicity of vibration and a variable moment of inertia. It will perhaps be sufficient to note that the method described by Mayer and Mayer,[46] or an elaboration of that method, has been used almost exclusively to calculate the thermodynamic functions of diatomic gases for the many compilations of such data which have been published in this country in recent years. For some molecules, the method, which treats $^1\Sigma$ states, may be adequate to several thousand degrees. For other molecules with small dissociation energies, it is demonstrably inadequate even below 1000°K. In addition to the need for modifications to treat rotational levels for configurations other than $^1\Sigma$ states, the inadequacies result from approximations used to replace direct summation of exponentials of the term values with expressions less tedious to evaluate. Simplification is achieved in part by replacing direct summation with respect to J by the first few terms of the Euler-Maclaurin summation formula between the limits $J = 0$ and $J = \infty$. Certain other exponentials are approximated by the first two terms of a power series expansion prior to integration or summation. Summation with respect to v is also from 0 to ∞. Three related sources of possible error are thereby introduced. The approximation of exponentials involving v and J by the first two terms of a power series expansion becomes increasingly unsatisfactory as v and J increase. For electronic states of an actual molecule dissociating into neutral atoms, v and J will not increase without limit, but each will have a limiting value. For some states an accurate representation of experimental energy levels from rotational and vibrational analyses requires higher order spectroscopic constants than are included in the Mayer and Mayer formulation or its elaborations. The combined effect of these factors is to increase the uncertainty of the calculation as the temperature increases. Although the particulars may vary, the same type of comments may be made regarding the earlier methods of eliminating direct summation, such as those of Kassel,[37,38] and Gordon and Barnes.[25] The treatment of Gordon and Barnes has been modified by Brounshtein,[8,9] who developed corrections to the partition functions to account for limiting values of J.

In all of the above procedures and the method explored here, quantum mechanical partition functions of the molecules are calculated for discrete bound states of the pairs of atoms. Another quite different approach has also been reported in the search for methods valid at high temperatures. The total classical partition function of a system of atoms and molecules may be calculated and formation of molecules treated as a gas imperfection. Thermodynamic functions of a diatomic molecule may be derived as corrections to those of the monatomic gas from expressions related to the second virial coefficient and its temperature derivative. The effects of quantization are accounted for in the form of corrections. It is necessary to select a suitable potential energy function to represent the interaction of the atoms. Beckett and Haar[7] adopted the Morse potential function and applied the virial coefficient approach to the calculation of the thermodynamic functions of a number of diatomic molecules to 25,000°K. Sinanoglu and Pitzer[65] evaluated the second virial coefficient of $Na_2(g)$ with the use of the Rydberg potential function. The elaboration of this approach using cluster theory to an equilibrium mixture of a number of molecules was reviewed by Beckett, Green, and Woolley[6] and discussed by Woolley.[81]

DESCRIPTION OF METHOD

As noted above, quantum mechanical partition functions are calculated here by the direct summation of suitably weighted exponentials of the energies of experimental and extrapolated vibrational and rotational levels of stable electronic states. Therefore, the purpose of the method explored is to perform an extrapolation of the experimental levels in a meaningful way that is consistent with appropriate limiting conditions. The dissociation energy of each experimentally observed electronic state (and in a few cases, of predicted electronic states) is assumed to be known. For the temperature range and the molecules considered, it has been necessary to treat only states dissociating to normal or excited neutral atoms and therefore having a finite number of vibrational levels between the minimum of the potential curve and the dissociation limit. Thus it has not been necessary to treat electronic states which dissociate to ions and for which there will be an infinite number of vibrational and rotational levels below the dissociation limit. Binding forces in states dissociating into neutral atoms can have an ionic contribution, resulting in "anomolous" potential energy curves. It is assumed that the Morse, Rydberg, or Hulburt-Hirschfelder potential function will approximately represent this stiuation. No electronic states have been treated for which maxima in the potential energy curves of the nonrotating molecule have been postulated, although in principle such states should offer no particular difficulty.

An expression for the effective potential energy of a vibrating-rotating diatomic molecule may be "derived" starting from a classical mechanical view of the rotating but vibrationless molecule. In the latter condition, the law of conservation of momentum will require the internuclear distance, r, to assume that value, r_c, at which the centrifugal force equals the attractive force; that is, for the rigid rotator

$$p^2/\mu r_c^3 = U_o'(r_c), \tag{1}$$

where p is the angular momentum, μ is the reduced mass, and $U_o'(r_c)$ is the first derivative of the potential energy, $U_o(r)$, at the equilibrium internuclear distance r_c. If now the internuclear distance is displaced from this equilibrium position by the addition of vibrational energy, the force restoring the atoms to that position is $-[U_o'(r)-p^2/\mu r^3]$. The restoring force is taken to be the negative of the derivative of an effective potential $U_{eff}(r)$. Therefore

$$U_{eff}(r) = U_o(r) + p^2/2\mu r^2. \tag{2}$$

Thus the potential energy is increased by an amount equal to the kinetic energy of rotation. Substituting for the rotational kinetic energy its value according to quantum mechanics, one obtains

$$U_{eff}(r) = U_o(r) + \frac{h}{8\pi^2 c\mu r^2}\ [J(J+1)-\lambda^2] \quad (\text{in cm}^{-1}). \tag{3}$$

If the interaction of electron spin and electronic orbital angular momentum with the angular momentum of nuclear rotation is neglected, λ becomes zero. The spectroscopic rotational constant B_e is given by

$$B_e = \frac{h}{8\pi^2 c\mu r_e^2}\ , \tag{4}$$

where r_e is the equilibrium internuclear distance for the hypothetical state $v = -1/2$ and $J = 0$. Thus

$$U_{eff}(r) = U_o(r) + (r_e/r)^2 B_e\, J(J+1) \; . \tag{5}$$

J is replaced by K for Hund's coupling case (b). The $1/r^2$ dependence of the kinetic energy of rotation is equivalent to representing the moment of inertia of the nonrigid rotator by

$$I(\zeta) = I_e(1+\zeta)^2 \; , \tag{6}$$

where $I_e = \mu r_e^2$ (the moment of inertia of the rigid rotator), and $\zeta = (r - r_e)/r_e$.

Calculation of effective potentials as a function of r and J requires that the potential energy function $U_o(r)$ be known. Two general approaches to its determination are possible. One is to calculate the function from the experimentally observed energy levels using one of the variations of the Rydberg-Klein-Rees (RKR) method.[60] This approach, although probably the more satisfactory in principle, has the disadvantage that the function will be defined only for the range of r corresponding to the experimental spectroscopic data. Because for most electronic states spectroscopic data will be lacking near the dissociation limit, we have preferred the alternate approach of approximating $U_o(r)$ by one of the proposed empirical or semi-empirical algebraic expressions whose parameters are determined from spectroscopic constants and the dissociation energy. From among the proposed expressions which are defined to the dissociation limit, two three-parameter functions, the Morse and the Rydberg, and one five-parameter function, the Hulburt-Hirschfelder, have been used and compared.

The Morse potential function[48] may be written

$$U_o(r) = D\,[1-\exp(-x)]^2 \; , \tag{7}$$

where D is the dissociation energy measured from the minimum of the potential energy curve, $x = [\omega_e/2(B_eD)^{\frac{1}{2}}]\zeta$, and ω_e and B_e are the usual spectroscopic constants. The value of D for a particular electronic state of a given diatomic molecule will in practice by derived from spectroscopic data, thermochemical data, or a combination of both.

The Rydberg potential[63] is given by

$$U_o(r) = D\,[1-(1+x)\exp(-x)]. \tag{8}$$

The Hulburt-Hirschfelder potential function[30,31] may be written

$$U_o(r) = D\,[1-\exp(-x)]^2 + D[cx^3(1+bx)\,\exp(-2x)]\,. \tag{9}$$

The coefficients b and c are algebraic functions of D and the spectroscopic constants ω_e, $\omega_e x_e$, α_e, and B_e. The first term on the right of this equation is the Morse potential, and the second is a correction to that potential which uses two additional parameters. The two additional parameters should provide a better fit to the "true" potential curve at large r, which is the region of interest for the present use of a potential energy function. The Huburt-Hirschfelder function can be expected to give a fit to the true potential which is as good or better than that provided by the other available empirical potential functions.[30,71,74] It is also possible to use the formalism of the Hulburt-Hirschfelder function to represent results of an RKR calculation over a significant range of r. This may be done by calculating "effective" Hulburt-Hirschfelder coefficients from a nonlinear least squares fit to the RKR data.

With the selection of an expression for $U_o(r)$, a family of effective potential curves may be calculated. Such a family of curves is illustrared in Figure 1 for the ground state of $Na_2(g)$. To calculate these curves a Hulburt-Hirschfelder potential and appropriate molecular constants from Table 24 were used. The effective potential curve of a given electronic state for the general J (or K)>0 first goes through a minimum at r_c ($>r_e$) with increasing r. As r continues to increase, the curve passes through a maximum and then asymptotically approaches the dissociation limit of that state. As J is permitted to increase, the potential difference between the minimum and the maximum becomes progressively smaller, and r_{max} approaches r_c. Finally, at some critical value of J, the minimum and maximum coincide at an inflection point on the effective potential curve. Higher rotational states are mechanically unstable, as they no longer correspond to effective potential curves with a minimum. By the same criterion, however, there will be stable rotational states with energies greater than that of the dissociation limit and separated from the latter by a potential barrier. The curves in Figure 1 were calculated at the intervals $\Delta J = 10$, and the critical J is at 270.

The critical J, J_{max}, is taken to be the rotational quantum number of the last stable rotational level for the lowest vibrational level, $v = 0$, of the molecule whose effective potential can be represented by the assumed formulation. As v increases, the value of J at which the potential barrier is exceeded decreases. The determination of a J_{max} for each v is made with the so-called limiting curve of dissociation, which is a plot of the maxima of the effective potential curves as a function of J(J+1) [or K(K+1)]. For a given vibrational level, the sum of the vibrational energy and the rotational energy cannot exceed the maximum of the effective potential appropriate to that J. The largest J for which this condition holds is J_{max} for that vibrational level. This procedure is illustrated for the ground state of HF(g) in Figure 2. These data are based on the Rydberg potential and the molecular constants tabulated in Table 8. The usefulness and validity of this procedure may be checked by a comparison of calculated values of J_{max} as a function of v with experimentally observed breakoff points in band spectra. A direct comparison is limited to those band spectra which correspond to Herzberg's case III of predissociation (predissociation by rotation - a

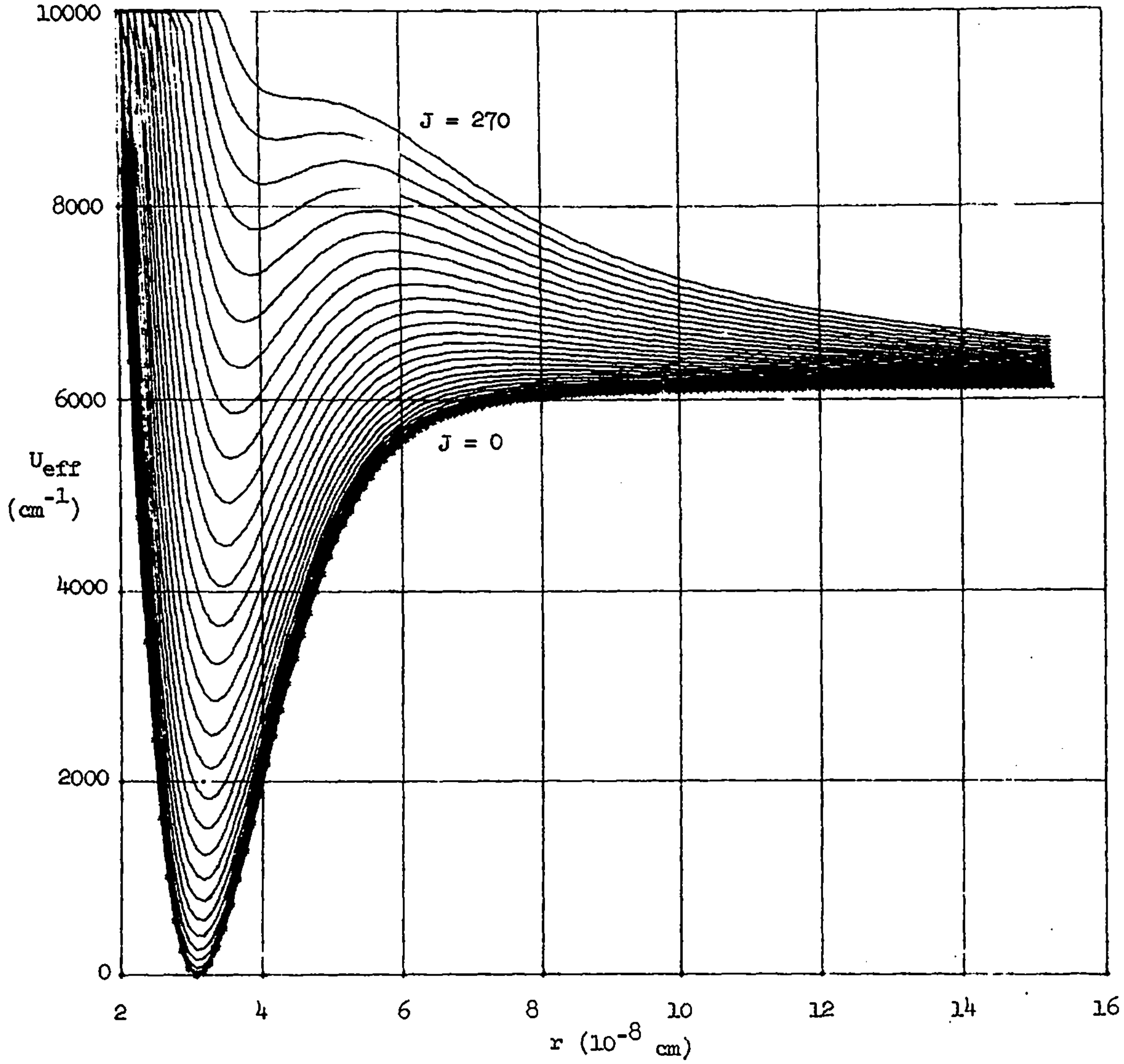

Fig. 1. Effective Potential Curves for the Ground State of Diatomic Sodium

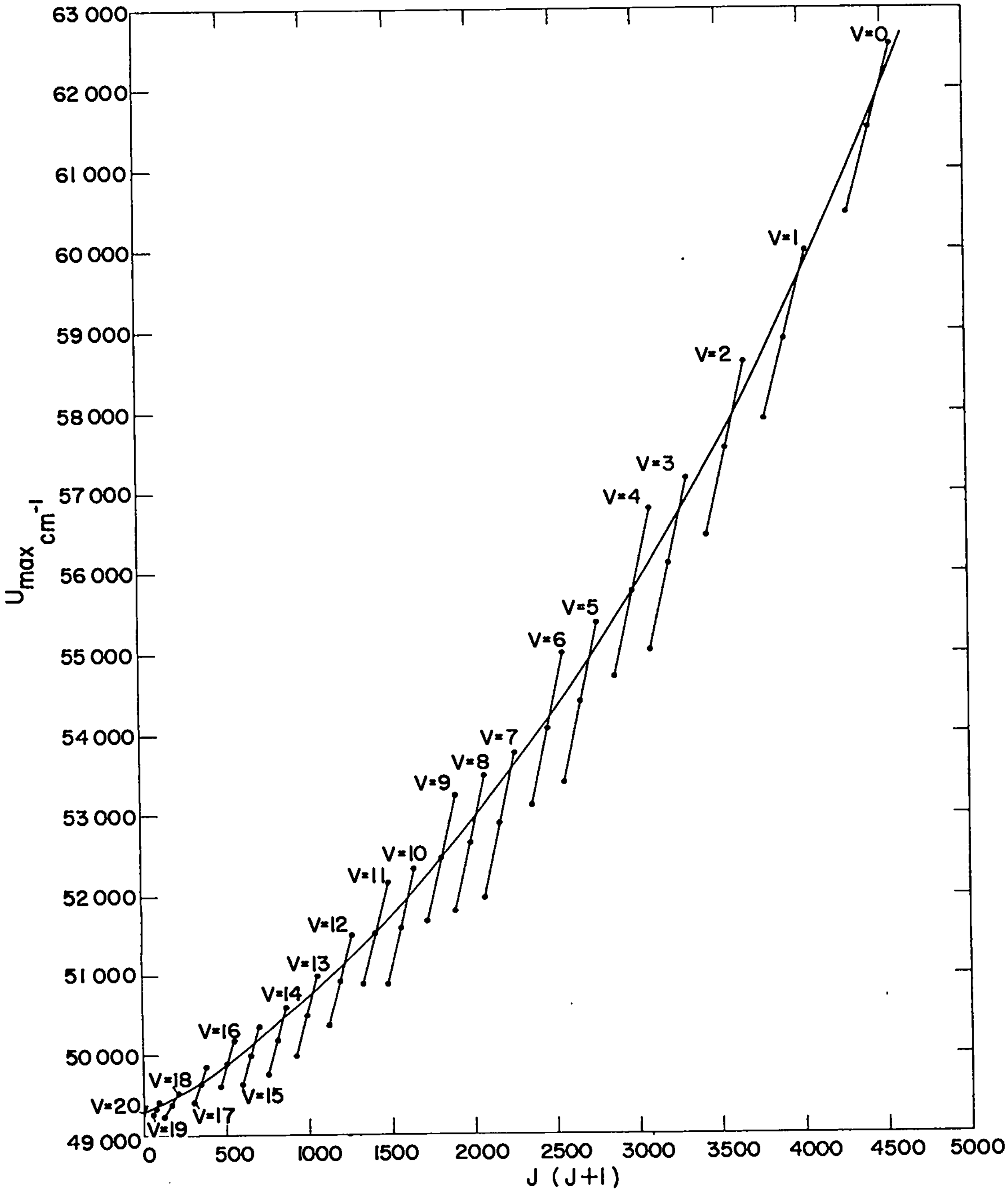

Fig. 2. Limiting Curve of Dissociation for the Ground State of Hydrogen Fluoride

radiationless molecular decomposition with no change of electronic state). The number of molecules with electronic states for which such a comparison is possible is not very great. Most observed predissociation effects are believed due to a radiationless transition between a stable electronic state and an unstable state or the continuum above the dissociation limit of another stable state (Herzberg's case I). In this case, the J at which rotational levels of the first stable state are observed to break off can be determined by the relative positions of the potential curves of the two electronic states. This J will not correspond to J_{max}.

It will, in general, be necessary to extrapolate vibrational term values from experimental low-lying levels to the dissociation limit. This is accomplished by assuming that the finite number of vibrational levels between the highest experimental level, v_i, and the limiting level, v_{max}, at or near the dissociation limit may be approximated by a cubic in v

$$G(v)_{v \geq v_i} = a_o + a_1 v + a_2 v^2 + a_3 v^3 \ . \tag{10}$$

The coefficients of this expression are determined from appropriate boundary conditions. At v_i both the term value $G(v_i)$ and its slope with respect to v calculated from equation (10) are set equal to the analogous experimental quantities. At the dissociation limit

$$G(v)_{v=v_{max}} = D, \quad \text{and } (\partial G/\partial v)_{v=vmax} = 0 \ . \tag{11}$$

In general, the value of v_{max} so calculated is not an integer and is therefore truncated. Experimental and extrapolated vibrational term values are then combined and fitted by a least-squares method to a power series in v up to a power of 10. The equation giving the best fit is used for subsequent calculations.

As noted above, a J_{max} for each v is calculated by finding the largest value of J which gives a sum of vibrational and rotational energies equal to or just less than the energy corresponding to the maximum of the effective potential for that J. Except for a final term, the expression for rotational term values is based on the usual formulation for the simple nonrigid rotator.

$$F(v,J) = B_v J(J+1) + D_v J^2(J+1)^2 + H_v J^3(J+1)^3 + L_v J^4(J+1)^4 + L_v^2 J^8(J+1)^8 / \left[H_v J^3(J+1)^3 - L_v J^4(J+1)^4\right], \tag{12}$$

where

$$B_v = B_e - \alpha_e(v+\tfrac{1}{2}) + \gamma_1(v+\tfrac{1}{2})^2 + \gamma_2(v+\tfrac{1}{2})^3 + \gamma_3(v+\tfrac{1}{2})^4 + \cdot\cdot\cdot\cdot,$$

$$D_v = D_e + \beta_1(v+\tfrac{1}{2}) + \beta_2(v+\tfrac{1}{2})^2 + \beta_3(v+\tfrac{1}{2})^3 + \cdot\cdot\cdot\cdot,$$

$$H_v = H_e + \delta_1(v+\tfrac{1}{2}) + \delta_2(v+\tfrac{1}{2})^2 + \delta_3(v+\tfrac{1}{2})^3 + \cdot\cdot\cdot\cdot, \tag{13}$$

and

$$L_v = L_e + \epsilon_1(v+\tfrac{1}{2}) + \epsilon_2(v+\tfrac{1}{2})^2 + \epsilon_3(v+\tfrac{1}{2})^3 + \cdot\cdot\cdot\cdot$$

The symbolism for the coefficients of $J^3(J+1)^3$ and $J^4(J+1)^4$ and the use of subscripted coefficients for the cross terms is arbitrary. Usage in the literature is not uniform. The last term on the right of the equation is added to the usual expression for rotational energy as an approximation to the contribution of terms involving powers of J(J+1) greater than the fourth. It is equal to the sum of a geometric series of added terms in which the ratio of consecutive terms is assumed to be $L_v J(J+1)/H_v$. This approximation was used by Woolley, Scott, and Brickwedde[82] in the course of the calculation of the thermal properties of hydrogen. It is intended to provide an improved extrapolation of rotational levels to large J. With the exception of the ground state of H_2, the maximum contribution of the correction terms to F(v,J) for any of the electronic states treated in this paper is of the order of 2000 cm^{-1}.

For multiplet electronic states encountered here, it is probably not necessary to generalize the expression for F(v,J) to include the effect of the interaction between rotational and electronic motions on the rotational levels. The effect on the thermodynamic functions would be either negligible or less than the uncertainties resulting from the extrapolation of vibrational-rotational levels to the dissociation limit. Such interactions are described to a first approximation by one or another of Hund's coupling cases. With increasing rotation, various uncoupling phenomena can also occur.

Rotational analyses of the band spectra involving a few of these electronic states are sufficiently complete to provide experimental values of H_e and L_e. However, for most states such data are lacking, and they are predicted with the use of Dunham's equations.[18] This use requires that ω_e, $\omega_e x_e$, B_e, and α_e be known. Indeed, for many states B_e and α_e are the only rotational constants experimentally known. Although D_e is frequently reported, it is commonly calculated from the approximation

$$D_e = 4\, B_e^3/\omega_e^2 \tag{14}$$

which may be derived starting with the classical picture of the harmonic oscillator and nonrigid rotator, and also follows with additional small correction terms from Dunham's equations.

The spectroscopic constant β_1 may also be predicted from Dunham's equations and ω_e, $\omega_e x_e$, B_e, and α_e. If, in addition, γ_1 is known, γ_2, β_2, and δ_1 may also be predicted from his equations. Sandeman[64] recast Dunham's potential function, and from relations given by him it is possible to predict γ_1 with the special assumption of the validity of the Morse potential function. Actually, limited use is made of predicted values for these quantities. Thus, in most cases, vibrational-rotational interaction terms are included in the expression for F(v,J) only if the appropriate experimental spectroscopic constants are available.

All necessary data are now at hand to calculate partition functions and their derivatives by direct summation over experimental and extrapolated energy levels, taking into account cutoff of vibrational and rotational quantum numbers. Calculations are made on an IBM-7094. A J_{max} for a given vibrational level with quantum number v_n is obtained by equating the vibrational-rotational energy $G(v_n) + F(v_n,J)$ to an expression for the limiting curve of dissociation and solving for J_{max} by the Newton-Raphson method. As noted above, limiting curves of dissociation and J_{max}'s were calculated using the Morse, Rydberg, and Hulburt-Hirschfelder potential functions, in turn. Among the molecules considered here, a direct comparison between predicted and observed J_{max}'s may be made for the ground states of HgH and HF. Experimental J_{max}'s for the ground state of HgH as reported by Hulthen[32] and from the more recent work of Porter[51] are compared in Table 1 with values predicted using the three potential functions.

Table 1

Breakoff of Rotational Levels of Mercury Hydride

	Vibrational Quantum Number, v				
J_{max}	0	1	2	3	4
Experimental					
Hulthen	30	23	16	8	5
Porter	31	24	16	8	-
Predicted					
Morse	30	23	16	8	5
Rydberg	31	24	17	9	5
Hulburt-Hirschfelder	34	26	18	9	6

As is shown the Morse or Rydberg potentials give a slightly better fit than the Hulburt-Hirschfelder potential. A similar comparison for the ground state of HF is given in Table 2. The experimental values of J_{max} are from the data of Johns and Barrow.[36]

Table 2

Breakoff of Rotational Levels of Hydrogen Fluoride

	Vibrational Quantum Number, v										
J_{max}	9	10	11	12	13	14	15	16	17	18	19
Experimental	≥42	≥40	37	34	31	28	25	21	17	13	8
Predicted											
Morse	41	38	36	33	30	27	24	21	17	13	8
Rydberg	42	39	37	34	31	28	25	22	18	13	8
Hulburt-Hirschfelder	41	38	36	33	30	27	24	21	17	13	8

The agreement is quite good with all potentials, although in this case the Rydberg potential is slightly superior.

Woolley, Scott, and Brickwedde[82] calculated values for the energies of unobserved higher rotational levels of molecular hydrogen, as well as limiting values of J as a function of v. For this purpose they first calculated the potential energy curve U (r) by a procedure equivalent to the RKR method using experimental vibrational levels to within 140 cm^{-1} of the dissociation limit. They then computed corresponding values of v, J(J+1), and the energy F of the vibrating-rotating system by applying the quantum integral to the effective potential curves.

$$\oint p\,dq = (2mr_e^2hc)^{\frac{1}{2}} \oint (F - U_{eff})^{\frac{1}{2}}\,d\xi = (v + \tfrac{1}{2})h. \qquad (15)$$

We have used the same spectroscopic constants they used in the application of the procedures tested here. Of the three analytical expressions for $U_0(r)$, the Rydberg potential gives the closest agreement with their potential energy curve in the region of large r, as shown in Figure 3. This region is the important one for establishing a limiting curve of dissociation. In Figure 3 the calculations of Woolley, Scott, and Brickwedde are plotted as dots. The solid line is a potential curve obtained from the Hulburt-Hirschfelder equation using effective coefficients. The effective coefficients are obtained by a nonlinear least-squares fit of the Hulburt-Hirschfelder equation to the RKR data. In Table 3 values of J_{max} calculated with the Morse, Rydberg, and Hulburt-Hirschfelder equations are compared with values derived from the calculations of Woolley, Scott, and Brickwedde. The heat capacity of para-H_2 as calculated by Woolley, Scott, and Brickwedde is compared in Table 4 with heat capacities calculated with J_{max}'s based on the indicated energy functions. Although above 3000°K the heat capacities calculated here are consistently lower than those based on the method of extrapolation of rotational levels used by Woolley, Scott, and Brickwedde, the magnitude of the difference is probably within the uncertainty of any extrapolation procedure.

Table 3

Breakoff of Rotational Levels of Diatomic Hydrogen

	J_{max}			
v	Woolley et al.	Morse	Rydberg	Hulburt-Hirschfelder
0	38	36	39	37
1	35	32	33	32
2	33	29	30	29
3	31	27	28	27
4	29	25	26	26
4	29	25	26	26
5	27	24	24	24
6	25	22	22	22
7	23	20	21	20
8	21	19	19	19
9	19	17	17	17
10	16	15	15	15
11	14	12	13	12
12	11	10	10	10
13	7	7	7	7
14	4	4	4	4
15	0	0	0	0

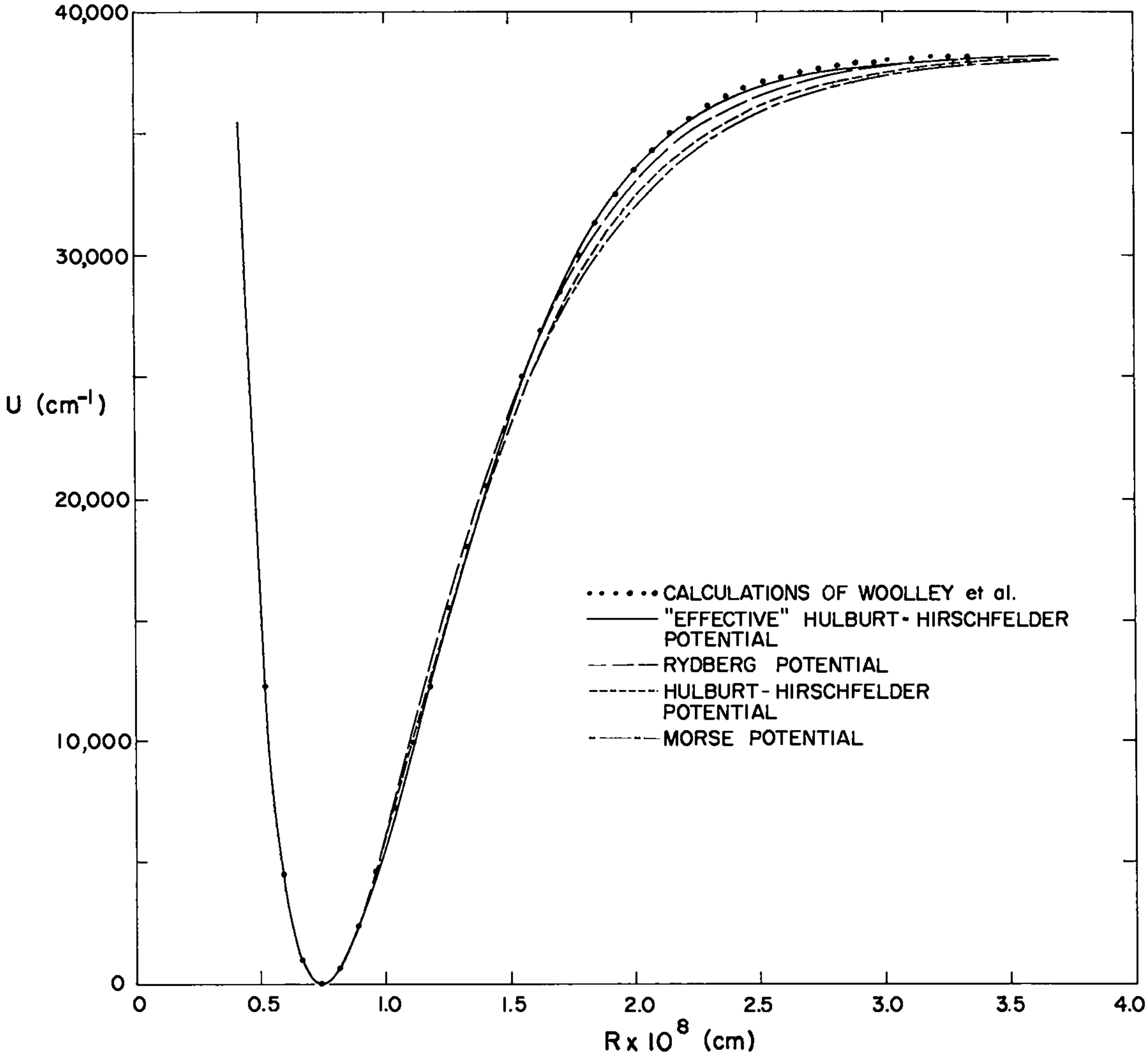

Fig. 3. Potential Energy Curves for Diatomic Hydrogen

Table 4

Heat Capacity of p - Hydrogen

T, °K	C_p, cal/deg/mole Woolley et al.	Morse	Rydberg	Hulburt-Hirschfelder
100	6.455	6.453	6.453	6.453
300	7.152	7.153	7.153	7.153
500	6.998	6.998	6.998	6.998
1000	7.219	7.219	7.219	7.219
1500	7.720	7.719	7.719	7.719
2000	8.195	8.192	8.192	8.192
3000	8.859	8.859	8.859	8.859
4000	9.342	9.325	9.327	9.326
5000	9.748	9.683	9.694	9.687
6000	--	9.872	9.904	9.882

RESULTS

In this section are given the values and sources of the molecular constants used and the thermodynamic functions calculated for the following diatomic molecules: HgH, HF, HCl, HBr, HI, F_2, Cl_2, Br_2, I_2, Li_2, Na_2, K_2, B_2, and C_2. Dissociation energies of electronic states of these molecules range from 650 cm^{-1} to 49,400 cm^{-1}.

In the tables of molecular constants are tabulated coefficients of the expressions for vibrational energy and of the expressions for the limiting curves of dissociation. The expressions for vibrational energy are of the form

$$G(v) = A_o + A_1v + A_2v^2 + A_3v^3 + \ldots\ldots\ldots$$

and, as described above, were derived to give experimental and extrapolated vibrational levels from v = 0 to the dissociation limits. The expressions for the limiting curves of dissociation are of the form

$$E(J) = B_0 + B_1J(J+1) + B_2J^2(J+1)^2 + B_3J^3(J+1)^3 + \ldots.$$

Atomic energy levels required to calculate dissociation energies of excited electronic states are taken from the National Bureau of Standards' Circular 467. Physical constants used in the calculations are given in Table 32.

Reference is occasionally made to a Mayer and Mayer-type calculation of thermodynamic functions. This refers to an elaboration of the Mayer and Mayer treatment which uses the spectroscopic constants ω_e, ω_ex_e, ω_ey_e, B_e, α_e, γ_1, and D_e. This elaboration originated at the National Bureau of Standards.

Mercury Hydride

HgH	Mol. Wt. = 201.598	
Molecular Constants		Table 6
Thermodynamic Functions		Table 7

Molecular constants for the $^2\Sigma^+$ ground state are those tabulated by Herzberg[29] from the work of Fujioka and Tanaka.[23] Herzberg corrected the value of ω_ex_e given by these authors. The dissociation energy is a spectroscopic value from the limiting curve of dissociation.

Dissociations of the $A^2\Pi_{\frac{1}{2}}$ and $A^2\Pi_{3/2}$ states are taken to be to unexcited hydrogen atoms and to the 6p $^3P^\circ_0$ and 6p $^3P^\circ_1$ states, respectively, of the separated mercury atoms. Vibrational constants for the $A^2\Pi_{\frac{1}{2}}$ state are calculated from data for the lowest three vibrational levels as given by Porter.[51] This calculation is somewhat uncertain, as strong perturbations are known to exist between the levels of the excited electronic states of HgH. Values of B_e and α_e for the $A^2\Pi_{\frac{1}{2}}$ state are those listed by Herzberg[29] from the work of Rydberg.[62] They fit Rydberg's results for B_v for the lowest three of four vibrational levels for which he reported rotational analyses. D_e is equal to D_v for $v = 0$ and $v = 1$ as reported by Rydberg.

The vibrational constants for the $A^2\Pi_{3/2}$ state are derived by combining the data of Porter[51] and Rydberg,[62] which extend to $v = 6$. Values of B_e, α_e, γ_1, D_e, and β_1 are from an analysis of Rydberg's tabulations of B_v and D_v.

The effect of a breakoff of vibrational and rotational levels on thermodynamic functions is particularly marked for HgH. In Table 5 the heat capacities to 1500°K calculated taking breakoff into account are compared with values from a Mayer and Mayer-type calculation. To that temperature the excited electronic states contribute nothing to the thermodynamic functions.

Table 5

Heat Capacity of Mercury Hydride

	C_p, cal/deg/mole	
Temp., °K	With Breakoff of Levels	Without Breakoff of Levels
100	6.693	6.692
200	6.999	6.695
300	7.211	7.198
400	7.579	7.544
500	7.966	7.914
600	8.266	8.255
700	8.426	8.558
800	8.443	8.830
900	8.343	9.079
1000	8.167	9.313
1100	7.948	9.538
1200	7.713	9.759
1300	7.480	9.979
1400	7.257	10.202
1500	7.051	10.427

Table 6

Summary of Constants for the Electronic States of Mercury Hydride

Molecular Constants, cm^{-1}

	$X^2\Sigma^+$	$A^2\Pi_{1/2}$	$A^2\Pi_{3/2}$
ν_{00}	0.0	24923.	28606.
D_0	3034.	15742.	13805.
ω_e	1387.09	2064.15	2066.9
ω_ex_e	83.01	63.12	41.85
B_e	5.5490	6.683	6.709
α_e	0.312	0.242	0.1865
γ_1	-0.0701	-	-5.77×10^{-3}
D_e	-3.44×10^{-4}	-2.9×10^{-4}	-2.67×10^{-4}
β_1	-6.6×10^{-5}	-	-1.02×10^{-5}
H_e	-7.79×10^{-9}*	5.34×10^{-9}*	6.82×10^{-9}*
δ_1	-4.16×10^{-8}*	-	-
L_e	-5.91×10^{-12}*	-1.41×10^{-12}*	-6.05×10^{-13}*

Coefficients of Expression for Vibrational Energy, cm^{-1}

A_0	672.325	1017.0	1022.9
A_1	1301.074	2001.014	1929.0563
A_2	-89.817	-63.1606	199.3407
A_3	-6.126	-0.02724533	-239.53664
A_4	-1.588		122.52364
A_5			-36.093028
A_6			6.3210421
A_7			-0.64697326
A_8			0.035543579
A_9			-8.073457×10^{-4}

Coefficients of Expression for Limiting Curve of Dissociation, cm^{-1}

B_0	3706.325	16759.	14827.9
B_1	0.975315	0.584165	0.649189
B_2	1.55701×10^{-3}	3.60061×10^{-4}	4.39327×10^{-4}
B_3	-9.14600×10^{-7}	-6.24447×10^{-8}	-8.60076×10^{-8}
B_4	3.24600×10^{-10}	7.55487×10^{-12}	1.15632×10^{-11}

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*Calculated from Dunham-Sandeman equations

Table 7

Thermodynamic Functions of Mercury Hydride

T, °Kelvin	$-(F^\circ_T-H^\circ_{298})/T$, cal/gfw/deg	$H^\circ_T-H^\circ_{298}$, kcal/gfw	S°_T, cal/gfw/deg	C°_p, cal/gfw/deg
0.	Infinite	-2.0834	0.0000	0.0000
100.00	58.7642	-1.3927	44.8376	6.9627
200.00	53.1466	-0.6954	49.6697	6.9986
298.15	52.4958	0.	52.4958	7.2056
300.00	52.4959	0.0133	52.5404	7.2113
400.00	52.7829	0.7522	54.6633	7.5791
500.00	53.3373	1.5297	56.3968	7.9655
600.00	53.9736	2.3423	57.8775	8.2660
700.00	54.6254	3.1782	59.1657	8.4263
800.00	55.2650	4.0228	60.2934	8.4426
900.00	55.8798	4.8629	61.2830	8.3432
1000.00	56.4646	5.6888	62.1534	8.1666
1100.00	57.0174	6.4948	62.9218	7.9480
1200.00	57.5384	7.2779	63.6033	7.7133
1300.00	58.0287	8.0375	64.2114	7.4797
1400.00	58.4902	8.7742	64.7575	7.2571
1500.00	58.9247	9.4895	65.2510	7.0508
1600.00	59.3344	10.1850	65.7000	6.8626
1700.00	59.7211	10.8626	66.1108	6.6929
1800.00	60.0867	11.5241	66.4890	6.5406
1900.00	60.4330	12.1713	66.8389	6.4046
2000.00	60.7615	12.8055	67.1643	6.2832
2100.00	61.0737	13.4283	67.4682	6.1749
2200.00	61.3709	14.0409	67.7532	6.0781
2300.00	61.6543	14.6443	68.0214	5.9916
2400.00	61.9249	15.2395	68.2747	5.9141
2500.00	62.1838	15.8274	68.5147	5.8445
2600.00	62.4317	16.4087	68.7427	5.7820
2700.00	62.6695	16.9840	68.9598	5.7257
2800.00	62.8979	17.5540	69.1671	5.6749
2900.00	63.1175	18.1191	69.3655	5.6291
3000.00	63.3289	18.6799	69.5556	5.5877
3100.00	63.5328	19.2368	69.7382	5.5503
3200.00	63.7294	19.7901	69.9139	5.5166
3300.00	63.9194	20.3402	70.0831	5.4863
3400.00	64.1031	20.8875	70.2465	5.4591
3500.00	64.2809	21.4322	70.4044	5.4349
3600.00	64.4532	21.9746	70.5572	5.4136
3700.00	64.6201	22.5150	70.7053	5.3950
3800.00	64.7822	23.0536	70.8489	5.3791
3900.00	64.9395	23.5909	70.9885	5.3658
4000.00	65.0925	24.1269	71.1242	5.3553
4100.00	65.2412	24.6620	71.2563	5.3474
4200.00	65.3859	25.1965	71.3851	5.3422
4300.00	65.5269	25.7305	71.5108	5.3398
4400.00	65.6643	26.2645	71.6335	5.3402
4500.00	65.7983	26.7987	71.7536	5.3435
4600.00	65.9291	27.3333	71.8711	5.3499
4700.00	66.0567	27.8687	71.9862	5.3593
4800.00	66.1814	28.4053	72.0992	5.3719
4900.00	66.3033	28.9432	72.2101	5.3878
5000.00	66.4226	29.4830	72.3192	5.4071
5100.00	66.5392	30.0248	72.4264	5.4298
5200.00	66.6535	30.5690	72.5321	5.4561
5300.00	66.7654	31.1161	72.6363	5.4859
5400.00	66.8750	31.6664	72.7392	5.5195
5500.00	66.9826	32.2201	72.8408	5.5568
5600.00	67.0881	32.7779	72.9413	5.5979
5700.00	67.1917	33.3399	73.0408	5.6427
5800.00	67.2934	33.9065	73.1393	5.6915
5900.00	67.3933	34.4783	73.2371	5.7441
6000.00	67.4915	35.0555	73.3341	5.8005

Hydrogen Fluoride

HF Mol. Wt. = 20.0064
Molecular Constants Table 8
Thermodynamic Functions Table 9

The expression for the energies of the vibrational levels of the $^1\Sigma^+$ ground state is obtained from a least-squares fit of the data of Mann et al.[44] for v = 0 to 9 and of Johns and Barrow[36] for v = 9 to 19.

Vibrational and rotational constants given by Mann et al. and by Johns and Barrow differ slightly. Constants from the latter source are used, as they were based on data to larger v's and J's. The dissociation energy used in the calculations is the quantity selected for the JANAF Interim Thermochemical Tables[35] from a consideration of spectroscopic and thermochemical data. Virtually the same value follows from data tabulated in the available part of NBS Revised Circular 500.[79] The Rydberg potential is the best fit to the RKR curve[20,21,71] for $r/r_e > 1.7$.

A calculation based on the Mayer and Mayer treatment is a good approximation for HF to 6000°K. At that temperature the heat capacity may be calculated to be 0.13 cal/deg/mole less and the free energy function 0.013 cal/deg/mole less than the values shown in Table 9.

Hydrogen Chloride

HCl Mol. Wt. = 36.461
Molecular Constants Table 8
Thermodynamic Functions Table 10

The value for the dissociation energy is a thermochemical quantity selected for the JANAF Interim Thermochemical Tables.[35] A value 54 cm^{-1} larger follows from tabulations in the available part of NBS Revised Circular 500.[79]

Molecular constants for the $^1\Sigma^+$ ground state of HCl^{35} are selected from the work of Rank, Rao, and Wiggins,[55] and have been isotopically weighted. The expression for vibrational energies is from an extrapolation

Table 8

Summary of Constants for the $^1\Sigma^+$ Ground States of the Hydrogen Halides

Molecular Constants, cm^{-1}

	HF	HCl	HBr	HI
ν_{00}	0.0	0.0	0.0	0.0
D_0	47140.	35735.	30308.	24650.
ω_e	4139.031	2990.3922	2649.183	2308.091
$\omega_e x_e$	90.43924	52.79900	45.2246	38.9810
B_e	20.9486	10.5895	8.466216	6.51083
α_e	0.797107	0.30701	0.233332	0.16864
γ_1	0.01402335	1.7711×10^{-3}	8.738×10^{-4}	-9.9×10^{-4}
γ_2	-1.181565×10^{-3}	-1.2000×10^{-4}	-1.203×10^{-4}	-
γ_3	1.00930×10^{-4}	-	-	-
γ_4	-4.14067×10^{-6}	-	-	-
D_e	-2.151×10^{-3}	-5.31641×10^{-4}	-3.4586×10^{-4}	-2.072×10^{-4}
β_1	5.87×10^{-5}	7.504×10^{-6}	3.97×10^{-6}	8.92×10^{-7}*
β_2	1.4427×10^{-6}	-4.000×10^{-7}	-3.8×10^{-7}	-
β_3	-3.2655×10^{-7}	-	-	-
H_e	1.64×10^{-7}*	1.74×10^{-8}	7.63×10^{-9}	3.10×10^{-9}*
δ_1	-2.73×10^{-10}*	-6.33×10^{-10}	-5.5×10^{-10}	-
L_e	-1.53×10^{-11}*	-9.92×10^{-13}	-3.27×10^{-13}*	-1.30×10^{-13}*

Coefficients of Expression for Vibrational Energy, cm^{-1}

	HF	HCl	HBr	HI
A_0	2047.0481	1482.0233	1313.285	1144.2758
A_1	4056.9693	2937.9771	2605.9391	2270.8046
A_2	-102.68719	-51.665191	-49.179415	-41.780081
A_3	10.532166	-1.1381796	2.6127479	0.64501057
A_4	-3.3473388	0.63499327	-0.74656052	0.031272143
A_5	0.65985898	-0.14008057	0.10416681	-0.055542409
A_6	-0.080132477	0.015731447	$-9.2492861 \times 10^{-3}$	9.4528208×10^{-3}
A_7	6.0493649×10^{-3}	$-1.0290891 \times 10^{-3}$	5.2548965×10^{-4}	$-7.9920002 \times 10^{-4}$
A_8	$-2.7675361 \times 10^{-4}$	3.9674295×10^{-5}	$-1.8506400 \times 10^{-5}$	3.7756826×10^{-5}
A_9	7.0122259×10^{-6}	$-8.3750036 \times 10^{-7}$	3.6805153×10^{-7}	$-9.5293187 \times 10^{-7}$
A_{10}	-7.550076×10^{-8}	7.4777718×10^{-9}	$-3.1601088 \times 10^{-9}$	1.0036622×10^{-8}

Coefficients of Expression for Limiting Curve of Dissociation, cm^{-1}

	HF	HCl	HBr	HI
B_0	49187.0	37217.0	31621.3	25794.3
B_1	0.879817	0.585303	0.380377	0.351069
B_2	6.37406×10^{-4}	2.90798×10^{-4}	2.99785×10^{-4}	2.85142×10^{-4}
B_3	-1.12456×10^{-7}	-3.68637×10^{-8}	-3.23007×10^{-8}	-3.18201×10^{-8}
B_4	1.51249×10^{-11}	3.36439×10^{-12}	2.40635×10^{-12}	2.07618×10^{-12}

*Calculated from Dunham-Sandeman equations

Table 9

Thermodynamic Functions of Hydrogen Fluoride

T, °Kelvin	$-(F^\circ_T-H^\circ_{298})/T$, cal/gfw/deg	$H^\circ_T-H^\circ_{298}$, kcal/gfw	S°_T, cal/gfw/deg	C°_p, cal/gfw/deg
0.	Infinite	-2.0552	0.0000	0.0000
100.00	47.6977	-1.3796	33.9022	6.9628
200.00	42.1446	-0.6834	38.7276	6.9617
298.15	41.5077	0.	41.5077	6.9639
300.00	41.5078	0.0129	41.5508	6.9639
400.00	41.7810	0.7094	43.5545	6.9668
500.00	42.2970	1.4063	45.1096	6.9723
600.00	42.8749	2.1042	46.3819	6.9861
700.00	43.4549	2.8040	47.4607	7.0148
800.00	44.0156	3.5077	48.4003	7.0624
900.00	44.5501	4.2172	49.2358	7.1287
1000.00	45.0570	4.9340	49.9910	7.2104
1100.00	45.5374	5.6596	50.6825	7.3033
1200.00	45.9931	6.3949	51.3222	7.4028
1300.00	46.4263	7.1403	51.9188	7.5052
1400.00	46.8388	7.8959	52.4787	7.6074
1500.00	47.2325	8.6617	53.0070	7.7075
1600.00	47.6092	9.4373	53.5075	7.8040
1700.00	47.9703	10.2223	53.9834	7.8960
1800.00	48.3171	11.0163	54.4372	7.9831
1900.00	48.6507	11.8188	54.8711	8.0653
2000.00	48.9722	12.6292	55.2868	8.1424
2100.00	49.2824	13.4471	55.6858	8.2148
2200.00	49.5823	14.2720	56.0695	8.2826
2300.00	49.8724	15.1035	56.4391	8.3462
2400.00	50.1535	15.9411	56.7956	8.4058
2500.00	50.4261	16.7845	57.1399	8.4618
2600.00	50.6908	17.6334	57.4728	8.5144
2700.00	50.9479	18.4873	57.7951	8.5641
2800.00	51.1981	19.3461	58.1074	8.6109
2900.00	51.4416	20.2094	58.4103	8.6553
3000.00	51.6788	21.0771	58.7045	8.6974
3100.00	51.9101	21.9488	58.9903	8.7375
3200.00	52.1357	22.8245	59.2683	8.7756
3300.00	52.3560	23.7039	59.5390	8.8122
3400.00	52.5711	24.5869	59.8025	8.8472
3500.00	52.7814	25.4733	60.0595	8.8809
3600.00	52.9871	26.3630	60.3101	8.9133
3700.00	53.1883	27.2559	60.5548	8.9447
3800.00	53.3853	28.1519	60.7937	8.9751
3900.00	53.5783	29.0509	61.0272	9.0046
4000.00	53.7674	29.9528	61.2556	9.0333
4100.00	53.9527	30.8575	61.4790	9.0613
4200.00	54.1346	31.7650	61.6977	9.0888
4300.00	54.3129	32.6752	61.9118	9.1156
4400.00	54.4880	33.5881	62.1217	9.1420
4500.00	54.6600	34.5036	62.3274	9.1679
4600.00	54.8289	35.4217	62.5292	9.1934
4700.00	54.9948	36.3423	62.7272	9.2186
4800.00	55.1579	37.2654	62.9216	9.2434
4900.00	55.3183	38.1910	63.1124	9.2679
5000.00	55.4761	39.1190	63.2999	9.2921
5100.00	55.6313	40.0494	63.4841	9.3160
5200.00	55.7841	40.9822	63.6653	9.3396
5300.00	55.9344	41.9173	63.8434	9.3629
5400.00	56.0825	42.8548	64.0186	9.3859
5500.00	56.2284	43.7945	64.1910	9.4086
5600.00	56.3721	44.7365	64.3608	9.4309
5700.00	56.5137	45.6007	64.5279	9.4529
5800.00	56.6533	46.6271	64.6925	9.4745
5900.00	56.7910	47.5756	64.8546	9.4956
6000.00	56.9267	48.5262	65.0144	9.5163

Table 10

Thermodynamic Functions of Hydrogen Chloride

T, °Kelvin	$-(F^\circ_T-H^\circ_{298})/T$, cal/gfw/deg	$H^\circ_T-H^\circ_{298}$, kcal/gfw	S°_T, cal/gfw/deg	C°_p, cal/gfw/deg
0.	Infinite	-2.0649	0.0000	0.0000
100.00	50.8326	-1.3793	37.0397	6.9589
200.00	45.2803	-0.6833	41.8637	6.9607
298.15	44.6434	0.	44.6434	6.9636
300.00	44.6436	0.0129	44.6865	6.9637
400.00	44.9168	0.7096	46.6908	6.9726
500.00	45.4331	1.4082	48.2495	7.0037
600.00	46.0124	2.1115	49.5316	7.0686
700.00	46.5953	2.8230	50.6282	7.1670
800.00	47.1609	3.5457	51.5930	7.2891
900.00	47.7023	4.2813	52.4593	7.4238
1000.00	48.2180	5.0305	53.2486	7.5614
1100.00	48.7088	5.7934	53.9756	7.6958
1200.00	49.1762	6.5694	54.6507	7.8230
1300.00	49.6218	7.3577	55.2816	7.9413
1400.00	50.0475	8.1574	55.8742	8.0500
1500.00	50.4547	8.9674	56.4330	8.1494
1600.00	50.8451	9.7870	56.9619	8.2399
1700.00	51.2198	10.6151	57.4640	8.3223
1800.00	51.5800	11.4512	57.9418	8.3973
1900.00	51.9270	12.2944	58.3977	8.4659
2000.00	52.2615	13.1442	58.8335	8.5288
2100.00	52.5844	14.0000	59.2511	8.5866
2200.00	52.8966	14.8613	59.6518	8.6399
2300.00	53.1988	15.7278	60.0369	8.6894
2400.00	53.4915	16.5991	60.4077	8.7355
2500.00	53.7753	17.4748	60.7652	8.7787
2600.00	54.0508	18.3547	61.1103	8.8194
2700.00	54.3185	19.2386	61.4439	8.8578
2800.00	54.5788	20.1262	61.7667	8.8943
2900.00	54.8320	21.0174	62.0794	8.9292
3000.00	55.0787	21.9120	62.3827	8.9626
3100.00	55.3191	22.8099	62.6771	8.9948
3200.00	55.5535	23.7110	62.9632	9.0259
3300.00	55.7823	24.6151	63.2414	9.0562
3400.00	56.0057	25.5222	63.5122	9.0857
3500.00	56.2239	26.4322	63.7760	9.1145
3600.00	56.4373	27.3450	64.0331	9.1427
3700.00	56.6460	28.2607	64.2840	9.1703
3800.00	56.8502	29.1791	64.5289	9.1975
3900.00	57.0502	30.1002	64.7682	9.2242
4000.00	57.2461	31.0239	65.0021	9.2505
4100.00	57.4381	31.9503	65.2308	9.2762
4200.00	57.6263	32.8791	65.4546	9.3015
4300.00	57.8109	33.8105	65.6738	9.3263
4400.00	57.9920	34.7444	65.8885	9.3505
4500.00	58.1699	35.6806	66.0989	9.3740
4600.00	58.3445	36.6192	66.3052	9.3968
4700.00	58.5160	37.5600	66.5075	9.4189
4800.00	58.6846	38.5029	66.7060	9.4401
4900.00	58.8503	39.4480	66.9009	9.4604
5000.00	59.0132	40.3950	67.0922	9.4797
5100.00	59.1735	41.3439	67.2801	9.4979
5200.00	59.3311	42.2945	67.4647	9.5149
5300.00	59.4863	43.2468	67.6461	9.5306
5400.00	59.6391	44.2006	67.8244	9.5450
5500.00	59.7895	45.1557	67.9996	9.5580
5600.00	59.9377	46.1121	68.1720	9.5695
5700.00	60.0836	47.0696	68.3414	9.5794
5800.00	60.2274	48.0279	68.5081	9.5878
5900.00	60.3692	48.9871	68.6721	9.5946
6000.00	60.5089	49.9468	68.8334	9.5996

of data for v = 0 to 5. Thermodynamic functions calculated using the three potential energy functions have at 6000°K a spread of 0.02 cal/deg/mole in calculated free energy functions. At that temperature the average heat capacity and free energy function are about 0.08 cal/deg/mole and 0.07 cal/deg/mole greater, respectively, than those computed by a Mayer and Mayer-type calculation.

Hydrogen Bromide

HBr Mol. Wt. = 80.917
Molecular Constants Table 8
Thermodynamic Functions Table 11

The molecular constants used for the $^1\Sigma^+$ ground state are those reported by Rank, Fink, and Wiggins,[53] and they have been isotopically weighted. Very similar constants have also been recently reported by James and Thibault.[34] The expression for vibrational energies is an extrapolation from data to v = 3. The dissociation energy is based on ΔH_{f298}HBr(g) = -8.71 kcal/mole, as calculated for the JANAF Interim Thermochemical Tables[35] from a number of reaction heats. The dissociation energy from data in the available part of NBS Revised Circular 500[79] is 5 cm^{-1} less. At 6000°K the heat capacity is 0.14 cal/deg/mole less and the free energy function is 0.025 cal/deg/mole greater than the corresponding quantities obtained by a Mayer and Mayer-type calculation.

Hydrogen Iodide

HI Mol. Wt. = 127.9124
Molecular Constants Table 8
Thermodynamic Functions Table 12

The selected dissociation energy of the $^1\Sigma^+$ ground state, a thermochemical value, is some 100 cm^{-1} less than the value calculated from data in the available part of NBS Revised Circular 500.[79] The molecular

Table 11

Thermodynamic Functions of Hydrogen Bromide

T, °Kelvin	$-(F^\circ_T-H^\circ_{298})/T$, cal/gfw/deg	$H^\circ_T-H^\circ_{298}$, kcal/gfw	S°_T, cal/gfw/deg	C°_p, cal/gfw/deg
0.	Infinite	-2.0669	0.0000	0.0000
100.00	53.6525	-1.3793	39.8594	6.9585
200.00	48.1001	-0.6834	44.6833	6.9607
298.15	47.4632	0.	47.4632	6.9647
300.00	47.4633	0.0129	47.5063	6.9649
400.00	47.7366	0.7101	49.5119	6.9836
500.00	48.2536	1.4109	51.0754	7.0394
600.00	48.8346	2.1195	52.3670	7.1394
700.00	49.4203	2.8399	53.4773	7.2729
800.00	49.9899	3.5746	54.4582	7.4237
900.00	50.5362	4.3247	55.3415	7.5782
1000.00	51.0576	5.0901	56.1477	7.7276
1100.00	51.5546	5.8699	56.8909	7.8671
1200.00	52.0284	6.6631	57.5810	7.9948
1300.00	52.4806	7.4685	58.2255	8.1104
1400.00	52.9127	8.2848	58.8305	8.2145
1500.00	53.3264	9.1110	59.4004	8.3080
1600.00	53.7231	9.9461	59.9394	8 3923
1700.00	54.1039	10.7892	60.4505	8.4683
1800.00	54.4701	11.6395	60.9365	8.5372
1900.00	54.8227	12.4964	61.3998	8.6000
2000.00	55.1627	13.3593	61.8424	8.6574
2100.00	55.4909	14.2277	62.2661	8.7104
2200.00	55.8082	15.1013	62.6724	8.7595
2300.00	56.1152	15.9795	63.0628	8.8053
2400.00	56.4125	16.8622	63.4385	8.8483
2500.00	56.7009	17.7491	63.8005	8.8889
2600.00	56.9807	18.6400	64.1499	8.9276
2700.00	57.2525	19.5346	64.4875	8.9645
2800.00	57.5168	20.4328	64.8142	9.0000
2900.00	57.7739	21.3346	65.1306	9.0343
3000.00	58.0242	22.2397	65.4375	9.0676
3100.00	58.2682	23.1480	65.7353	9.1000
3200.00	58.5061	24.0596	66.0247	9.1315
3300.00	58.7382	24.9743	66.3062	9.1624
3400.00	58.9649	25.8921	66.5802	9.1925
3500.00	59.1863	26.8128	66.8471	9.2219
3600.00	59.4027	27.7364	67.1073	9.2505
3700.00	59.6144	28.6629	67.3611	9.2784
3800.00	59.8215	29.5921	67.6089	9.3054
3900.00	60.0243	30.5240	67.8510	9.3315
4000.00	60.2229	31.4584	68.0875	9.3565
4100.00	60.4176	32.3952	68.3188	9.3804
4200.00	60.6084	33.3344	68.5452	9.4029
4300.00	60.7956	34.2757	68.7667	9.4241
4400.00	60.9792	35.2191	68.9836	9.4437
4500.00	61.1594	36.1644	69.1960	9.4617
4600.00	61.3364	37.1114	69.4041	9.4780
4700.00	61.5103	38.0600	69.6081	9.4923
4800.00	61.6811	39.0098	69.8081	9.5047
4900.00	61.8489	39.9608	70.0042	9.5151
5000.00	62.0140	40.9128	70.1965	9.5233
5100.00	62.1763	41.8654	70.3852	9.5293
5200.00	62.3359	42.8185	70.5702	9.5331
5300.00	62.4930	43.7719	70.7518	9.5345
5400.00	62.6476	44.7254	70.9301	9.5337
5500.00	62.7998	45.6786	71.1050	9.5306
5600.00	62.9496	46.6315	71.2767	9.5251
5700.00	63.0972	47.5836	71.4452	9.5173
5800.00	63.2425	48.5348	71.6106	9.5072
5900.00	63.3858	49.4850	71.7730	9.4949
6000.00	63.5269	50.4337	71.9325	9.4804

Table 12

Thermodynamic Functions of Hydrogen Iodide

T, °Kelvin	$-(F^\circ_T-H^\circ_{298})/T$, cal/gfw/deg	$H^\circ_T-H^\circ_{298}$, kcal/gfw	S°_T, cal/gfw/deg	C°_p, cal/gfw/deg
0.	Infinite	-2.0689	0.0000	0.0000
100.00	55.5390	-1.3794	41.7449	6.9583
200.00	49.9860	-0.6835	46.5687	6.9608
298.15	49.3490	0.	49.3490	6.9685
300.00	49.3491	0.0129	49.3921	6.9688
400.00	49.6228	0.7114	51.4013	7.0096
500.00	50.1413	1.4167	52.9748	7.1073
600.00	50.7255	2.1345	54.2830	7.2538
700.00	51.3163	2.8684	55.4139	7.4256
800.00	51.8923	3.6198	56.4170	7.6020
900.00	52.4462	4.3885	57.3222	7.7702
1000.00	52.9757	5.1733	58.1490	7.9245
1100.00	53.4811	5.9728	58.9109	8.0628
1200.00	53.9634	6.7854	59.6179	8.1857
1300.00	54.4240	7.6095	60.2775	8.2944
1400.00	54.8644	8.4438	60.8957	8.3906
1500.00	55.2861	9.2873	61.4776	8.4762
1600.00	55.6904	10.1388	62.0271	8.5526
1700.00	56.0786	10.9975	62.5477	8.6214
1800.00	56.4518	11.8628	63.0423	8.6838
1900.00	56.8112	12.7341	63.5134	8.7408
2000.00	57.1576	13.6109	63.9631	8.7933
2100.00	57.4920	14.4927	64.3933	8.8421
2200.00	57.8151	15.3792	64.8057	8.8879
2300.00	58.1277	16.2702	65.2017	8.9310
2400.00	58.4305	17.1653	65.5827	8.9719
2500.00	58.7240	18.0645	65.9498	9.0110
2600.00	59.0087	18.9675	66.3039	9.0485
2700.00	59.2853	19.8741	66.6461	9.0845
2800.00	59.5541	20.7843	66.9771	9.1191
2900.00	59.8156	21.6979	67.2977	9.1524
3000.00	60.0702	22.6148	67.6085	9.1843
3100.00	60.3183	23.5347	67.9101	9.2148
3200.00	60.5601	24.4577	68.2032	9.2437
3300.00	60.7961	25.3834	68.4880	9.2708
3400.00	61.0264	26.3118	68.7652	9.2962
3500.00	61.2514	27.2426	69.0350	9.3194
3600.00	61.4713	28.1756	69.2978	9.3405
3700.00	61.6863	29.1106	69.5540	9.3592
3800.00	61.8966	30.0473	69.8038	9.3753
3900.00	62.1025	30.9856	70.0475	9.3888
4000.00	62.3041	31.9250	70.2854	9.3994
4100.00	62.5016	32.8653	70.5176	9.4071
4200.00	62.6952	33.8063	70.7443	9.4117
4300.00	62.8850	34.7476	70.9658	9.4132
4400.00	63.0711	35.6888	71.1822	9.4116
4500.00	63.2537	36.6298	71.3937	9.4069
4600.00	63.4329	37.5701	71.6003	9.3990
4700.00	63.6088	38.5095	71.8024	9.3880
4800.00	63.7816	39.4476	71.9999	9.3740
4900.00	63.9513	40.3842	72.1930	9.3569
5000.00	64.1180	41.3189	72.3818	9.3370
5100.00	64.2819	42.2515	72.5665	9.3142
5200.00	64.4429	43.1817	72.7471	9.2888
5300.00	64.6013	44.1092	72.9238	9.2608
5400.00	64.7570	45.0337	73.0966	9.2303
5500.00	64.9102	45.9551	73.2657	9.1976
5600.00	65.0609	46.8732	73.4311	9.1628
5700.00	65.2092	47.7876	73.5929	9.1259
5800.00	65.3551	48.6983	73.7513	9.0873
5900.00	65.4987	49.6050	73.9063	9.0469
6000.00	65.6401	50.5076	74.0580	9.0050

constants are from the work of Haeusler, Meyer, and Barchewitz,[27] who based their analyses on vibrational-rotational data to $v = 4$. A Mayer and Mayer-type calculation gives at 6000°K a heat capacity 0.8 cal/deg/mole greater and a free energy function 0.024 cal/deg/mole greater than the corresponding quantities tabulated in Table 12.

Fluorine

F_2	Mol. Wt. = 37.9968
Molecular Constants	Table 13
Thermodynamic Functions	Table 14

Molecular constants for the $^1\Sigma_g^+$ ground state are based on the values for B_0 and $\Delta G_{\frac{1}{2}}$ obtained by Andrychuk[1] from the Raman spectrum of the gas. The dissociation energy is calculated from $D_{298} = 37.72 \pm 0.13$ kcal/mole derived by Stamper and Barrow[70] from dissociation pressure measurements. The same value follows from data in the revised version of NBS Circular 500.[79] The thermodynamic functions given in Table 14 are based on data for the ground state only. However, in the course of an analysis of the continuous absorption spectrum of molecular fluorine, Rees[59] deduced a portion of the repulsive limb of the potential energy curve for a stable $^3\Pi_{0^+u}$ state. From the position of the potential curve segment, estimates of spectroscopic constants, and a consideration of likely dissociation products, the dissociation energy of this state is probably about 2000 cm^{-1} and ν_{00} is probably about 11300 cm^{-1}. The estimated contribution of this state to the heat capacity is indicated in Table 15. Rees[59] also computed the potential energy curve of the repulsive A $^1\Pi_u$ state. Herzberg[29] listed data for two other stable states whose distances above the ground state have not been established. Iczkowski and Margrave[33] have reported the vacuum ultraviolet bands of a (V,N) transition.

Table 13

Summary of Constants for the Ground State of Diatomic Fluorine

Molecular Constants, cm^{-1}

	$X^1\Sigma_g^+$
ν_{00}	0.0
D_0	12857.
ω_e	922.94
$\omega_e x_e$	15.54
B_e	0.891
α_e	0.0164*
D_e	-3.32×10^{-6}**
H_e	-1.46×10^{-11}**
L_e	-2.07×10^{-16}**

Coefficients of Expression for Vibrational Energy, cm^{-1}

A_0	457.6
A_1	907.38332
A_2	-15.567200
A_3	-0.016455473

Coefficients of Expression for Limiting Curve of Dissociation, cm^{-1}

B_0	13314.6
B_1	0.129242
B_2	1.05647×10^{-5}
B_3	-2.89208×10^{-10}
B_4	5.00902×10^{-15}

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* Calculated from Pekeris equation

** Calculated from Dunham-Sandeman equations

Table 14

Thermodynamic Functions of Diatomic Fluorine

T, °Kelvin	$-(F^\circ_T-H^\circ_{298})/T$, cal/gfw/deg	$H^\circ_T-H^\circ_{298}$, kcal/gfw	S°_T, cal/gfw/deg	C°_p, cal/gfw/deg
0.	Infinite	-2.1096	0.0000	0.0000
100.00	54.8423	-1.4149	40.6938	6.9584
200.00	49.1153	-0.7147	45.5417	7.0969
298.15	48.4440	0.	48.4440	7.4873
300.00	48.4441	0.0139	48.4903	7.4953
400.00	48.7432	0.7841	50.7034	7.8960
500.00	49.3204	1.5898	52.5001	8.2031
600.00	49.9800	2.4219	54.0165	8.4269
700.00	50.6525	3.2733	55.3286	8.5924
800.00	51.3107	4.1391	56.4846	8.7192
900.00	51.9439	5.0163	57.5176	8.8207
1000.00	52.5487	5.9027	58.4515	8.9055
1100.00	53.1247	6.7970	59.3038	8.9795
1200.00	53.6727	7.6984	60.0880	9.0465
1300.00	54.1945	8.6062	60.8146	9.1091
1400.00	54.6918	9.5201	61.4919	9.1686
1500.00	55.1665	10.4398	62.1264	9.2258
1600.00	55.6203	11.3652	62.7236	9.2803
1700.00	56.0549	12.2958	63.2877	9.3314
1800.00	56.4717	13.2313	63.8224	9.3781
1900.00	56.8721	14.1712	64.3306	9.4189
2000.00	57.2572	15.1148	64.8146	9.4524
2100.00	57.6282	16.0614	65.2765	9.4775
2200.00	57.9859	17.0100	65.7178	9.4931
2300.00	58.3313	17.9597	66.1399	9.4984
2400.00	58.6652	18.9094	66.5441	9.4930
2500.00	58.9881	19.8579	66.9313	9.4769
2600.00	59.3008	20.8044	67.3025	9.4502
2700.00	59.6038	21.7476	67.6585	9.4134
2800.00	59.8976	22.6867	68.0000	9.3670
2900.00	60.1827	23.6207	68.3278	9.3119
3000.00	60.4595	24.5488	68.6424	9.2490
3100.00	60.7284	25.4703	68.9446	9.1791
3200.00	60.9897	26.3845	69.2348	9.1033
3300.00	61.2438	27.2908	69.5137	9.0225
3400.00	61.4910	28.1889	69.7818	8.9377
3500.00	61.7316	29.0783	70.0397	8.8496
3600.00	61.9658	29.9587	70.2877	8.7591
3700.00	62.1940	30.8300	70.5264	8.6669
3800.00	62.4163	31.6920	70.7563	8.5736
3900.00	62.6330	32.5447	70.9778	8.4799
4000.00	62.8443	33.3880	71.1913	8.3863
4100.00	63.0504	34.2220	71.3973	8.2932
4200.00	63.2515	35.0467	71.5960	8.2010
4300.00	63.4478	35.8622	71.7879	8.1100
4400.00	63.6395	36.6687	71.9733	8.0204
4500.00	63.8267	37.4664	72.1526	7.9326
4600.00	64.0096	38.2553	72.3260	7.8466
4700.00	64.1883	39.0358	72.4938	7.7626
4800.00	64.3631	39.8079	72.6564	7.6807
4900.00	64.5339	40.5720	72.8139	7.6010
5000.00	64.7011	41.3282	72.9667	7.5235
5100.00	64.8646	42.0768	73.1150	7.4483
5200.00	65.0247	42.8179	73.2589	7.3754
5300.00	65.1813	43.5519	73.3987	7.3048
5400.00	65.3348	44.2790	73.5346	7.2364
5500.00	65.4851	44.9993	73.6668	7.1702
5600.00	65.6323	45.7131	73.7954	7.1062
5700.00	65.7767	46.4206	73.9206	7.0444
5800.00	65.9181	47.1220	74.0426	6.9847
5900.00	66.0568	47.8176	74.1615	6.9270
6000.00	66.1929	48.5075	74.2775	6.8713

Table 15

Estimated Contribution of the First Excited State to the Heat Capacity of Molecular Fluorine

Temp., °K	ΔC_p, cal/deg/mole
1000	0.000
1500	0.013
2000	0.078
2500	0.172
3000	0.232
3500	0.242
4000	0.219
5000	0.144

Chlorine

Cl_2 Mol. Wt. = 70.906

Molecular Constants	Table 16
Thermodynamic Functions	Table 17

Molecular constants for Cl_2 have been isotopically weighted.

Three recent sources of spectroscopic data for the $^1\Sigma_g^+$ ground state of Cl_2 are the work of Douglas, Møller, and Stoicheff,[16] of Rao and Venkateswarlu,[56] and of Richards and Barrow.[61] The data of Rao and Venkateswarlu, obtained from resonance spectra in the vacuum ultraviolet, are used, as the authors observed vibrational levels to within about 140 cm^{-1} of the dissociation limit which they determined to be 20062 ± 10 cm^{-1}. The same value follows from thermodynamic data in the revised version of NBS Circular 500.[79] Douglas, Møller, and Stoicheff reported 19999 ± 2 cm^{-1} from the convergence limit of upper state vibrational levels. The expression used for vibrational levels involves an extrapolation of the data of Rao and Venkateswarlu from $v = 49$ to a dissociation limit of 20001 cm^{-1}. For $r > r_e$, the Rydberg potential energy function is in much better agreement with the RKR curve calculated by Rao and Venkateswarlu than is the Morse or Hulburt-Hirschfelder potential.

Table 16

Summary of Constants for the Electronic States of Diatomic Chlorine

Molecular Constants, cm^{-1}

	$X^1\Sigma_g^+$	$^3\Pi_2$	$^3\Pi_1$	$A^3\Pi_{0^+u}$
ν_{00}	0.0	16945.	17226.	17531.
D_0	20001.	3056.	2775.	3350.
ω_e	555.979	253.3*	247.6*	258.95
$\omega_e x_e$	2.66	5.69*	5.83*	5.403
B_e	0.2406	0.162*	0.161*	0.1658
α_e	1.65×10^{-3}	3.07×10^{-3}*	3.15×10^{-3}*	3.65×10^{-3}
γ_1	-1.93×10^{-5}	-	-	-
D_e	-1.772×10^{-7}**	-2.67×10^{-7}**	-2.72×10^{-7}**	-2.72×10^{-7}**
β_1	-4.6×10^{-10}**	-	-	-
H_e	-8.66×10^{-14}**	-1.28×10^{-12}**	-1.39×10^{-12}**	-1.66×10^{-12}**
L_e	-1.44×10^{-19}**	-1.31×10^{-17}**	-1.49×10^{-17}**	-1.42×10^{-17}**

Coefficients of Expression for Vibrational Energy, cm^{-1}

A_0	277.324	125.2	122.312	128.122
A_1	553.46047	247.62475	241.77241	255.52442
A_2	-2.735895	-5.6495813	-5.794846	-7.4869239
A_3	6.572864×10^{-3}	0.024790936	0.022421775	0.74200982
A_4	-5.0661526×10^{-4}			-0.13623701
A_5	-1.5365969×10^{-5}			0.014022228
A_6	1.8253381×10^{-6}			-8.5485597×10^{-4}
A_7	-7.5307×10^{-8}			3.1642835×10^{-5}
A_8	1.6907592×10^{-9}			-6.9485705×10^{-7}
A_9	-2.0390907×10^{-11}			8.3105835×10^{-9}
A_{10}	1.0065583×10^{-13}			-4.168667×10^{-11}

Coefficients of Expression for Limiting Curve of Dissociation, cm^{-1}

B_0	20278.3	3181.2	2897.3	3478.1
B_1	0.0185557	0.0345616	0.0355557	0.0337871
B_2	1.00966×10^{-6}	1.59453×10^{-6}	1.71792×10^{-6}	1.51806×10^{-6}
B_3	-8.28978×10^{-12}	-3.02875×10^{-11}	-3.49669×10^{-11}	-2.73571×10^{-11}
B_4	2.75640×10^{-17}	3.30938×10^{-16}	4.06383×10^{-16}	2.86443×10^{-16}

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* Estimated

** Calculated from Dunham-Sandeman equations

Table 17

Thermodynamic Functions of Diatomic Chlorine

T, °Kelvin	$-(F^\circ_T-H^\circ_{298})/T$, cal/gfw/deg	$H^\circ_T-H^\circ_{298}$, kcal/gfw	S°_T, cal/gfw/deg	C°_p, cal/gfw/deg
0.	Infinite	-2.1943	0.0000	0.0000
100.00	60.1324	-1.4983	45.1492	7.0023
200.00	54.0195	-0.7723	50.1579	7.5813
298.15	53.2926	0.	53.2926	8.1146
300.00	53.2928	0.0150	53.3428	8.1223
400.00	53.6157	0.8445	55.7268	8.4373
500.00	54.2347	1.6982	57.6311	8.6217
600.00	54.9364	2.5666	59.2140	8.7377
700.00	55.6465	3.4445	60.5672	8.8165
800.00	56.3369	4.3292	61.7484	8.8740
900.00	56.9975	5.2189	62.7963	8.9185
1000.00	57.6253	6.1126	63.7378	8.9548
1100.00	58.2204	7.0096	64.5928	8.9859
1200.00	58.7845	7.9096	65.3759	9.0135
1300.00	59.3197	8.8123	66.0984	9.0388
1400.00	59.8281	9.7174	66.7691	9.0628
1500.00	60.3120	10.6248	67.3951	9.0863
1600.00	60.7732	11.5346	67.9823	9.1100
1700.00	61.2137	12.4468	68.5353	9.1345
1800.00	61.6351	13.3616	69.0582	9.1605
1900.00	62.0389	14.2790	69.5542	9.1892
2000.00	62.4265	15.1995	70.0263	9.2210
2100.00	62.7992	16.1234	70.4770	9.2567
2200.00	63.1581	17.0510	70.9086	9.2971
2300.00	63.5042	17.9829	71.3228	9.3425
2400.00	63.8383	18.9196	71.7215	9.3930
2500.00	64.1614	19.8617	72.1060	9.4487
2600.00	64.4741	20.8095	72.4778	9.5092
2700.00	64.7772	21.7639	72.8379	9.5737
2800.00	65.0714	22.7247	73.1873	9.6415
2900.00	65.3571	23.6923	73.5269	9.7117
3000.00	65.6350	24.6670	73.8573	9.7829
3100.00	65.9054	25.6489	74.1793	9.8539
3200.00	66.1689	26.6377	74.4932	9.9235
3300.00	66.4258	27.6335	74.7996	9.9903
3400.00	66.6766	28.6357	75.0988	10.0532
3500.00	66.9214	29.6437	75.3910	10.1112
3600.00	67.1606	30.6573	75.6766	10.1632
3700.00	67.3946	31.6759	75.9556	10.2081
3800.00	67.6235	32.6988	76.2284	10.2455
3900.00	67.8475	33.7251	76.4950	10.2748
4000.00	68.0670	34.7537	76.7554	10.2958
4100.00	68.2820	35.7840	77.0098	10.3081
4200.00	68.4928	36.8150	77.2583	10.3117
4300.00	68.6995	37.8460	77.5009	10.3067
4400.00	68.9022	38.8760	77.7377	10.2933
4500.00	69.1011	39.9043	77.9688	10.2717
4600.00	69.2964	40.9300	78.1942	10.2423
4700.00	69.4880	41.9525	78.4141	10.2056
4800.00	69.6762	42.9709	78.6285	10.1620
4900.00	69.8611	43.9846	78.8375	10.1121
5000.00	70.0427	44.9931	79.0413	10.0563
5100.00	70.2211	45.9957	79.2398	9.9953
5200.00	70.3964	46.9920	79.4333	9.9295
5300.00	70.5686	47.9817	79.6218	9.8596
5400.00	70.7380	48.9642	79.8054	9.7860
5500.00	70.9045	49.9390	79.9843	9.7092
5600.00	71.0682	50.9060	80.1586	9.6299
5700.00	71.2292	51.8649	80.3283	9.5484
5800.00	71.3875	52.8155	80.4936	9.4652
5900.00	71.5432	53.7577	80.6547	9.3806
6000.00	71.6964	54.6915	80.8116	9.2950

All data for the $^3\Pi_1$ and $^3\Pi_2$ states are estimated, as experimental data are not available. The electronic energies of these configurations are obtained from Mulliken's Interpretation I of N → Q absorption continuum data.[49] The results of his calculations were given in the form of predicted relative energies of the $^3\Pi_1$, $^3\Pi_2$, the experimentally established $^3\Pi_{0^+}$, and the repulsive $^1\Pi$ states. The $^3\Pi_{0^-}$ state is repulsive. The $^3\Pi_1$ and $^3\Pi_2$ states are both taken to dissociate to normal atoms.

Recent vibrational-rotational analyses of spectra involving the A $^3\Pi_{0^+}$ state have been made by Douglas, Møller, and Stoicheff ($6 \le v \le 31$),[16] and by Richards and Barrow ($6 \le v \le 22$).[61] A vibrational analysis has been given by Venkateswarlu and Khanna ($0 \le v \le 25$).[76] There has been past uncertainty concerning the vibrational numbering of this state,[29] a history of which is described by Khanna.[39] The present expression for vibrational energies is obtained by extrapolation of the data of Venkateswarlu and Khanna. Dissociation of this state is to one normal atom and one excited atom at an energy 881 cm^{-1} greater. The electronic energy is calculated by correcting T_e as given by Richards and Barrow with the data of Venkateswarlu and Khanna for the vibrational energy at $v = 6$. The rotational constants of Douglas, Møller, and Stoicheff are used.

There are numerous higher electronic states known for Cl_2 which will not affect the present calculation.

When the thermodynamic functions of chlorine or the other halogens are calculated by a Mayer and Mayer-type approximation and the excited states are included in the calculation, the results become completely meaningless as the temperature increases. The reason is, of course, that the excited states have low dissociation energies. The effect of the assumption of the Mayer and Mayer treatment that v and J increase without limit thus becomes pronounced.

Bromine

Br_2 Mol. Wt. = 159.818

Molecular Constants Table 18

Thermodynamic Functions Table 19

Molecular Constants for Br_2 have been isotopically weighted.

Vibrational and rotational constants for the $^1\Sigma_g^+$ ground state are from Rao and Venkateswarlu,[57] who studied the vacuum ultraviolet resonance spectrum. Vibrational levels were observed to $v = 35$. The dissociation energy of the ground state is taken from Herzberg[29] and is based on the convergence limit of a band system involving excited states. The available part of NBS Revised Circular 500[79] uses the same dissociation energy.

Constants for the as yet unobserved $^3\Pi_2$ state are estimated. The dissociation energy follows from the assumption of dissociation to neutral atoms and Mulliken's prediction of the electronic energy (Interpretation I).[49]

Numbering of the vibrational levels of the $A^3\Pi_{1u}$ state is uncertain. Although the numbering proposed by Darbyshire[14] is used, the vibrational constants calculated are slightly different from his, as the extrapolated values of $\Delta G_{v+\frac{1}{2}}$ ($v = 6$ to $v = 0$) are somewhat different. In the absence of a rotational analysis, rotational constants are estimated. This state also dissociates to neutral atoms. With the adopted numbering, Darbyshire's vibrational data extended to $v = 23$.

The expression for vibrational levels of the $B^3\Pi_{0^+u}$ state is based on the data to $v = 30$ of Brown,[10] Darbyshire,[14] and Venkateswarlu and Verma.[77] The rotational constants tabulated by Herzberg[29] are used. This state dissociates to a normal atom and an excited atom at 3685 cm^{-1}.

Table 18

Summary of Constants for the Electronic States of Diatomic Bromine

Molecular Constants, cm^{-1}

	$X^1\Sigma_g^+$	$^3\Pi_2$	$A^3\Pi_{1u}$	$B^3\Pi_{0^+u}$
ν_{00}	0.0	12790.	13737.	15814.
D_0	15903.0	3113.	2166.	3774.
ω_e	323.23	172.*	176.5	165.132
$\omega_e x_e$	1.0283	3.*	4.55	1.644
B_e	0.08107	0.060*	0.059*	0.0595
α_e	2.65×10^{-4}	7.65×10^{-4}*	9.2×10^{-4}*	6.25×10^{-4}
γ_1	-1.395×10^{-5}	-	-	-
γ_2	2.48×10^{-7}**	-	-	-
D_e	-2.04×10^{-8}**	-2.94×10^{-8}**	-2.67×10^{-8}	-3.09×10^{-8}**
β_1	-1.50×10^{-10}**	-	-	-
H_e	-8.84×10^{-16}**	-5.84×10^{-14}**	-6.86×10^{-14}**	-4.59×10^{-14}**
L_e	-3.84×10^{-21}**	-2.29×10^{-19}**	-3.33×10^{-19}**	-1.08×10^{-19}**

Coefficients of Expression for Vibrational Energy, cm^{-1}

A_0	161.348	85.212	86.622	82.155
A_1	323.48413	168.96696	167.68368	165.67424
A_2	-1.6607633	-2.983957	-3.6961822	-2.5410224
A_3	0.10801727	0.016977843	9.2310941×10^{-3}	0.11083058
A_4	-9.2262762×10^{-3}		-3.1794584×10^{-3}	-6.8670688×10^{-3}
A_5	4.2921364×10^{-4}		2.0074174×10^{-4}	1.9991646×10^{-4}
A_6	-1.182641×10^{-5}		-2.9137044×10^{-6}	-2.9364987×10^{-6}
A_7	1.9645867×10^{-7}			2.1224503×10^{-8}
A_8	-1.9411086×10^{-9}			-5.8497769×10^{-11}
A_9	1.0530819×10^{-11}			
A_{10}	-2.4194675×10^{-14}			

Coefficients of Expression for Limiting Curve of Dissociation, cm^{-1}

B_0	16064.3	3198.2	2252.6	3856.2
B_1	9.48887×10^{-3}	0.0123947	0.0159086	9.63623×10^{-3}
B_2	9.18758×10^{-8}	2.40011×10^{-7}	3.20546×10^{-7}	2.19708×10^{-7}
B_3	-2.23882×10^{-13}	-1.62734×10^{-12}	-2.78421×10^{-12}	-1.49835×10^{-12}
B_4	3.06686×10^{-19}	6.25619×10^{-18}	1.26694×10^{-17}	5.46868×10^{-18}

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* Estimated

** Calculated from Dunham-Sandeman equations

Table 19

Thermodynamic Functions of Diatomic Bromine

T, °Kelvin	$-(F^\circ_T-H^\circ_{298})/T$, cal/gfw/deg	$H^\circ_T-H^\circ_{298}$, kcal/gfw	S°_T, cal/gfw/deg	C°_p, cal/gfw/deg
0.	Infinite	-2.3241	0.0000	0.0000
100.00	66.0286	-1.6195	49.8338	7.3823
200.00	59.4177	-0.8312	55.2616	8.2674
298.15	58.6384	0.	58.6384	8.6189
300.00	58.6386	0.0159	58.6918	8.6230
400.00	58.9790	0.8870	61.1967	8.7806
500.00	59.6265	1.7697	63.1660	8.8657
600.00	60.3555	2.6592	64.7874	8.9196
700.00	61.0895	3.5532	66.1655	8.9585
800.00	61.8005	4.4506	67.3637	8.9896
900.00	62.4787	5.3509	68.4241	9.0165
1000.00	63.1216	6.2538	69.3754	9.0411
1100.00	63.7300	7.1591	70.2382	9.0647
1200.00	64.3057	8.0667	71.0279	9.0883
1300.00	64.8511	8.9768	71.7563	9.1128
1400.00	65.3688	9.8894	72.4326	9.1393
1500.00	65.8610	10.8048	73.0642	9.1692
1600.00	66.3299	11.7231	73.6568	9.2042
1700.00	66.7775	12.6454	74.2160	9.2448
1800.00	67.2055	13.5725	74.7458	9.2920
1900.00	67.6157	14.5044	75.2496	9.3468
2000.00	68.0095	15.4422	75.7306	9.4090
2100.00	68.3883	16.3864	76.1913	9.4780
2200.00	68.7531	17.3379	76.6339	9.5526
2300.00	69.1051	18.2970	77.0603	9.6312
2400.00	69.4452	19.2641	77.4719	9.7118
2500.00	69.7741	20.2399	77.8701	9.7920
2600.00	70.0930	21.2231	78.2557	9.8700
2700.00	70.4023	22.2138	78.6296	9.9434
2800.00	70.7026	23.2112	78.9924	10.0106
2900.00	70.9946	24.2150	79.3446	10.0693
3000.00	71.2787	25.2243	79.6868	10.1181
3100.00	71.5553	26.2380	80.0192	10.1559
3200.00	71.8249	27.2549	80.3420	10.1822
3300.00	72.0878	28.2739	80.6556	10.1963
3400.00	72.3442	29.2939	80.9601	10.1980
3500.00	72.5946	30.3138	81.2557	10.1876
3600.00	72.8392	31.3316	81.5424	10.1656
3700.00	73.0782	32.3466	81.8205	10.1324
3800.00	73.3118	33.3577	82.0902	10.0888
3900.00	73.5403	34.3639	82.3516	10.0356
4000.00	73.7638	35.3644	82.6049	9.9736
4100.00	73.9824	36.3584	82.8503	9.9038
4200.00	74.1964	37.3449	83.0881	9.8271
4300.00	74.4059	38.3235	83.3183	9.7445
4400.00	74.6110	39.2936	83.5414	9.6569
4500.00	74.8119	40.2547	83.7574	9.5652
4600.00	75.0086	41.2064	83.9666	9.4701
4700.00	75.2014	42.1488	84.1692	9.3724
4800.00	75.3902	43.0811	84.3654	9.2728
4900.00	75.5753	44.0035	84.5556	9.1719
5000.00	75.7568	44.9156	84.7399	9.0703
5100.00	75.9347	45.8175	84.9185	8.9685
5200.00	76.1091	46.7092	85.0917	8.8670
5300.00	76.2802	47.5907	85.2596	8.7661
5400.00	76.4480	48.4623	85.4225	8.6661
5500.00	76.6126	49.3239	85.5806	8.5674
5600.00	76.7742	50.1757	85.7341	8.4702
5700.00	76.9327	51.0179	85.8832	8.3746
5800.00	77.0882	51.8506	86.0280	8.2809
5900.00	77.2410	52.6740	86.1688	8.1892
6000.00	77.3909	53.4883	86.3056	8.0996

Iodine

I_2 Mol. Wt. = 253. 8088

Molecular Constants Table 20

Thermodynamic Functions Table 21

Spectroscopic data for the $^1\Sigma_g^+$ ground state have been published recently by Rank and Rao[54] and by Verma.[78] The dissociation energy used for this state is from Verma, whose vibrational data extended to very near the dissociation limit ($v = 114$), and whose rotational analysis was based on data to $v = 84$. Verma's observations were of the ultraviolet resonance spectrum. The rotational constants reported by Rank and Rao were based on a combination of interferometric measurements of the green-line resonance series to $v = 39$ with the results of Verma. Because the rotational constants of Rank and Rao give a negative B_v near the dissociation limit, Verma's constants are preferred. Verma also computed a potential energy curve for the ground state by the RKR method. Weissman, Vanderslice, and Battino[80] and Zare[84] refined these calculations. The Hulburt-Hirschfelder potential function is a much better approximation to the RKR curves than is the Morse or Rydberg potential.

In the absence of experimental data for the $^3\Pi_2$ state, all constants are estimated. The dissociation energy is estimated from Mulliken's[49] prediction of the electronic energy (Interpretation I) and the assumption that dissociation is to neutral atoms.

The electronic energy and vibrational data for the $A^3\Pi_{1u}$ state are from Brown.[11] The extrapolation of vibrational levels is from $v = 22$. Dissociation is to neutral atoms. Rotational constants for this state are all estimated, as experimental values are not available.

Dissociation of the B $^3\Pi_{0^+u}$ state is to one normal atom and one excited atom at 7603.15 cm^{-1}. Vibrational and rotational data for this state are from the recent paper of Steinfeld et al.[72] The expression for vibrational levels is an extrapolation from $v = 29$. The authors

Table 20

Summary of Constants for the Electronic States of Diatomic Iodine

Molecular Constants, cm^{-1}

	$X^1\Sigma_g^+$	$^3\Pi_2$	$A^3\Pi_{1u}$	$B^3\Pi_{0^+u}$
ν_{00}	0.0	10596.	11803.	15725.94
D_0	12452.5	1856.	650.	4329.7
ω_e	214.51886	76.8*	43.772	125.273
$\omega_e x_e$	0.60738	0.91*	1.051	0.7016
B_e	0.03734	0.0273*	0.0259*	0.028969
α_e	1.208×10^{-4}	2.78×10^{-4}*	4.94×10^{-4}*	1.562×10^{-4}
γ_1	4.44×10^{-7}	-	-	-4.0×10^{-7}
γ_2	-1.839×10^{-8}	-	-	-3.5×10^{-8}
γ_3	-5.7×10^{-12}	-	-	-
D_e	-1.99×10^{-9}	-1.38×10^{-8}**	-3.64×10^{-8}**	-6.20×10^{-9}**
β_1	-1.236×10^{-10}	-	-	-7.81×10^{-11}**
H_e	-6.02×10^{-16}**	-1.93×10^{-14}**	-1.72×10^{-13}**	-2.5×10^{-15}**
L_e	-2.50×10^{-22}**	-5.83×10^{-20}**	-1.67×10^{-18}**	-2.56×10^{-21}**

Coefficients of Expression for Vibrational Energy, cm^{-1}

A_0	107.24133	38.175	21.601	62.46
A_1	214.13629	75.902517	42.378755	124.26112
A_2	-0.69932384	-0.90503411	-0.54948173	-0.521929
A_3	0.012057338	2.516942×10^{-3}	-0.088415127	-0.046217921
A_4	-9.6662638×10^{-4}		9.5748248×10^{-4}	4.296168×10^{-3}
A_5	3.9016628×10^{-5}		1.4945641×10^{-3}	-2.480347×10^{-4}
A_6	-9.5401828×10^{-7}		-1.7759066×10^{-4}	8.4892911×10^{-6}
A_7	1.4126614×10^{-8}		9.5699682×10^{-6}	-1.7476962×10^{-7}
A_8	-1.2483757×10^{-10}		-2.7623962×10^{-7}	2.1350045×10^{-9}
A_9	6.0582981×10^{-13}		4.1448187×10^{-9}	-1.4291955×10^{-11}
A_{10}	-1.2367088×10^{-15}		-2.5444454×10^{-11}	4.0447143×10^{-14}

Coefficients of Expression for Limiting Curve of Dissociation, cm^{-1}

B_0	12559.7	1894.2	671.60	4392.2
B_1	5.88911×10^{-3}	4.16841×10^{-3}	3.96550×10^{-3}	4.97453×10^{-3}
B_2	3.65169×10^{-8}	8.90338×10^{-8}	1.84233×10^{-7}	5.71741×10^{-8}
B_3	-5.64756×10^{-14}	-6.38285×10^{-13}	-3.57182×10^{-12}	-1.75524×10^{-13}
B_4	3.62258×10^{-20}	2.50187×10^{-18}	4.02504×10^{-17}	2.38926×10^{-19}

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* Estimated

** Calculated from Dunham-Sandeman equations

Table 21

Thermodynamic Functions of Diatomic Iodine

T, °Kelvin	$-(F^\circ_T-H^\circ_{298})/T$, cal/gfw/deg	$H^\circ_T-H^\circ_{298}$, kcal/gfw	S°_T, cal/gfw/deg	C°_p, cal/gfw/deg
0.	Infinite	-2.4172	0.0000	0.0000
100.00	69.9530	-1.6918	53.0346	7.9177
200.00	63.0786	-0.8570	58.7936	8.6172
298.15	62.2773	0.	62.2773	8.8137
300.00	62.2775	0.0163	62.3318	8.8159
400.00	62.6245	0.9026	64.8810	8.9006
500.00	63.2822	1.7953	66.8727	8.9493
600.00	64.0209	2.6920	68.5075	8.9836
700.00	64.7633	3.5918	69.8945	9.0115
800.00	65.4817	4.4942	71.0995	9.0367
900.00	66.1662	5.3991	72.1652	9.0611
1000.00	66.8147	6.3064	73.1211	9.0868
1100.00	67.4280	7.2163	73.9883	9.1150
1200.00	68.0083	8.1295	74.7828	9.1476
1300.00	68.5580	9.0461	75.5165	9.1868
1400.00	69.0795	9.9675	76.1992	9.2338
1500.00	69.5757	10.8936	76.8381	9.2900
1600.00	70.0486	11.8258	77.4397	9.3548
1700.00	70.5003	12.7647	78.0090	9.4265
1800.00	70.9326	13.7111	78.5499	9.5028
1900.00	71.3472	14.6646	79.0654	9.5811
2000.00	71.7454	15.6271	79.5589	9.6564
2100.00	72.1288	16.5963	80.0318	9.7266
2200.00	72.4984	17.5721	80.4858	9.7883
2300.00	72.8553	18.5536	80.9221	9.8391
2400.00	73.2002	19.5394	81.3416	9.8771
2500.00	73.5340	20.5284	81.7454	9.9010
2600.00	73.8574	21.5190	82.1339	9.9102
2700.00	74.1708	22.5103	82.5080	9.9043
2800.00	74.4750	23.5005	82.8680	9.8841
2900.00	74.7704	24.4873	83.2143	9.8504
3000.00	75.0575	25.4702	83.5475	9.8042
3100.00	75.3366	26.4478	83.8681	9.7466
3200.00	75.6080	27.4185	84.1763	9.6795
3300.00	75.8722	28.3824	84.4730	9.6034
3400.00	76.1294	29.3385	84.7584	9.5199
3500.00	76.3799	30.2858	85.0330	9.4305
3600.00	76.6240	31.2240	85.2974	9.3363
3700.00	76.8619	32.1528	85.5518	9.2383
3800.00	77.0937	33.0723	85.7970	9.1374
3900.00	77.3199	33.9812	86.0330	9.0350
4000.00	77.5406	34.8795	86.2605	8.9318
4100.00	77.7560	35.7675	86.4798	8.8283
4200.00	77.9662	36.6451	86.6913	8.7251
4300.00	78.1715	37.5124	86.8954	8.6227
4400.00	78.3721	38.3695	87.0924	8.5217
4500.00	78.5680	39.2166	87.2828	8.4222
4600.00	78.7595	40.0539	87.4668	8.3246
4700.00	78.9467	40.8815	87.6448	8.2291
4800.00	79.1297	41.6996	87.8171	8.1359
4900.00	79.3087	42.5086	87.9839	8.0450
5000.00	79.4838	43.3085	88.1455	7.9567
5100.00	79.6552	44.1000	88.3023	7.8708
5200.00	79.8229	44.8837	88.4544	7.7873
5300.00	79.9872	45.6584	88.6020	7.7066
5400.00	80.1480	46.4252	88.7453	7.6284
5500.00	80.3056	47.1844	88.8846	7.5527
5600.00	80.4600	47.9360	89.0200	7.4796
5700.00	80.6113	48.6805	89.1518	7.4090
5800.00	80.7597	49.4180	89.2800	7.3407
5900.00	80.9052	50.1486	89.4050	7.2748
6000.00	81.0479	50.8729	89.5267	7.2112

revised the vibrational numbering by $\Delta v = -1$ from the previously accepted assignments. Zare[84] calculated an RKR curve for this state using earlier spectroscopic data.

In addition to a repulsive state dissociating to neutral atoms, a number of additional ionic states ($T_e > 39000$ cm^{-1}) are known.[28,29,45]

Lithium

Li_2 Mol. Wt. = 13.878
Molecular Constants Table 22
Thermodynamic Functions Table 23

Molecular constants have been isotopically weighted.

Vibrational and rotational constants for the $^1\Sigma_g^+$ ground state are those tabulated by Herzberg[29] from the work of Loomis and Nusbaum.[41] Extrapolation of vibrational levels is from v = 15. The dissociation energy is that recommended by Evans et al.,[19] and is an average of spectroscopic and molecular-beam data.

Spectroscopic constants for the $A^1\Sigma_u^+$ and $B^1\Pi_u$ states are those tabulated by Herzberg.[29] These states dissociate to one neutral (2s) and one excited (2p) atom at 14904 cm^{-1}. Extrapolation of levels for the A state is from v = 5 and for the B state, from v = 14.

Recent rotational analyses of C-X systems[3,75] have shown the upper state to be $^1\Pi_u$ rather than $^1\Sigma_u^+$ as proposed earlier.[29] The spectroscopic constants reported by Barrow, Travis, and Wright[3] are used. The authors preferred a correlation of this state with a neutral atom and an excited atom (3p) at 30925.38 cm^{-1}. The dissociation energy used accords with this assumption. Barrow, Travis, and Wright also gave incomplete and tentative data for a $D^1\Pi_u$ state at $T_e = 34140$ cm^{-1}. This state has not been included in the present calculation.

Table 22

Summary of Constants for the Electronic States of Diatomic Lithium

Molecular Constants, cm^{-1}

	$X^1\Sigma_g^+$	$A^1\Sigma_u^+$	$B^1\Pi_u$	$C^1\Pi_u$
ν_{00}	0.0.	14020.34	20398.2	30491.7
D_0	9010.	9893.46	3515.6	9443.4
ω_e	353.544	256.989	271.30	239.3
$\omega_e x_e$	2.624	1.594	2.778	3.37
B_e	0.68112	0.5037	0.56418	0.51389
α_e	7.18×10^{-3}	5.52×10^{-3}	8.20×10^{-3}	9.83×10^{-3}
γ_1	-8.0×10^{-5}	-	-	1.38×10^{-4}
D_e	-1.005×10^{-5}	-7.74×10^{-6}*	-9.717×10^{-6}	-9.48×10^{-6}*
β_1	-2.88×10^{-8}	5.98×10^{-8}*	-1.487×10^{-8}	-
H_e	1.63×10^{-10}*	1.27×10^{-10}*	1.41×10^{-10}*	9.01×10^{-11}*
δ_1	-1.31×10^{-12}*	-	4.99×10^{-12}*	2.02×10^{-11}*
L_e	-4.49×10^{-15}*	-2.66×10^{-15}*	-4.34×10^{-15}*	-3.82×10^{-15}*

Coefficients of Expression for Vibrational Energy, cm^{-1}

A_0	176.115	128.096	134.947	118.815
A_1	350.43382	255.39839	270.5042	236.32858
A_2	-2.2814263	-1.5450438	-6.821413	-3.0185184
A_3	-0.08774838	-0.012368695	2.7621396	-0.064773442
A_4	7.6652964×10^{-3}	8.5822964×10^{-4}	-1.0228949	0.016923995
A_5	-2.1837829×10^{-4}	-3.6003379×10^{-5}	0.21181976	-1.0053486×10^{-3}
A_6	-9.8766668×10^{-6}	9.4357717×10^{-7}	-0.026537951	3.0792493×10^{-5}
A_7	8.5318493×10^{-7}	-1.5598918×10^{-8}	2.0394314×10^{-3}	-5.5132287×10^{-7}
A_8	-2.4359356×10^{-8}	1.5807345×10^{-10}	-9.3665004×10^{-5}	5.8259161×10^{-9}
A_9	3.2383052×10^{-10}	-8.966005×10^{-13}	2.3523712×10^{-6}	-3.3732591×10^{-11}
A_{10}	-1.6888656×10^{-12}	2.1799778×10^{-15}	-2.481024×10^{-8}	8.2645279×10^{-14}

Coefficients of Expression for Limiting Curve of Dissociation, cm^{-1}

B_0	9186.1	10021.5	3650.5	9562.2
B_1	0.0222594	0.0116824	0.0646704	0.0121745
B_2	5.77483×10^{-6}	1.40938×10^{-6}	1.72123×10^{-5}	6.31702×10^{-7}
B_3	-1.57734×10^{-10}	-2.63907×10^{-11}	-1.32003×10^{-9}	-9.34330×10^{-12}
B_4	3.13936×10^{-15}	4.13955×10^{-16}	4.77104×10^{-14}	8.96413×10^{-17}

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* Calculated from Dunham-Sandeman equations

Table 23

Thermodynamic Functions of Diatomic Lithium

T, °Kelvin	$-(F^\circ_T-H^\circ_{298})/T$, cal/gfw/deg	$H^\circ_T-H^\circ_{298}$, kcal/gfw	S°_T, cal/gfw/deg	C°_p, cal/gfw/deg
0.	Infinite	-2.3123	0.0000	0.0000
100.00	54.4093	-1.6101	38.3085	7.3093
200.00	47.8300	-0.8293	43.6836	8.2163
298.15	47.0518	0.	47.0518	8.6281
300.00	47.0519	0.0160	47.1051	8.6332
400.00	47.3934	0.8906	49.6198	8.8392
500.00	48.0443	1.7813	51.6068	8.9663
600.00	48.7789	2.6828	53.2502	9.0609
700.00	49.5203	3.5930	54.6532	9.1418
800.00	50.2401	4.5110	55.8789	9.2182
900.00	50.9283	5.4366	56.9690	9.2946
1000.00	51.5823	6.3700	57.9523	9.3719
1100.00	52.2028	7.3110	58.8491	9.4479
1200.00	52.7915	8.2593	59.6743	9.5178
1300.00	53.3507	9.2141	60.4385	9.5752
1400.00	53.8826	10.1738	61.1496	9.6144
1500.00	54.3895	11.1362	61.8136	9.6304
1600.00	54.8731	12.0990	62.4350	9.6207
1700.00	55.3353	13.0594	63.0173	9.5845
1800.00	55.7774	14.0150	63.5635	9.5232
1900.00	56.2008	14.9633	64.0762	9.4396
2000.00	56.6067	15.9023	64.5579	9.3373
2100.00	56.9962	16.8303	65.0107	9.2204
2200.00	57.3703	17.7461	65.4367	9.0934
2300.00	57.7298	18.6488	65.8380	8.9601
2400.00	58.0756	19.5380	66.2165	8.8243
2500.00	58.4085	20.4138	66.5740	8.6889
2600.00	58.7291	21.2761	66.9122	8.5569
2700.00	59.0381	22.1254	67.2327	8.4301
2800.00	59.3363	22.9621	67.5370	8.3104
2900.00	59.6241	23.7874	67.8267	8.1985
3000.00	59.9022	24.6020	68.1028	8.0955
3100.00	60.1710	25.4067	68.3667	8.0018
3200.00	60.4311	26.2026	68.6194	7.9176
3300.00	60.6829	26.9905	68.8619	7.8430
3400.00	60.9269	27.7717	69.0951	7.7775
3500.00	61.1635	28.5466	69.3197	7.7211
3600.00	61.3931	29.3162	69.5365	7.6734
3700.00	61.6160	30.0815	69.7462	7.6338
3800.00	61.8327	30.8433	69.9493	7.6018
3900.00	62.0433	31.6021	70.1464	7.5770
4000.00	62.2483	32.3588	70.3380	7.5587
4100.00	62.4479	33.1140	70.5245	7.5463
4200.00	62.6424	33.8683	70.7063	7.5394
4300.00	62.8320	34.6220	70.8836	7.5373
4400.00	63.0170	35.3758	71.0569	7.5396
4500.00	63.1975	36.1300	71.2264	7.5458
4600.00	63.3739	36.8850	71.3924	7.5553
4700.00	63.5462	37.6411	71.5550	7.5678
4800.00	63.7148	38.3986	71.7145	7.5828
4900.00	63.8796	39.1577	71.8710	7.5999
5000.00	64.0409	39.9191	72.0248	7.6187
5100.00	64.1990	40.6820	72.1758	7.6390
5200.00	64.3538	41.4469	72.3244	7.6604
5300.00	64.5056	42.2141	72.4705	7.6827
5400.00	64.6544	42.9835	72.6143	7.7056
5500.00	64.8004	43.7552	72.7559	7.7287
5600.00	64.9437	44.5292	72.8954	7.7521
5700.00	65.0845	45.3056	73.0328	7.7753
5800.00	65.2227	46.0842	73.1682	7.7984
5900.00	65.3585	46.8652	73.3017	7.8210
6000.00	65.4920	47.6484	73.4334	7.8432

Extrapolation of vibrational levels is from v = 15. The dissociation energy is that recommended by Evans et al.,[19] and is an average of spectroscopic and molecular-beam data.

Spectroscopic constants for the A $^1\Sigma_u^+$ and B $^1\Pi_u$ states are those tabulated by Herzberg.[29] These states dissociate to one neutral (2s) and one excited (2p) atom at 14904. cm^{-1}. Extrapolation of levels for the A state is from v = 5 and for the B state, from v = 14.

Recent rotational analyses of C-X systems[3,75] have shown the upper state to be $^1\Pi_u$ rather than $^1\Sigma_u^+$ as proposed earlier.[29] The spectroscopic constants reported by Barrow, Travis, and Wright[3] are used. The authors preferred a correlation of this state with a neutral atom and an excited atom (3p) at 30925.38 cm^{-1}. The dissociation energy used accords with this assumption. Barrow, Travis, and Wright also gave incomplete and tentative data for a D $^1\Pi_u$ state at T_e = 34140 cm^{-1}. This state has not been included in the present calculation.

Sodium Na_2 Mol. Wt. = 45.9796
Molecular Constants Table 24
Thermodynamic Functions Table 25

Molecular constants used for the $^1\Sigma_g^+$ ground state are those listed by Herzberg.[29] Extrapolation of vibrational levels is from v = 22. The dissociation energy of the ground state is the value recommended by Gaydon[24] and Cottrell[12] from a consideration of spectroscopic and thermochemical data. An uncertainly of ± 240 cm^{-1} was assigned to this quantity. Thermodynamic data adopted in the JANAF Interim Thermochemical Tables[35] correspond to a dissociation energy of 6350 cm^{-1}. The latter value was preferred as being consistent with vapor pressure data. Evans et al.[19] selected a spectroscopic value of 6131 ± 50 cm^{-1}.

Spectroscopic constants for the A $^1\Sigma_u^+$ and B $^1\Pi_u$ states are also as listed by Herzberg.[29] Dissociation of these states is to a neutral atom (3s ^2S) and an excited atom (3p $^2P^o$). Extrapolation of vibrational levels for the A state is from v = 13,[22] and for the B state, is from v = 26.[43]

Table 24

Summary of Constants for the Electronic States of Diatomic Sodium

Molecular Constants, cm^{-1}

	$X^1\Sigma_g^+$	$A^1\Sigma_u^+$	$B^1\Pi_u$	$C^1\Pi_u$	$D^1\Pi_u$
ν_{00}	0.0	14659.7	20302.5	29372.1	33415.5
D_0	6050.	8346.5	2703.7	6944.8	7674.8
ω_e	159.23	117.6	123.79	117.3	110.
$\omega_e x_e$	0.726	0.38	0.6303	0.55	0.5
B_e	0.15471	0.1107	0.12588	0.12815	0.1185
α_e	7.9×10^{-4}	5.4×10^{-4}	9.4×10^{-4}	8.4×10^{-4}	8.0×10^{-4}*
γ_1	-3.0×10^{-5}	-	-	-	2.0×10^{-6}*
γ_2	5.5×10^{-7}**	-	-	-	-
D_e	-5.84×10^{-7}	-3.92×10^{-7}**	-5.21×10^{-7}**	-6.12×10^{-7}**	-5.1×10^{-7}**
β_1	-5.0×10^{-9}	-	-	-	-
H_e	2.48×10^{-12}**	1.58×10^{-12}**	1.67×10^{-12}**	2.92×10^{-12}**	2.42×10^{-12}**
L_e	-2.30×10^{-17}**	-9.8×10^{-18}**	-1.13×10^{-17}**	-2.60×10^{-17}**	-2.01×10^{-17}**

Coefficients of Expression for Vibrational Energy, cm^{-1}

A_0	79.434	58.785	61.73	58.36	53.604
A_1	157.9109	117.2216	122.1702	116.9284	109.6398
A_2	-0.6441034	-0.3768885	0.02480714	-0.5707556	-0.5214668
A_3	-5.452238×10^{-3}	-2.487947×10^{-4}	-0.1607073	6.321917×10^{-4}	8.2558399×10^{-4}
A_4			0.01517175		
A_5			-7.225900×10^{-4}		
A_6			1.565723×10^{-5}		
A_7			-1.294059×10^{-7}		

Coefficients of Expression for Limiting Curve of Dissociation, cm^{-1}

B_0	6129.4	8405.2	2765.4	7003.2	7728.4
B_1	7.18560×10^{-3}	2.78646×10^{-3}	0.0282462	3.54480×10^{-3}	2.63244×10^{-3}
B_2	7.73064×10^{-7}	9.78466×10^{-8}	5.24509×10^{-7}	1.31709×10^{-7}	9.05159×10^{-8}
B_3	-9.43741×10^{-12}	-5.31840×10^{-13}	-7.96405×10^{-12}	-1.1153×10^{-12}	-6.68453×10^{-13}
B_4	5.80780×10^{-17}	2.33708×10^{-18}	9.02481×10^{-17}	6.72192×10^{-18}	2.86026×10^{-18}

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*Estimated

**Calculated from Dunham-Sandeman equations

Table 25

Thermodynamic Functions of Diatomic Sodium

T, °Kelvin	$-(F^\circ_T-H^\circ_{298})/T$, cal/gfw/deg	$H^\circ_T-H^\circ_{298}$, kcal/gfw	S°_T, cal/gfw/deg	C°_p, cal/gfw/deg
0.	Infinite	-2.4866	0.0000	0.0000
100.00	62.8654	-1.7378	45.4874	8.3063
200.00	55.8231	-0.8748	51.4494	8.8240
298.15	55.0058	0.	55.0058	8.9820
300.00	55.0060	0.0166	55.0614	8.9841
400.00	55.3596	0.9202	57.6602	9.0836
500.00	56.0306	1.8330	59.6966	9.1723
600.00	56.7857	2.7548	61.3770	9.2643
700.00	57.5466	3.6860	62.8123	9.3607
800.00	58.2849	4.6267	64.0683	9.4512
900.00	58.9907	5.5755	65.1857	9.5190
1000.00	59.6613	6.5292	66.1905	9.5475
1100.00	60.2969	7.4833	67.0999	9.5264
1200.00	60.8988	8.4328	67.9261	9.4531
1300.00	61.4687	9.3724	68.6783	9.3325
1400.00	62.0086	10.2979	69.3642	9.1734
1500.00	62.5201	11.2061	69.9909	8.9863
1600.00	63.0052	12.0945	70.5643	8.7817
1700.00	63.4656	12.9621	71.0903	8.5687
1800.00	63.9028	13.8082	71.5740	8.3548
1900.00	64.3184	14.6331	72.0201	8.1456
2000.00	64.7139	15.4375	72.4327	7.9452
2100.00	65.0907	16.2225	72.8157	7.7564
2200.00	65.4501	16.9893	73.1725	7.5811
2300.00	65.7931	17.7396	73.5059	7.4203
2400.00	66.1210	18.4744	73.8187	7.2747
2500.00	66.4348	19.1952	74.1129	7.1443
2600.00	66.7356	19.9037	74.3908	7.0292
2700.00	67.0240	20.6015	74.6542	6.9290
2800.00	67.3010	21.2899	74.9046	6.8432
2900.00	67.5674	21.9704	75.1434	6.7712
3000.00	67.8238	22.6444	75.3719	6.7125
3100.00	68.0708	23.3127	75.5911	6.6667
3200.00	68.3091	23.9772	75.8020	6.6328
3300.00	68.5393	24.6389	76.0056	6.6101
3400.00	68.7617	25.2996	76.2028	6.5978
3500.00	68.9771	25.9590	76.3939	6.5958
3600.00	69.1857	26.6187	76.5798	6.6031
3700.00	69.3880	27.2796	76.7608	6.6191
3800.00	69.5843	27.9426	76.9376	6.6433
3900.00	69.7751	28.6085	77.1106	6.6748
4000.00	69.9606	29.2778	77.2800	6.7134
4100.00	70.1411	29.9514	77.4463	6.7583
4200.00	70.3170	30.6297	77.6098	6.8090
4300.00	70.4885	31.3134	77.7707	6.8649
4400.00	70.6558	32.0028	77.9292	6.9257
4500.00	70.8192	32.6985	78.0855	6.9908
4600.00	70.9788	33.4009	78.2399	7.0597
4700.00	71.1350	34.1104	78.3925	7.1320
4800.00	71.2878	34.8273	78.5434	7.2072
4900.00	71.4374	35.5518	78.6928	7.2850
5000.00	71.5840	36.2842	78.8408	7.3650
5100.00	71.7277	37.0246	78.9875	7.4467
5200.00	71.8687	37.7734	79.1329	7.5299
5300.00	72.0070	38.5321	79.2772	7.6141
5400.00	72.1429	39.2981	79.4203	7.6991
5500.00	72.2765	40.0724	79.5624	7.7847
5600.00	72.4078	40.8551	79.7034	7.8704
5700.00	72.5371	41.6464	79.8435	7.9560
5800.00	72.6643	42.4462	79.9826	8.0412
5900.00	72.7895	43.2544	80.1208	8.1259
6000.00	72.9128	44.0711	80.2580	8.2096

The earlier characterization[29,67] of a C state at $T_e = 29342\ cm^{-1}$ as probably $^1\Sigma_u^+$ has been revised to a $^1\Pi_u$ designation by Barrow, Travis, and Wright.[3] The revision has been confirmed by Morales.[47] The constants of Barrow, Travis, and Wright are used. The suggestion by the latter authors that the most probably dissociation would be to a neutral atom and Na(4p $^2P^o$) is adopted. Singh and Rai[66] inferred that dissociation of this state is to Na(3s ^2S) + Na(3d ^2D) from a comparison of values of the potential energy calculated by the RKR method and from the Hulburt-Hirschfelder potential function. The dissociation energy of the C state would thereby be reduced by about 1100 cm^{-1}. However, Singh and Rai appear to have used an expression for one of the parameters in the Hulburt-Hirschfelder function from the original paper of Hulburt and Hirschfelder[30] which contains a typographical error.[31] Our calculations show that the Morse potential provides the best fit to the RKR data for the C state.

Singh and Rai[66] also calculated RKR curves for the X, A, and B states. The Hulburt-Hirschfelder potential function is in best agreement with the RKR calculations for these three states.

Morales[47] was unable to confirm the existence of Sinha's system 2.[68] The upper state of this system was designated by Herzberg[29] as the D state. Apparently Barrow, Travis, and Wright[3] were also unable to confirm the system, as the position of a state designated by them as D $^1\Pi_u$ is identical to that of the upper state of Sinha's system 3 (Herzberg's E state). The data of Barrow, Travis, and Wright for their D $^1\Pi_u$ are used, except for a modification of α_e. Also used is their suggested correlation of this state with Na(3s) + Na(5p). Extrapolation of vibrational levels is from v = 13.

Potassium

K_2 Mol. Wt. = 78.204

Molecular Constants	Table 26
Thermodynamic Functions	Table 27

The constants used for the $^1\Sigma_g^+$ ground state are those tabulated by Herzberg[29] from the results of Loomis and Nusbaum[42] and Loomis.[40] Extrapolation of vibrational levels is from v = 19. The value of the dissociation energy is a spectroscopic one recommended by Evans et al.[19] from the convergence limit of the B $^1\Pi_u$ state. The same value has been used in the JANAF Interim Thermochemical Tables.[35]

A vibrational analysis only is available for the A $^1\Sigma_u^+$ state, making use of levels to v = 16.[13,29] In the absence of a rotational analysis, rotational constants are estimated. This state correlates with one neutral atom (4s) and one excited atom (4p).

The B $^1\Pi_u$ state also correlates with K(4s) and K(4p). Herzberg's tabulation [29] of spectroscopic constants for this state are from Loomis and Nusbaum[42] and Loomis.[40] Extrapolation of vibrational levels is from v = 27.

Rai and Tripathi[52] reported RKR curves for the X and B states. The Hulburt-Hirschfelder function gives potentials which agree best with the RKR potentials for both of these states. The calculations of Rai and Tripathi using the Hulburt-Hirschfelder function appear to be in error for the reason noted above for the analogous calculations of Singh and Rai.[66]

Herzberg[29] tabulates the results of a vibrational analysis of a C-X system studied by Sinha.[69] This state had been tentatively characterized as $^1\Sigma_u^+$, but because of the revision necessary for analogous states of lithium and sodium, the C state is arbitrarily taken to be $^1\Pi$. Vibrational levels are extrapolated from v = 10. Rotational constants are estimated. The state is assumed to dissociate to K(4s) and K(5p).

Sinha[69] also gave a vibrational analysis for a D $^1\Pi_u$(?) state at T_e = 24627.7 cm^{-1}. This state has not been included in the present calculation. Herzberg[29] also lists vibrational constants for three additional higher, but uncharacterized, states from the work of Yoshinaga.[83]

Table 26

Summary of Constants for the Electronic States of Diatomic Potassium

Molecular Constants, cm^{-1}

	$X^1\Sigma_g^+$	$A^1\Sigma_u^+$	$B^1\Pi_u$	$C^1\Pi_u$(?)
ν_{00}	0.0	11670.9	15369.2	22954.0
D_0	4145.	5488.1	1789.8	5901.8
ω_e	92.48	68.97	74.87	60.5
$\omega_e x_e$	0.353	0.152	0.3863	0.199
B_e	0.05603	0.0417*	0.04808	0.0488*
α_e	2.18×10^{-4}	1.39×10^{-4}*	2.34×10^{-4}	1.51×10^{-4}*
D_e	-8.23×10^{-8}	-6.10×10^{-8}**	-8.02×10^{-8}	-1.27×10^{-7}**
β_1	-8.26×10^{-10}	-4.12×10^{-12}**	-7.4×10^{-10}	-1.31×10^{-9}**
H_e	1.12×10^{-13}**	9.58×10^{-14}**	9.64×10^{-14}**	4.50×10^{-13}**
δ_1	-	-	-	1.77×10^{-14}**
L_e	-5.06×10^{-19}**	-2.36×10^{-19}**	-6.71×10^{-19}**	-3.14×10^{-18}**

Coefficients of Expression for Vibrational Energy, cm^{-1}

A_0	46.152	34.447	37.341	30.197
A_1	91.996362	68.784156	74.573441	60.323689
A_2	-0.26591024	-0.13386059	-0.47858078	-0.2035236 4
A_3	-0.019179035	$-2.7107457 \times 10^{-3}$	0.046353242	2.2613939×10^{-4}
A_4	1.9324356×10^{-3}	1.7182257×10^{-4}	$-9.2747120 \times 10^{-3}$	
A_5	$-1.0159241 \times 10^{-4}$	$-5.4215482 \times 10^{-6}$	1.1040283×10^{-3}	
A_6	3.0159127×10^{-6}	9.3457601×10^{-8}	$-7.9683102 \times 10^{-5}$	
A_7	$-5.4052965 \times 10^{-8}$	$-9.5960220 \times 10^{-10}$	3.4180133×10^{-6}	
A_8	5.809991×10^{-10}	$5.8654467 \times 10^{-12}$	$-8.2719460 \times 10^{-8}$	
A_9	$-3.4546111 \times 10^{-12}$	$-1.9737944 \times 10^{-14}$	$9.8408010 \times 10^{-10}$	
A_{10}	$8.7470255 \times 10^{-15}$	$2.8188533 \times 10^{-17}$	$-3.9980314 \times 10^{-12}$	

Coefficients of Expression for Limiting Curve of Dissociation, cm^{-1}

B_0	4191.15	5522.55	1827.14	5932.0
B_1	3.43544×10^{-3}	1.29098×10^{-3}	0.0155846	1.07604×10^{-3}
B_2	2.10928×10^{-7}	4.69826×10^{-8}	4.19572×10^{-8}	1.68547×10^{-8}
B_3	-1.60671×10^{-12}	-1.61176×10^{-13}	2.05615×10^{-13}	-6.53151×10^{-14}
B_4	5.30102×10^{-18}	3.09571×10^{-19}	-4.26864×10^{-19}	1.47414×10^{-19}

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*Estimated

**Calculated from Dunham-Sandeman equations

Table 27
Thermodynamic Functions of Diatomic Potassium

T, °Kelvin	$-(F^\circ_T-H^\circ_{298})/T$, cal/gfw/deg	$H^\circ_T-H^\circ_{298}$, kcal/gfw	S°_T, cal/gfw/deg	C°_p, cal/gfw/deg
0.	Infinite	-2.5678	0.0000	0.0000
100.00	67.6800	-1.7748	49.9322	8.7244
200.00	60.5118	-0.8866	56.0788	8.9787
298.15	59.6842	0.	59.6842	9.0815
300.00	59.6844	0.0168	59.7404	9.0832
400.00	60.0417	0.9297	62.3658	9.1740
500.00	60.7195	1.8517	64.4230	9.2667
600.00	61.4822	2.7823	66.1194	9.3383
700.00	62.2503	3.7173	67.5608	9.3501
800.00	62.9937	4.6495	68.8056	9.2770
900.00	63.7011	5.5700	69.8899	9.1201
1000.00	64.3685	6.4713	70.8398	8.8981
1100.00	64.9956	7.3483	71.6758	8.6359
1200.00	65.5837	8.1979	72.4153	8.3564
1300.00	66.1350	9.0194	73.0730	8.0772
1400.00	66.6520	9.8135	73.6616	7.8098
1500.00	67.1372	10.5818	74.1918	7.5614
1600.00	67.5934	11.3265	74.6724	7.3357
1700.00	68.0228	12.0498	75.1110	7.1340
1800.00	68.4279	12.7542	75.5136	6.9568
1900.00	68.8108	13.4421	75.8855	6.8037
2000.00	69.1733	14.1157	76.2311	6.6736
2100.00	69.5171	14.7774	76.5540	6.5654
2200.00	69.8440	15.4293	76.8573	6.4778
2300.00	70.1550	16.0739	77.1437	6.4093
2400.00	70.4520	16.7119	77.4153	6.3591
2500.00	70.7357	17.3458	77.6740	6.3256
2600.00	71.0074	17.9772	77.9217	6.3076
2700.00	71.2679	18.6075	78.1595	6.3039
2800.00	71.5181	19.2382	78.3889	6.3133
2900.00	71.7589	19.8705	78.6108	6.3348
3000.00	71.9909	20.5056	78.8261	6.3672
3100.00	72.2147	21.1444	79.0355	6.4096
3200.00	72.4311	21.7878	79.2398	6.4610
3300.00	72.6404	22.4368	79.4395	6.5204
3400.00	72.8433	23.0920	79.6351	6.5870
3500.00	73.0401	23.7542	79.8271	6.6599
3600.00	73.2313	24.4240	80.0157	6.7382
3700.00	73.4169	25.1032	80.2016	6.8211
3800.00	73.5978	25.7898	80.3846	6.9082
3900.00	73.7742	26.4851	80.5652	6.9985
4000.00	73.9462	27.1895	80.7436	7.0914
4100.00	74.1142	27.9033	80.9198	7.1863
4200.00	74.2783	28.6267	81.0942	7.2826
4300.00	74.4388	29.3597	81.2667	7.3796
4400.00	74.5959	30.1025	81.4374	7.4769
4500.00	74.7499	30.8550	81.6065	7.5739
4600.00	74.9008	31.6172	81.7741	7.6702
4700.00	75.0488	32.3889	81.9400	7.7652
4800.00	75.1941	33.1700	82.1045	7.8586
4900.00	75.3368	33.9604	82.2675	7.9501
5000.00	75.4770	34.7598	82.4290	8.0391
5100.00	75.6149	35.5680	82.5891	8.1255
5200.00	75.7506	36.3847	82.7477	8.2089
5300.00	75.8841	37.2096	82.9048	8.2891
5400.00	76.0156	38.0423	83.0604	8.3658
5500.00	76.1451	38.8825	83.2146	8.4388
5600.00	76.2727	39.7299	83.3673	8.5081
5700.00	76.3985	40.5839	83.5185	8.5733
5800.00	76.5226	41.4443	83.6681	8.6345
5900.00	76.6449	42.3106	83.8162	8.6915
6000.00	76.7657	43.1824	83.9628	8.7444

Boron

B_2 Mol. Wt. = 21.622
Molecular Constants Table 28
Thermodynamic Functions Table 29

Spectroscopic data for the X $^3\Sigma_u^-$ state are from Douglas and Herzberg[15] and have been isotopically weighted. The dissociation energy of the ground state is based on thermochemical data adopted in the JANAF Interim Thermochemical Tables.[35] From this source $\Delta H^\circ_{0f}B(g) = 131.6 \pm 4$ kcal/mole and $\Delta H^\circ_{0f}B_2(g) = 193.5 \pm 6.4$ kcal/mole. The excited electronic state is taken to dissociate to one normal atom and one excited atom at 28805 cm^{-1}. The latter quantity is uncertain, as necessary intersystem combinations between doublet and quartet terms have not been observed. Extrapolation of vibrational levels of both electronic states is from $v = 4$.

Carbon

C_2 Mol. Wt. = 24.0223
Molecular Constants Table 30
Thermodynamic Functions Table 31

Molecular constants used for the ground and nine excited states of C_2 are taken from sources summarized by Ballik and Ramsay.[2] Dissociation energies are determined with the aid of potential curves for the states given in the same paper. An inferred but unidentified $^1\Pi_g$ state with $T_e \sim 44000$ cm^{-1} and $D_0 \sim 26000$ cm^{-1} is not included in the calculation.

The dissociation energy of the ground state is a mass spectrometric value given by Drowart et al.[17] The spectroscopic value,[50] when corrected to the singlet ground state, is significantly less.

Read and Vanderslice[58] calculated parts of the potential energy curves for nine of the states by the RKR method. The Hulburt-Hirschfelder function agrees very well with their data for six of these states. None of the potential functions is a particularly good representation for the RKR curves of the A $^3\Pi_g$, c $^1\Pi_g$, and B $^3\Pi_g$ states. This fact is not

Table 28

Summary of Constants for the Electronic States of Diatomic Boron

Molecular Constants, cm^{-1}

	$X^3\Sigma_g^-$	$A^3\Sigma_u^-$
ν_{00}	0.0	30518.1
D_0	24370.	22660.
ω_e	1060.9	946.0
$\omega_e x_e$	9.58	2.65
B_e	1.235	1.182
α_e	0.0144	0.0113
D_e	$-6.70\text{x}10^{-6}$*	$-7.38\text{x}10^{-6}$*
β_1	$-6.08\text{x}10^{-8}$*	-
H_e	$1.20\text{x}10^{-11}$*	$3.34\text{x}10^{-11}$*
δ_1	$8.18\text{x}10^{-13}$*	$-4.88\text{x}10^{-12}$*
L_e	$-2.50\text{x}10^{-16}$*	$2.32\text{x}10^{-16}$*

Coefficients of Expression for Vibrational Energy, cm^{-1}

A_0	528.102	472.347
A_1	1050.8579	941.21931
A_2	-9.2645123	-1.4295165
A_3	-0.039523007	-0.14399283
A_4	$-5.0599163\text{x}10^{-4}$	$-4.8924239\text{x}10^{-3}$
A_5	$1.6156798\text{x}10^{-5}$	$1.8053689\text{x}10^{-4}$
A_6	$-2.6046966\text{x}10^{-7}$	$-3.3678633\text{x}10^{-6}$
A_7	$1.6713995\text{x}10^{-9}$	$2.5034088\text{x}10^{-8}$

Coefficients of Expression for Limiting Curve of Dissociation, cm^{-1}

B_0	24898.1	23316.3
B_1	0.0773201	0.244776
B_2	$9.65482\text{x}10^{-6}$	$3.69838\text{x}10^{-6}$
B_3	$-1.89032\text{x}10^{-10}$	$-5.12705\text{x}10^{-11}$
B_4	$2.61682\text{x}10^{-15}$	$7.47325\text{x}10^{-16}$

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* Calculated from Dunham-Sandeman equations

Table 29

Thermodynamic Functions of Diatomic Boron

T, °Kelvin	$-(F^\circ_T-H^\circ_{298})/T$, cal/gfw/deg	$H^\circ_T-H^\circ_{298}$, kcal/gfw	S°_T, cal/gfw/deg	C°_p, cal/gfw/deg
0.	Infinite	-2.0935	0.0000	0.0000
100.00	54.5316	-1.3991	40.5409	6.9577
200.00	48.8813	-0.7015	45.3738	7.0230
298.15	48.2239	0.	48.2239	7.3011
300.00	48.2240	0.0135	48.2691	7.3077
400.00	48.5150	0.7624	50.4210	7.6680
500.00	49.0761	1.5453	52.1667	7.9772
600.00	49.7174	2.3554	53.6430	8.2141
700.00	50.3716	3.1861	54.9232	8.3917
800.00	51.0126	4.0323	56.0530	8.5260
900.00	51.6297	4.8903	57.0634	8.6297
1000.00	52.2195	5.7575	57.9771	8.7119
1100.00	52.7814	6.6322	58.8106	8.7787
1200.00	53.3162	7.5129	59.5769	8.8344
1300.00	53.8254	8.3988	60.2860	8.8820
1400.00	54.3107	9.2891	60.9458	8.9235
1500.00	54.7738	10.1833	61.5627	8.9606
1600.00	55.2164	11.0811	62.1421	8.9943
1700.00	55.6400	11.9821	62.6883	9.0254
1800.00	56.0461	12.8861	63.2050	9.0547
1900.00	56.4359	13.7930	63.6953	9.0827
2000.00	56.8106	14.7026	64.1619	9.1097
2100.00	57.1713	15.6149	64.6070	9.1360
2200.00	57.5191	16.5298	65.0326	9.1619
2300.00	57.8547	17.4473	65.4405	9.1875
2400.00	58.1790	18.3674	65.8320	9.2129
2500.00	58.4927	19.2899	66.2086	9.2382
2600.00	58.7964	20.2150	66.5714	9.2634
2700.00	59.0909	21.1426	66.9215	9.2884
2800.00	59.3767	22.0726	67.2598	9.3131
2900.00	59.6542	23.0051	67.5870	9.3373
3000.00	59.9239	23.9400	67.9039	9.3608
3100.00	60.1863	24.8772	68.2112	9.3834
3200.00	60.4418	25.8166	68.5095	9.4049
3300.00	60.6907	26.7582	68.7992	9.4250
3400.00	60.9333	27.7016	69.0808	9.4434
3500.00	61.1700	28.6468	69.3548	9.4601
3600.00	61.4011	29.5936	69.6215	9.4746
3700.00	61.6268	30.5416	69.8813	9.4868
3800.00	61.8474	31.4908	70.1344	9.4965
3900.00	62.0630	32.4408	70.3812	9.5035
4000.00	62.2740	33.3914	70.6219	9.5078
4100.00	62.4805	34.3423	70.8567	9.5092
4200.00	62.6827	35.2931	71.0858	9.5075
4300.00	62.8807	36.2437	71.3095	9.5029
4400.00	63.0747	37.1936	71.5278	9.4953
4500.00	63.2650	38.1426	71.7411	9.4847
4600.00	63.4515	39.0905	71.9494	9.4711
4700.00	63.6345	40.0369	72.1530	9.4547
4800.00	63.8140	40.9815	72.3518	9.4355
4900.00	63.9902	41.9240	72.5462	9.4136
5000.00	64.1633	42.8641	72.7361	9.3892
5100.00	64.3332	43.8017	72.9218	9.3623
5200.00	64.5001	44.7366	73.1033	9.3332
5300.00	64.6641	45.6681	73.2807	9.3021
5400.00	64.8253	46.5967	73.4543	9.2690
5500.00	64.9837	47.5218	73.6241	9.2341
5600.00	65.1395	48.4434	73.7901	9.1975
5700.00	65.2927	49.3613	73.9526	9.1596
5800.00	65.4434	50.2753	74.1116	9.1203
5900.00	65.5916	51.1853	74.2671	9.0800
6000.00	65.7375	52.0912	74.4194	9.0386

Table 30

Summary of Constants for the Electronic States of Diatomic Carbon

Molecular Constants, cm^{-1}

	$x^1\Sigma_g^+$	$X^3\Pi_u$	$A'^3\Sigma_g^-$	$b^1\Pi_u$	$A''^3\Sigma_u^+$
ν_{00}	0.0	610.0	6242.7	8268.2	13365.5
D_0	49400.	48790.	43157.3	41131.8	36034.5
ω_e	1854.71	1641.35	1470.45	1608.35	1961.6
$\omega_e x_e$	13.340	11.67	11.19	12.078	13.65
B_e	1.81984	1.63246	1.49852	1.61634	1.87
α_e	0.01765	0.01661	0.01634	0.01685	0.0182*
γ_1	$-2.3x10^{-4}$	-	-	$-5.4x10^{-5}$	-
D_e	$-6.92x10^{-6}$	$-6.46x10^{-6}$**	$-6.23x10^{-6}$**	$-6.44x10^{-6}$	$-6.8x10^{-6}$**
β_1	$-8.10x10^{-8}$	$-1.08x10^{-8}$**	$-9.32x10^{-9}$**	$-3.6x10^{-8}$	$-1.9x10^{-8}$**
H_e	$9.52x10^{-12}$**	$7.54x10^{-12}$**	$-5.60x10^{-12}$**	$7.15x10^{-12}$**	$7.38x10^{-12}$**
L_e	$-1.11x10^{-16}$**	$-7.46x10^{-17}$**	$-7.25x10^{-17}$**	$-9.26x10^{-17}$**	$-7.64x10^{-17}$**

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* Estimated

** Calculated from Dunham-Sandeman equations

Coefficients of Expression for Vibrational Energy, cm^{-1}

A_0	924.00	817.8	732.4	801.2	977.4
A_1	1842.165	1628.986	1459.083	1593.722	1949.188
A_2	-14.29403	-11.31652	-10.96333	-11.16155	-12.55418
A_3	-0.05578831	-0.03955319	-0.02375443	-0.08796477	-0.4138394

Coefficients of Expression for Limiting Curve of Dissociation, cm^{-1}

B_0	50324.0	49607.8	43889.7	41933.0	37011.9
B_1	0.116564	0.0932111	0.0863754	0.105314	0.336999
B_2	$1.21059x10^{-5}$	$7.86714x10^{-6}$	$6.77614x10^{-6}$	$1.14827x10^{-5}$	$1.83279x10^{-5}$
B_3	$-1.86850x10^{-10}$	$-1.06036x10^{-10}$	$-9.18755x10^{-11}$	$-1.90805x10^{-10}$	$-4.29950x10^{-10}$
B_4	$1.72558x10^{-15}$	$1.01183x10^{-15}$	$9.59303x10^{-16}$	$1.89095x10^{-15}$	$4.82104x10^{-15}$

Table 30 (cont.)

Molecular Constants, cm^{-1}

	$A^3\Pi_g$	$c^1\Pi_g$	$B^3\Pi_g$	$d^1\Sigma_u^+$	$e^1\Sigma_g^+$
ν_{00}	19988.5	34239.	40416.4	43227.5	54936.4
D_0	29411.5	15161.	19177.3	38014.6	14851.
ω_e	1788.22	1809.1	1106.56	1829.57	1671.5
$\omega_e x_e$	16.440	15.81	39.26	13.97	40.02
B_e	1.7560	1.7834	1.1922	1.8334	1.793
α_e	0.02156*	0.0180	0.0242	0.0204	0.0421
γ_1	8.5555×10^{-4}*	-	-	-	-
γ_2	-2.548×10^{-4}*	-	-	-	-
γ_3	9.2219×10^{-6}*	-	-	-	-
D_e	-6.74×10^{-6}	-7.00×10^{-6}**	-6.225×10^{-6}	-7.36×10^{-6}**	-8.3×10^{-6}
β_1	-1.03×10^{-7}	-1.05×10^{-7}**	-2.5×10^{-7}	-2.23×10^{-7}**	-6.0×10^{-7}
H_e	1.14×10^{-11}**	7.91×10^{-12}**	-2.93×10^{-11}**	4.42×10^{-12}**	-6.26×10^{-11}**
δ_1	-	-	4.32×10^{-12}**	-	4.34×10^{-12}**
L_e	-2.75×10^{-16}**	-1.97×10^{-16}**	-1.77×10^{-15}**	-6.54×10^{-17}**	-1.34×10^{-15}**

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* Recalculated from data in Ref. 52

** Calculated from Dunham-Sandeman equations

Coefficients of Expression for Vibrational Energy, cm^{-1}

A_0	890.0	900.1	543.8	911.3	825.8
A_1	1773.29	1769.586	997.88	1813.484	1608.328
A_2	-18.6215	15.3593	-8.45995	-12.55609	-29.3545
A_3	-0.260802	-22.23338	-0.126558	-0.2357358	-0.8233686
A_4		3.186425			
A_5		-0.2392492			
A_6		9.164796×10^{-3}			
A_7		-1.408116×10^{-4}			

Coefficients of Expression for Limiting Curve of Dissociation, cm^{-1}

B_0	30301.5	16709.0	19721.1	38925.9	15676.8
B_1	0.294914	0.751363	0.103427	0.174271	0.271440
B_2	2.25983×10^{-5}	1.02344×10^{-5}	4.89758×10^{-6}	2.04600×10^{-5}	4.61756×10^{-5}
B_3	-6.05073×10^{-10}	-2.01332×10^{-10}	-1.02003×10^{-10}	-4.66734×10^{-10}	-2.09277×10^{-9}
B_4	7.51131×10^{-15}	4.25071×10^{-15}	1.20516×10^{-15}	5.12295×10^{-15}	5.34195×10^{-14}

Table 31

Thermodynamic Functions of Diatomic Carbon

T, °Kelvin	$-(F_T^\circ - H_{298}^\circ)/T$, cal/gfw/deg	$H_T^\circ - H_{298}^\circ$, kcal/gfw	S_T°, cal/gfw/deg	C_p°, cal/gfw/deg
0.	Infinite	-2.5281	0.0000	0.0000
100.00	56.2423	-1.8324	37.9180	7.1139
200.00	48.5713	-1.0047	43.5477	9.6691
298.15	47.6266	0.	47.6266	10.3118
300.00	47.6268	0.0191	47.6903	10.3010
400.00	48.0216	1.0091	50.5444	9.4766
500.00	48.7403	1.9236	52.5874	8.8772
600.00	49.5187	2.7956	54.1781	8.6049
700.00	50.2811	3.6505	55.4961	8.5146
800.00	51.0055	4.5013	56.6322	8.5105
900.00	51.6876	5.3539	57.6364	8.5452
1000.00	52.3283	6.2109	58.5393	8.5973
1100.00	52.9309	7.0736	59.3615	8.6575
1200.00	53.4987	7.9426	60.1175	8.7219
1300.00	54.0351	8.8181	60.8183	8.7887
1400.00	54.5432	9.7004	61.4721	8.8569
1500.00	55.0258	10.5895	62.0855	8.9260
1600.00	55.4853	11.4856	62.6638	8.9953
1700.00	55.9238	12.3886	63.2112	9.0644
1800.00	56.3432	13.2984	63.7312	9.1327
1900.00	56.7452	14.2151	64.2268	9.1998
2000.00	57.1312	15.1383	64.7004	9.2652
2100.00	57.5025	16.0680	65.1539	9.3287
2200.00	57.8603	17.0040	65.5893	9.3899
2300.00	58.2055	17.9459	66.0080	9.4487
2400.00	58.5390	18.8937	66.4114	9.5050
2500.00	58.8617	19.8469	66.8005	9.5588
2600.00	59.1743	20.8054	67.1764	9.6099
2700.00	59.4775	21.7687	67.5400	9.6586
2800.00	59.7717	22.7368	67.8920	9.7047
2900.00	60.0577	23.7094	68.2333	9.7484
3000.00	60.3357	24.6863	68.5645	9.7898
3100.00	60.6064	25.6673	68.8862	9.8291
3200.00	60.8701	26.6520	69.1988	9.8663
3300.00	61.1271	27.6405	69.5030	9.9017
3400.00	61.3778	28.6325	69.7991	9.9353
3500.00	61.6225	29.6276	70.0875	9.9674
3600.00	61.8616	30.6259	70.3688	9.9980
3700.00	62.0952	31.6271	70.6431	10.0272
3800.00	62.3237	32.6313	70.9109	10.0553
3900.00	62.5472	33.6381	71.1724	10.0822
4000.00	62.7661	34.6477	71.4280	10.1081
4100.00	62.9804	35.6597	71.6779	10.1332
4200.00	63.1904	36.6743	71.9224	10.1575
4300.00	63.3963	37.6913	72.1617	10.1810
4400.00	63.5982	38.7105	72.3960	10.2039
4500.00	63.7962	39.7321	72.6256	10.2263
4600.00	63.9906	40.7558	72.8505	10.2482
4700.00	64.1814	41.7818	73.0712	10.2696
4800.00	64.3689	42.8097	73.2876	10.2906
4900.00	64.5531	43.8398	73.5000	10.3111
5000.00	64.7341	44.8720	73.7085	10.3313
5100.00	64.9121	45.9061	73.9133	10.3511
5200.00	65.0871	46.9422	74.1145	10.3705
5300.00	65.2593	47.9801	74.3122	10.3897
5400.00	65.4288	49.0200	74.5066	10.4085
5500.00	65.5956	50.0618	74.6977	10.4269
5600.00	65.7598	51.1052	74.8857	10.4450
5700.00	65.9216	52.1505	75.0708	10.4627
5800.00	66.0809	53.1976	75.2529	10.4799
5900.00	66.2379	54.2464	75.4322	10.4967
6000.00	66.3926	55.2968	75.6087	10.5130

surprising, because in these cases obedience to the noncrossing rule causes atypical curve shapes.

DISCUSSION

The general approach used in this paper to determine v_{max} and J_{max} is similar to that used by Baumann,[4,5] Gurvich and Yungman,[26] and Stupochenko et al.[73] Gurvich and Yungman and Stupochenko et al. used the Morse potential to calculate effective potential curves, and Baumann used the Hulburt-Hirschfelder potential. In their formulation of the effective potential, Gurvich and Yungman added the term $-r_e^6 D_e J^2(J+1)^2$ to correct for centrifugal stretching.* This does not seem appropriate, as, in the sense the correction was intended, it is already implicit in the term for rotational energy in Eq. (5). That is, a solution to the wave equation with the effective potential in the form of Eq. (5) will give an expression for the levels of the nonrigid rotator which includes a centrifugal stretching correction term.

The main difference between the method used in this paper and that used by Baumann or by Gurvich and Yungman is the technique for establishing J_{max} as a function of v. The authors mentioned plotted the height of the potential barrier $U_{eff}(r_{max}) - U_{eff}(r_{min})$ against J. A J_{max} for each v was then determined by drawing a line parallel to the J axis at a height equal to the energy of that v. The J corresponding to the intersection of the line with the curve of the potential barrier was taken to be J_{max}. This, of course, is equivalent to taking the energy of the minimum $U_{eff}(r_{min})$ as a measure of the rotational energy, and finding the maximum vibrational energy which will fit into the potential barrier

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* The equation containing this term in the paper of Gurvich and Yungman contains typographical errors.

to give the total permissible energy $U_{eff}(r_{max})$. It is thereby assumed that the rotational constants B_v, D_v, --- are in fact independent of v. Because the rotational constants are not permitted to change with v, the values of J_{max} predicted by this procedure are consistently smaller than the experimental values for HgH and HF and the values calculated for H_2 by the RKR method, except at $v = 0$ and $v = v_{max}$. As was demonstrated above, the procedure we have used gives quite good agreement for these molecules. Stupochenko et al. appear to have used a procedure analogous to ours.

The procedure outlined in this report has the advantage that it may be applied to electronic states for which the Mayer and Mayer treatment is adequate over the temperature range of interest, to states for which a virial coefficient treatment is applicable, and to intermediate cases.

Table 32. Physical Constants

Gas constant, $R = 1.98717$ cal./deg./mole

Planck constant, $h = 6.6256 \times 10^{-27}$ erg sec.

Thermochemical calorie $= 4.1840 \times 10^{7}$ erg

Boltzmann constant, $k = 1.38054 \times 10^{-16}$ erg/deg.

$\alpha = hc/k = 1.43879$ cm./deg.

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